EMAC 276 Polymer Properties and Design

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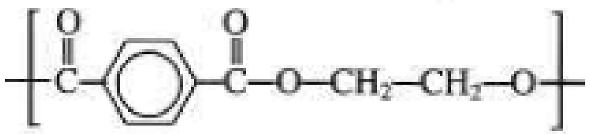
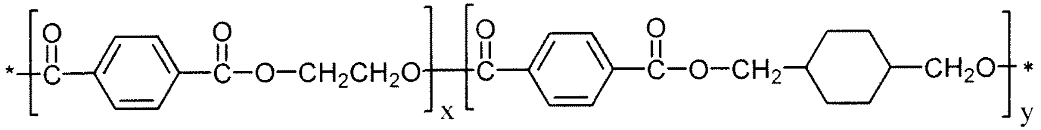
MWF 10:35-11:25 am
Spring 2025

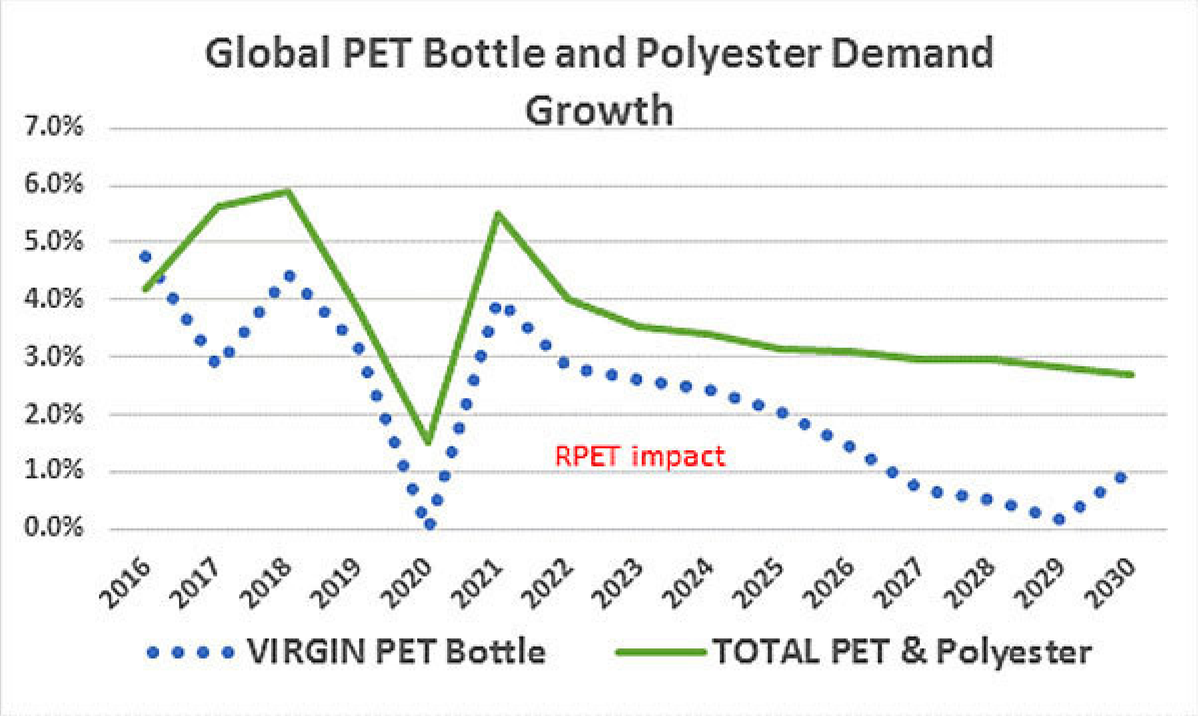
Polyesters – Poly(ethylene terephthalate) (PET)

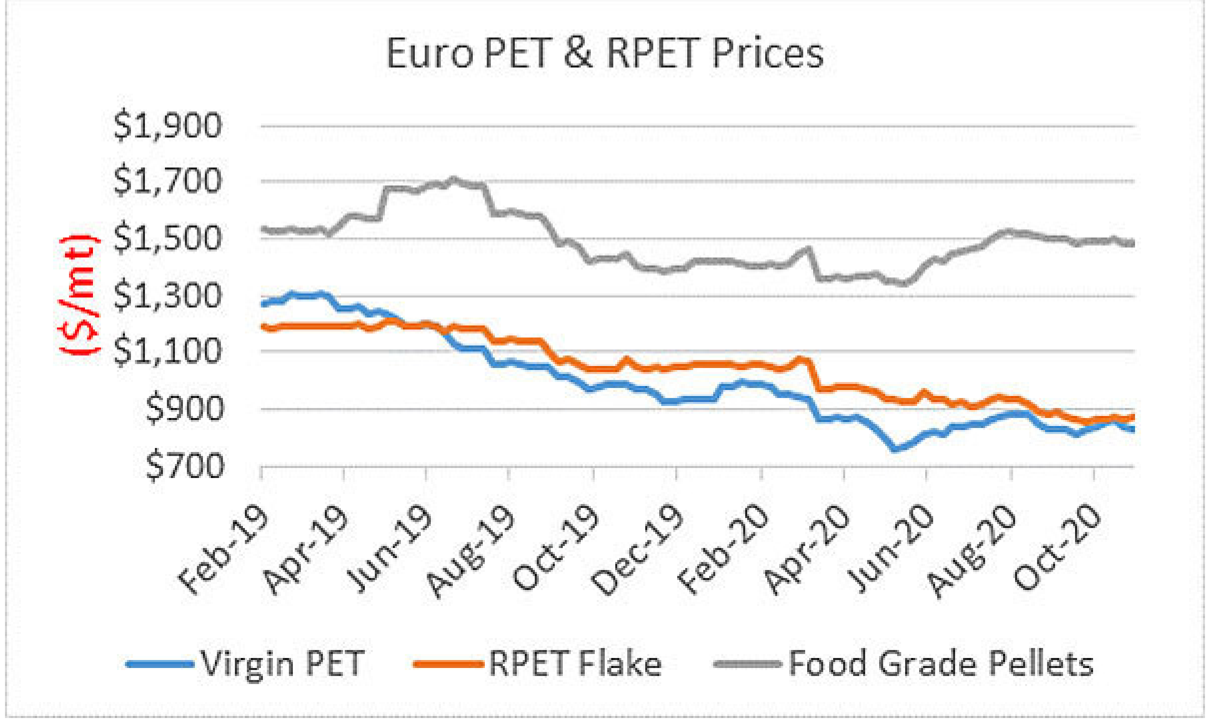


Homopolymers and copolymers (e.g., PETG)
"G" means other "glycols"



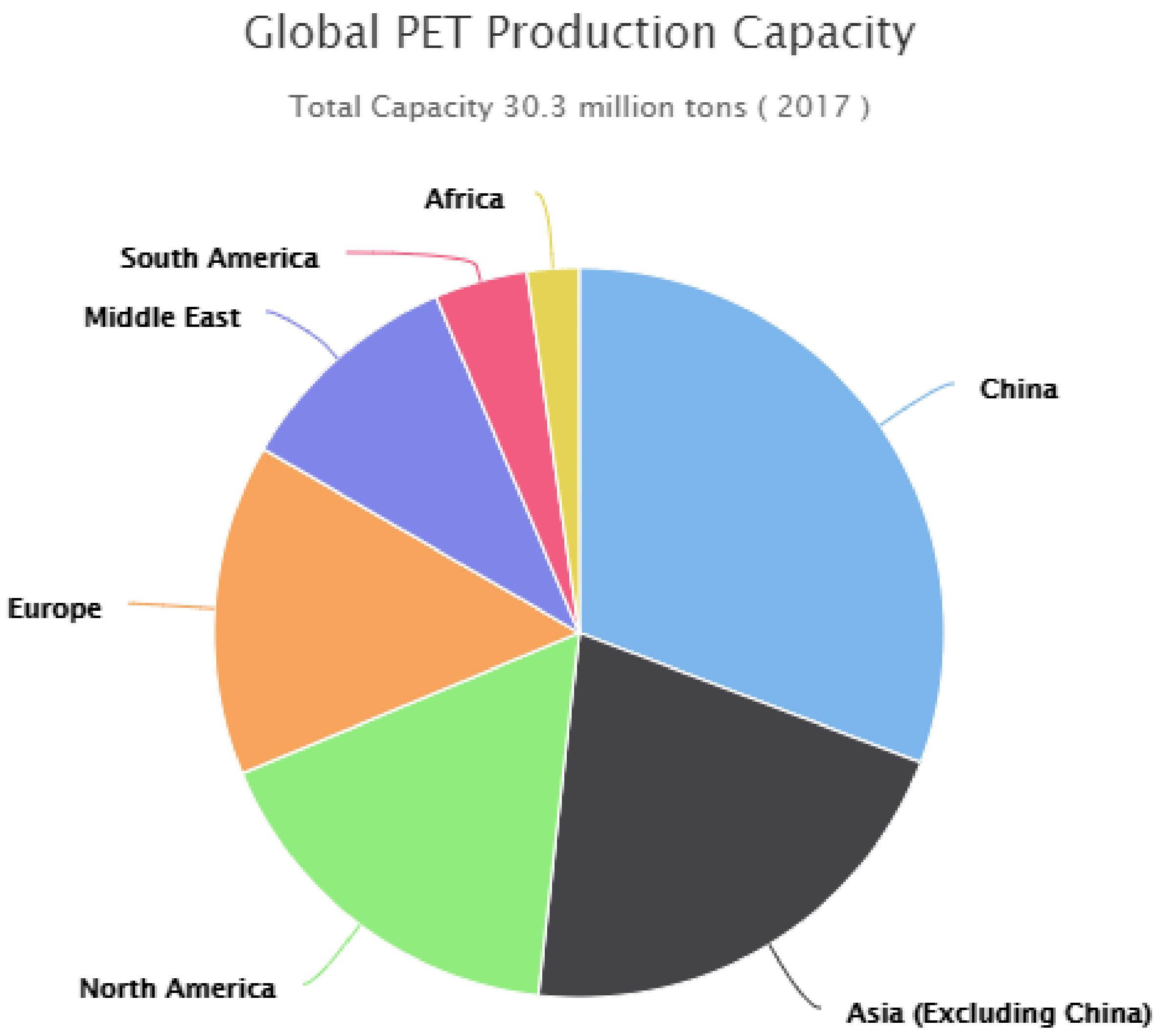
PETG

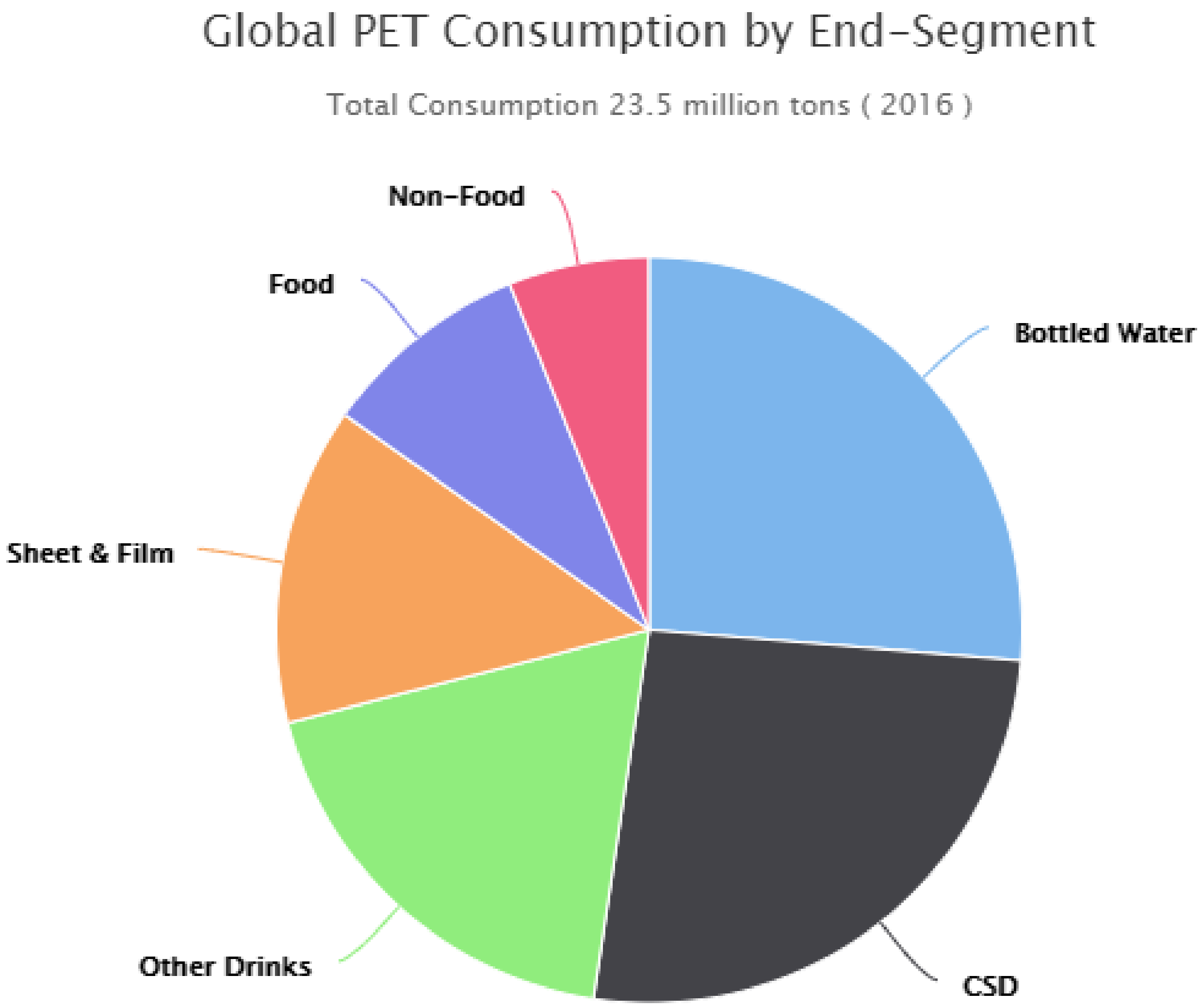




https://www.prnewswire.com/news-releases/sp-global-platts-to-assess-prices-for-food-grade-recycled-pet-packaging-pellets-301173672.html

World PET Resin Production and Consumption





carbonate soft drink (CSD)

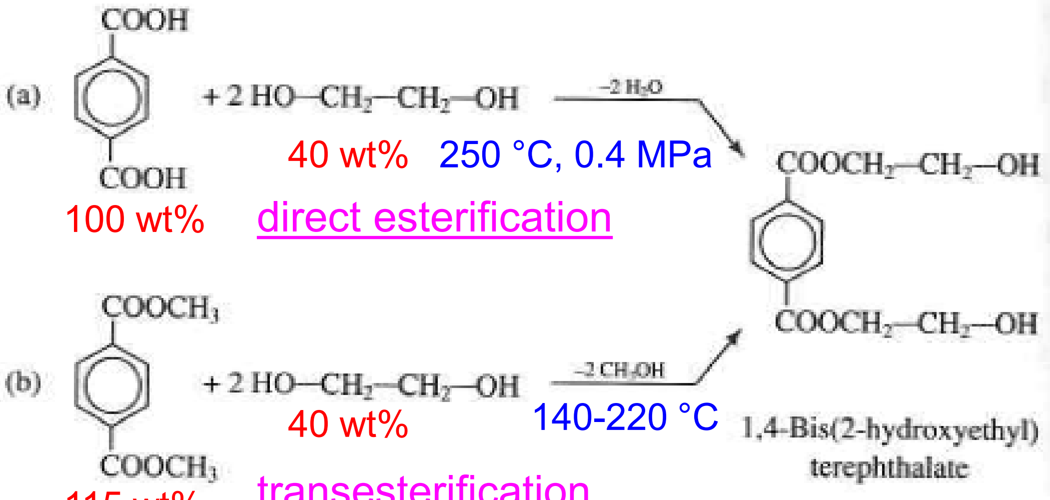
https://www.plasticsinsight.com/resin-intelligence/resin-prices/polyethylene-terephthalate/

Typical PET Synthesis

Step I:

Method (a)

Method (b)



100 wt% 40 wt% 250 °C, 0.4 MPa

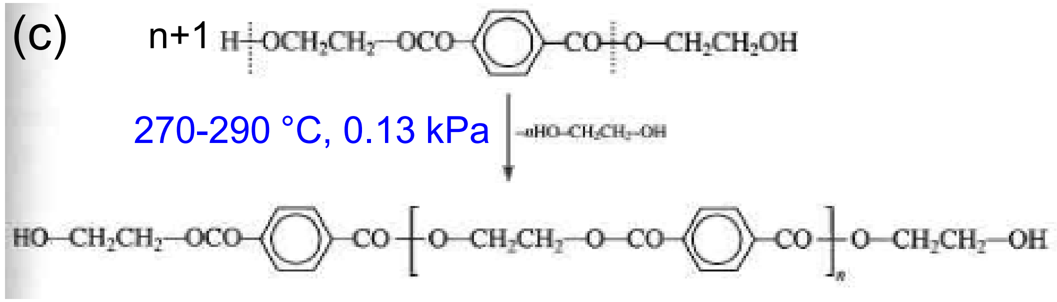
direct esterification

115 wt% 40 wt% 140-220 °C

transesterification

Step II:

