Poly lactic acid

Properties and processing

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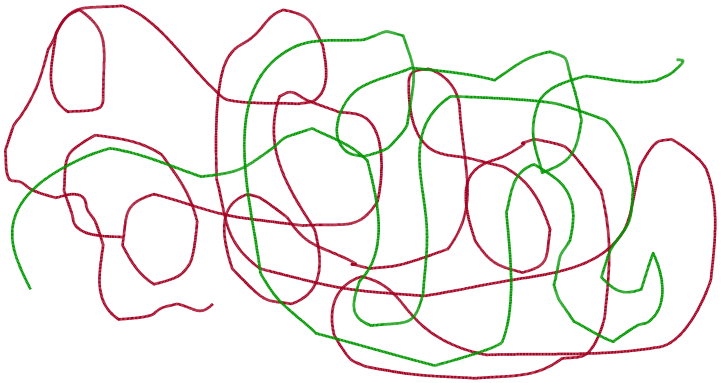
Outline

- Polymers
- Polymerization
  - methods
  - reactors
- Biodegradable polymers
  - Poly lactic acid
    - polymerization
    - processing
- Possibilities
  - composites
  - rheology

POLYMERS - MACROMOLECULES



Very Long Molecules

Based on:

- Carbon
- Hydrogen
- Oxygen
- Silicon
- Nitrogen, Sulfur, Chlorine etc.

Synthetic

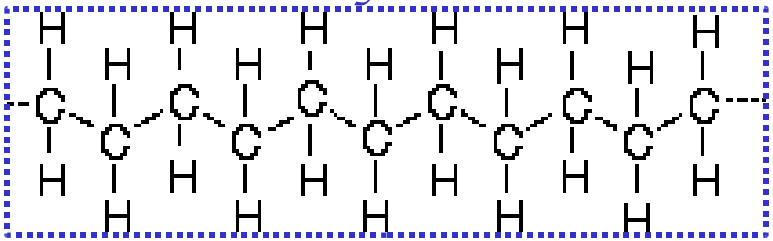
- Polyethylene, polyester

Natural

- DNA, proteins, cellulose, starch

EXAMPLES

Polymer



Polyethylene

Monomer

$CH_2 = CH_2$

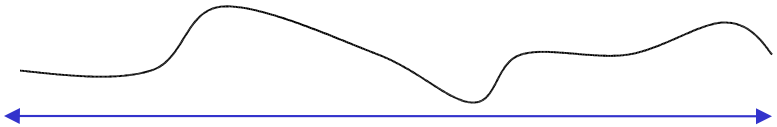
Ethylene

Repeating Unit

$—(CH_2 – CH_2)_n—$

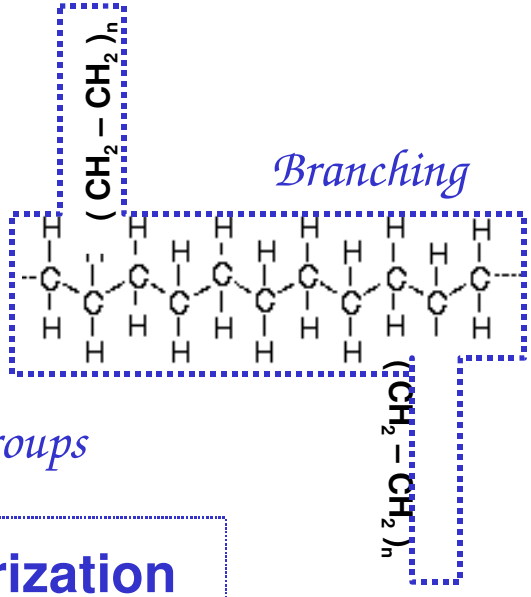
Ethylene

Main chain - Backbone



Molecular weight

Branching



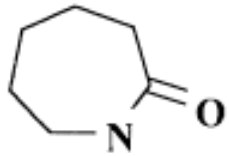
Side groups

Free Radical, Ionic or Coordination Polymerization
Chain Polymerization

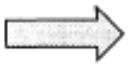
EXAMPLES

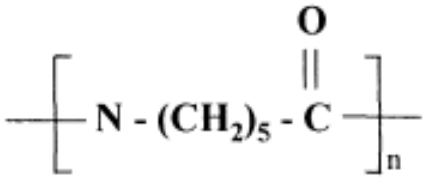
NYLONS

Monomer(s) | **Polymer**



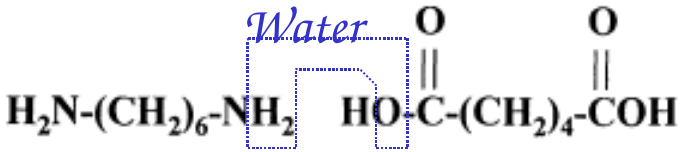
ε - caprolactam





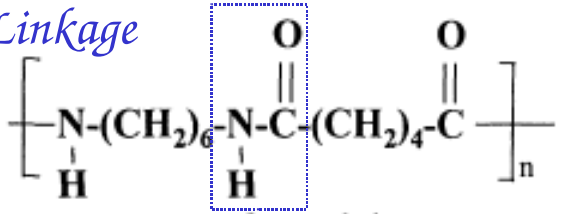
nylon - 6

Water

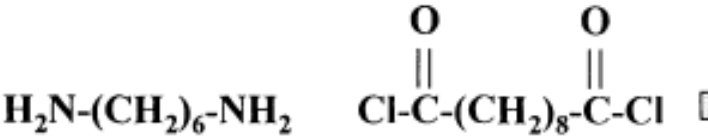


1,6-hexanediamine *adipic acid*

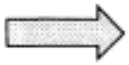
Amide Linkage

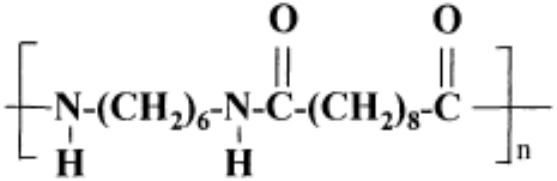


nylon - 6,6



1,6-hexamethylene diamine *decanedioyl chloride*

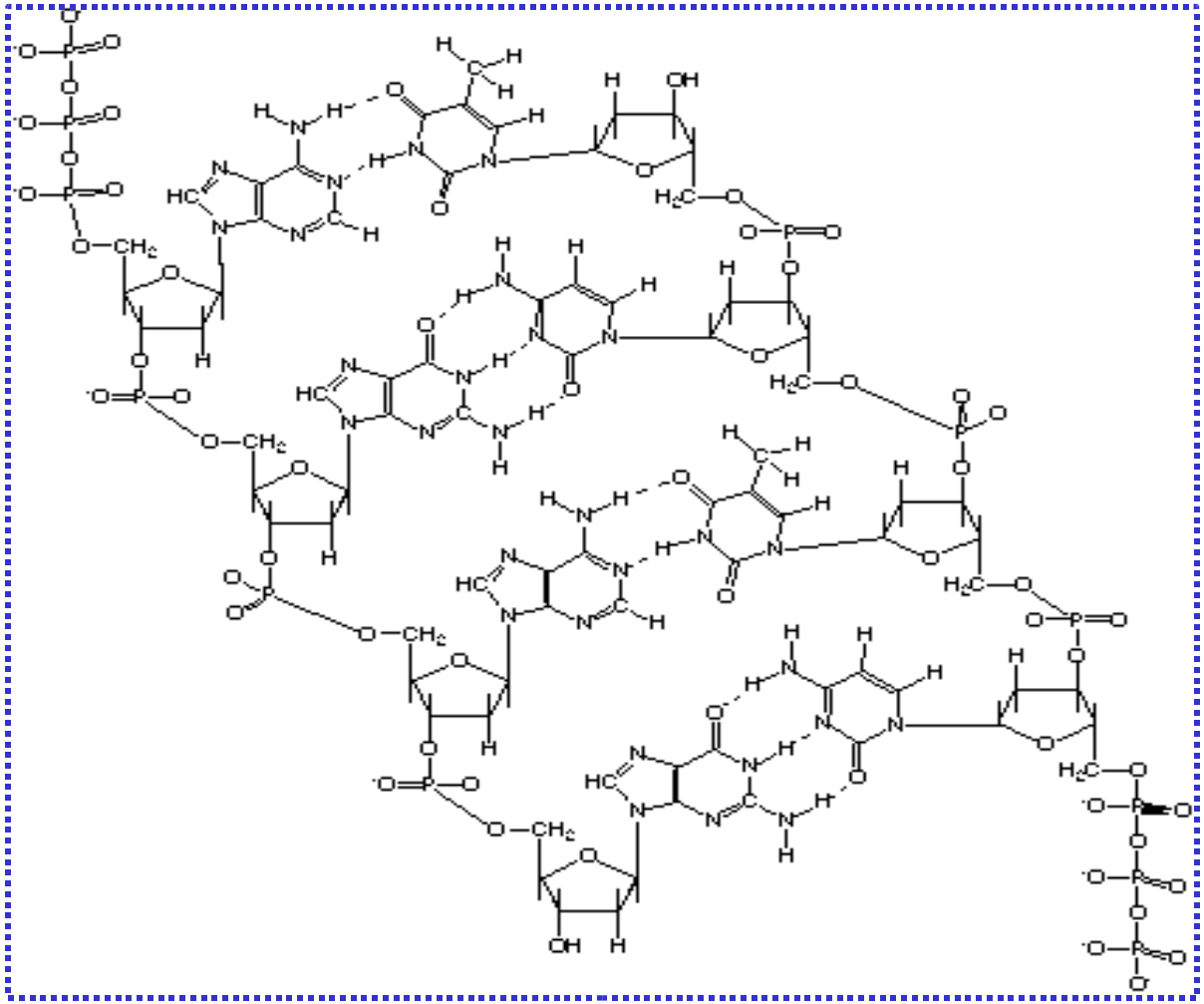




nylon - 6,10

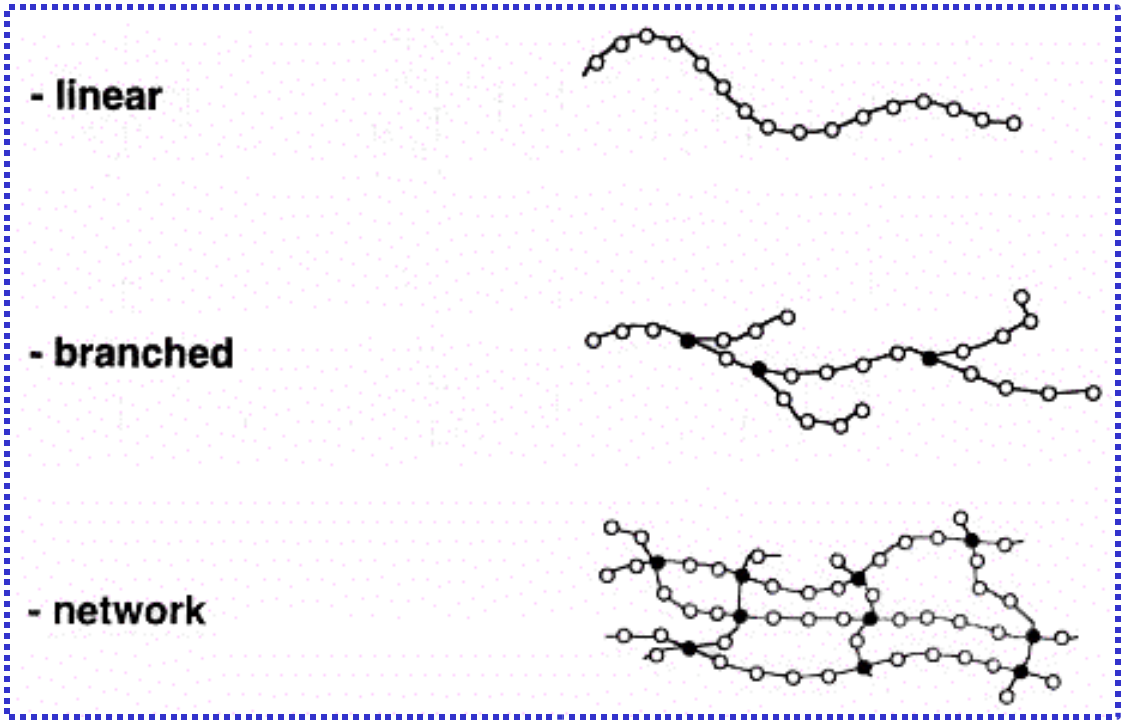
Condensation or Step Addition Polymerization

EXAMPLES



DNA structure

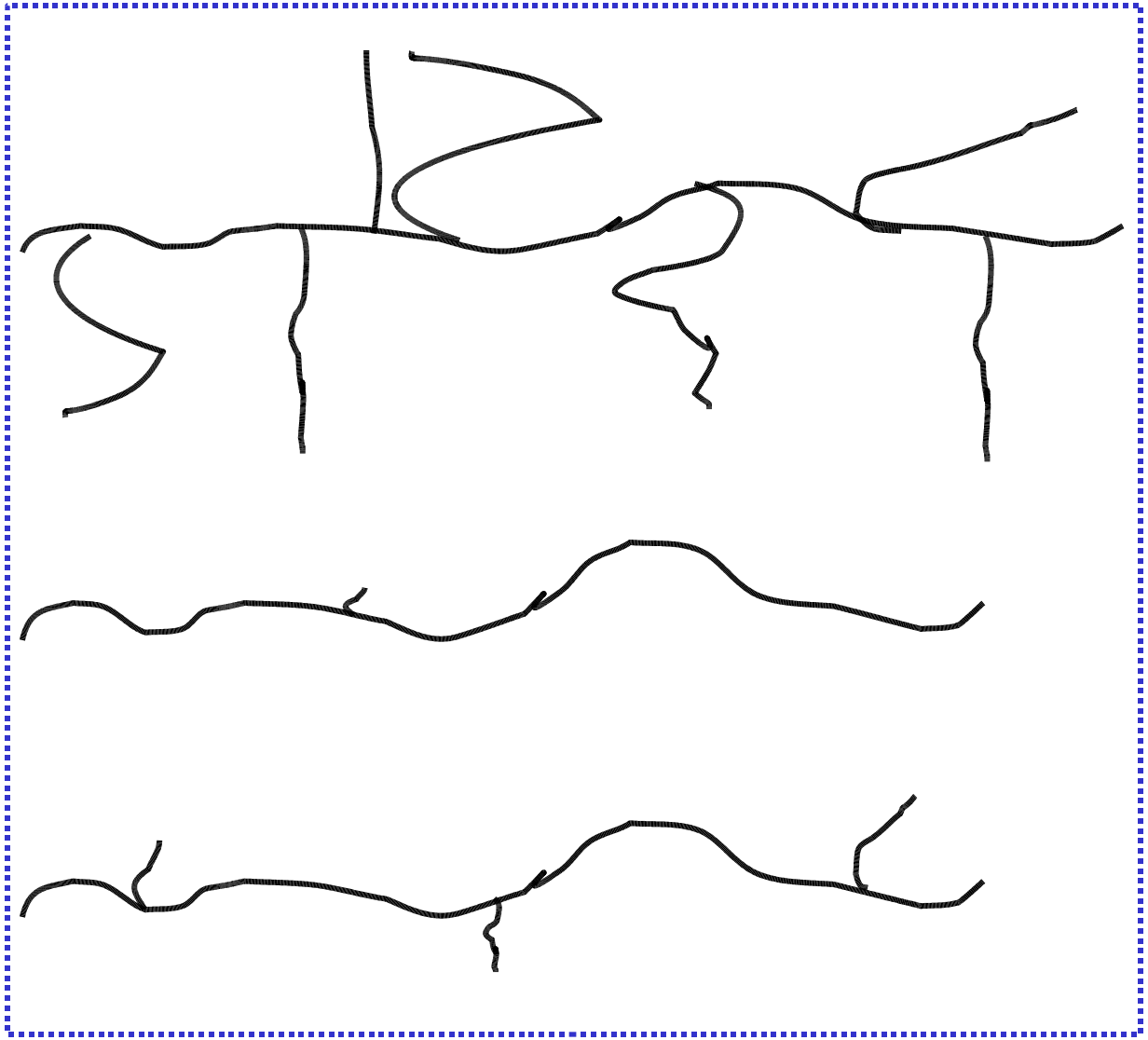
Molecular Architecture



Homopolymers and Copolymers

- *Polyethylene, Polypropylene, Polystyrene, Polybutadiene*
- *Ethylene-Propylene Copolymer, Styrene-Butadiene Copolymer*