(c) n+1



270-290 °C, 0.13 kPa

Molecular weight:

20 kDa for textile fibers

30 kDa for bottles and tire cord

Method (a) Method (b)

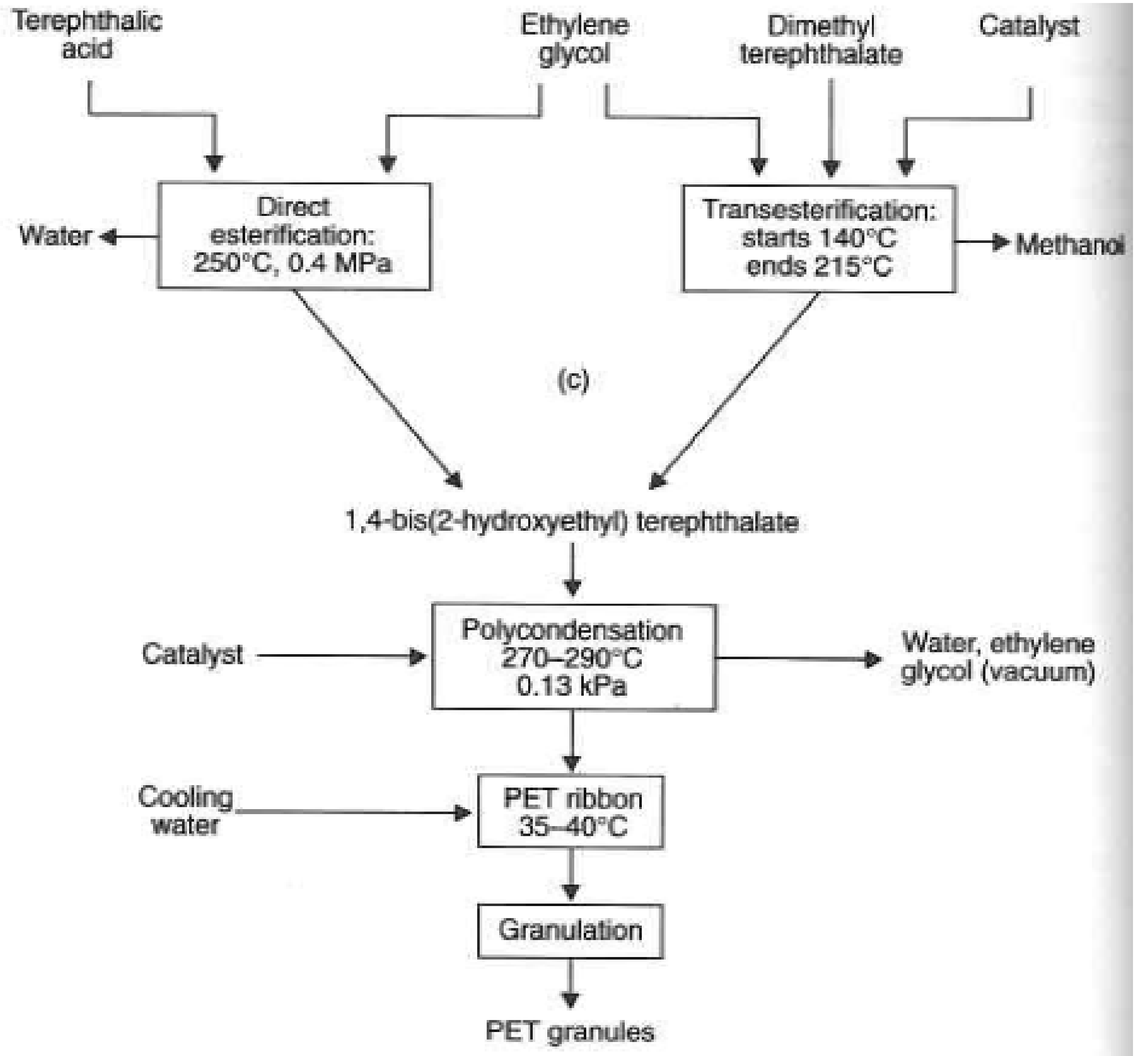
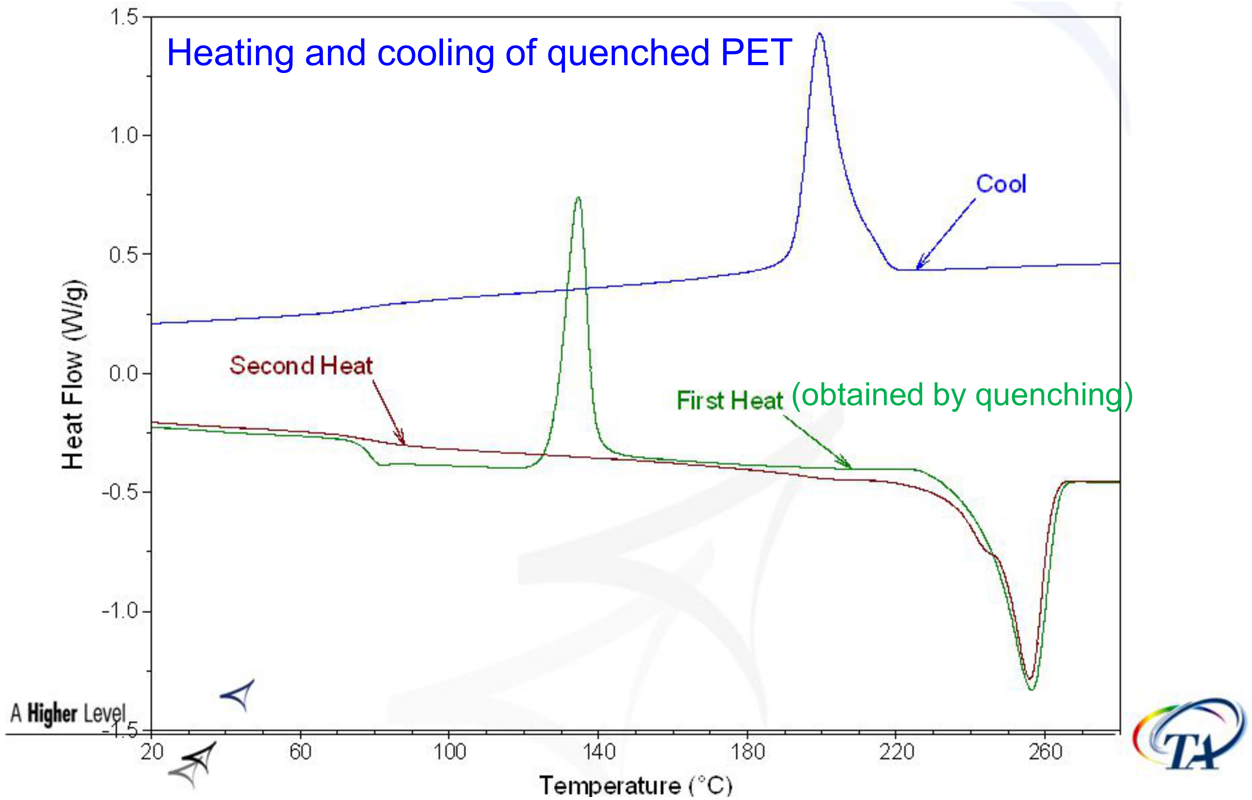


Figure 4.1 Preparation of poly(ethylene terephthalate).

Typical PET Properties: Thermal, Mechanical, Electrical

Glass transition temperature T_g	K	DSC	(72-100°C) 342–388
Melting temperature T_m	K	DSC	(255-265°C) 538
Heat of fussion ΔH	kJ mol^{-1}	DSC	24.1
Breaking strength σ_B	MPa	Tensile	50
Tensile (Young's) modulus E	MPa	–	1,700
Flexural modulus (rigidity) E	MPa	3-point flexure	2,000
Ultimate strain ε_B	%	Tensile	180
Yield strain ε_Y	%	Tensile	4
Impact strength	J m^{-1}	Notched Izod, ASTM D256-86	90
Hardness	–	Rockwell	R105
Deflection temperature	K	HDT	
		At 264 psi	336
		At 66 psi	344
Thermal expansion coefficient α	K^{-1}	TMA	9.1×10^{-5}
Water absorption	%	After 24 h	0.5
Dielectric strength	kV mm^1	Thermal	
		1/8 in	15.7
		1/16 in	22.1
		Electrical; ASTM D149	26
Dielectric constant	10^6 Hz	Thermal	3.2
		Electrical; ASTM D150	3.3
Volume resistivity	ohm cm	ASTM D257	0.1×10^{16}

Crystallization Behavior

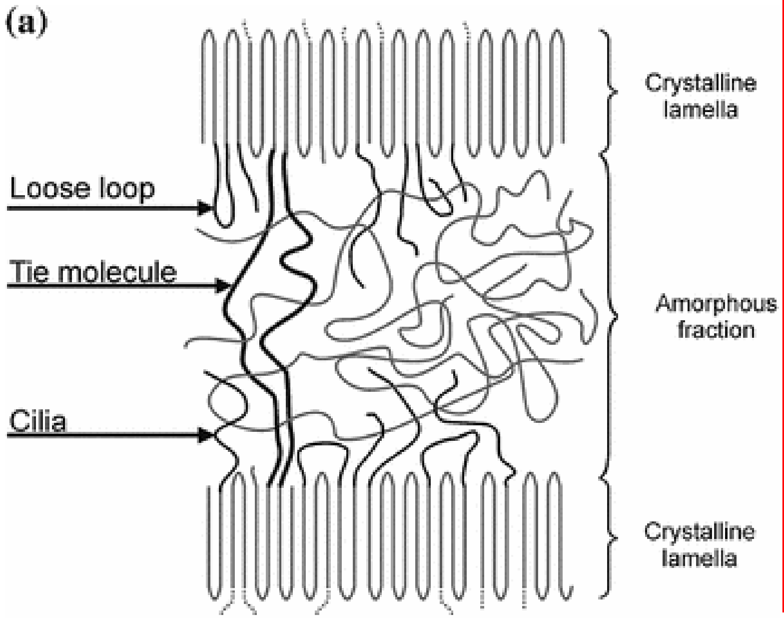


https://www.americanlaboratory.com/914-Application-Notes/132221-Differential-Scanning-Calorimetry-DSC-as-an-Analytical-Tool-in-Plastics-Failure-Analysis/

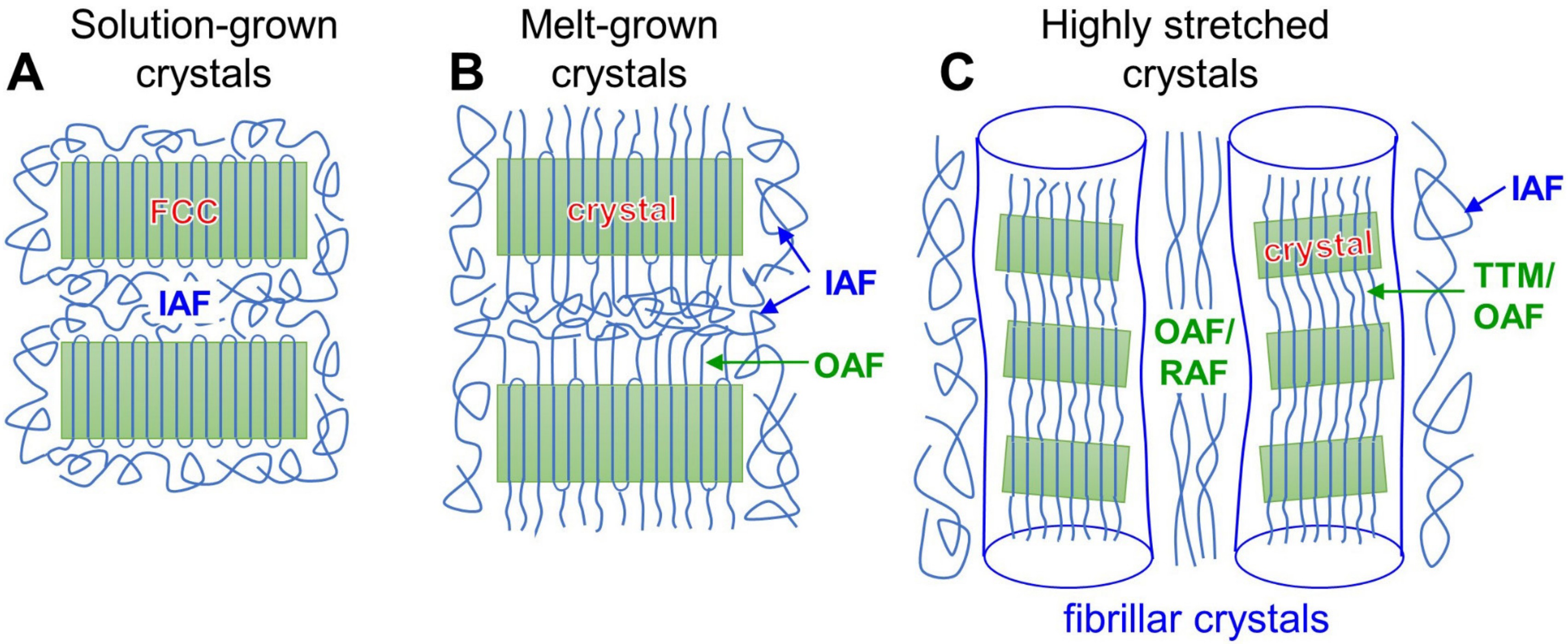
- Crystallinity ranges from 0% to 45%;
- Amorphous PET is transparent – PET preform or parison;
- Crystalline PET is non-transparent – heat resistant products.

Rigid Amorphous Fraction for Better Properties

Old Understanding

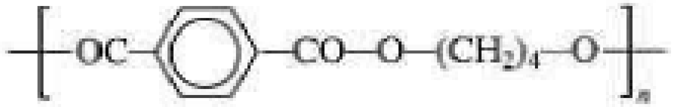


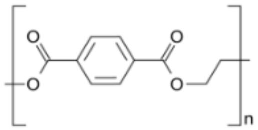
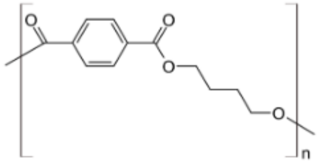
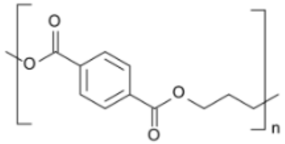
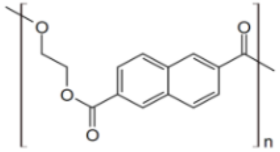
New Understanding



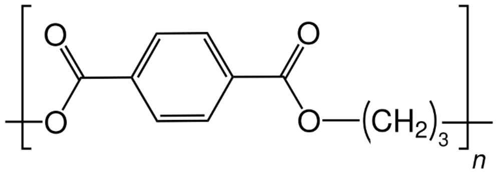
FCC: Folded-chain crystal
IAF: Isotropic amorphous fraction. If mobile, it is also called mobile amorphous fraction (MAF)
OAF: oriented amorphous fraction. If rigid, it is also called rigid amorphous fraction (RAF)
TTM: Taut-tie molecules
Important: It is RAF and TTM that promote polymer high mechanical, barrier, electrical properties!!! For PET, T_g(MAF) = 75°C, but T_g(RAF) = 100°C, and RAF% ~ 30% for ultradrawn PET fibers (crystal% ~ 40% and MAF% ~30%)!

Poly(butylene terephthalate) (PBT)

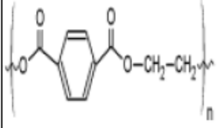
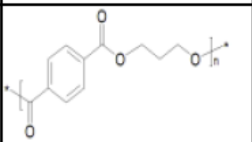
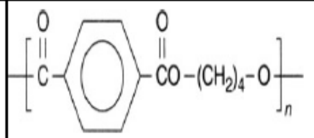
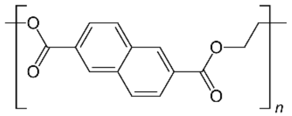


Polyester	Structure of Repeat Unit	Trade Name
Polyethylene terephthalate (PET,PETE)		Mylar®, Rynite®, Impet®, DuPont Celanese
Polybutylene terephthalate (PBT)		Crastin®, Celanex®, DuPont Celanese
Polytrimethylene terephthalate (PTT)		Sorona® DuPont
Polyethylene naphthalate (PEN)		Teonex® Teijin

Poly(trimethylene terephthalate) (PTT)



Poly(ethylene naphthalate) (PEN)

Physical Property	PET	PTT	PBT	PEN
Chemical structure				
Specific Gravity (measured as per ASTM D792 specifications)	1.40	1.35	1.34	1.35
T_m (°C) (Using DSC for injection molded samples at a heating rate of 10 °C min^{-1}*)	265	227	228	270
T_g* (°C)	80	45-60	25	120-135
Onset of decomposition temperature by using TGA (°C)	350	373	378	384

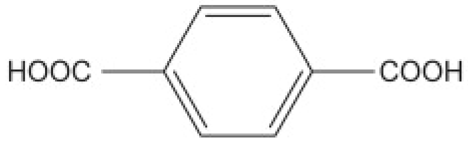
*indicates that the same experimental conditions were used in both

http://dx.doi.org/10.5772/50317

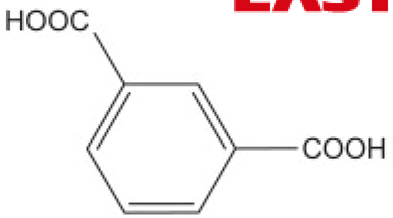
Glycol-Modified PET (PETG) Copolymers

Diacid	+	Diol	→	Polyester	
TPA	+	EG	→	PET	
TPA	+	EG + CHDM	→	PETG	(copolyester where EG > CHDM)
TPA	+	CHDM + EG	→	PCTG	(copolyester where CHDM > EG)
TPA + IPA	+	CHDM	→	PCTA	(copolyester)
TPA	+	CHDM	→	PCT	

EASTMAN

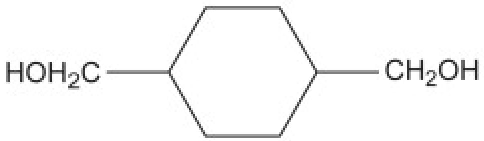


Terephthalic acid (TPA)



Isophthalic acid (iPA)

Ethylene Glycol (EG)



1,4 Cyclohexanedimethanol (CHDM)

Property	Unit	PETG	PCTG	PCTA
Density	g/cc	1.27	1.23	1.2
Transparency	%	91	89	91
Glass transition temperature	°C	81	83	87
HDT at (0.46 MPa or 66 psi)	°C	70	74	75
HDT at (1.8 MPa or 264 psi)	°C	63	64	65
Tensile strength @ break	MPa	28	30	51
Tensile elongation	%	110	330	300
Flexural modulus	GPa	2.1	1.8	2
Impact strength, notched, 23°C	J/m	101	No break	80
Processing temperature	°C	250–270	250–270	230–280
Softening point	°C	85	88	—

1. PCT has rather stiff chains, T_g=130°C and T_m=290°C. It has good weathering and water resistance and is used for film and fibers.
2. PCTA is amorphous (T_g~100 °C), and has a high clarity and good mechanical and processing characteristics.
3. A similar copolyester (PETG/PCTG) is prepared from terephthalic acid and a mixture of CHDM and EG.

Bisphenol A-free – To replace PC

aligners

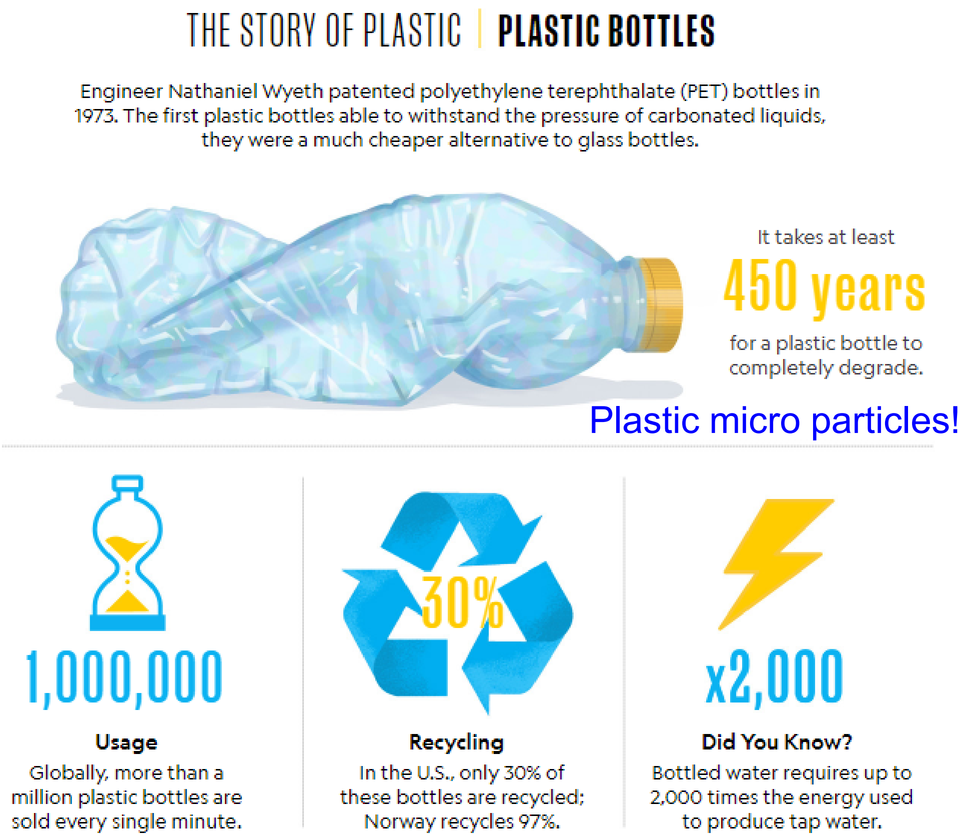
milk/water bottles

medical containers

Applications: Injection Molding and Drink Bottles

PETE

https://www.youtube.com/watch?v=vBpNp0wYV8I



Plastic micro particles!

https://www.youtube.com/watch?v=AAvOYz7qOsw

Injection Molding:

i) mold < 50°C, amorphous PET, clear parts;

ii) mold > 130°C, crystalline PET (20-40%), opaque parts.

How the plastic bottle went from miracle container to hated garbage?

https://www.nationalgeographic.com/environment/2019/08/plastic-bottles/

Applications: Polyester Fibers for Textiles and Tires

https://www.youtube.com/watch?v=fNdsOraykNI

https://www.tiresafety.com/en_us/tires-101/tire-design/tire-construction

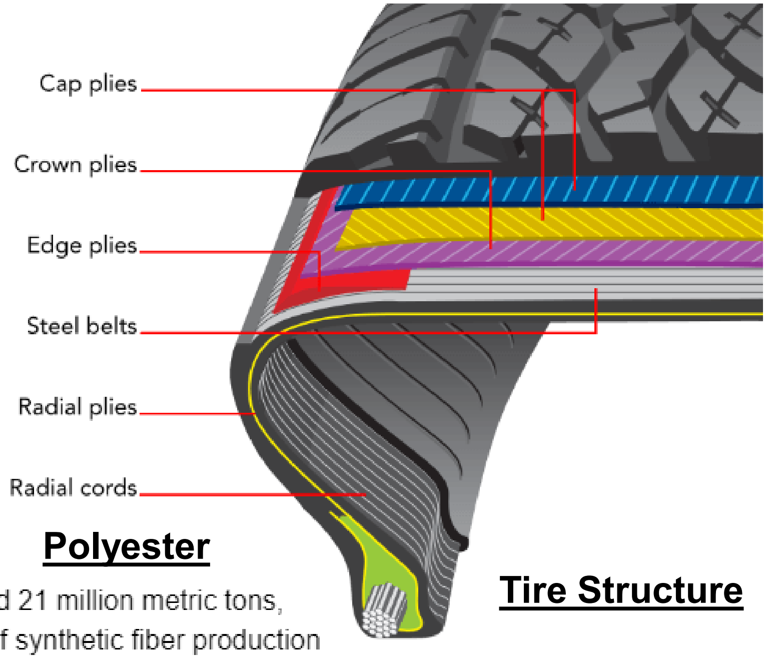
Physical properties

1. *Tenacity*: 5 – 7 gm/den
2. *Elongation at break*: 15 – 30%
3. *Elastic modulus*: 90
4. *Elasticity*: Good
5. *Moisture Regain (MR%)*: 0.40%
6. *Specific Gravity*: 1.38
7. *Melting point*: 250^{0}C
8. *Volumetric Swelling*: None
9. *Ability to protest friction*: Excellent
10. *Color*: White
11. *Light reflection ability*: Good
12. *Lusture*: Bright

Chemical properties

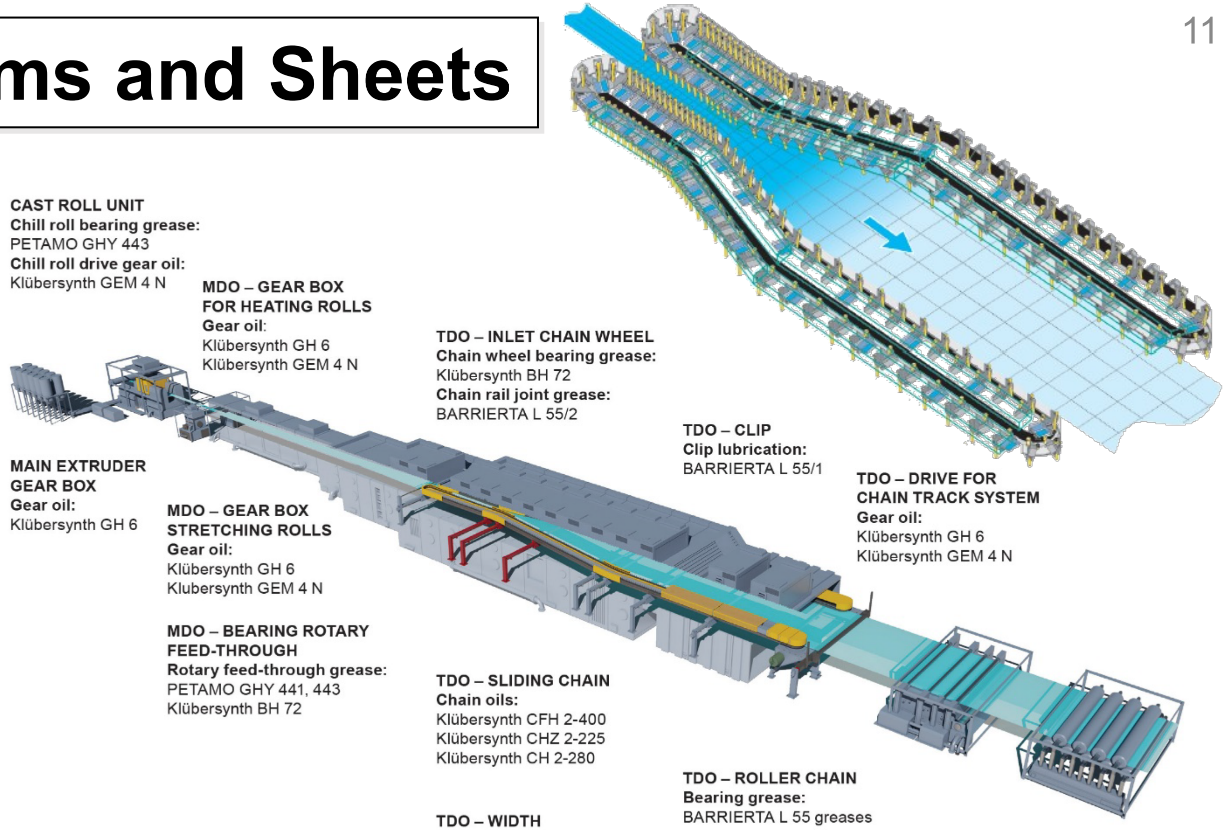
1. *Acids*: Good resistance to acids in cold condition. But polyester degrades by H_2SO_4 at high temperature.
2. *Basic*: Good resistance to basic in cold condition but Strong NaOH dissolves polyester in boiling.
3. *Effect of bleaching*: Polyester does not affected by bleaching process.
4. *Organic solvent*: Organic solvent does not affect on polyester fiber.
5. *Protection ability against mildew*: Good
6. *Protection ability against insects*: Good
7. *Dyes*: Polyester could be dye with disperse, azoic color and some pigments.
8. *Solvents of polyester*: Following are the solvents of polyester:
   - Chlorinated hydrocarbon.
   - F_3CCOOH
   - Phenol (in hot condition)

	Nylon	**Polyester**
Worldwide Production	Around 3.9 million metric tons, 11% of synthetic fiber production	Around 21 million metric tons, 58% of synthetic fiber production



Tire Structure

Applications: Films and Sheets

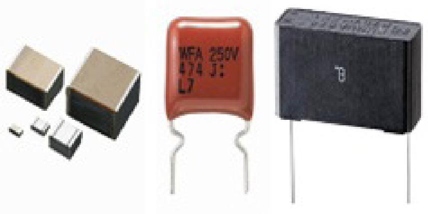


https://www.youtube.com/watch?v=8uxn6oe4p7c

Thin film metallization

Packaging

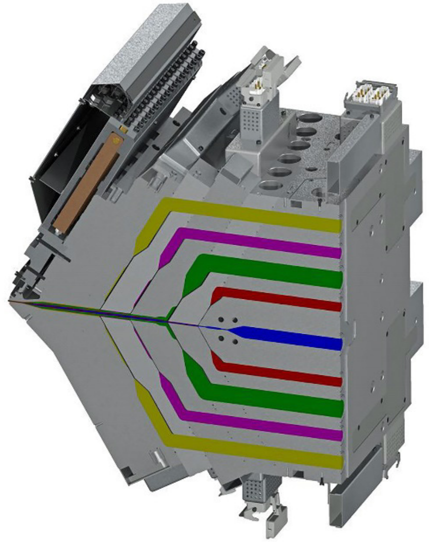
Capacitors

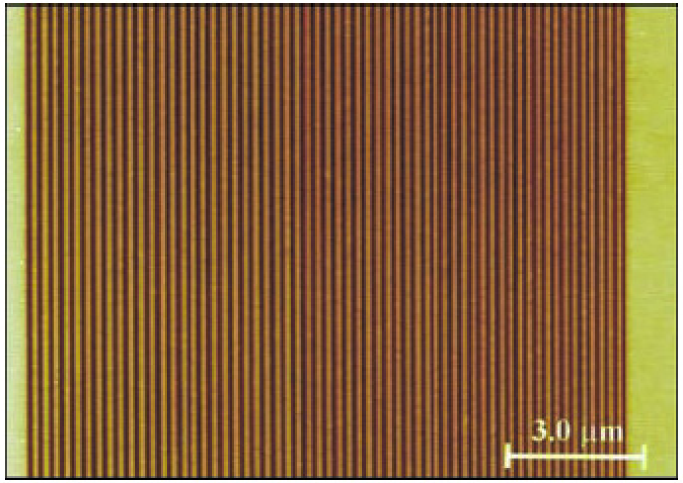


power and electrical applications

Applications: Multilayer Film Coextrusion

Polyester-based Multilayer Films (MLFs)





Reflectivity R:

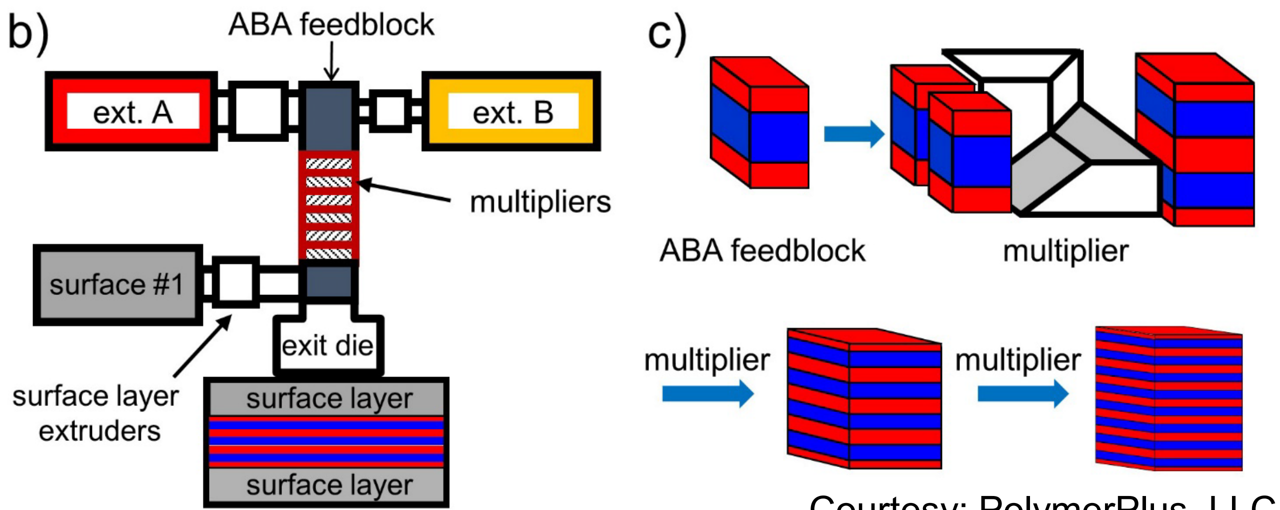
$$R(\omega_s) \approx 1 - 4\left(\frac{n_1}{n_2}\right)^{2N}$$