Molecular Architecture



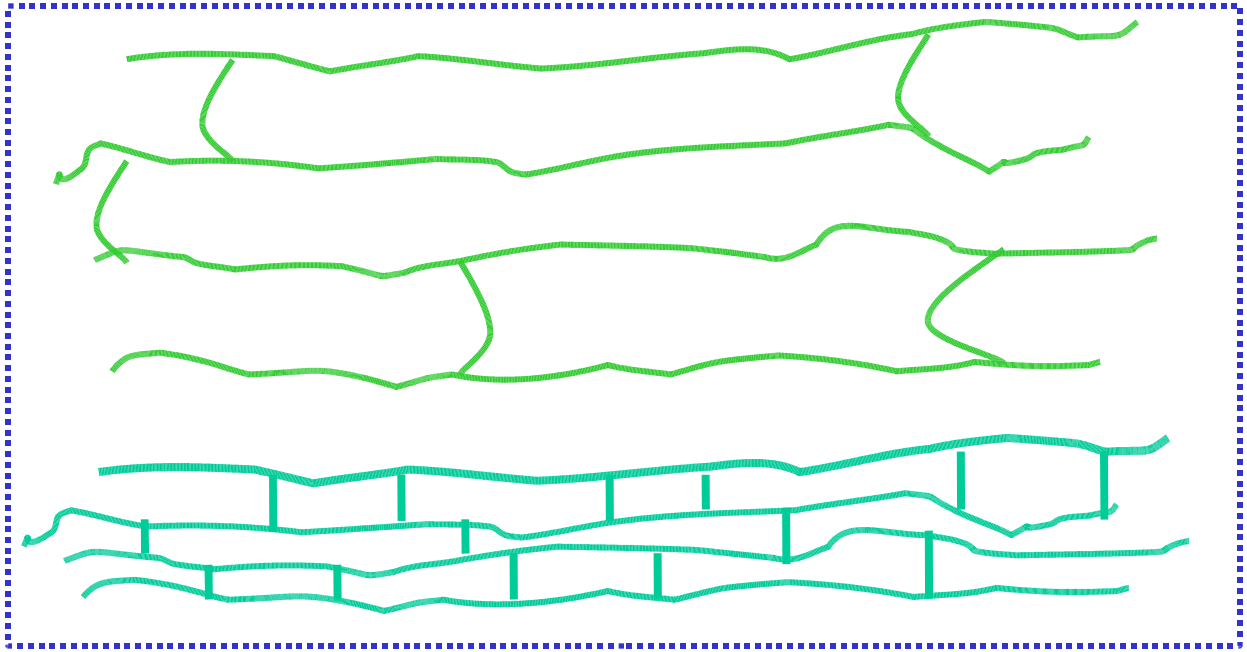
Low Density Polyethylene ***(LDPE)***

High Density Polyethylene ***(HDPE)***

Linear Low Density Polyethylene ***(LLDPE)***

Networked Polymers

Degree of Crosslinking or Crosslinking density



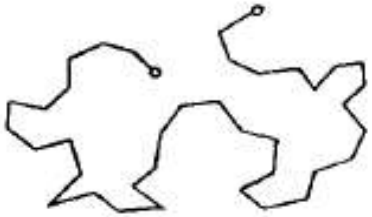
Low
Rubbers

High
Thermosets

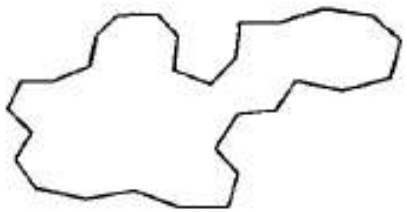
<u>Curing</u> : *Process of crosslinking or networking*

Prepolymer or Resin + Curing Agent = Polymer

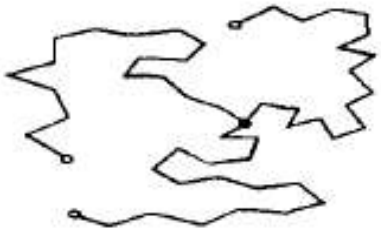
Molecular Architecture



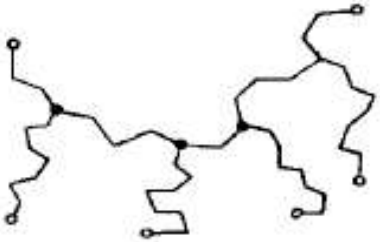
Linear



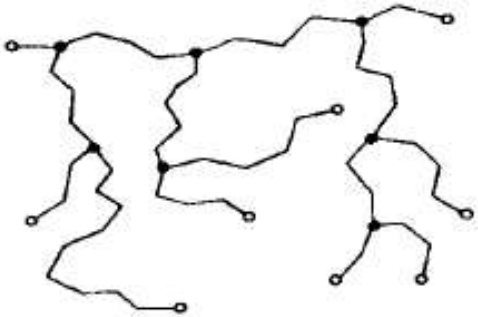
Ring



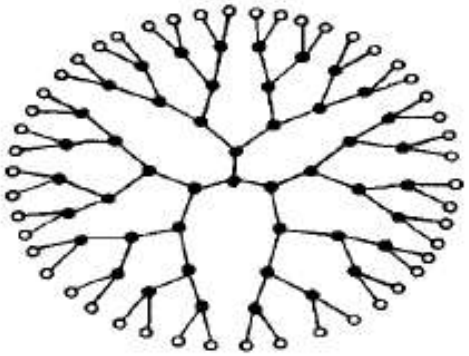
Star



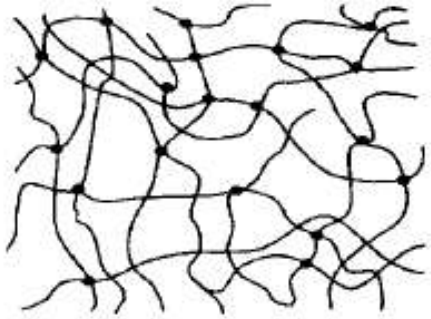
Comb



Sub-branch



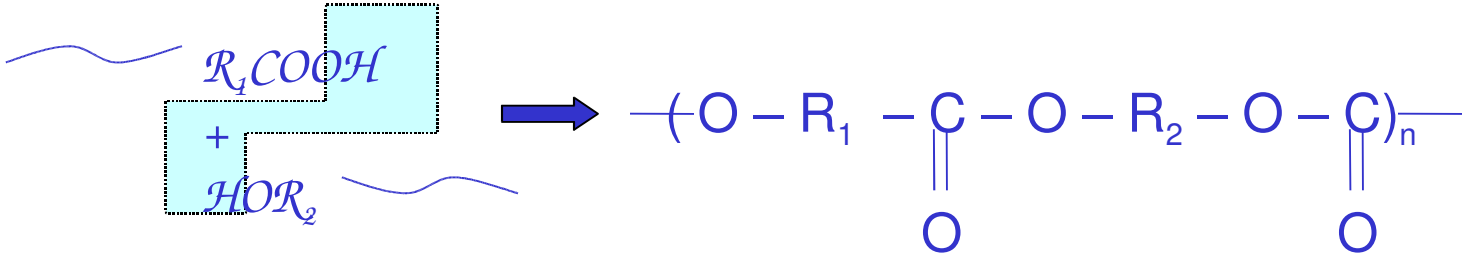
Dendrimer

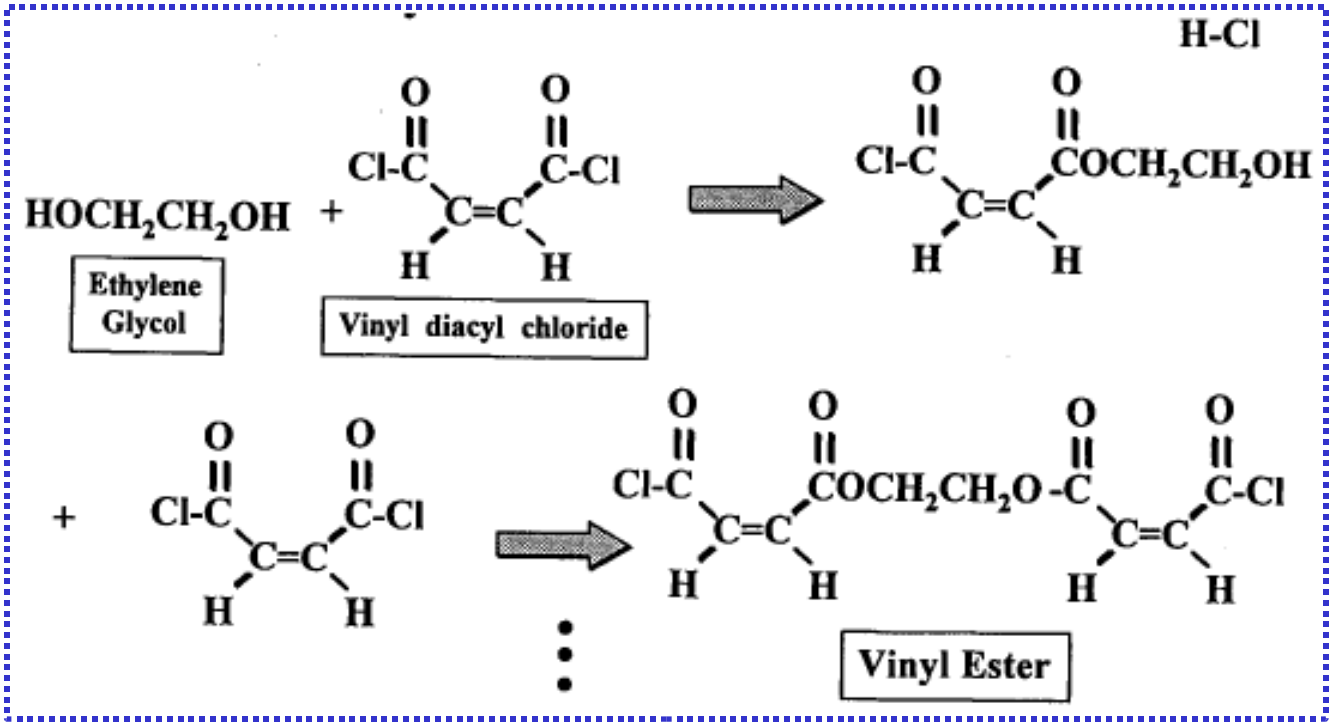


Network

Polyesters

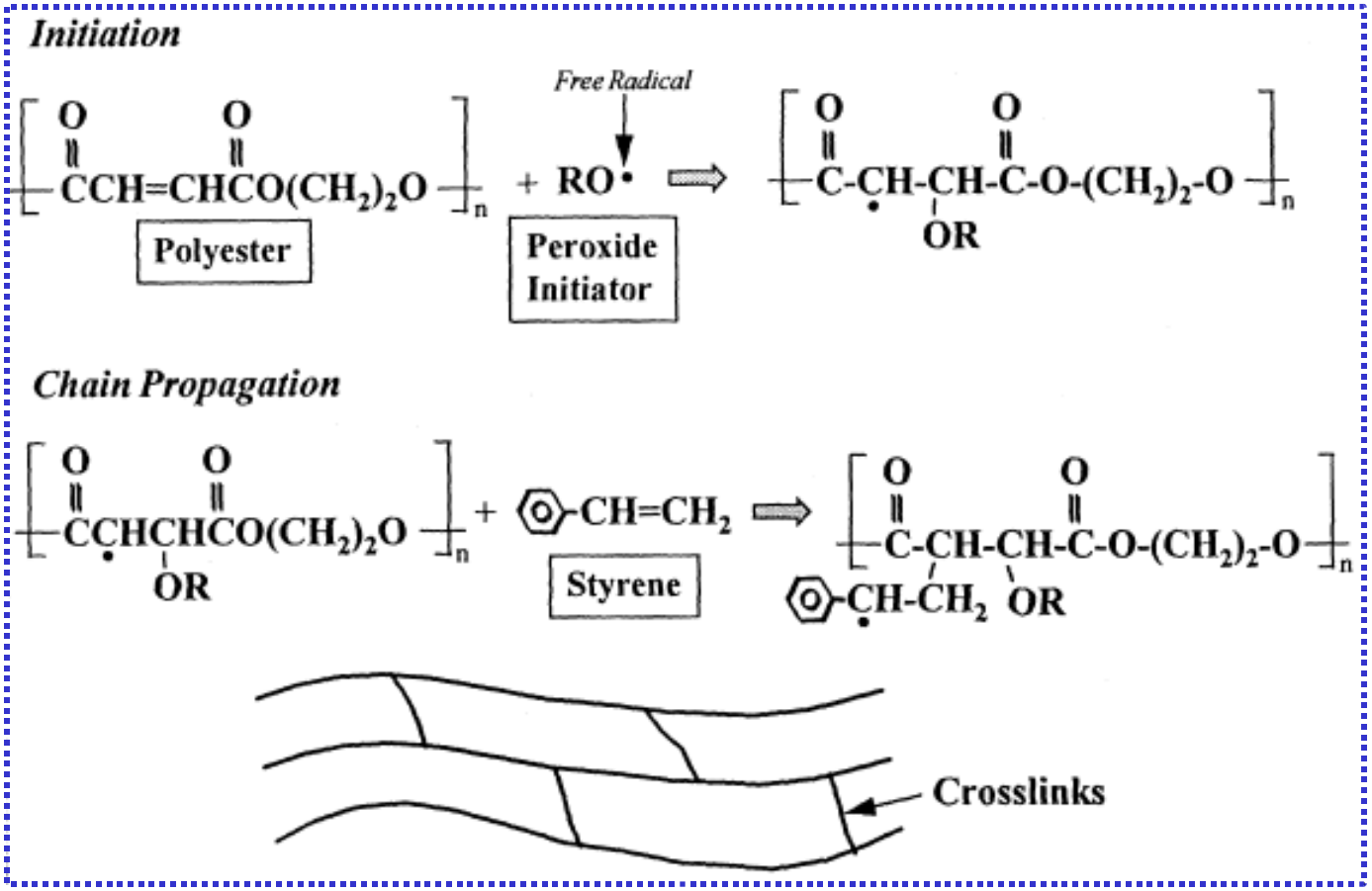
(Alcohol & Carboxylic acid or Salt)





Polyesters

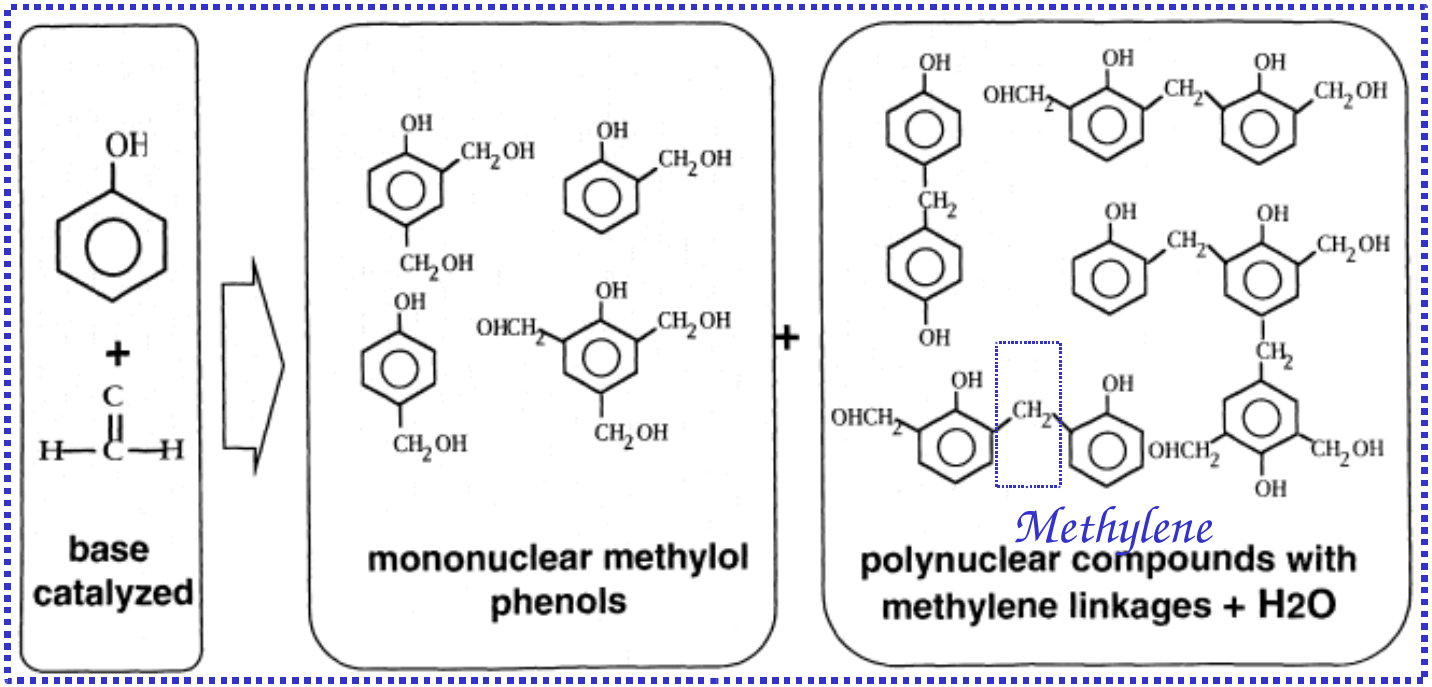
Curing or Crosslinking Reactions

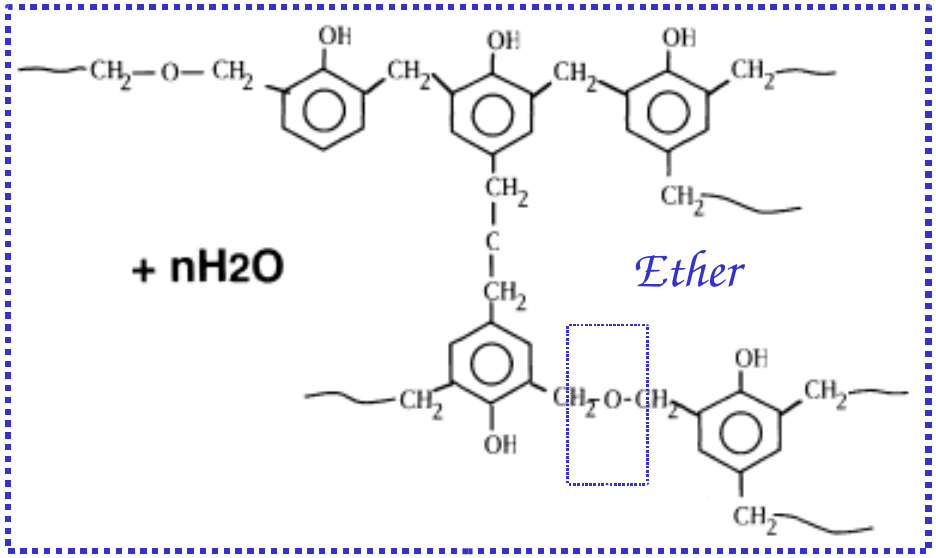


Phenol

+

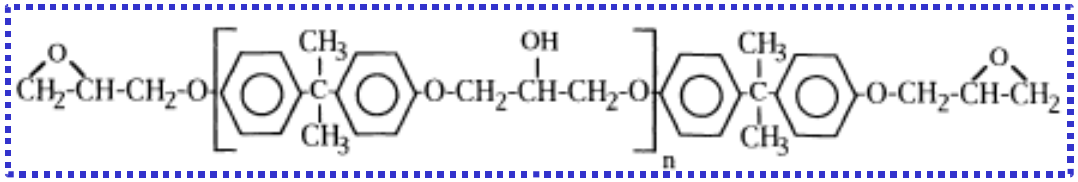
Formaldehyde



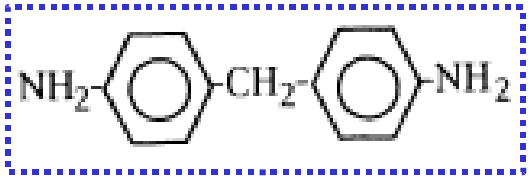


Phenolics

EPOXY

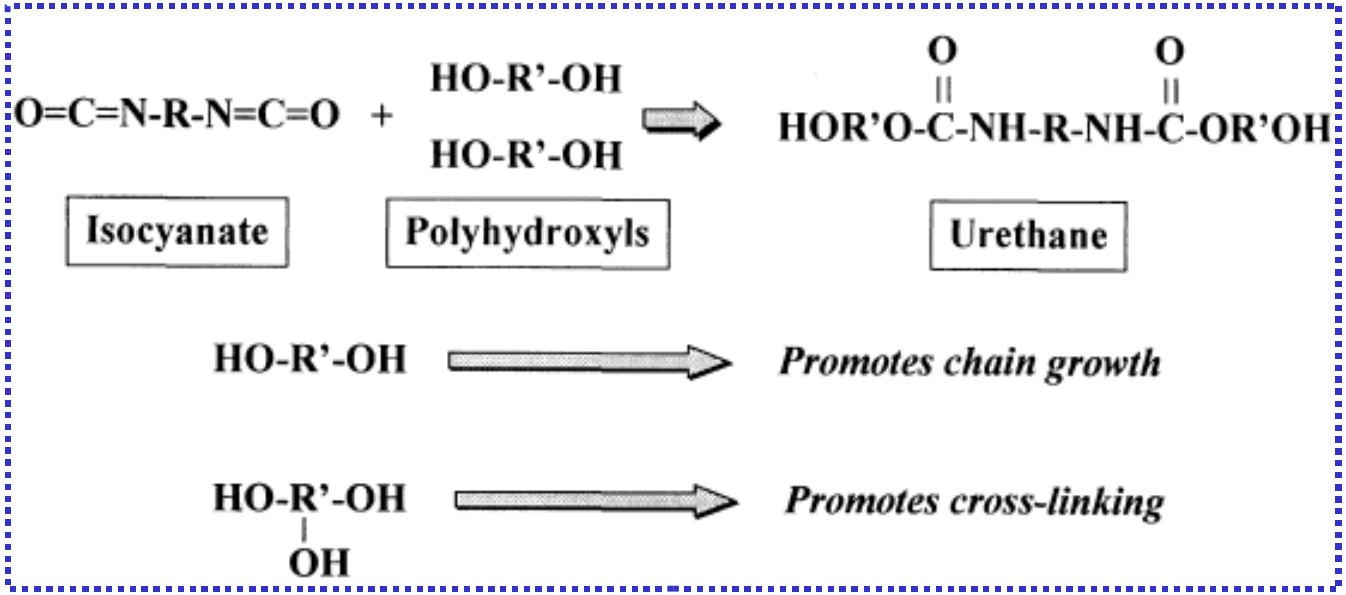


DGEBA

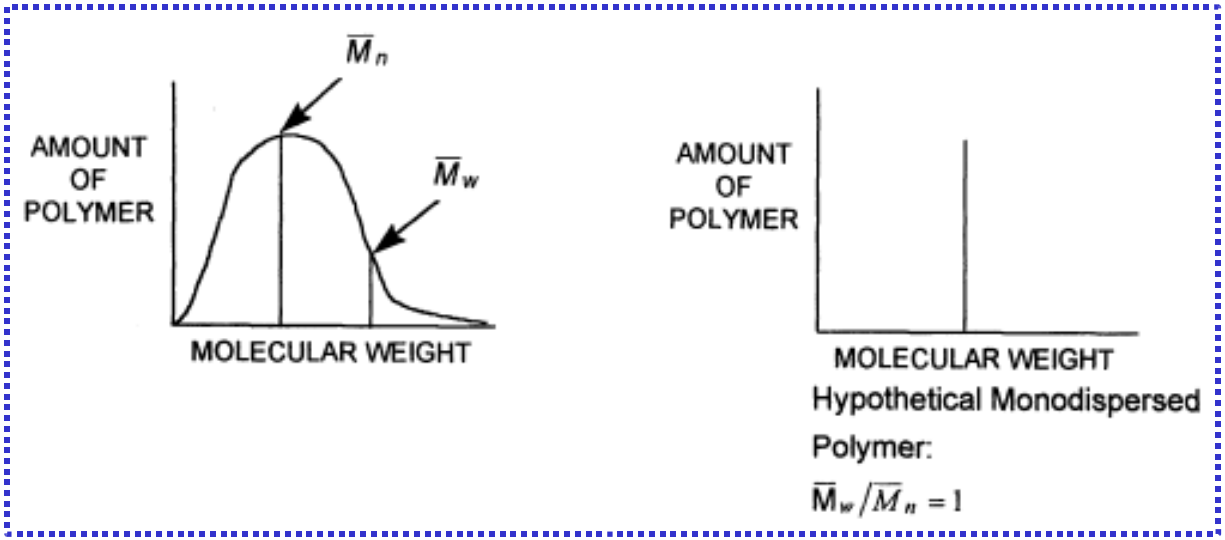


MDA

POLYURETHANE



Molecular Weight Distribution (MWD)



Number Average Molecular Weight

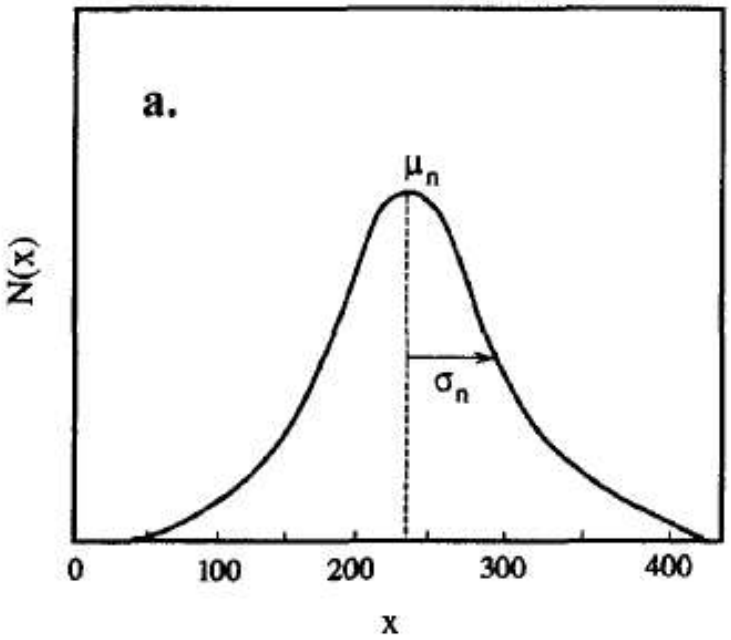
$$\overline{M}_n = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i}$$

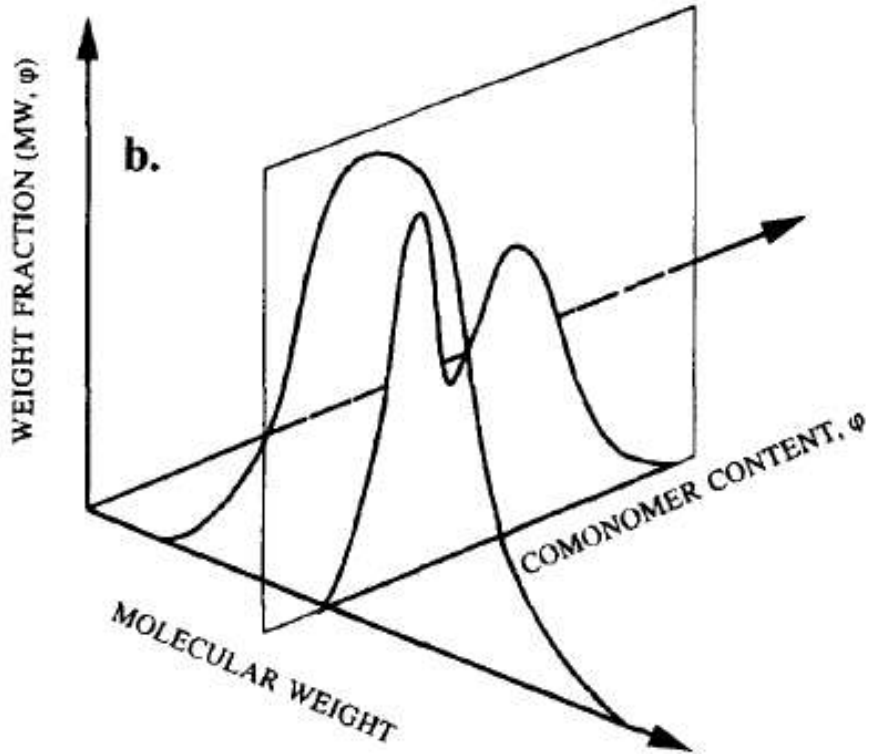
$$\overline{M}_w = \frac{\sum_{i=1}^{\infty} M_i^2 N_i}{\sum_{i=1}^{\infty} M_i N_i}$$

Weight Average Molecular Weight

$$\text{Polydispersity} = \frac{\overline{M}_w}{\overline{M}_n}$$

Molecular Weight Distribution (MWD)





Factors to be controlled

- molar mass
- molecular weight distribution (MWD)
- copolymer composition distribution (CCD)
- chain sequence length distribution (CSLD)
- branching distribution (BD)
- stereoregularity
- ...

Factors to be controlled depend on ...

- chemical nature of the monomers
- the type of polymerization mechanism
- the physical state of the reacting system (or polymerization process)
- the type of reactor configuration

Outline

- Polymers
- Polymerization
  - methods
  - reactors
- Biodegradable polymers
  - Poly lactic acid
    - polymerization
    - processing
- Possibilities
  - composites
  - rheology

Step addition: reactions

Polymer Type	I (A-BA-B)	II (A-AB-B)	III (A-AB-BA-A)
Monomer Type	A-B, A-X, B-X	A-A, B-B, A-X, B-X	A-A, B-B, A-X, B-X
Polycondensation I	$P_m + P_n \leftrightarrow P_{m+n} + C$ $P_m + X'_n \leftrightarrow X'_{m+n} + C$ $P_m + X''_n \leftrightarrow X''_{m+n} + C$ $X'_m + X''_n \leftrightarrow D_{m+n} + C$	$P_m + P_n \leftrightarrow P_{m+n} + C$ $P_m + P'_n \leftrightarrow P'_{m+n} + C$ $P_m + P''_n \leftrightarrow P''_{m+n} + C$ $P'_m + P''_n \leftrightarrow P_{m+n} + C$ $P_m + X'_n \leftrightarrow X'_{m+n} + C$ $P_m + X''_n \leftrightarrow X''_{m+n} + C$ $P'_m + X''_n \leftrightarrow X'_{m+n} + C$ $P''_m + X'_n \leftrightarrow X''_{m+n} + C$ $X'_m + X''_n \leftrightarrow D_{m+n} + C$	$P_m + P_n \leftrightarrow P_{m+n} + C$ $P_m + P'_n \leftrightarrow P'_{m+n} + C$ $P_m + P''_n \leftrightarrow P''_{m+n} + C$ $P'_m + P''_n \leftrightarrow P_{m+n} + C$ $P_m + X'_n \leftrightarrow X'_{m+n} + C$ $P_m + X''_n \leftrightarrow X''_{m+n} + C$ $P'_m + X''_n \leftrightarrow X'_{m+n} + C$ $P''_m + X'_n \leftrightarrow X''_{m+n} + C$ $X'_m + X''_n \leftrightarrow D_{m+n} + C$
Ring Addition	$P_m + R_n \leftrightarrow P_{m+n}$	$P_m + R_n \leftrightarrow P_{m+n}$ $P'_m + R_n \leftrightarrow P'_{m+n}$ $P''_m + R_n \leftrightarrow P''_{m+n}$	$P_m + R_n \leftrightarrow P_{m+n}$ $P'_m + R_n \leftrightarrow P'_{m+n}$ $P''_m + R_n \leftrightarrow P''_{m+n}$
Ring Opening	$R_m + C \leftrightarrow P_m$	$R_m + C \leftrightarrow P_m$	$R_m + C \leftrightarrow P_m$
			Polycondensation II $P_m + P'_n \leftrightarrow P''_{m+n-1} + P'_1$ $P_m + P'_n \leftrightarrow P_{m+n-1} + P'_1$ $P'_m + P'_n \leftrightarrow P'_{m+n-1} + P'_1$ $P_m + X'_n \leftrightarrow X''_{m+n-1} + P'_1$ $P'_m + X'_n \leftrightarrow X'_{m+n-1} + P'_1$ $X'_m + X'_n \leftrightarrow D_{m+n-1} + P'_1$
Symbols	C ≡ condensate molecule P ≡ bifuctional polymer X ≡ monofuntional polymer D ≡ nonfuctional polymer R ≡ cyclic compound m, n, r ≡ # of repeat units $'$ ≡ only A end groups $''$ ≡ only B end groups		

Chain polymerization: reactions

Initiation (by oxygen, peroxides or azo compounds):

$$I_i \xrightarrow{k_{di}} 2R^{\bullet} \quad ; \quad i = 1, 2, \ldots, N_i$$

Chain Initiation Reactions:

$$R^{\bullet} + M_j \xrightarrow{k_{ij}} R^{j}_{2-j,j-1} \; ; \; j = 1, 2$$

Propagation Reactions:

$$R^{i}_{p,q} + M_j \xrightarrow{k_{pij}} R^{j}_{p+2-j,q+j-1} \; ; \; i = 1, 2 \text{ and } j = 1, 2$$

Chain Transfer to Monomer Reactions:

$$R^{i}_{p,q} + M_j \xrightarrow{k_{tmij}} R^{j}_{2-j,j-1} + D_{p,q} \; ; \; i = 1, 2 \text{ and } j = 1, 2$$

Chain Transfer to Solvent (Chain Transfer Agent Reactions):

$$R^{i}_{p,q} + S \xrightarrow{k_{tsi}} R^{i}_{2-i,i-1} + D_{p,q} \; ; \; i = 1, 2$$

Chain Transfer to Polymer:

$$R^{i}_{p,q} + D_{x,y} \xrightarrow{k_{tpij}} R^{j}_{x,y} + D_{p,q} \; ; \; i = 1, 2 \text{ and } j = 1, 2$$

Termination by Disproportionation:

$$R^{i}_{p,q} + R^{j}_{x,y} \xrightarrow{k_{tdij}} D_{p,q} + D_{x,y} \; ; \; i = 1, 2 \text{ and } j = 1, 2$$

Termination by Combination:

$$R^{i}_{p,q} + R^{j}_{x,y} \xrightarrow{k_{tcij}} D_{p+x,q+y} \; ; \; i = 1, 2 \text{ and } j = 1, 2$$

Intramolecular Transfer (Short Chain Branching):

$$R^{i}_{p,q} \xrightarrow{k_{bi}} R^{i}_{p,q} \text{ or } R^{j}_{p,q} \quad ; \quad i = 1, 2$$

β-Scission of sec- and tert-radicals:

$$R^{i}_{p,q} \xrightarrow{k_{\beta i}} D^{*}_{p+j-2,q-j+1} + R^{j}_{2-j,j-1} \quad ; \quad i = 1, 2 \quad ; \quad j = 1,2$$

Coordination polymerization: reactions

adsorption from solution of the monomer M

$$| + \text{MeR} \underset{}{\overset{k_1}{\rightleftharpoons}} |\text{MeR} \quad ; \quad | + \text{M} \overset{k_2}{\rightleftharpoons} |\text{M}$$

followed by initiation via reaction between the adsorbed species

$$\begin{matrix} |\text{MeR} \\ |\text{M} \end{matrix} \xrightarrow{k_i} | \text{Me - M - R}$$

and propagation in a like manner

$$\begin{matrix} |\text{Me - M}_n\text{ - R} \\ |\text{M} \end{matrix} \xrightarrow{k_p} |\text{Me - M}_{(n+1)}\text{ - R}$$

Termination can occur by chain transfer with monomer

$$\begin{matrix} |\ \text{Me - M}_n\text{ - R} \\ |\ \text{M} \end{matrix} \xrightarrow{k_{tr,M}} |\text{Me - M - R} \quad + \quad \text{P}_n$$

or by spontaneous internal hydride transfer

$$|\text{Me - M}_n\text{ - R} \xrightarrow{k_s} |\text{Me-H} \quad + \text{P}_n$$

or by transfer to Me-R

$$\begin{matrix} |\ \text{Me - M}_n\text{ - R} \\ |\ \text{Me - R} \end{matrix} \xrightarrow{k_{tr,C}} | \text{Me-R} \quad + \text{P}_n$$

Polymerization processes

- Bulk polymerization
- Solution polymerization
- Suspension polymerization
- Emulsion polymerization
- Solid catalyzed polymerization
  - gas
  - slurry
  - liquid
- Interfacial, solid state ....