PMMA/PEN MLFs

(n_1=1.49)/(n_2=1.58)

DOI: 10.1126/science.287.5462.2451

- 1965 Dow Chemical: Interfacial Surface Generator by Walter Schrenk and co-workers
- 1995 patents sold to 3M
- Since then, 3M developed multilayer birefringent optical films with a billion-dollar market

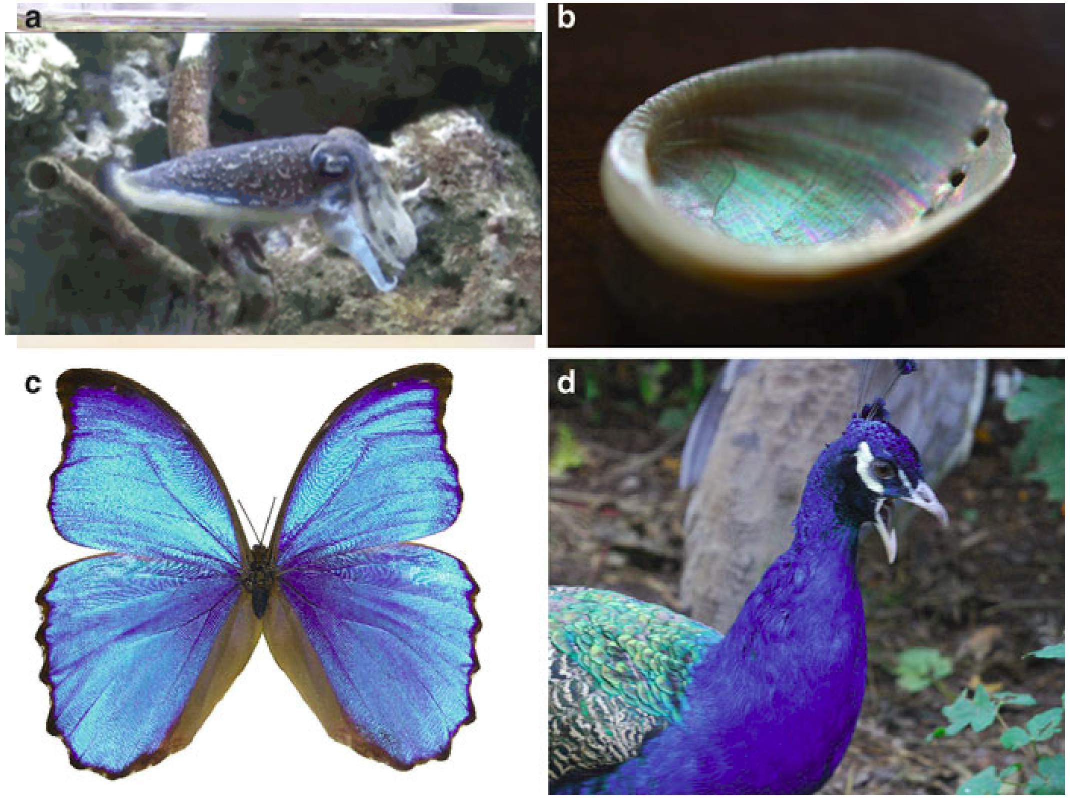


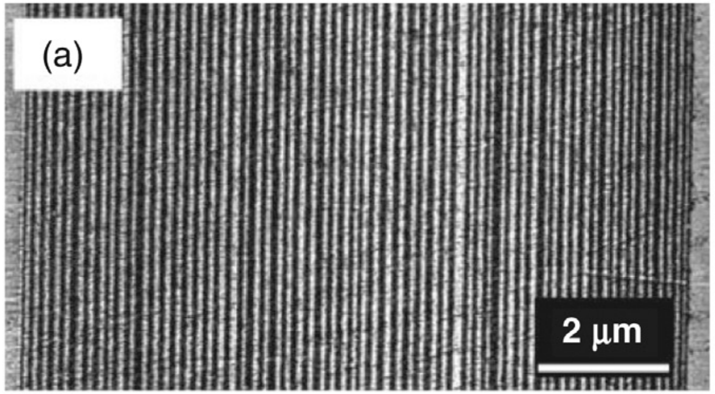
Courtesy: PolymerPlus, LLC

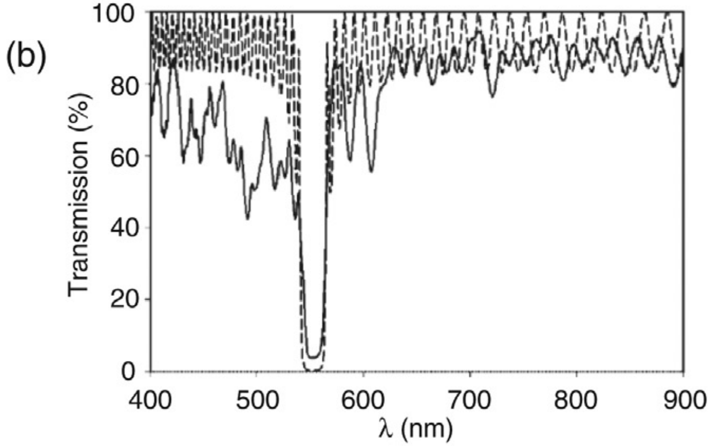
- Prof. Baer at CWRU keeps a simple coextrusion line
- 2006 Awarded $40M NSF Science & Technology Center
- Versatile coextrusion of multilayer films for optical, gas barrier, and electronic applications

Reading Material: https://www.ptonline.com/articles/microlayer-films-new-uses-for-hundreds-of-layers

Applications: 1D Photonic Crystals

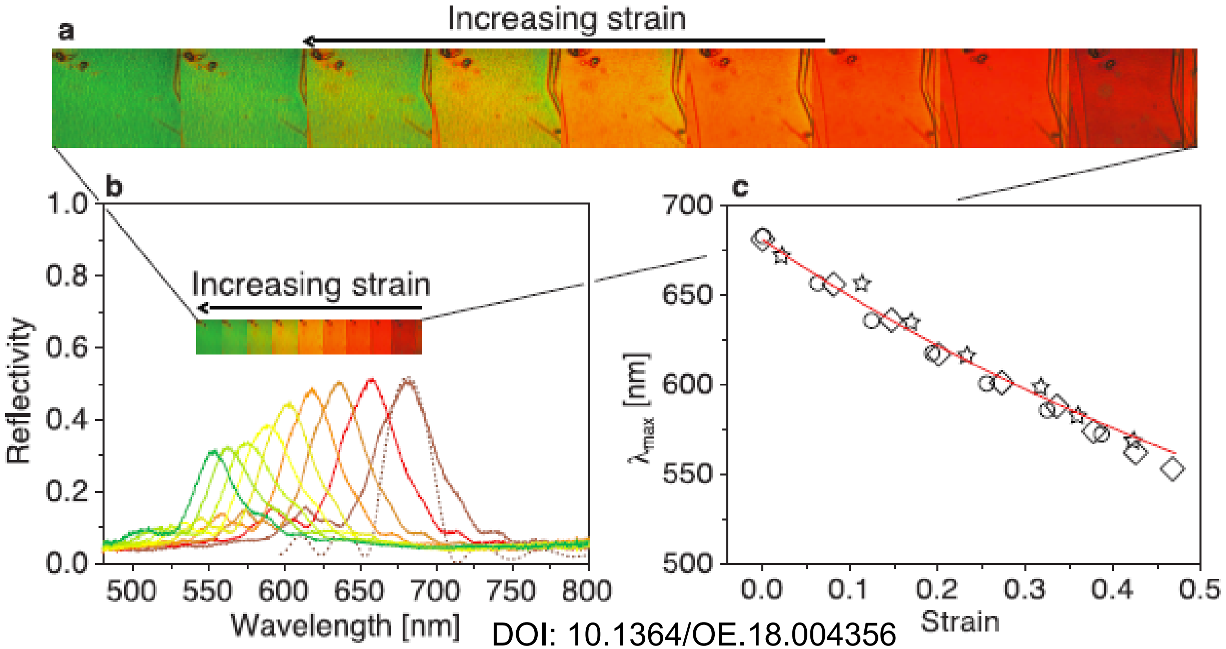






$$\bar{\lambda} = 4d_i\sqrt{n_i^2 - \sin^2\theta}$$

with $\bar{\lambda}$ being the central reflection stopband wavelength, θ is the angle of light incidence and d_i, n_i are the thickness and refractive index of the i-th layer. The multilayer structures here are



DOI: 10.1364/OE.18.004356

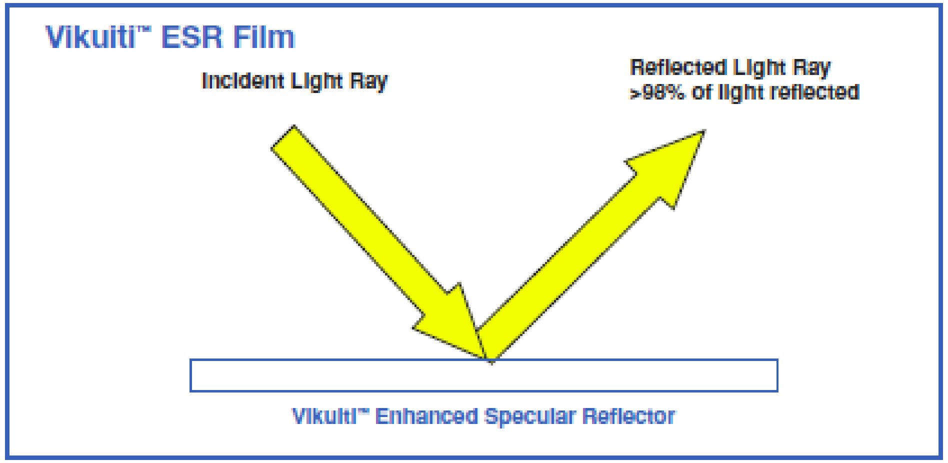
Applications: 3M Enhanced Specular Reflection (ESR) Films

How does LED light work in LCDs?

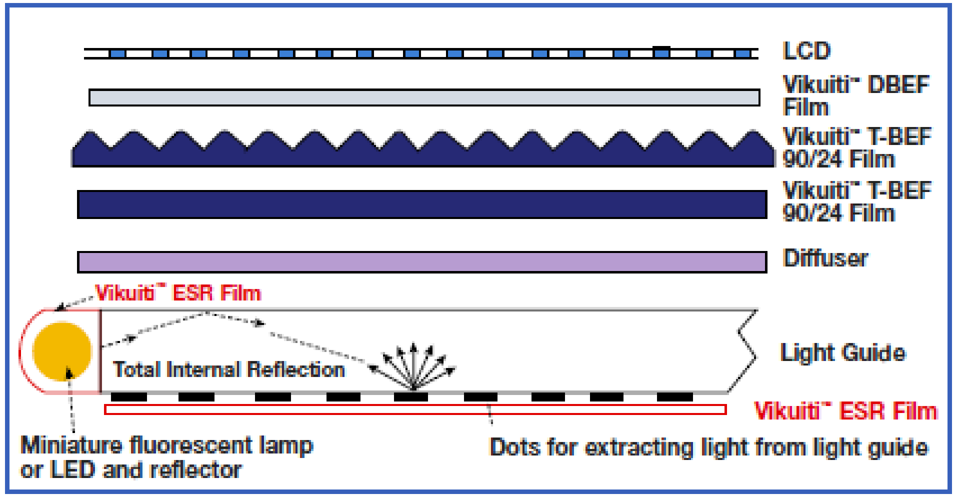
https://www.youtube.com/watch?v=jiejNAUwcQ8&t=288s

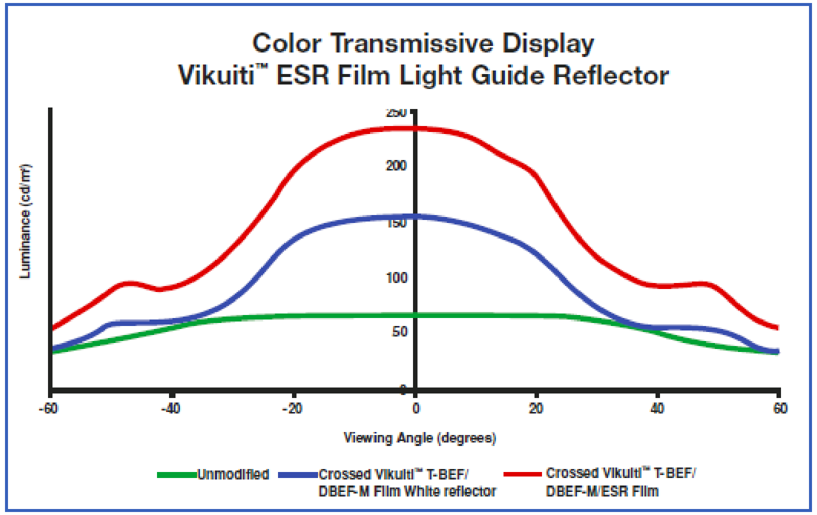
Applications: 3M Enhanced Specular Reflection (ESR) Films

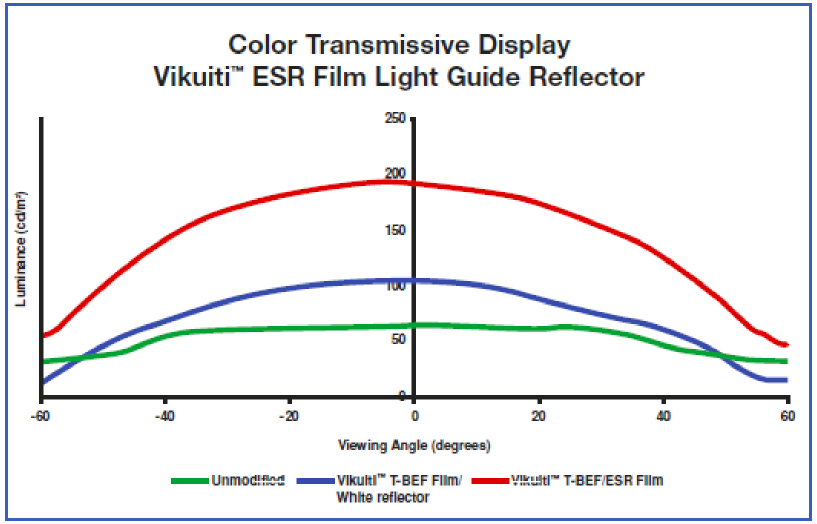
PMMA (n_1=1.49)/Polyester (n_2=1.58) multilayer films



Vikuiti™ ESR Film in a typical LCD







Weber, M. F., et al., Giant birefringent optics in multilayer polymer mirrors. *Science* **2000**, *287*, 2451-2456. DOI: 10.1126/science.287.5462.2451

DBEF: dual brightness enhancement film
T-BEF: Thin brightness enhancement film

Thermoplastic Polyester Elastomers (TPEs or TPEEs)

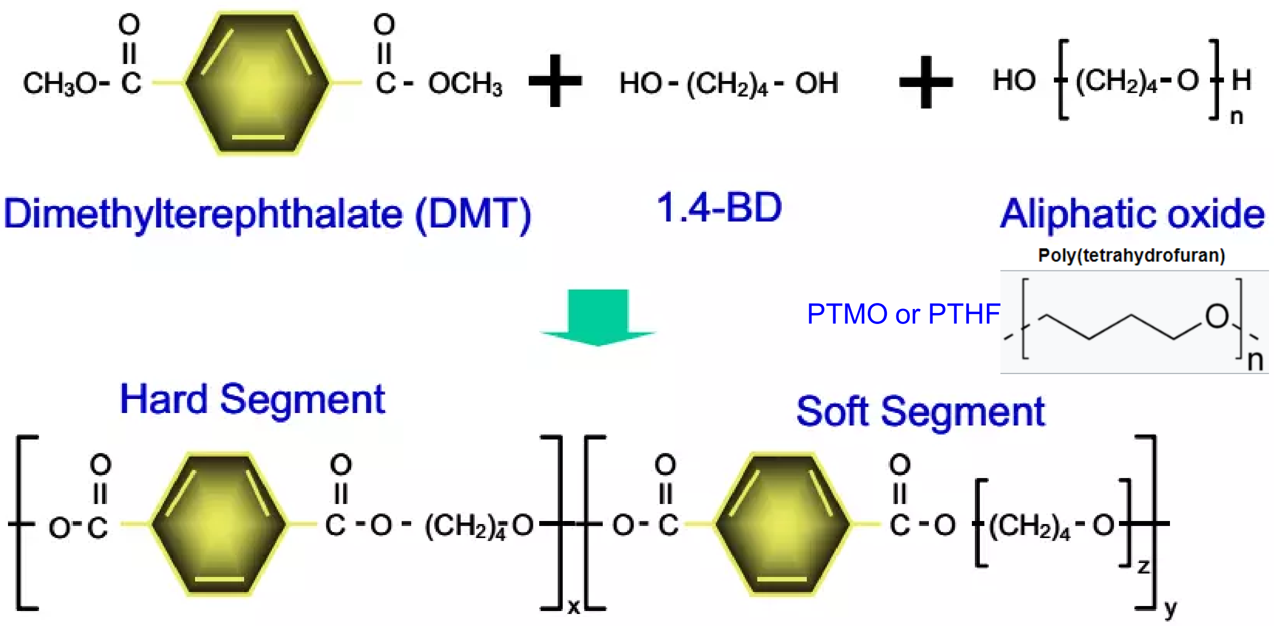


Table 4.3 Some properties of thermoplastic polyester elastomers

	Hard block content (%)		
Property	*33*	*58*	*76*
Specific gravity	1.15	1.20	1.22
Melting temperature (°C)	176	202	212
Glass transition temperature (°C)	−78	−50	−2
Shore hardness	92A	55D	63D
Tensile strength (MPa)	39.3	44.1	47.5
10% Modulus (MPa)	3.58	10.0	16.9
Flexural modulus (MPa)	44.8	206	496
Elongation at break (%)	810	760	510

Physical Properties

These polar rubbers have good oil and petrol resistance, superior tensile and tear strength, high resilience, good flex fatigue resistance and abrasion resistance. Increasing the polyether content results in more elastic polymers of lower modulus. The properties can be further modified by incorporation of various fillers such as carbon black, clays and fiber glass which increase the modulus.