Reactors

1. Polymerization mechanism
   a) Elementary reactions and reacting species (e.g. monomer(s), initiator(s), chain transfer agent(s), "live" polymer chains and "dead" polymer chains)
   b) Polymerization rate functions (T & P effects)
2. Number of phases in the reactor
   1. Homogeneous versus heterogeneous
   2. Particle size distribution (polymer particles)
3. Reactor configuration: batch, semi-batch, continuous
4. Mixing conditions (ideal, non-ideal micro-, macromixing)
5. Thermodynamics
   1. distribution in different phases
   2. enthalpies of the different reacting species
6. Interphase and intraphase heat and mass transfer rates
7. Gel and glass effects (diffusion-controlled reactions)

Polymerization process for common polymers

Chain polymerization

Process:	Bulk and Solution	Precipitation	Liquid Slurry	Gas Dispersion	Emulsion	Micro Emulsion	Suspension
Particle Size (μm)	---	$100\text{-}10^4$	$10\text{-}10^4$	$10\text{-}10^4$	0.1-1.0	1.0-10	100-500
Commercial Reactor Types	Batch, CSTR, Tube, Extruder	Batch, CSTR Extruder	Batch, CSTR Loop	Fluid Bed Stirred Bed	Batch CSTR	Batch	Batch
Kinetic Mechanism	All	All	ZN	ZN	FR, I	FR, I	FR, I
Examples (including co-polymers)	PS, LDPE, PMMA, PVAC	PVC, PTFE, PF	HDPE, PP, EP	HDPE, LLDPE, PP EP	PS, PMMA PVA PTFE	PS, PMMA	PMMA PS PVC

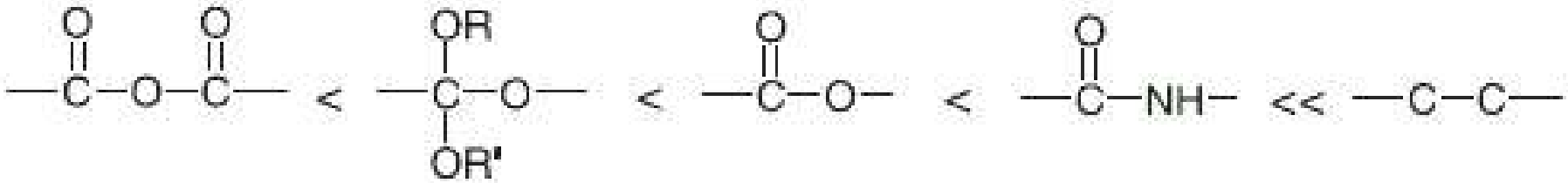
Mechanisms: FR - Free Radical, I- Ionic, ZN- Ziegler-Natta

Monomers : PS - Polystyrene, PMMA- Polymethacrylate, PVA - Polyvinylacetate, LDPE - Low density Polythylene, HDPE - High density polyethylene, LLDPE - Linear low density polyethylene, PTFE - Polytetrafluorethylene, PF - Polyformaldehyde, EP - Ethylene- Propylene copolymers, PP - Polypropylene

Outline

- Polymers
- Polymerization
  - methods
  - reactors
- Biodegradable polymers
  - Poly lactic acid
    - polymerization
    - processing
- Possibilities
  - composites
  - rheology

Relative stability of backbone linkages



Biodegradable polymers: requirements

- Biocompatibility of the polymer and its degradation products
- Mechanical strength sufficient to meet the needs of specific applications
- Degradability with degradation kinetics matching a biological process such as wound healing
- Processibility using available equipment
- Solubility in various solvents
- Chemical, structural and application versatility
- Economically acceptable shelf life
- Regulatory approval

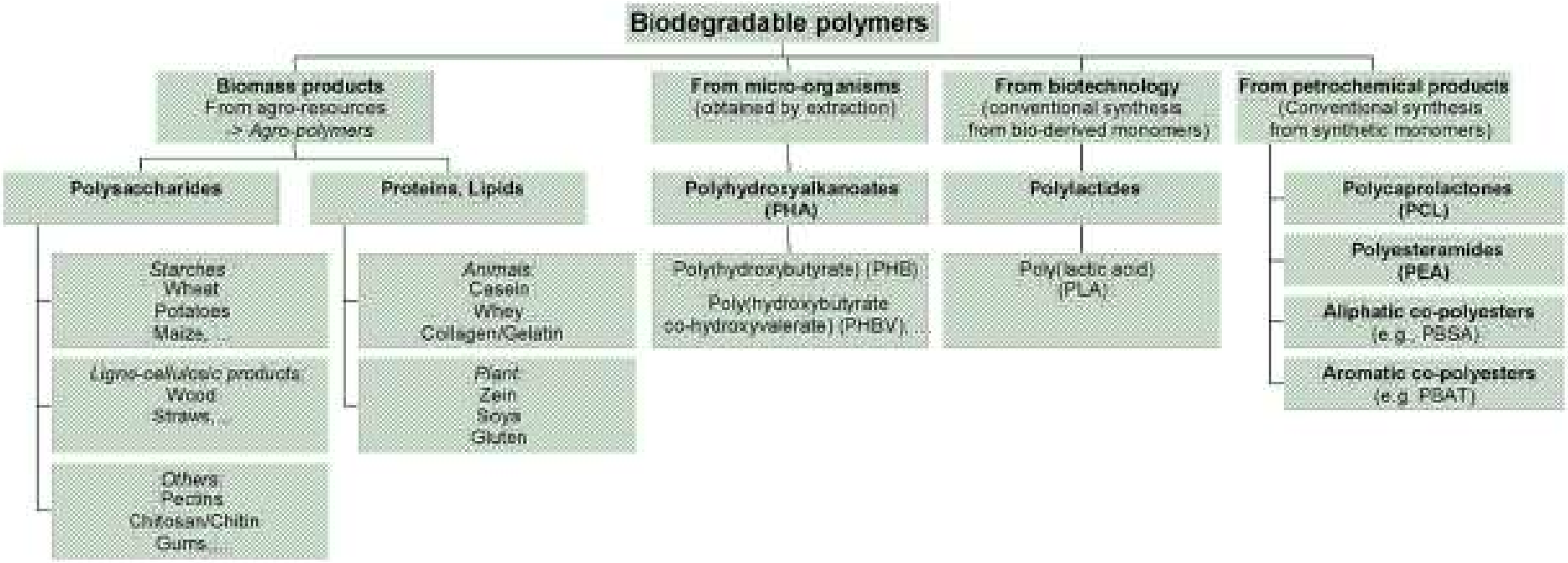
Examples of biodegradable polymers

Synthetic biodegradable Polymers	
Polyesters	Polyoxalates
Polyorthoesters	Polyiminocarbonates
Polyanhydrides	Polyurethanes
Polydioxanones	Polyphosphazenes
Poly(α-cyanoacrylates)	—
Natural biodegradable polymers	
Starch	Albumin
Hyaluronic acid	Dextran
Heparin	Chitosan
Gelatin	—
Poly(β-hydroxyalkanoate)s	

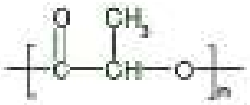
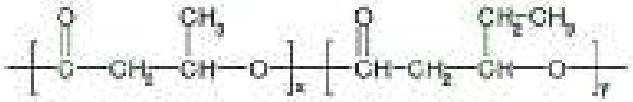
Biodegradable polymers classification

- polymers from biomass such as the agro-polymers from agro-resources, e.g., starch, cellulose,
- polymers obtained by microbial production, e.g., the poly hydroxyalkanoates
- polymers chemically synthesized using monomers obtained from agro-resources, e.g., poly(lactic acid)
- polymers whose monomers and polymers are both obtained by chemical synthesis from fossil resources

Biodegradable polymers classification



Commercial biodegradable polyesters

	Trade Name	Company
Agro-resources based polyesters:		
Poly(lactic acid) (PLA)		
	Natureworks	Cargill (USA)
	Lacty	Shimadzu (Japan)
	Lacea	Mitsui Chemicals (Japan)
	Heplon	Chronopol (USA)
	CPLA	Dainippon Ink Chem. (Japan)
	PLA	Galactic/Total (Belgium)
	Eco Plastic	Toyota (Japan)
	Treofan	Treofan (Netherland)
	PDLA	Purac (Netherland)
	Ecoloju	Mitsubishi (Japan)
	Biomer L	Biomer (Germany)
Polyhydroxyalkanoate (PHA)		
		
(PHBV, PHB)	Biopol	Monsanto (USA)*
(PHBV, PHB)	Mirel	Metabolix/ADM (USA)
(PHB, PHBV)	Biocycle	PHB Industrial (Brazil)
(PHB, PHBV)	Biomer P	Biomer (Germany)
(PHB, PHBV)	Enmat	Tianan (China)
(PHBHx, PHBO, PHBOd)	Nodax	Procter & Gamble (USA)*

Commercial biodegradable polyesters

Petroleum-based polyesters:

Polycaprolactone (PCL)

CAPA
Tone

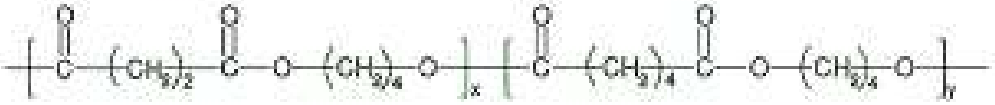
Solvay (Belgium)
Union Carbide (USA)

Polyesteramide (PEA)

BAK

Bayer (Germany)*

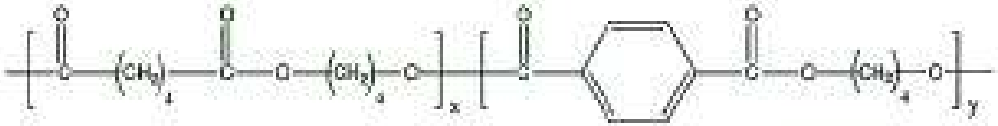
Aliphatic copolyesters (e.g., PBSA)



Bionolle
EnPol
Skygreen
Lunare SE

Showa Highpolymer (Japan)
Ire Chemical ltd (Korea)
SK Chemicals (Korea)
Nippon shokubai (Japan)

Aromatic copolyesters (e.g., PBAT)



Eastar Bio
Ecoflex
Biomax
Origo-Bi

Eastman Chemical (USA)*
BASF (Germany)
Dupont (USA)
Novamont (Italy)

(*) These polyesters productions have been stopped.

Commercially available biopolyesters: properties

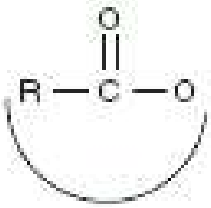
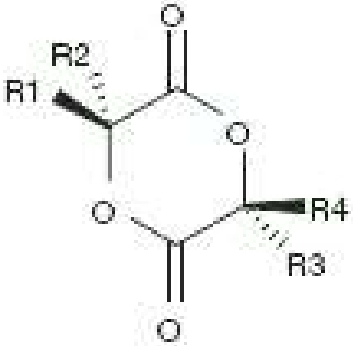
	PLA Dow–Cargill (NatureWorks)	PHBV Monsanto (Biopol D400G – HV = 7 mol%)	PCL Solvay (CAPA 680)	PEA Bayer (BAK 1095)	PBSA Showa (Bionolle 3000)	PBAT Eastman (Eastar bio 14766)
Density	1.25	1.25	1.11	1.07	1.23	1.21
Melting point (°C)[a]	152	153	65	112	114	110–115
Glass transition (°C)[a]	58	5	−61	−29	−45	−30
Crystallinity[b] (in %)	0–1	51	67	33	41	20–35
Modulus (MPa) (NFT 51-035)	2050	900	190	262	249	52
Elongation at break (%) (NFT 51-035)	9	15	>500	420	>500	>500
Tensile stress at break or max. (MPa) (NFT 51-035)	–	–	14	17	19	9
Biodegradation[c] (mineralization in %)	100	100	100	100	90	100
Water permeability WVTR at 25 °C ($g/m^2/day$)	172	21	177	680	330	550
Surface tension (γ) (mN/m)	50	–	51	59	56	53
γ_d (dispersive component)	37	–	41	37	43	43
γ_p (polar component)	13	–	11	22	14	11

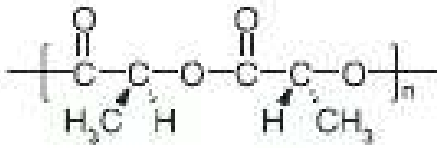
[a] Measured by DSC.
[b] Determined on granules, before processing.
[c] After 60 days in controlled composting according to ASTM 5336.

Synthesis of biodegradable polyesters

- A step-growth process or polycondensation
  - from a mixture of diol and diacid (or diacid derivatives)
  - from hydroxyacid
- Ring-opening polymerization (ROP)
  - of cyclic esters and related compounds

Ring opening polymerization

Monomer	Polymer	T_g (°C)	T_m (°C)
	Polylactone poly(ω-hydroxy acid)		
$R = -(CH_2)_2-$ βPL, β-propiolactone	PβPL	−24	93
$R = -(CH_2)_3-$ γBL, γ-butyrolactone	PγBL	−59	65
$R = -(CH_2)_4-$ δVL, δ-valerolactone	PδVL	−63	60
$R = -(CH_2)_5-$ εCL, ε-caprolactone	PεCL	−60	65
$R = -(CH_2)_2-O-(CH_2)_2-$ DXO, 1,5-dioxepan-2-one	PDXO	−36	-
$R = -(CH_2-CH(CH_3))-$ βBL, β-butyrolactone	PβBL isotactic	5	180
	PβBL actatic	−2	—
$R = -(C(CH_3)_2-CH_2)-$ PVL, pivalolactone	PPVL	−10	245
$R = -CH_2-CH(CO_2C_7H_7)-$ βMLABz, benzyl β- malolactonate	P(R,S)MLABz	25	—
	P(*R*)MLABz	20–25	150
	P(*S*)MLABz		
	Polydilactone		
			
$R_1 = R_2 = R_3 = R_4 = H$ GA, glycolide	Poly(α-hydroxyacid) PGA	34	225
$R_1 = R_4 = CH_3$, $R_2 = R_3 = H$ L,L-LA, L,L-lactide	PL,L-LA	55–60	170–190
$R_1 = R_4 = H$, $R_2 = R_3 = CH_3$ D,D-LA, D,D-lactide	PD,D-LA	55–60	170–190
$R_1 = R_3 = CH_3$, $R_2 = R_4 = H$ meso-LA, meso-lactide	Pmeso LA	45–50	—
D,D-LA/L,L-LA (50-50) D,L-LA, (D,L) racemic lactide	PDLLA	45–50	—

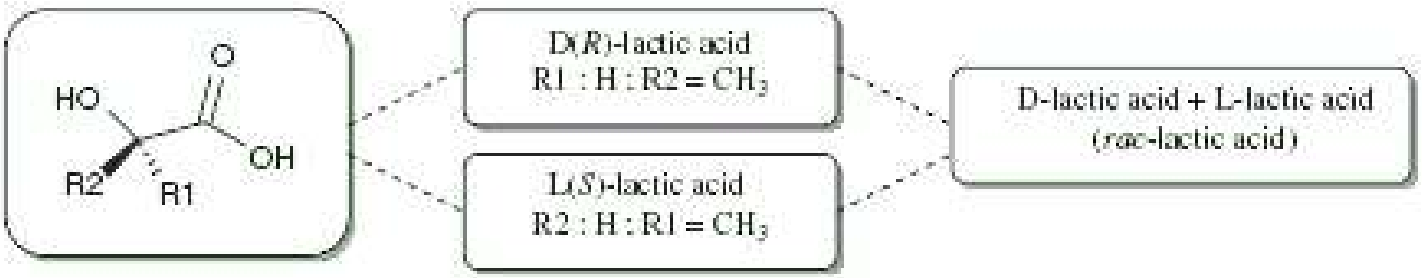


Polylactide (P(D,L)-LA)

Poly(ε-caprolactone) (PCL)

Poly(β-malic acid) (PMLA)

Lactic acid

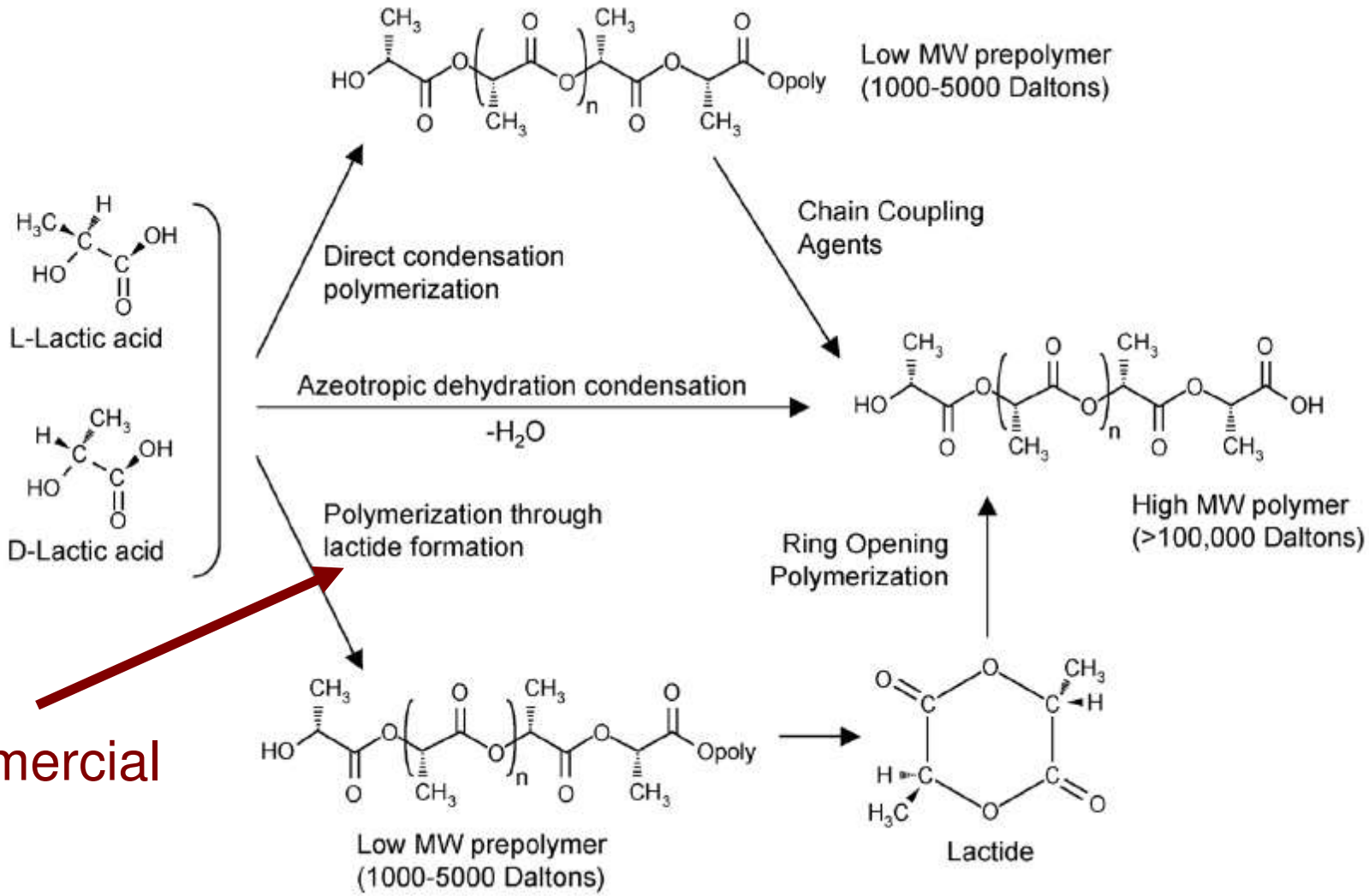


Routes to PLA

Direct condensation of lactic acid – single step

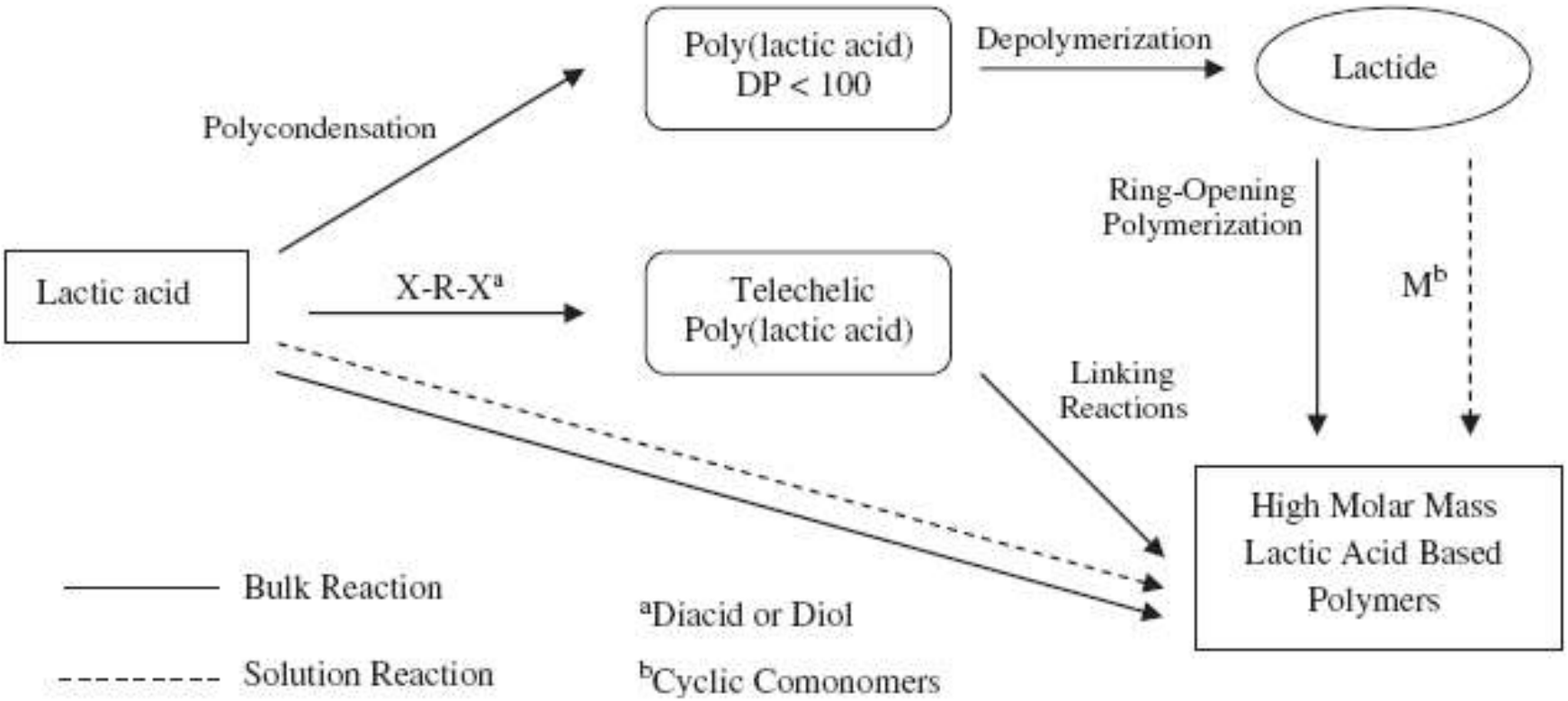
Ring opening polymerization- Multi step process

Routes to PLA



Commercial route

Routes to PLA



Production of PLA by Direct Condensation

- Equilibrium between free acid, water, and polyesters
- Difficulty in removing the trace amount of water in the late stages of poly

To overcome the above

Kinetic control over the reaction

Efficient removal of Water : Reletively high temperatures
Reduced pressure
Entraining agent such as various solvents

Suppression of De-polymerization

Production of PLA by ring opening polymerization

- Polymerization methods
  - solution polymerization
  - bulk polymerization
  - melt polymerization
  - suspension polymerization
- Polymerization mechanism
  - ionic
  - coordination
- Catalysts
  - by transition metal compounds of tin, aluminum, lead, zinc, bismuth, iron, yttrium
  - by metal-free catalysts such as DMAP, Pph3, N-heterocyclic carbenes and enzymes

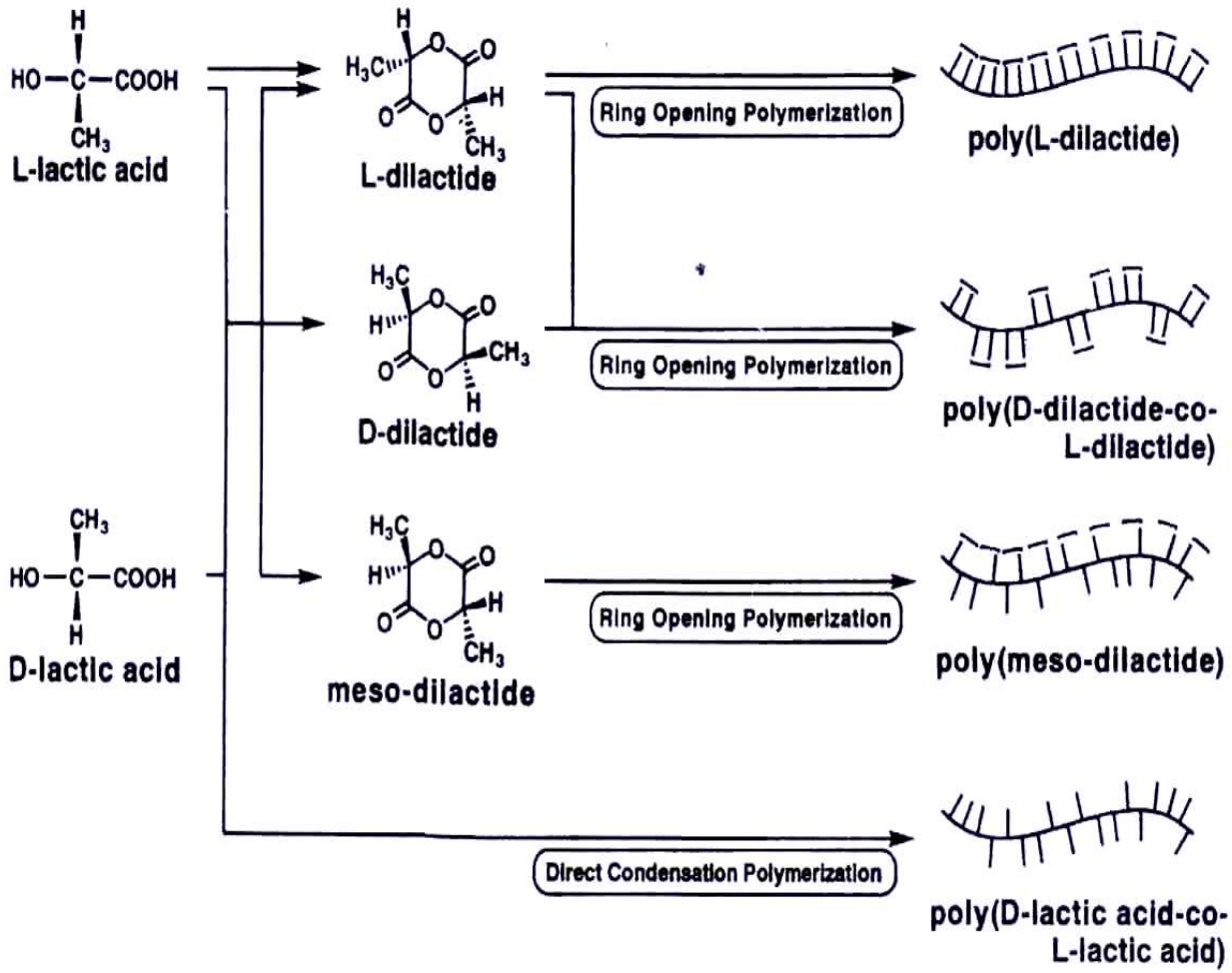
PLA polymerization

S.No.	Polymer	Catalyst	Solvent(s)	Reaction temp. °C	Reaction time	Molecular weight	Reference
1	D,L PLA L-PLA	Al Isopropoxide	Toluene	70–100	Up to 100 hrs.	$M_n > 90{,}000$	Dubois et al. (35)
2	L-PLA	Stannous octoate	Glycerol	130	6 hrs.	$DP_n = 43\text{-}178$	Han et al. (36)
3	D-L PLA L-PLA	Stannous octoate	Alcohols	200	60–75 min.	$M_w < 3{,}50{,}000$	Korhonen et al. (37)
4	L-PLA D-L PLA	Stannous octoate	Alcohols, carboxylic acid	130	2–72 hrs.	$M_n < 250{,}000$	Zhang et al. (38)
5	L-PLA	Stannous octoate	No solvent	130	72 hrs.	$M_v: = 20{,}000\text{–}680{,}000$	Hyon et al. (39)
6	L-PLA	Stannous octoate and triphenylamine	No solvent	180–185	7 min.	$M_n = 91{,}000$	Jacobsen et al. (40)
7	L-PLA D-L PLA	Stannous octoate and compounds of titanium and zirconium	Toluene	180–235	15–180 min.	$M_n = 40{,}000\text{–}100{,}000$	Rafier et al. (41)
8	D-PLA L-PLA D-L PLA	Stannous trifluoromethane sulphonate, Scandium(III) trifluoromethane sulfonate	Ethanol	40–65	50–100 hrs.	$DP_n = 15\text{–}30$	Moller et al. (42)
9	L-PLA	Sn substituted mesoporous silica molecular sieve	No slovent	130	72 hrs.	$M_n < 36{,}000$	Fattah et al. (43)
10	L-PLA	Mg, Al, Zn, Titanium alkoxides	Methylene chloride	100	—	$DP_n < 400$	Kricheldorf (44)

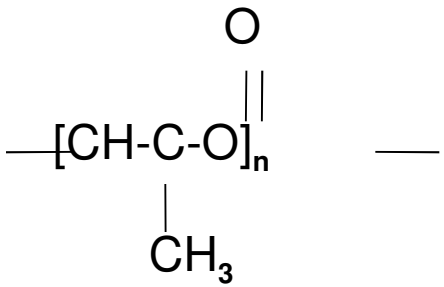
PLA polymerization

S.No.	Polymer	Catalyst	Solvent(s)	Reaction temp. °C	Reaction time	Molecular weight	Reference
11	L- PLA	Yttrium tris(2,6-di-tert butyl phenolate) (in toluene)	2-propanol, butanol, ethanol	22	2–5 min.	$M_n < 25{,}000$	Stevels et al. (45)
12	D-L PLA	Butyl lithium, butyl magnesium (in hexane)	THF	—	30 min	$M_n < 45{,}000$	Kasperczyk et al. (33)
13	D-L PLA	Zn lactate	No solvent	140	96 hrs.	$M_n = 212{,}000$	Schwach et al. (46)
14	D-L PLA L-PLA	Butylmagnesium, Grignard reagent	Ethers	0–25	4–8 days	$M_n < 300{,}000$	Kricheldorf et al. (47)
15	L-PLA	Potassium naphthalenide	THF, toluene	40	48–120 hrs.	$M_n < 16{,}000$	Stere et al.(48)
16	L-PLA	Complexes of iron with acetic, butyric, siobutyric and dichlor-oacetic acids	No solvent	170–210.	0.5–25 hrs.	$M_w = 150{,}000$	Stolt et al. (49)
17	D-L PLA	(Trimethyl triazacyclohexane) praseodymium triflate	No solvent	120–200	18 hrs.	$M_v = 10{,}000–20{,}000$	Kohn et al. (50)
18	D-L PLA	Lanthanum isopropoxide	Dichloromethane/ toluene (70/30)	21	30 min.	$M_n = 5300–21{,}900$	Save et al. (51)
19	PLA (type not specified)	Lead monoxide, lead stearate, basic lead carbonate, antimony trioxide, zinc oxide, zinc borate, cadmium oxide, titanyl stearate, magnesium oxide and calcium formate	No solvent	140–180	10–111 hrs.	IV (in benzene) = 1.21	Schneider et al. (16)