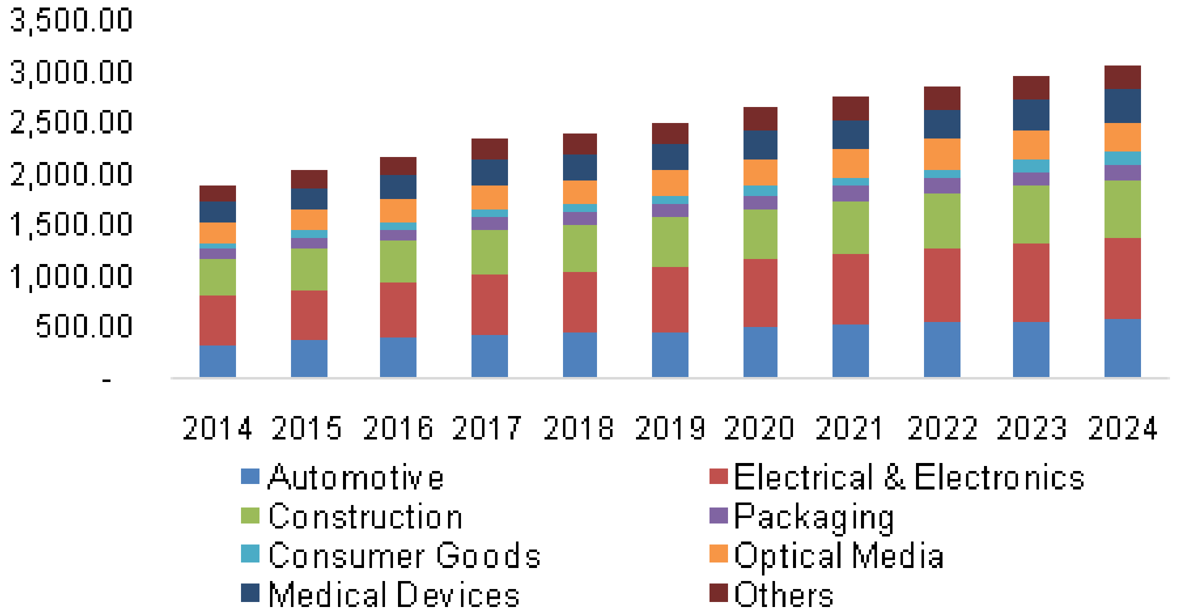
Applications

NOT suitable for use in pneumatic tires for motor vehicles. TPEs are toxicologically safer and can be used in direct contact with living tissues. They have found applications in the medical field as synthetic materials for vascular grafts and reconstruction of damaged organs.

Thermoplastic Polyester Elastomer | Kent Elastomer

Polycarbonates (PCs)

U.S. PC Market Revenue By Application, 2014 - 2024 (USD $M)



https://www.grandviewresearch.com/industry-analysis/polycarbonate-market

List of the Top Key Players of PC Market:

Covestro AG
LG Chem
Mitsubishi Gas Chemical Company
Sabic
Teijin Limited
Trinseo

Synthesis

(a) Ester Exchange

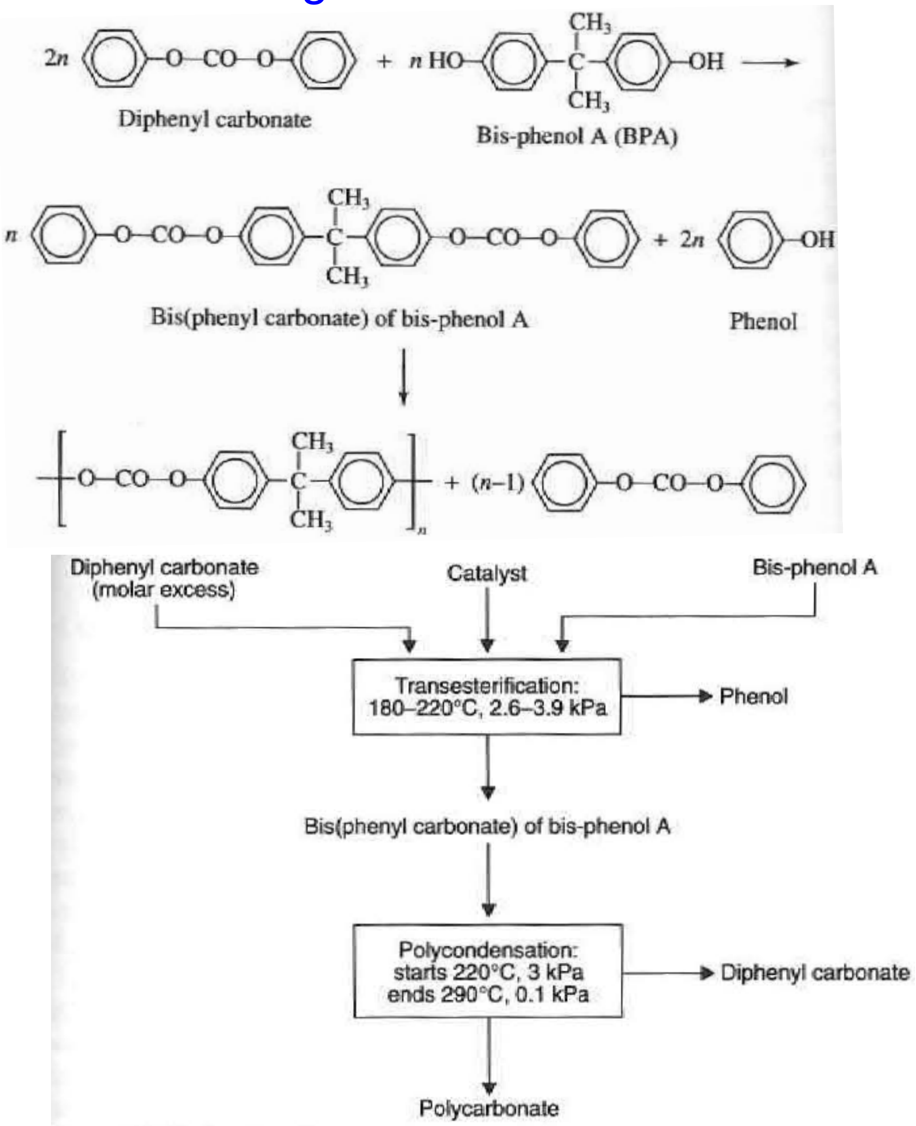
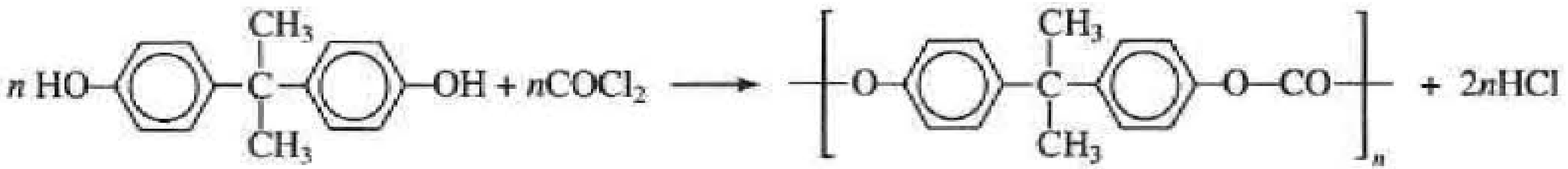


Figure 4.2 Polycarbonate preparation by the melt ester exchange process.

Polycarbonates (PCs)

Synthesis

(b) Phosgenation



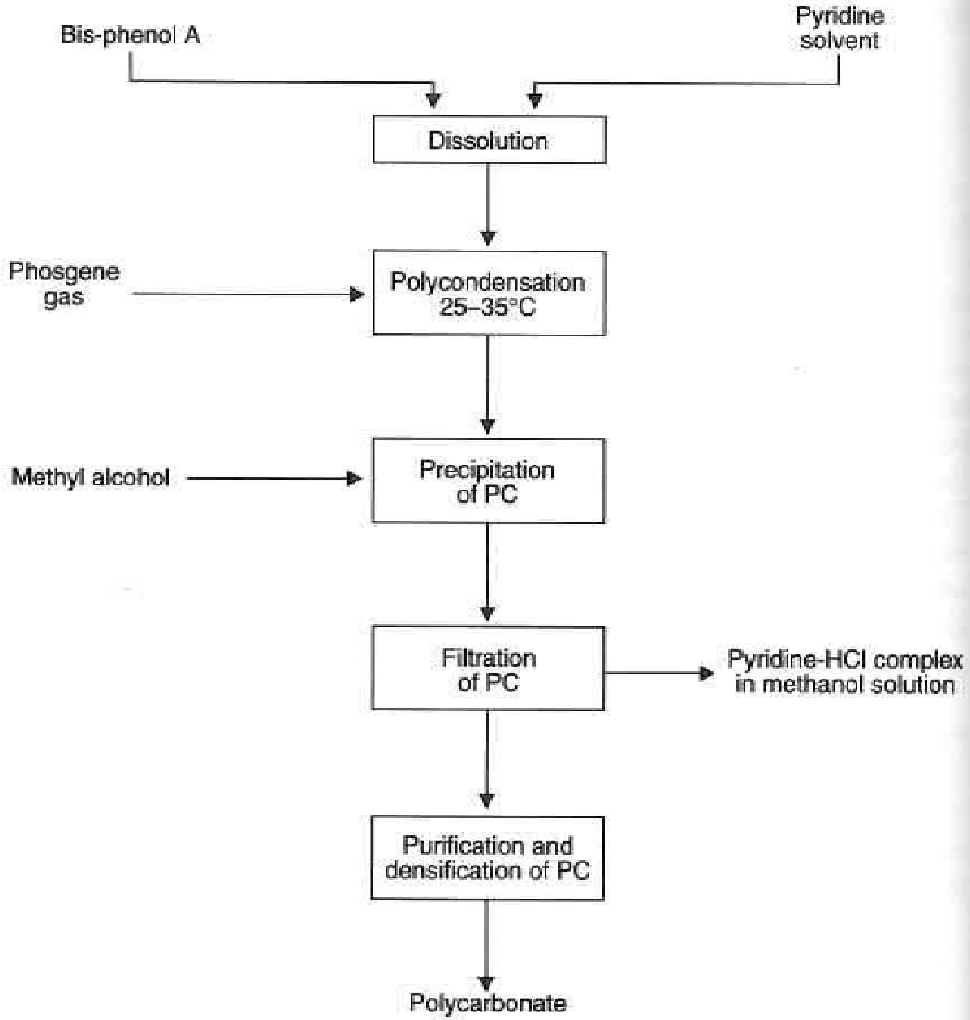


Figure 4.3 Polycarbonate preparation by the solution phosgenation process.

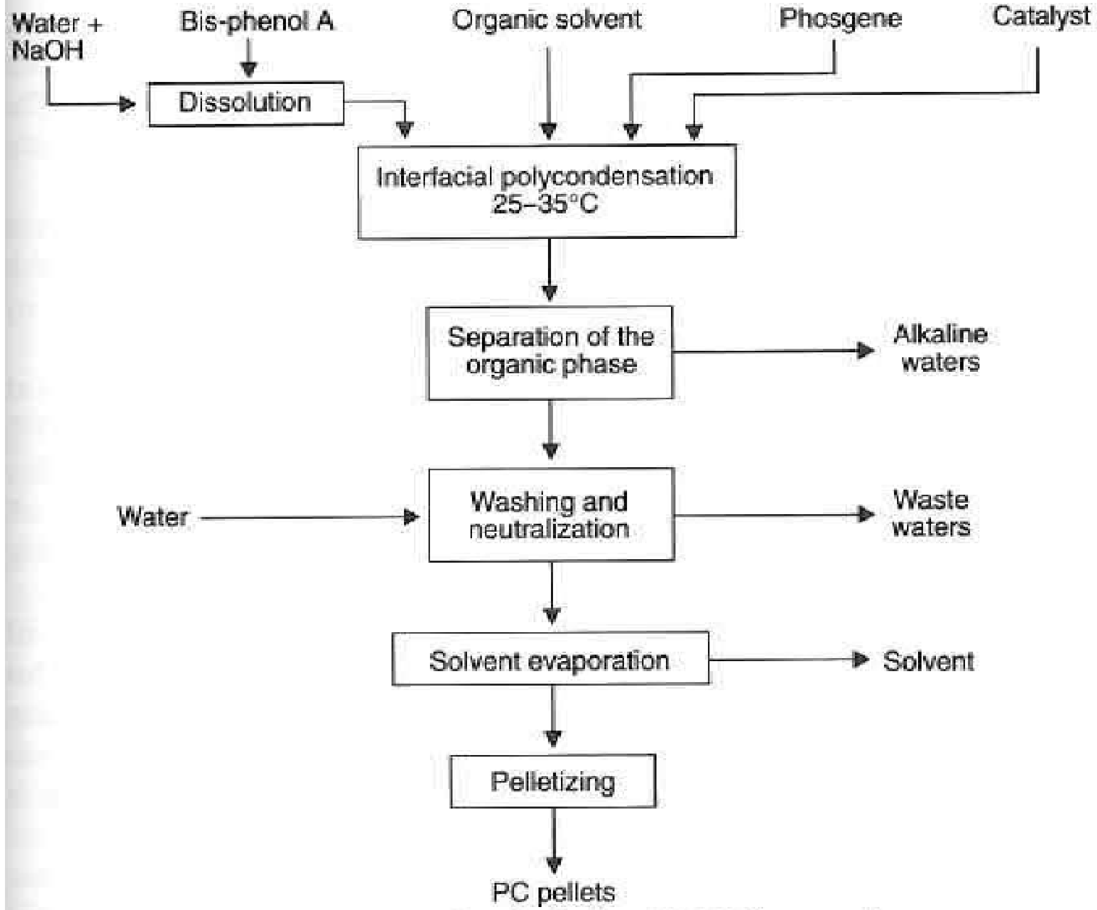


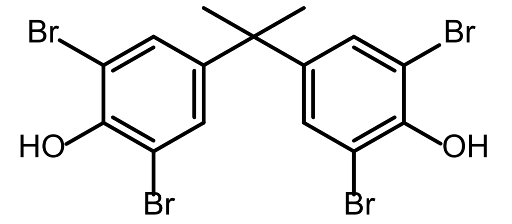
Figure 4.4 Polycarbonate preparation by the interfacial phosgenation process.