Polymerization scheme of copolymers from L-lactic acid and D-lactic acid



General properties of Polylactic acid

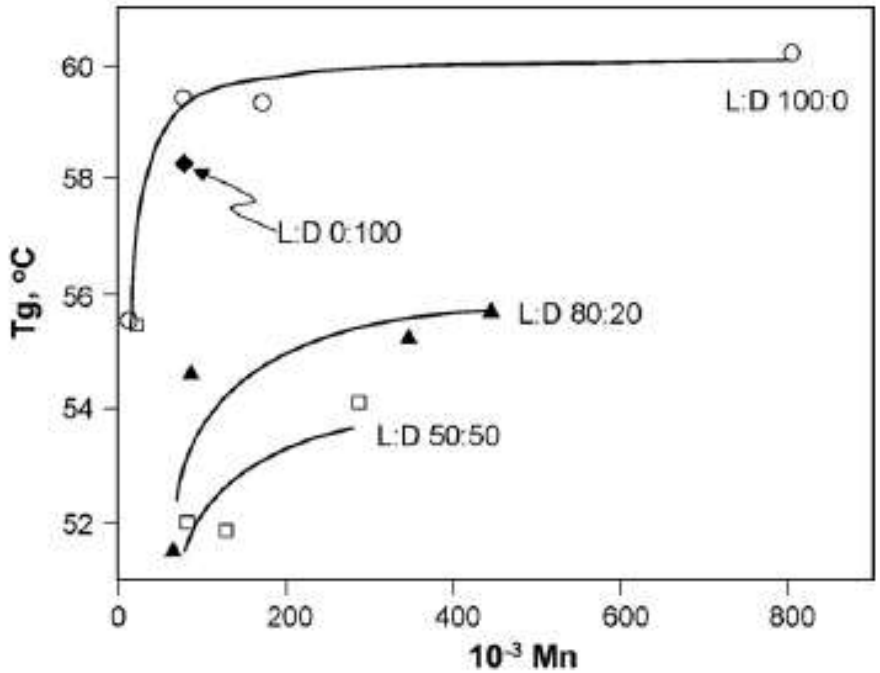


- Transperancy
- Glass Transition temperature 50-60^{0}C
- Melting Point 130-180^{0}C
- Crystallinity : 35-40 %
- Tensile Strength : 4-6 Kg/mm^2
- Elongation : 3-4 %, brittle
- Flexural Strength : 9~11 Kg/mm^2
- Impact Strength :~50 Kg-cm/cm^2

Crystallization in PLA:

- α structure - more stable with melting temperature of 185 C
- β structure with melting temperature of 175 C
- > 90 % L – content crystallizes more

Thermal transitions with molecular weight / copolymers



Copolymer ratio	Glass transition temperature (°C)	Melting temperature (°C)
100/0 (L/D,L)-PLA	63	178
95/5 (L/D,L)-PLA	59	164
90/10 (L/D,L)-PLA	56	150
85/15 (L/D,L)-PLA	56	140
80/20 (L/D,L)-PLA	56	125

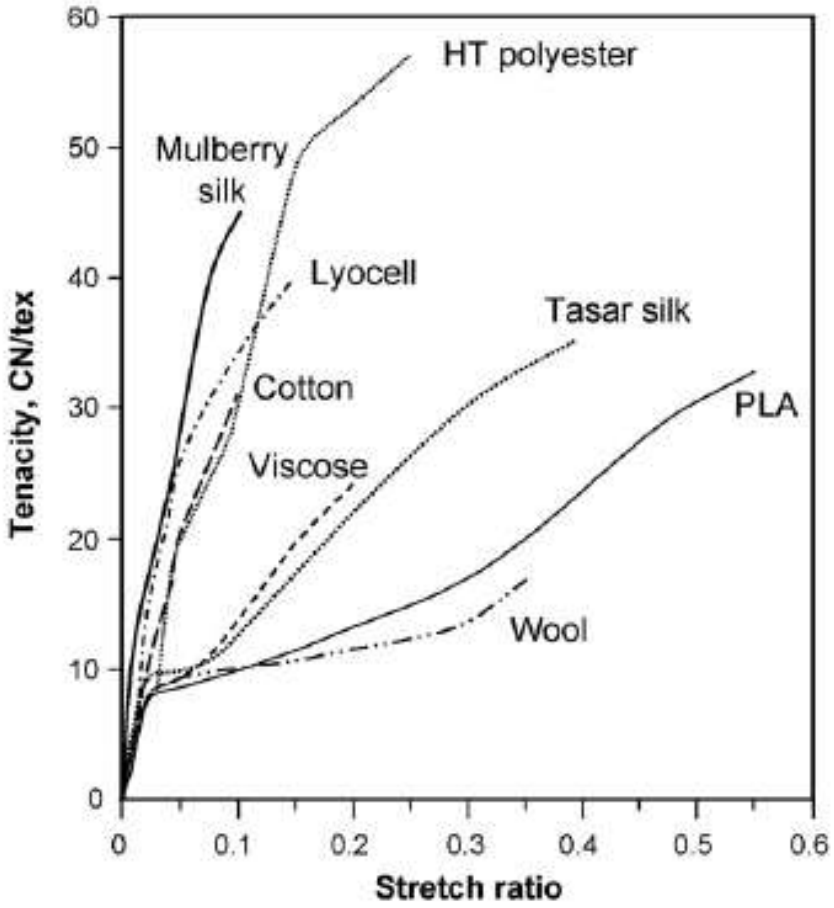
Properties of PLA: comparison

- PLA
  - reasonably good optical, physical, mechanical, and barrier properties compared to existing petroleum-based polymers
- The permeability coefficients
  - of CO_2, O_2, N_2, and H_2O for PLA are lower than for polystyrene (PS), but higher than poly(ethylene terephthalate) (PET)
  - The barrier properties of PLA against organic permeants such as ethyl acetate and d-limonene, are comparable to PET
- Mechanical properties
  - unoriented PLA is quite brittle, but possesses good strength and stiffness
  - Oriented PLA provides better performance than oriented PS, but comparable to PET
  - Compared to high density polyethylene (HDPE), polypropylene (PP) and PS
    - Tensile and flexural moduli of PLA are higher
    - Izod impact strength and elongation at break values are smaller

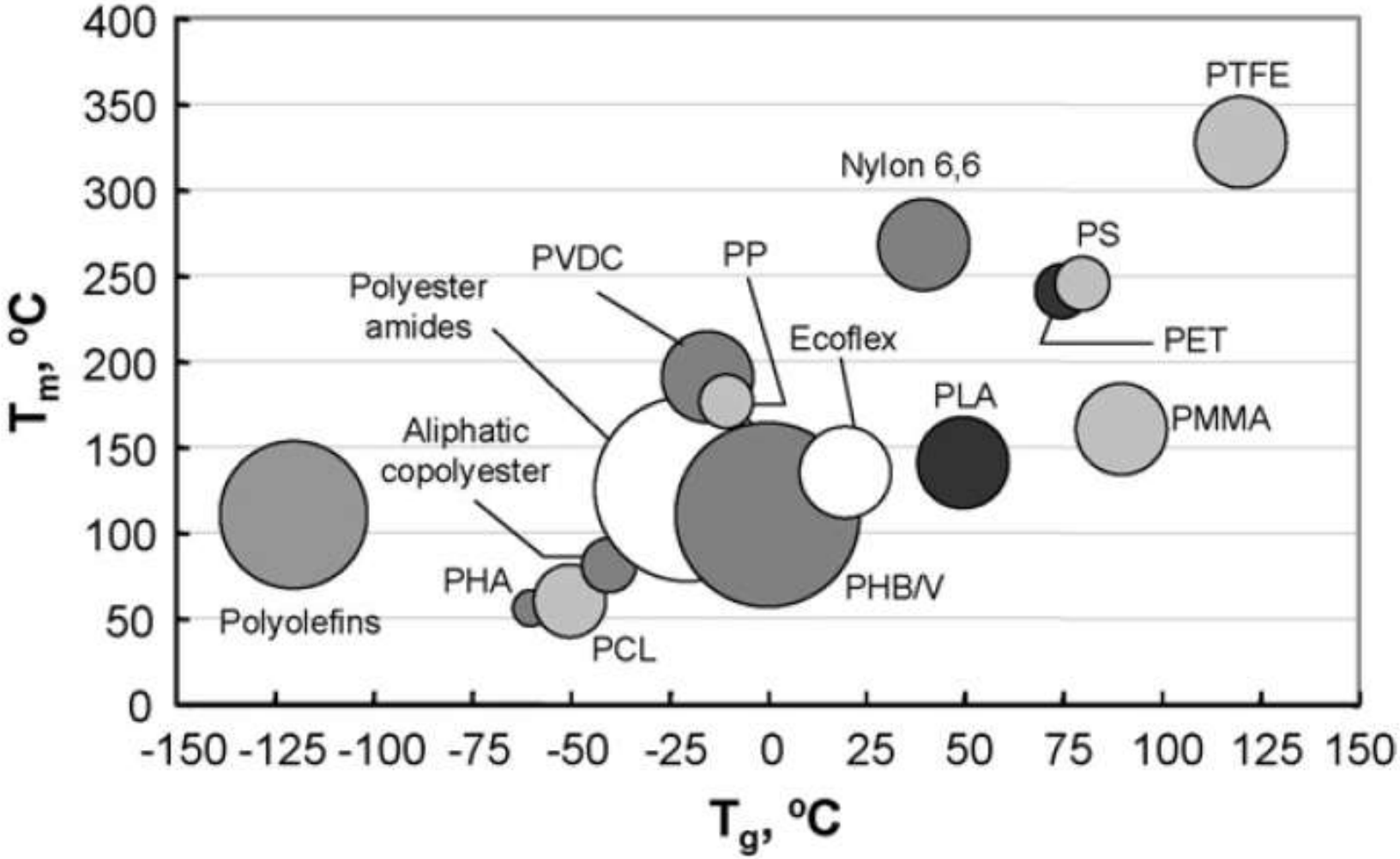
Biaxially oriented films

	PLA	PP	PET	Nylon	Cellophane
Density, g/cc	1.25	0.9	1.4	1.2	1.45
Haze, %	2.1	1–4	2–5	2–3	1–2
Tensile str., psi, MD,	15,950	27,550[a]	29,725[a]	36,250	13,050[a]
Tensile mod., psi, MD	478,500	348,000	551,000[a]	264,625	594,500[a]
Ult. elongation, %, MD	160	110[a]	140[a]	125[a]	23[a]
Tear, g/mil, MD	15	4–6	18	13	4

PLA fibers


HT polyester
Mulberry silk
Lyocell
Tasar silk
Cotton
PLA
Viscose
Wool
Tenacity, CN/tex
Stretch ratio
0
10
20
30
40
50
60
0
0.1
0.2
0.3
0.4
0.5
0.6

PLA properties: comparison



Processing of PLA

- Drying and extrusion
- Processing methods
  - Injection molding
  - Stretch blow molding
  - Cast film and sheet
  - Extrusion blown film
  - Thermoforming
  - Foaming
  - Fiber spinning
  - Electrospinning of ultrafine fibers

Outline

- Polymers
- Polymerization
  - methods
  - reactors
- Biodegradable polymers
  - Poly lactic acid
    - polymerization
    - processing
- Possibilities
  - composites
  - rheology

POLYMERIC COMPOSITES

Polymer Matrix + Reinforcement + Additives

↓

Thermoplastics

- *Linear or branched*

Thermosets

- *Crosslinked*

Processing

- ❑ *Prepreg / pellets*
  Matrix + Fibers
- ❑ *Bonding / Fusing*
  Heat + Pressure

- ❑ *Fiber preforms + Resin injection*
- ❑ *Prepregs / Charge (moulding compound)*
  Partially cured resin + Fibers
- ❑ *Reaction and Bonding*
  Heat + Pressure

Fiber Forms: Short, long, continuous, fabric, mat, 3-d Preform

Polymer Matrices : Some Examples

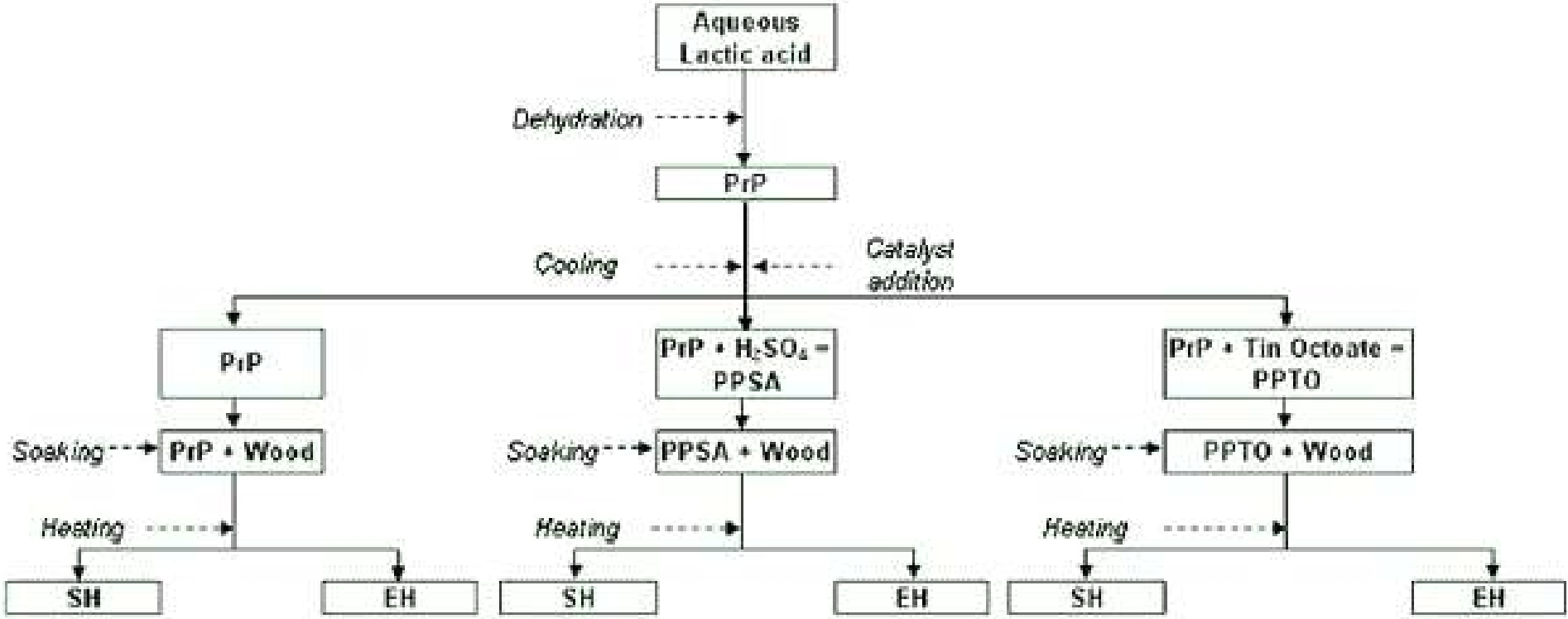
Composite Matrix Resin Classifications

- Resin (or matrix) type
  - Thermoset resins- those that undergo a chemical cross-linking reaction
    - Epoxy: reaction of bisphenol A and epichlorohydrin
    - Polyester: reaction of difunctional acid (or anhydride) and a difunctional alcohol (glycol)
    - Polyurethane: reaction of alcohol and isocyanate
    - Phenolic
    - Silicone
    - Melamine
  - Thermoplastic resins- those that are formed under heat
    - Polyamines (nylon) (short and long fibers)
    - Polyesters (short and long fibers)
    - Polypropylene (short, long fibers and continuous fibers)
    - Other thermoplastic resins (short and long fibers)
      - **High performance thermoplastics, PEEK**

Additives and Reinforcements to Polyesters

- Additives-
  - UV stabilizers, colorants, heat stabilizers, blowing agents
  - Catalyst, inhibitors, promotors
- Fillers
  - Talc
  - Calcium carbonate
- Reinforcements
  - Glass fiber- short fiber (1/8" or long fiber 1/4")
  - Mineral fiber (wolastonite)
  - Mica
  - carbon fibers