PC Properties

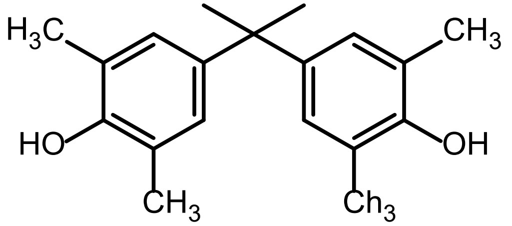
1. Typical MW: 20-50 kDa
2. Mechanical property
   Tough (high impact strength: 60-80 kJ/m^2 at RT); creep and scratch resistant
3. Thermal property
   Heat resistant; can crystallize upon solution-casting (T_m=250-300°C), but is amorphous upon melt-processing
4. Optical property
   High transparency and high refractive index (n = 1.586)
5. Electrical property
   Good insulator with very low dielectric loss; reasonable permittivity
6. Processing methods
   Extrusion, injection molding, blow molding, rotational molding, structural foam molding and film casting
7. Additives (UV stabilizers) and composites

Property			Units	Test Method
General				
Specific gravity	1.2		-	ASTM D-792
Water Absorption 24 hrs.	0.15		%	ASTM D-570
Refractive Index	1.586		-	ASTM D-542
Mechanical				
Tensile Strength, Yield, .125″	9,000		psi	ASTM D-638
Tensile Strength, Ultimate	9,500	65 MPa	psi	ASTM D-638
Tensile Modulus	345,000	2.4 GPa	psi	ASTM D-638
Shear Strength	6,000		psi	ASTM D-732
Compressive Strength	12,500		psi	ASTM D-695
Flexural Strength at 5% Strain	13,500		psi	ASTM D-790
Flexural Modulus .125″	345,000		psi	ASTM D-790
Izod Impact Notched .125″	12-16	25-34 kJ/m^2	ft.lb/in of notch	ASTM D-256
Rockwell Hardness	118		R Scale	ASTM D-785
Gardner Impact 1/2″ Diameter Dart .125″	>320		in.lbs	ASTM D-5420
Instrumented Impact .125″	>45		ft.lbs	ASTM D-3763
Thermal	T_g = 145 °C			
Heat Deflection Temperature 264 psi	270		°F	ASTM D-648
Heat Deflection Temperature 68 psi	280	138 °C	°F	ASTM D-648
Coefficient of Thermal Expansion	3.75 x 10^{-5}		in/in/°F	ASTM D-696
Coefficient of Thermal Conductivity	1.35		BTU/hr/ft^2/°F	ASTM D-177
Smoke Density	68		-	ASTM D-2843
Shading Coefficient Clear .125″	1.02		-	ASHRAE
Shading Coefficient Gray/Bronze .125″	.70		-	ASHRAE
Shading Coefficient Dark Gray .125″	.58		-	ASHRAE
Brittle Temperature	-200		°F	ASTM D-746
Flammability				
Horizontal Burn, AEB .125″	<1		in	ASTM D-635
Horizontal Burn, ATB .125″	<1		min	ASTM D-635
Self Ignition Temperature	1070		°F	ASTM D-1929
Flash Ignition Temperature	800		°F	ASTM D-1929
UL 94 Clear ≥ .060″	V-2		-	UL 94
UL 94 Clear ≥ .250″	V-0		-	UL 94
Optical				
Transmittance Clear .125″	>88		%	ASTM D-1003
Haze Clear .125″	<1		%	ASTM D-1003
Electrical				
Dielectric Constant 10 Hz	2.96		-	ASTM D-150
Dielectric Constant 60 Hz	3.17		-	ASTM D-150
Volume Resistivity	8.2 x 10^{16}		ohm-cm	ASTM D-257
Dissipation Factor 60 Hz	0.0009		-	ASTM D-150
Dissipation Factor 1 MHz	0.010		-	ASTM D-150
Arc Resistance				
Stainless Steel Strip Electrodes	10-11		sec	ASTM D-495
Tungsten Electrodes	120		sec	ASTM D-495

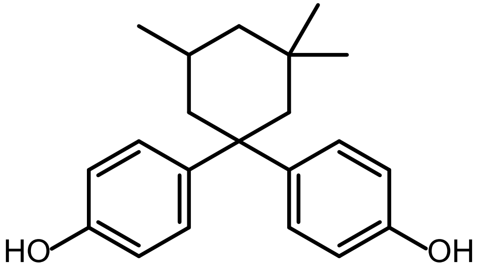
PC Copolymers



Flame-retardant
Tetrabromo-bis-phenol A



Hydrolysis & heat-retardant
Tetramethyl bis-phenol A
T_g = 196 °C

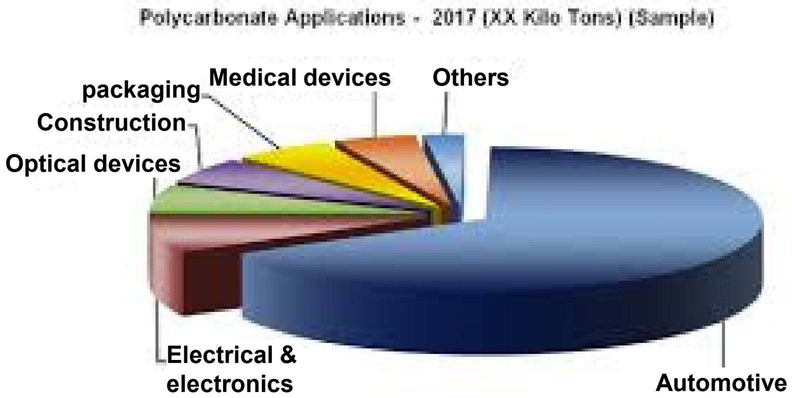


Heat-resistant
trimethyl-cyclohexanone-bis-phenol (TMC-BP)
Apec® PC series

- PC from BPA: T_g = 145°C;
- PC from TMC-BP: T_g = 239°C;
- Copolymers: 45% BPA & 55% TMC-BP, T_g = 205°C.

1. Injection molding: https://www.youtube.com/watch?v=RgItoijF30M
2. Tough PC sheets: https://www.youtube.com/watch?v=r7GCkVKLbc8

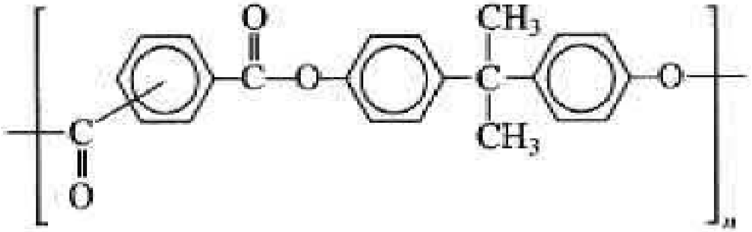
PC Applications



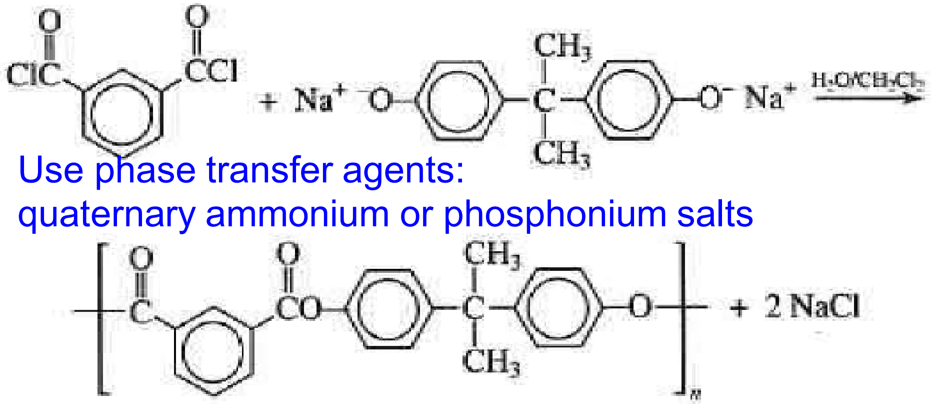
Applications

- Electronic components (capacitors, but stopped in 2000)
- Construction materials
- Data storage
- Automotive, aircraft, and security components
- Medical applications

Polyarylates – Aromatic Polyesters

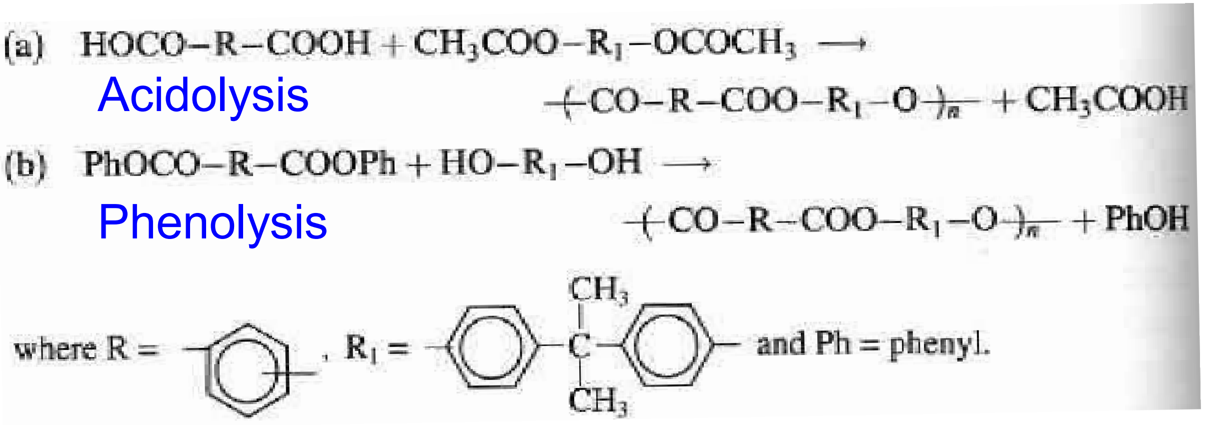


1) Interfacial polycondensation (low temp.)



Use phase transfer agents:
quaternary ammonium or phosphonium salts

2) High temp. polycondensation in melt or slurry



Properties

- Polyarylates are amorphous, aromatic polyesters (T_g ~190°C)
- They are flame retardant and show good toughness and UV resistance
- Polyarylates are transparent and have good electrical properties
- The abrasion resistance is superior to that of PC
- They show very high recovery from deformation
- Injection molding should be performed at 260-380°C with mold temperature at 65-150°C
- Extrusion and blow molding grades are available
- Can react with water, so should be dried prior to processing

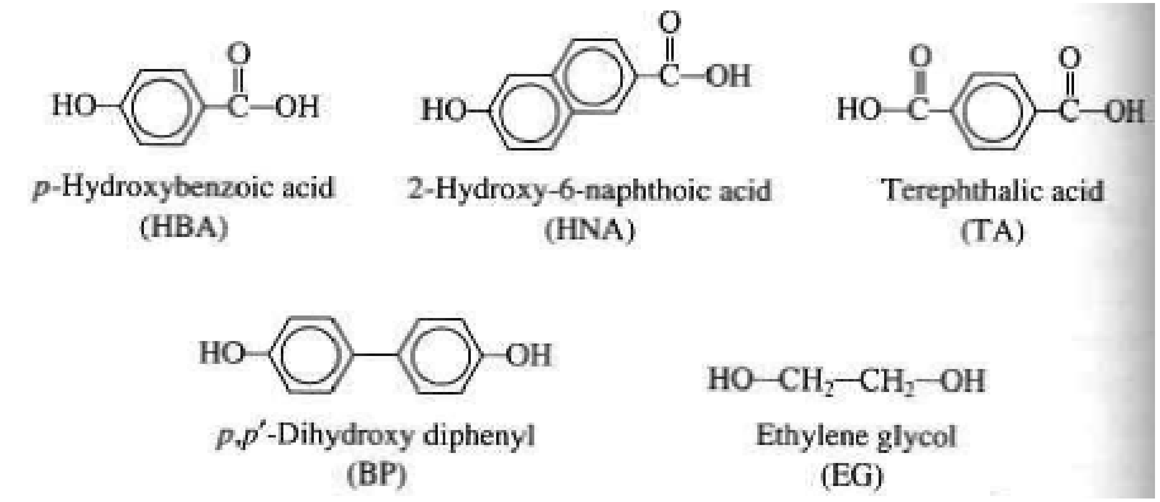
Applications

- Automobile applications such as door handles, brackets, and headlamp and mirror housings
- Used in electrical applications for connectors and fuses
- Used in circuit board applications due to its high temperature resistance, which can survive soldering
- Excellent UV resistance for coating of other plastics
- Heat resistance for fire helmets and shields

https://polymerdatabase.com/polymer%20classes/Polyarylate%20type.html

Liquid Crystalline Polyesters (LCPs)

LCP Monomers



Global LCP market volume by application, 2012 - 2020 (Kilo Tons)

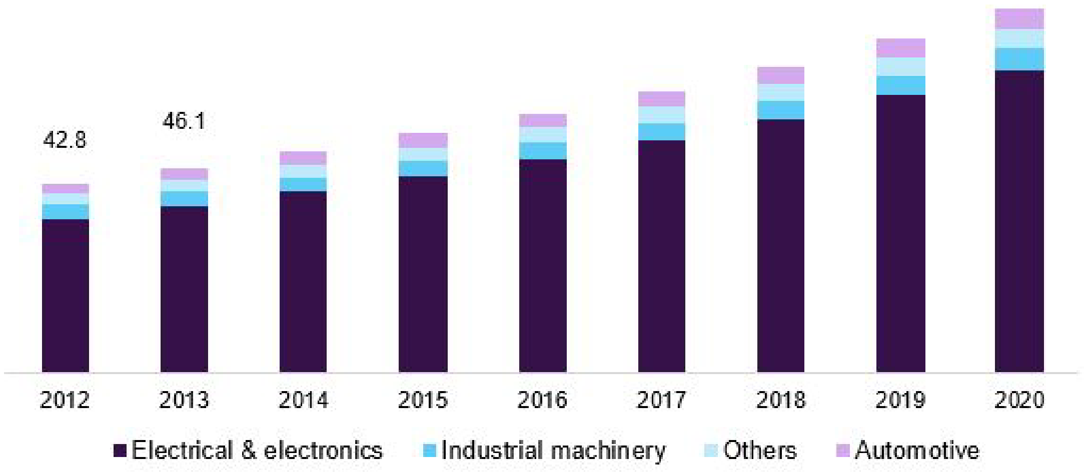
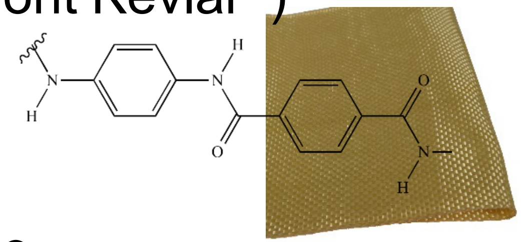


Table 4.5 Classification of LCP [57]

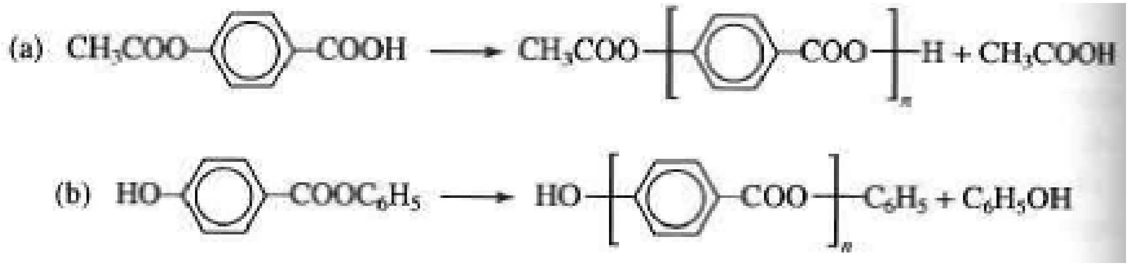
Type of LCP	*Heat deflection temperatures (°C)*	*Monomers*
Type I	60–216	*p*-Hydroxybenzoic acid Terephthalic acid Ethylene glycol
Type II	210–260	*p*-Hydroxybenzoic acid 2-Hydroxy-6-naphthoic acid Terephthalic acid
Type III	260–354	*p*-Hydroxybenzoic acid Terephthalic acid *p, p′*-Dihydroxybiphenyl

- 1970's: *lyotropic* LCPs (DuPont Kevlar®)
  - poly(*p*-benzamide)
  - ultra-high strength fibers



- 1980's: *thermotropic* (Vectra®)

  Synthesis: batch or continuous



Liquid Crystalline Polyesters (LCPs)

Properties

- High temperature stability
- Strong with highly oriented skin structure
- low CTE for precision parts
- low viscosity for extrusion or injection molding
- very low flammability, low smoke emission and 15 min at 1095°C flame by building a char layer
- Excellent electrical insulation and transparent to microwaves (~1-10 GHz)