PLA wood composites

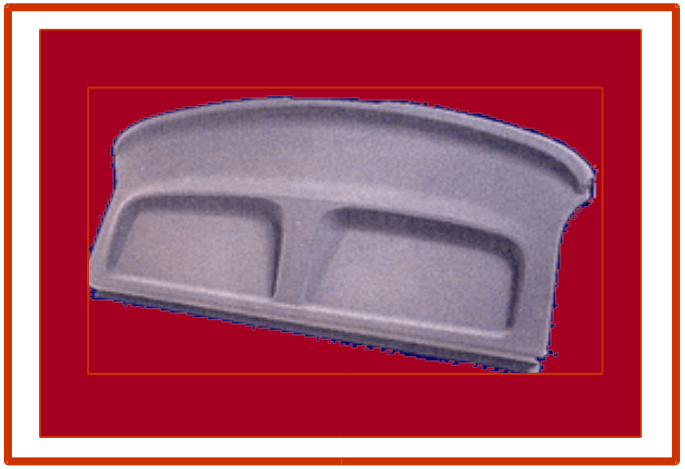


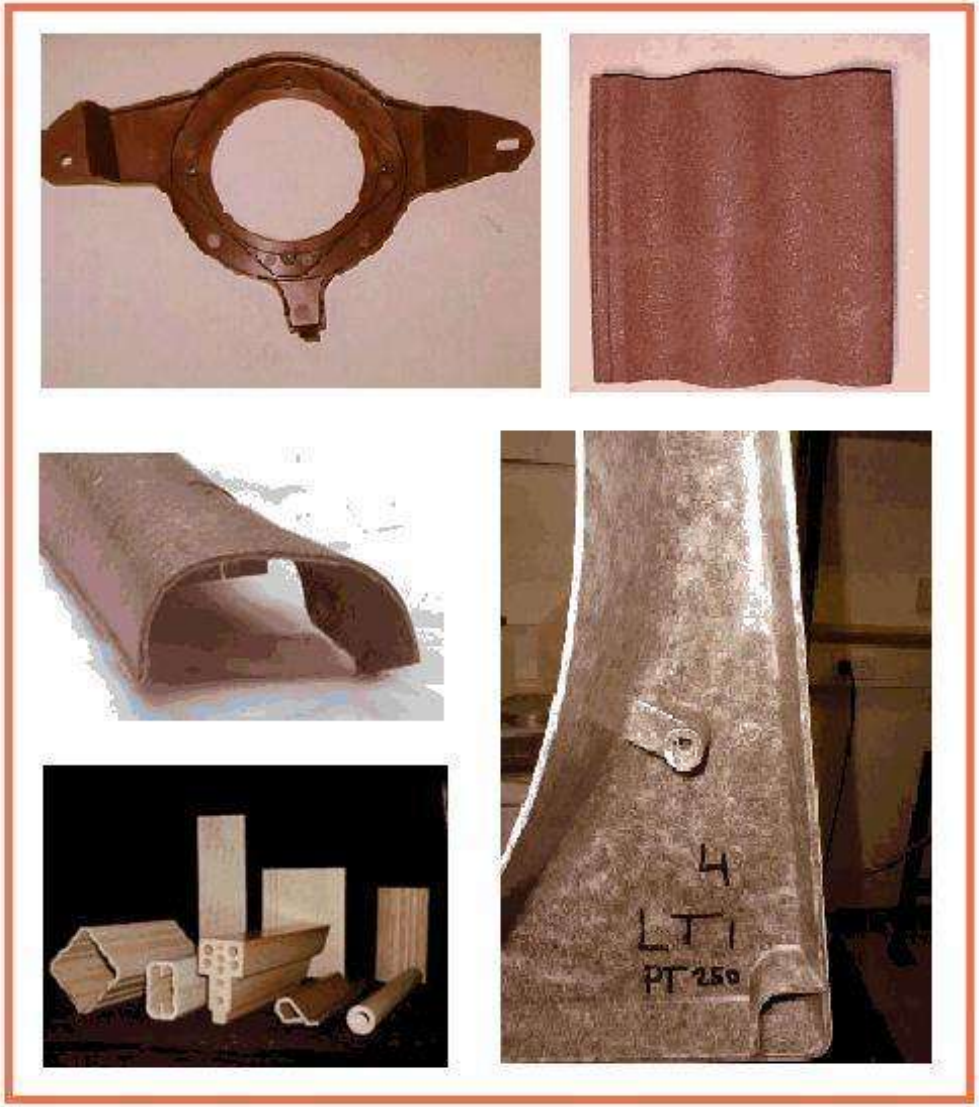
short heating extended heating

Natural fibers

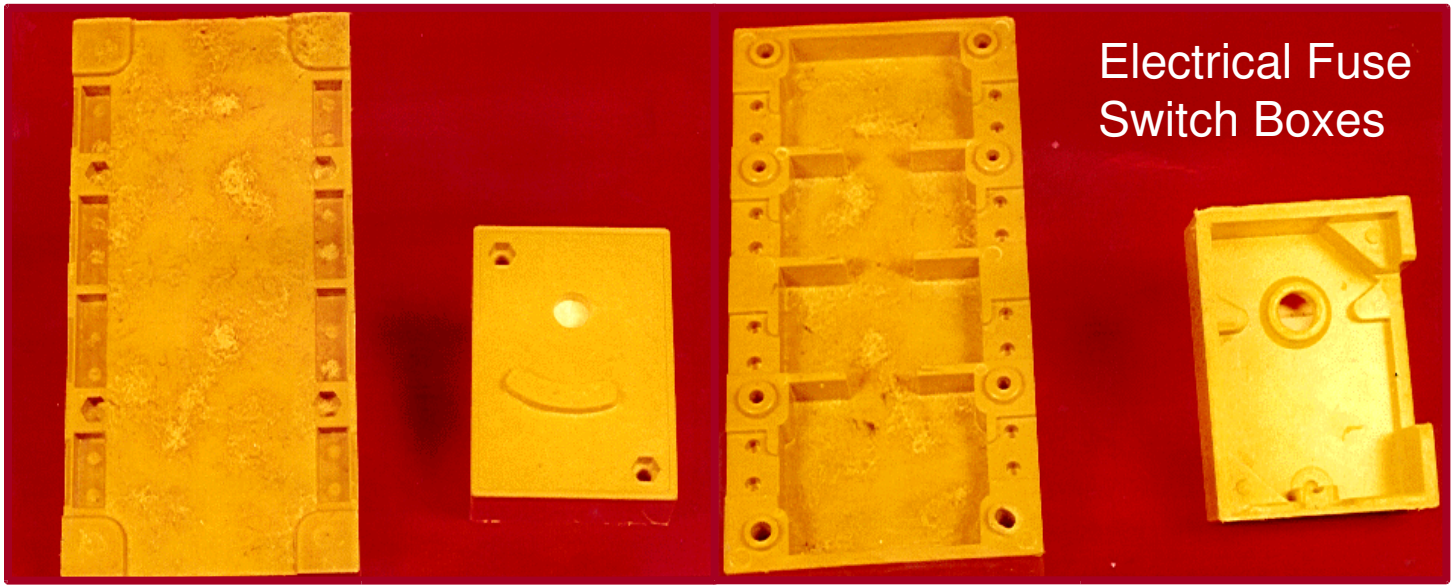
Fibre	Sp.gr.	Specific tensile strength (GPa)	Specific tensile modulus (Gpa)	Cost (US$/tonne)	Energy content GT/tonne
Plant Fibre	0.6-1.2	1.60-2.95	10-130	200-1000	4
Glass	2.6	1.35	30	1,200-1,800	30
Kevlar	1.4	2.71	90	7,500	25

NATURAL FIBER COMPOSITES: APPLICATIONS



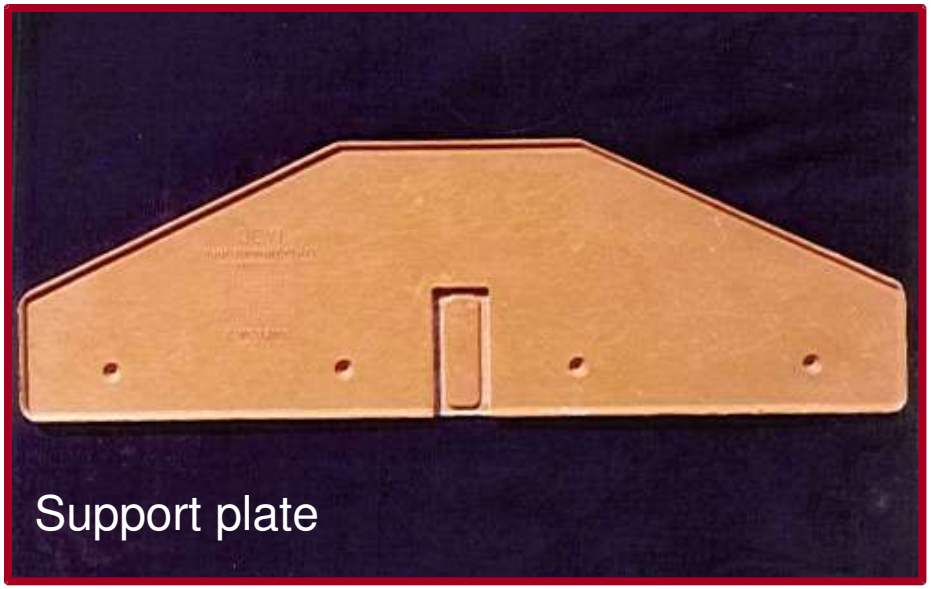


Polyester – sisal / jute composites

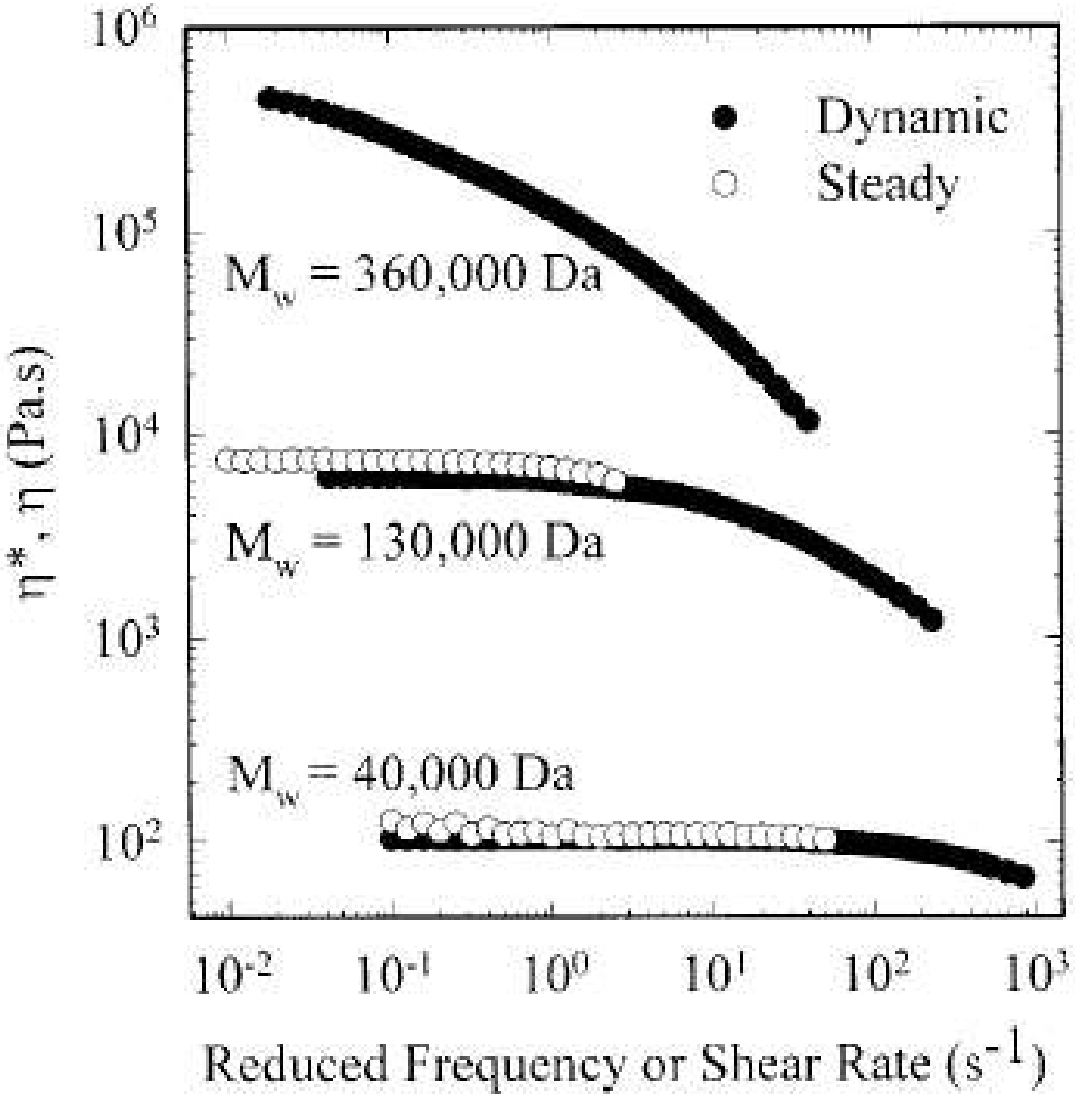


Processing Conditions:

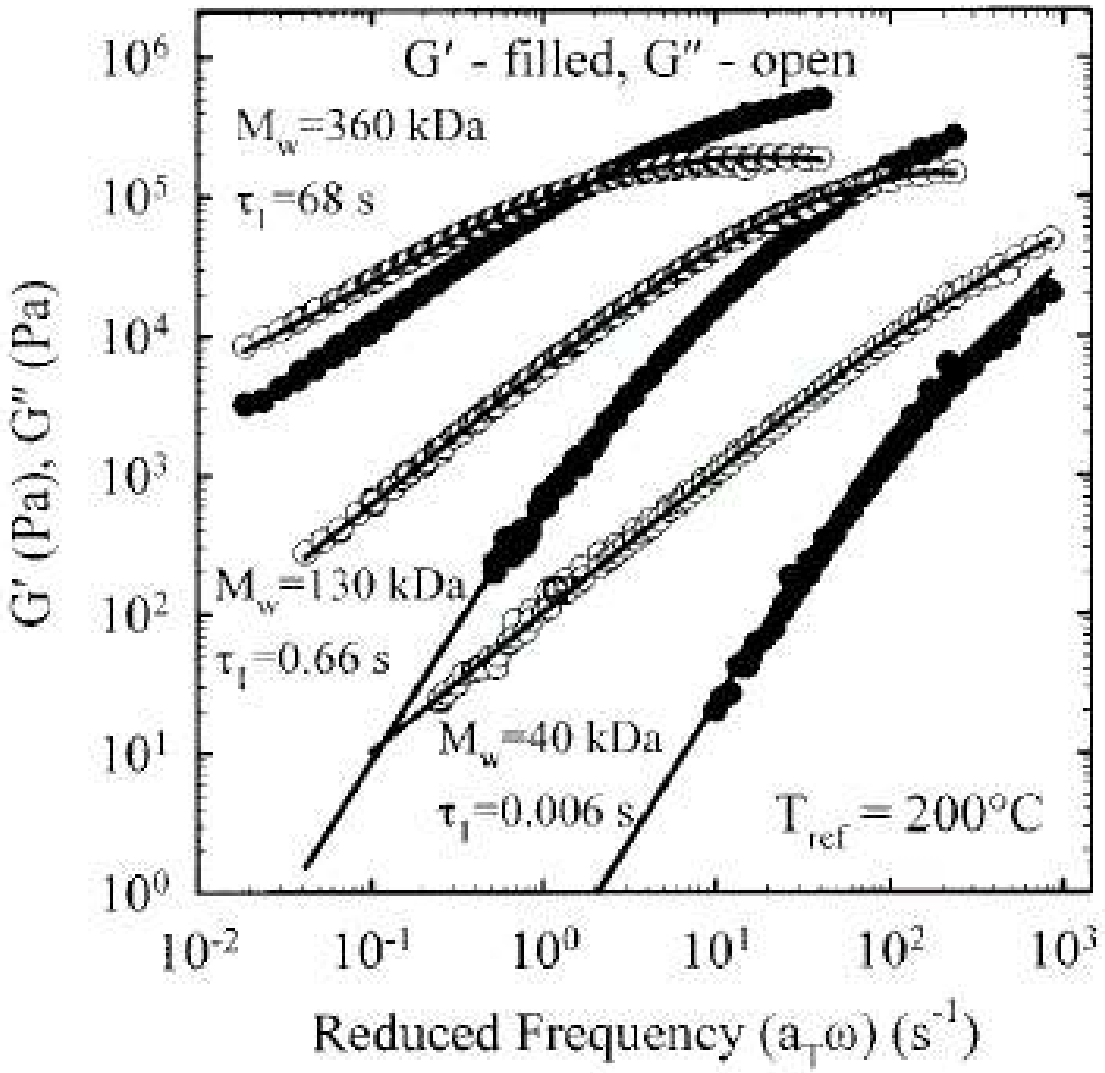
Temperature:	130 ºC
Pressure:	3 MPa
Time:	5 min



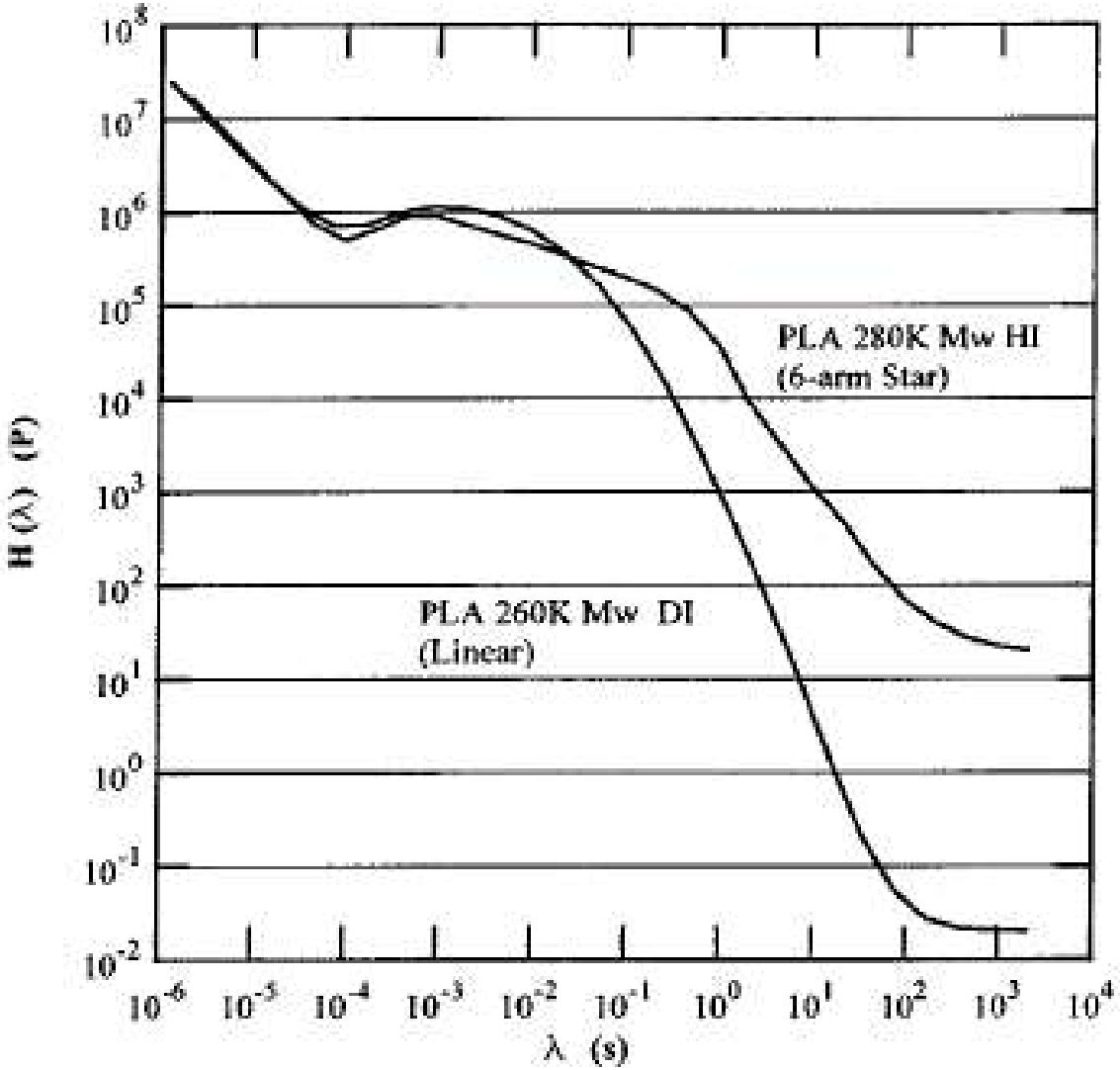
Viscosity with PLA molecular weight



Viscoelasticity with PLA molecular weight



Viscoelasticity with PLA architecture

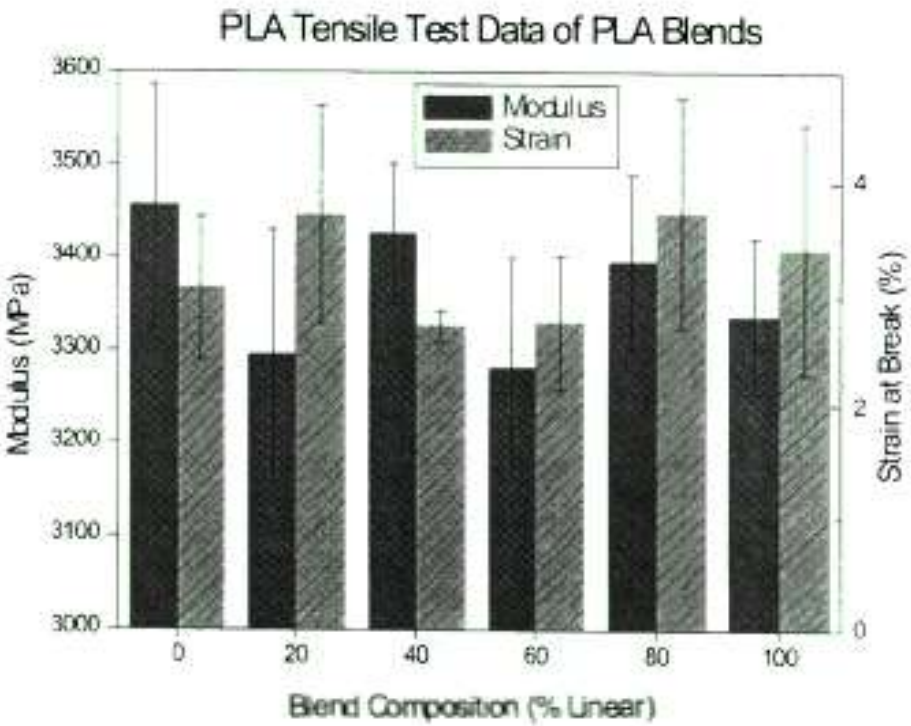


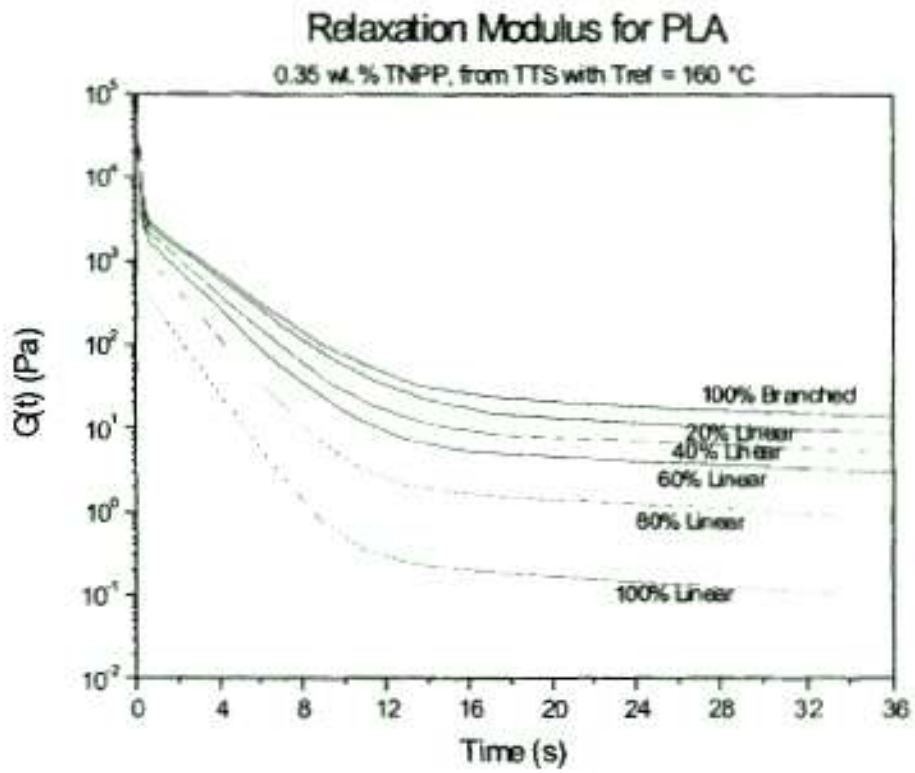
Relaxation time spectrum

Linear and branched PLA

- Cargill-Dow Polymers
- melt polymerization with stannous octoate
- LD ratio of 96:4
- peroxide initiated crosslinking for branching
- Tris(nony1-phenyl) phosphite (TNPP) stabilizer
  - TNPP acts as a chain extender reconnecting polymer chains that have broken due to moisture and elevated testing temperatures

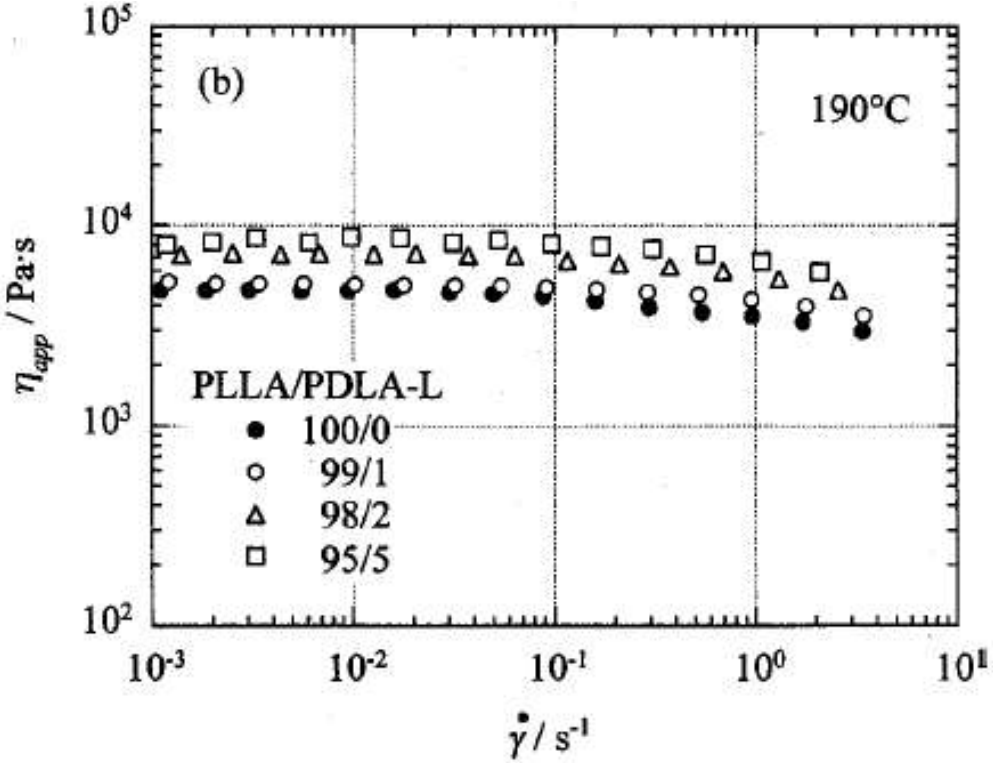
Linear and branched PLA



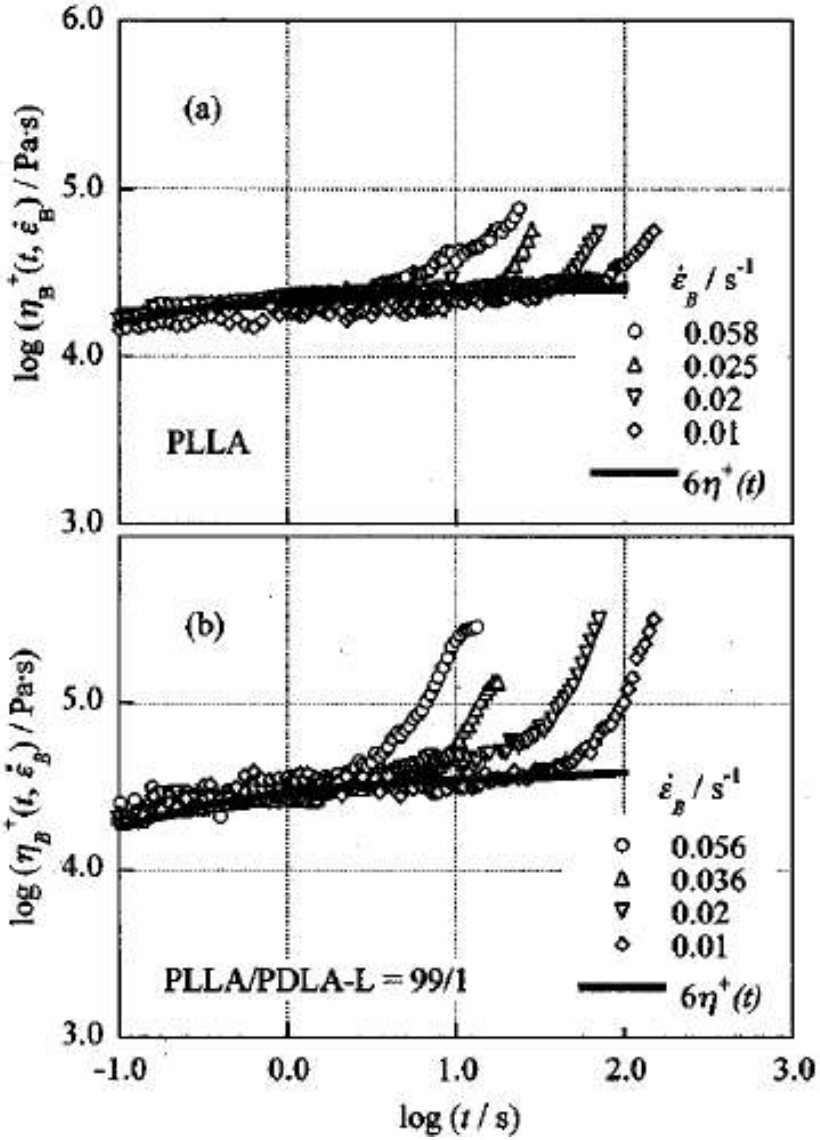


PLA blending

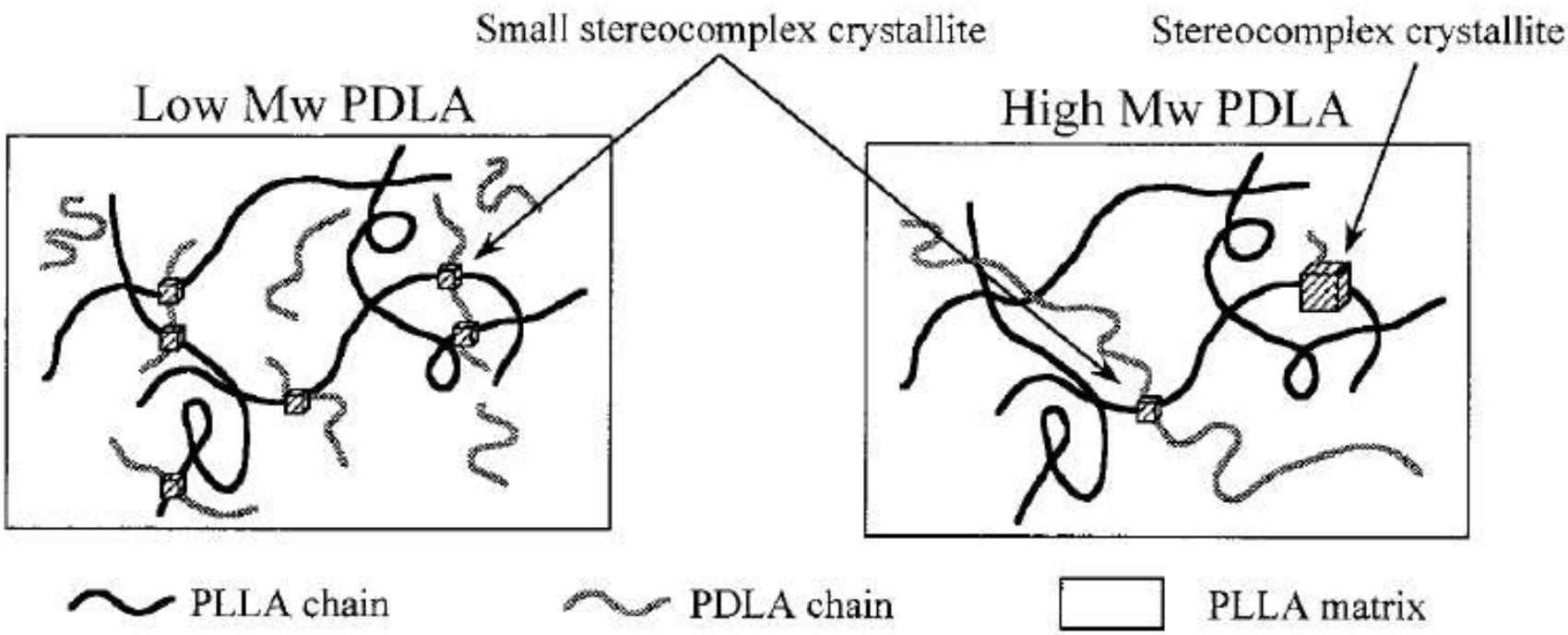
Sample	M_w	M_w/M_n
PLLA	2.3×10^5	2.30
PDLA–L	4.5×10^4	1.51
PDLA–H	2.6×10^5	1.60



PLA blending: biaxial stretching



PLA blending: biaxial stretching



Introduction of the long chain branching.
Increase in molecular weight.

Introduction of few long chain branching.
Appearance of the stereocomplex crystal.

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