Table 4.6 Some properties of LCP

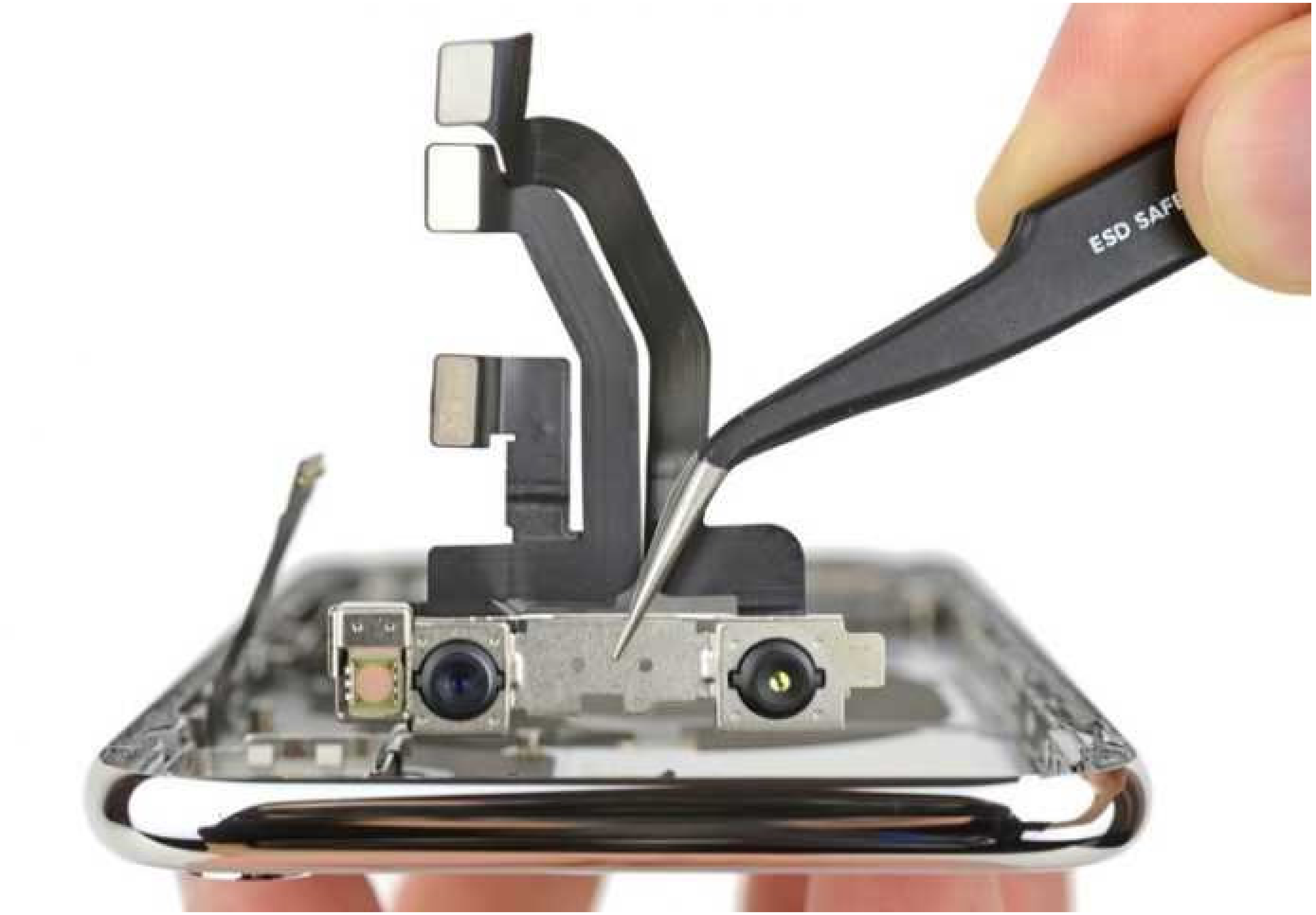
Property	*Value*
Density	1.70 g/cm^3
Melting temperatures	370–455°C
Heat deflection temperatures	260–355°C
Tensile strength, unfilled	165–230 MPa
filled	149–207 MPa
Flexural strength, unfilled	169–256 MPa
filled	207–317 MPa
Flexural modulus, unfilled	9–15.2 GPa
filled	13.8–27.6 GPa
Elongation	1–3%
Izod impact strength	53–160 J/m
Coefficient of thermal expansion	
in flow direction	$(2–5) \times 10^{-5}$ cm/cm · °C
in perpendicular direction approximately twice these values	

Applications

For electrical and mechanical parts, food containers, and any other applications requiring chemical inertness and high strength.

- Good for microwave frequency electronics due to low relative dielectric constants, low dissipation factors, and commercial availability of laminates, e.g., flexible 5G antenna for cell phones
  Apple iPhone 12 uses LCP flexible PCBs
- Packaging microelectromechanical systems (MEMS).
- Automotive ignition system components, heater plug connectors, lamp sockets, transmission system components, pump components, coil forms and sunlight sensors and sensors for car safety belts.
- About 70% of the total amount of LCP consists of various fillers: milled glass, glass and carbon fibers, graphite flakes, mineral fillers and powdered metals. This allows the tailoring of the mechanical, thermal, electrical and processing characteristics.

Liquid Crystalline Polyesters (LCPs)

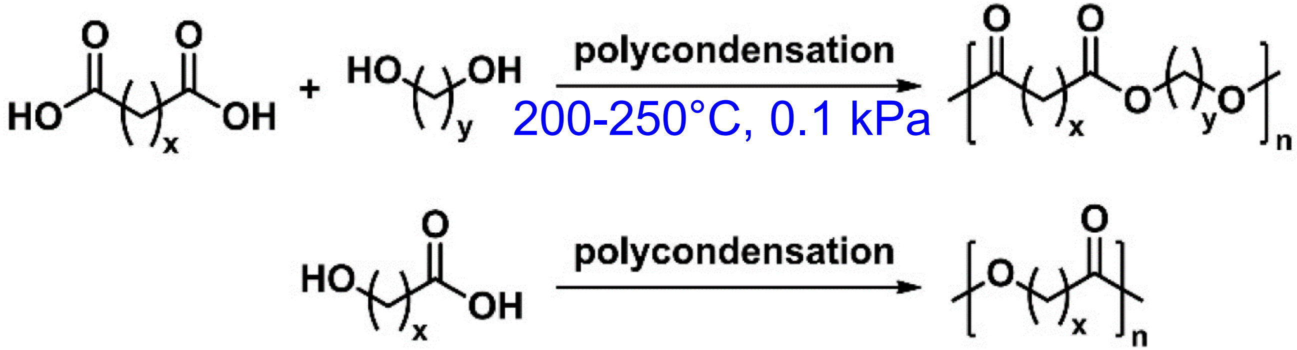


https://www.x-pcb.com/lcp-fpcs-benefits-applications/

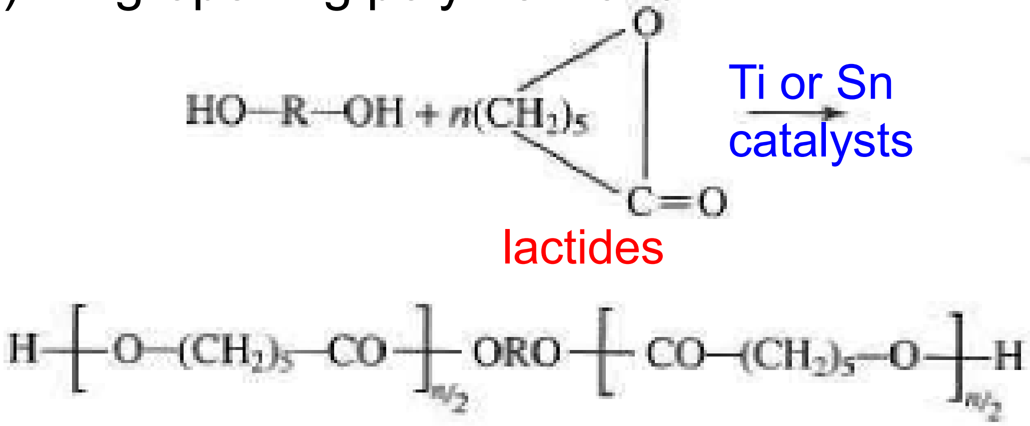
Low MW Aliphatic Polyesters as Precursor/Additive Polymers

Synthesis

a) Direct polycondensation



b) Ring-opening polymerization



Diols:

i) linear: ethylene glycol, diethylene glycol, 1,4-butane diol

ii) branched: glycerol, trimethylolpropane

Diacids:

Succinic, adipic, azelaic, sebacic or phthalic acid

ω-hydroxyacids

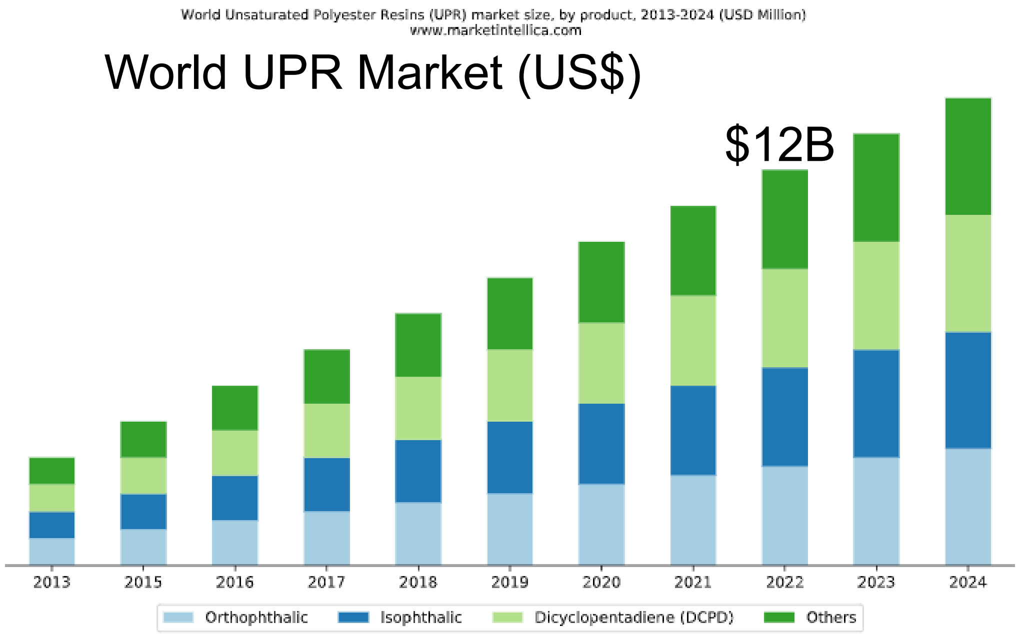
Properties

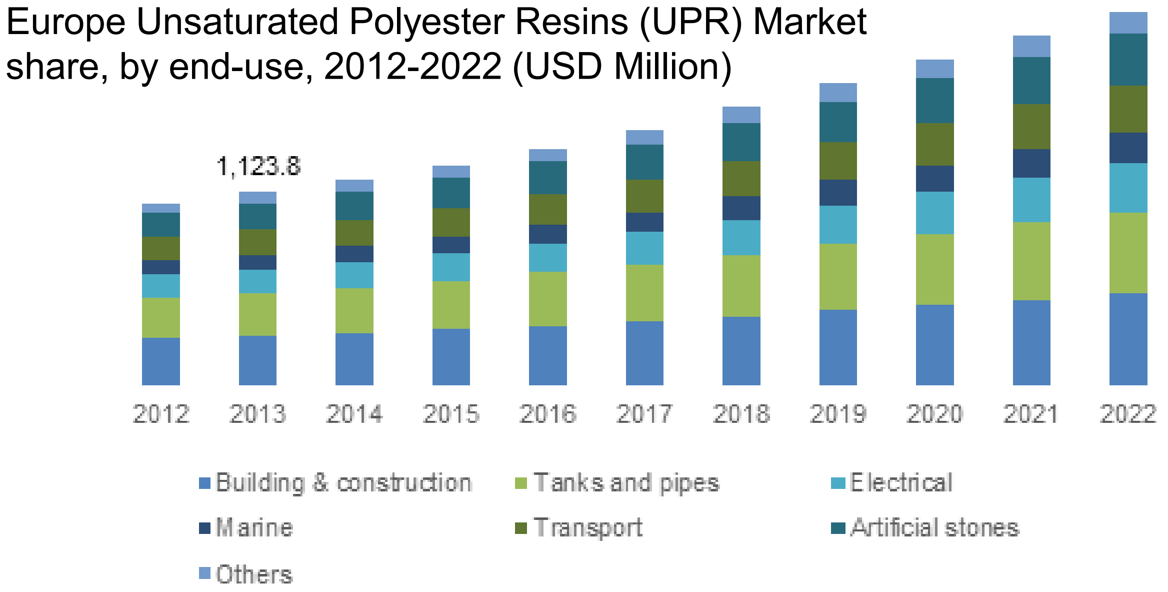
- Low molecular weights (MWs): 2000-4000 g/mol
- Difunctional with diols
- Low glass transition temperatures (Tg, < -30 °C)
- low viscosity for additives

Applications

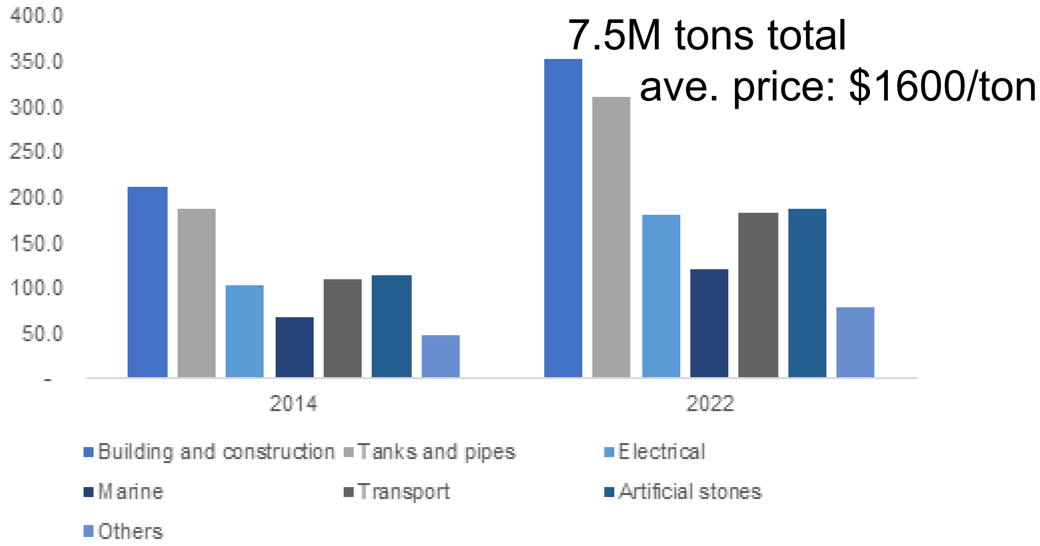
- Additives for PE, PP, PVC to increase dyability
- Precursor polymers for polyurethanes (Lubrizol)
- Biodegradable polymers to replace polyolefins and for biomedical applications

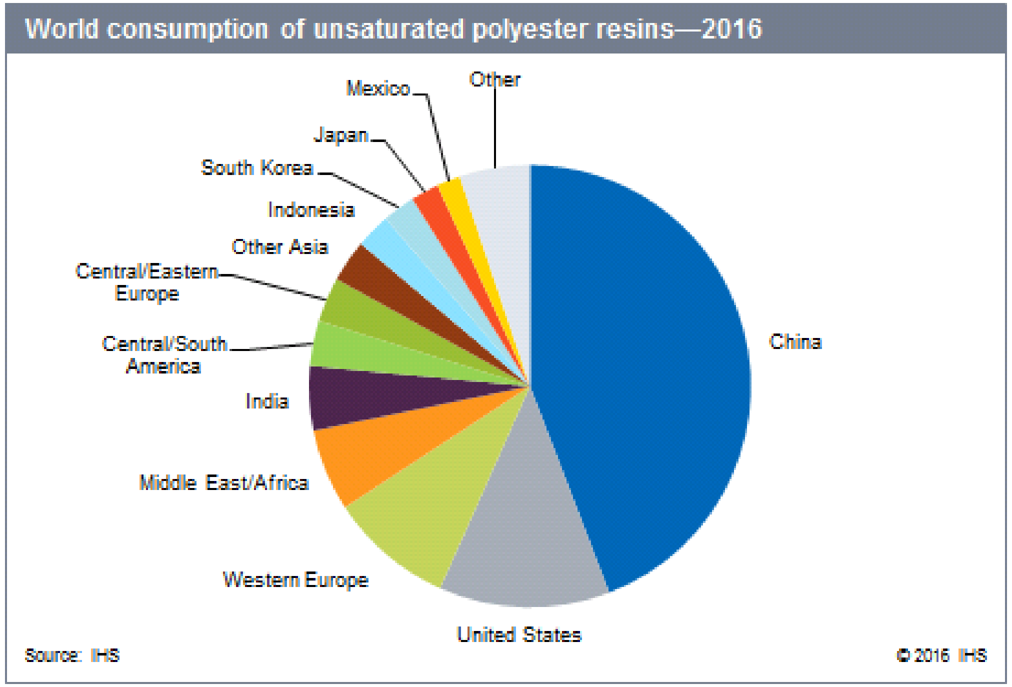
Thermoset Polyesters – Unsaturated Polyester Resins (UPR)





North America UPR Market Share, By Application, 2014 & 2022, (Kilo Tons)





UPR Synthesis

https://www.youtube.com/watch?v=O_-rINqV3JY

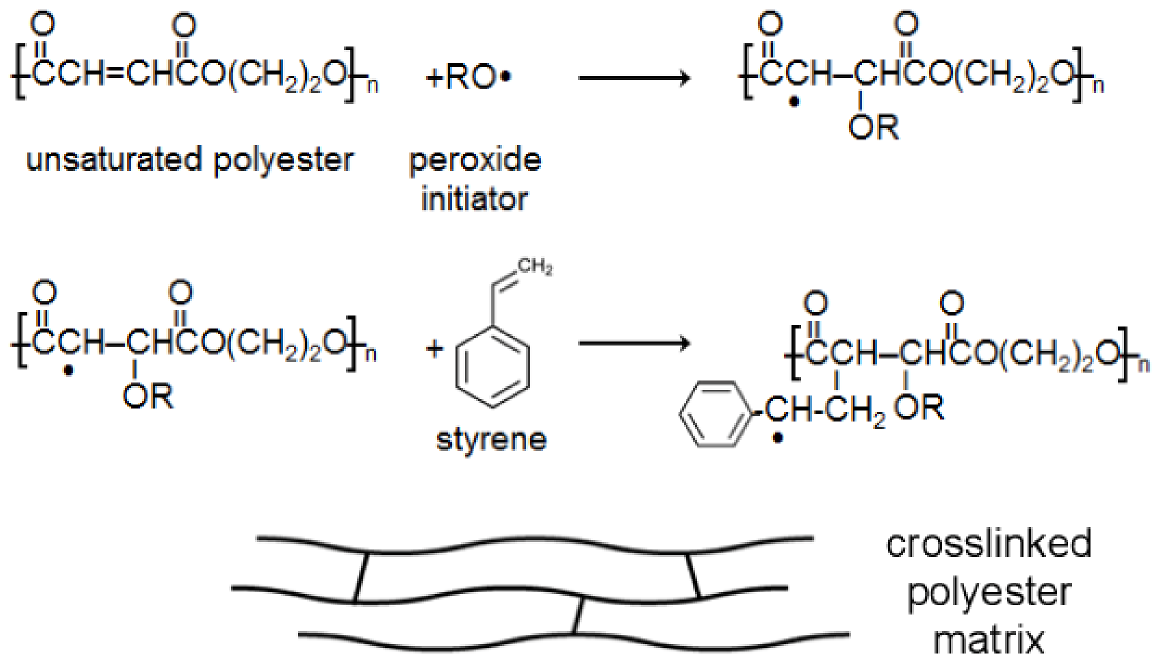


Fig. 1. Crosslink formation within a polyester resin.

UPRs are prepared in two steps:

1) Unsaturated polyester

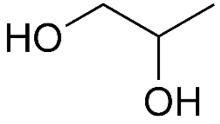
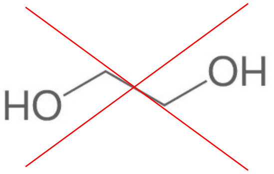
A linear polyester of low MW of about 700-4000, containing C=C bonds in the polymer chain, is synthesized in the first step and is dissolved in a vinyl monomer and stabilized with an inhibitor. This composition may be stored for months.

2) Curing

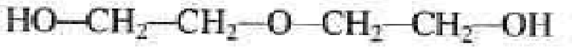
When used, the resin composition is mixed with a catalyst system (peroxide), compounded with fillers, reinforced with glass fibers and crosslinked by the copolymerization of the unsaturated double bonds in the polyester with the vinyl monomer used as solvent. The polymerization takes place during the molding or laminating operation.

UPR Components

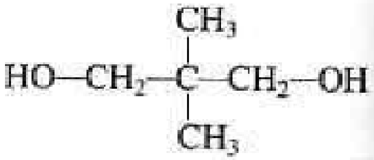
Glycols

Mostly used:  

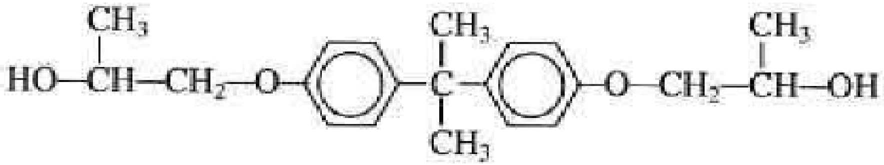
1,2-propylene glycol to avoid crystallization



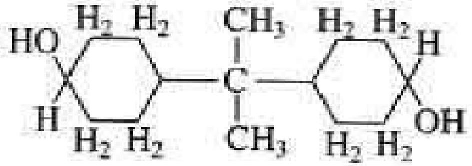
Di- or tri-ethylene glycol to increase flexibility



Thermal and UV resistance

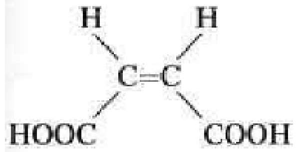


bis-glycol: resistance to alkali

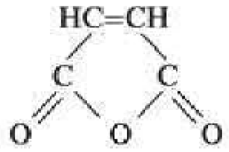


Hydrogenated bis-phenol A

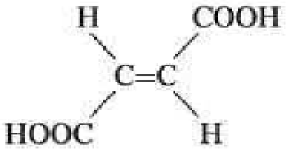
Unsaturated Acids



Maleic acid



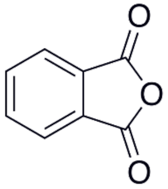
Maleic anhydride



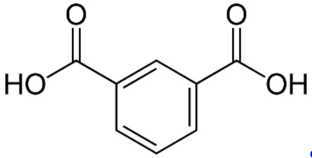
Fumaric acid
More reactive with St

Saturated Modifying Acids

To decrease crosslinking density. Saturated acid/ unsaturated acid = 40-60/60-40

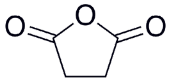


phthalic anhydride

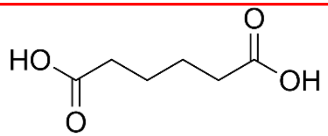


isophthalic acid

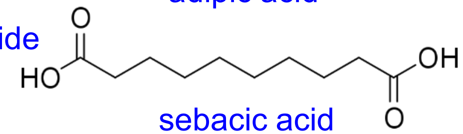
hard segments – heat resistant



succinic anhydride

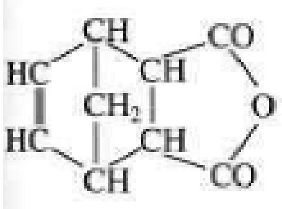


adipic acid

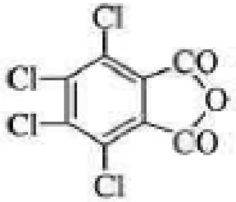


sebacic acid

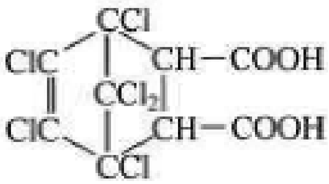
soft segments – flexibility



nadic anhydride
heat/chemical resistance



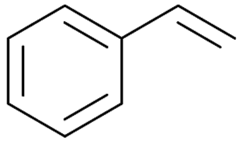
tetrachlorophthalic anhydride
flame-retardant



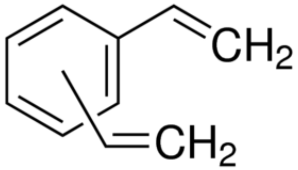
chlorendic acid
flame-retardant

UPR Components – cont'd

Crosslinking Monomer (solvent for UP)



styrene



divinyl benzene

Best property with styrene/fumaric acid = 1.9-2.4
To avoid evaporation of styrene, barrier agents are used, or vinyl toluene and divinyl benzene are used.

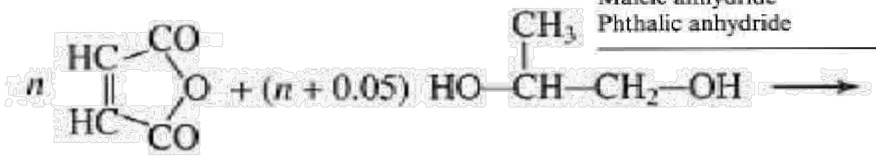
Table 4.8 A typical resin–styrene blend prepared for storage

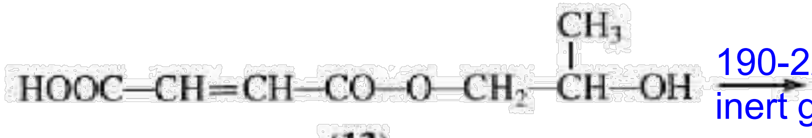
	Parts by weight
Polyester resin	200
Styrene	100
Benzyltrimethylammonium chloride	0.26
Hydroquinone	0.034
Quinone	0.0034

inhibitor

Synthesis of UPR

	Parts by weight	*Molar ratio*
Propylene glycol	100	1.1
Maleic anhydride	59	0.33
Phthalic anhydride	78	0.67





190-220°C
inert gas

(13)

MW: 1000-2000 g/mol

azeotropic distillation w/ toluene

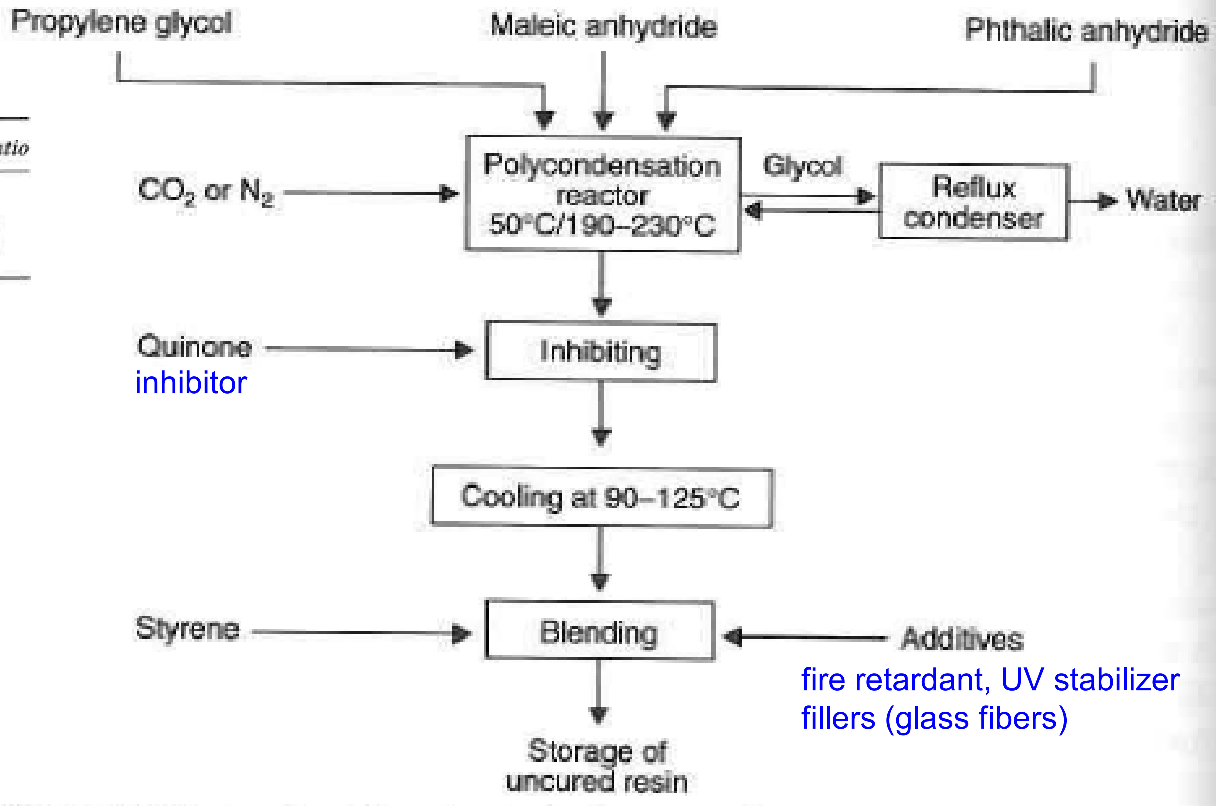


Figure 4.6 Preparation of unsaturated polyester resins.

UPR Curing: A Balance among Catalyst, Inhibitor, and Accelerator

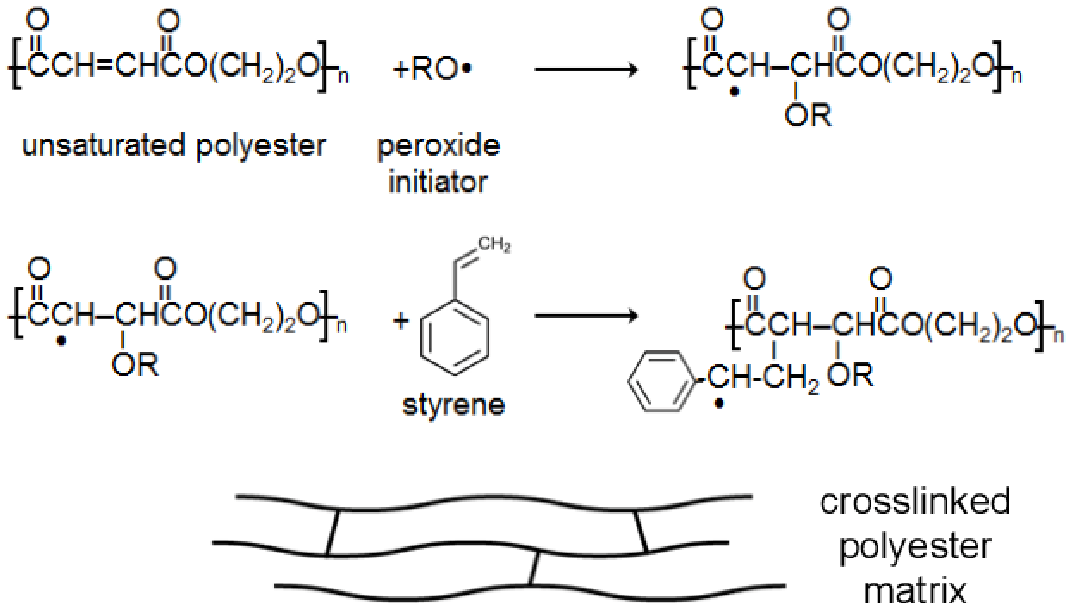
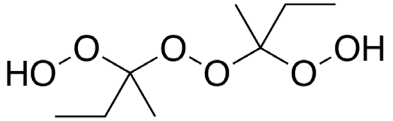


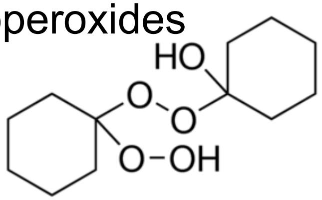
Fig. 1. Crosslink formation within a polyester resin.

Room Temp. Initiator System

1. Initiators: peroxides or hydroperoxides

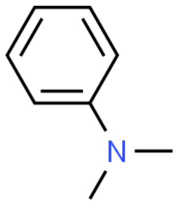


methyl ethyl ketone peroxide

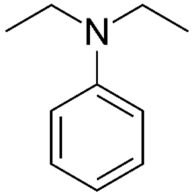


cyclohexanone peroxide

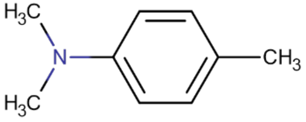
Accelerators: tertiary amines (for peroxides)



dimethylaniline



diethylaniline



dimethyl-*p*-toluidine

2. Metal soaps: cobalt or vanadium napththenates or octoates

Metal soaps should be used in combination of hydroperoxides

Warning: initiator and metal soap cannot mix directly.
Should be added separately into the UPR!
Otherwise, Explosion!

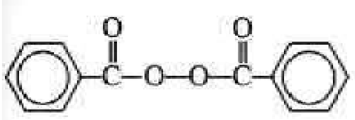
$$ROOH + Co^{2+} \rightarrow RO^{\cdot} + OH^{-} + Co^{3+}$$

$$ROOH + Co^{3+} \rightarrow ROO^{\cdot} + H^{+} + Co^{2+}$$

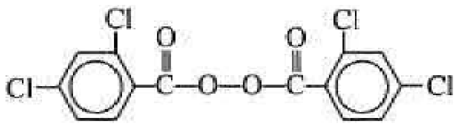
Curing and Gelation:

Exothermic reaction;
4-12% volume shrinkage, can be mitigated by adding fillers

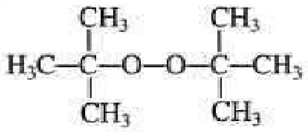
High Temp. Initiators



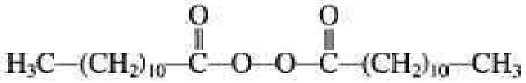
benzoyl peroxide (BPO)



2,4-dicblorobenzoyl peroxide



di-*tert*-butyl peroxide



lauroyl peroxide

UPR Properties and Applications

Properties

- Thermosetting, infusible and insoluble
- Many varieties of UPRs ranging from hard and brittle to soft and flexible. Almost every property can cover a broad range of values.
- Use temperature: up to 100°C for cured resins, 150°C for reinforced composites
- Resist to acids, but not alkaline
- Not good for high freq. electrical insulation
- Thixotropic (shear-thinning) with fine silica fillers
- Silane-treated glass fiber fillers for reinforcement
- Foams from water extended UPRs (i.e., artificial wood)
- Can be applied by hand lay-up or spray-up

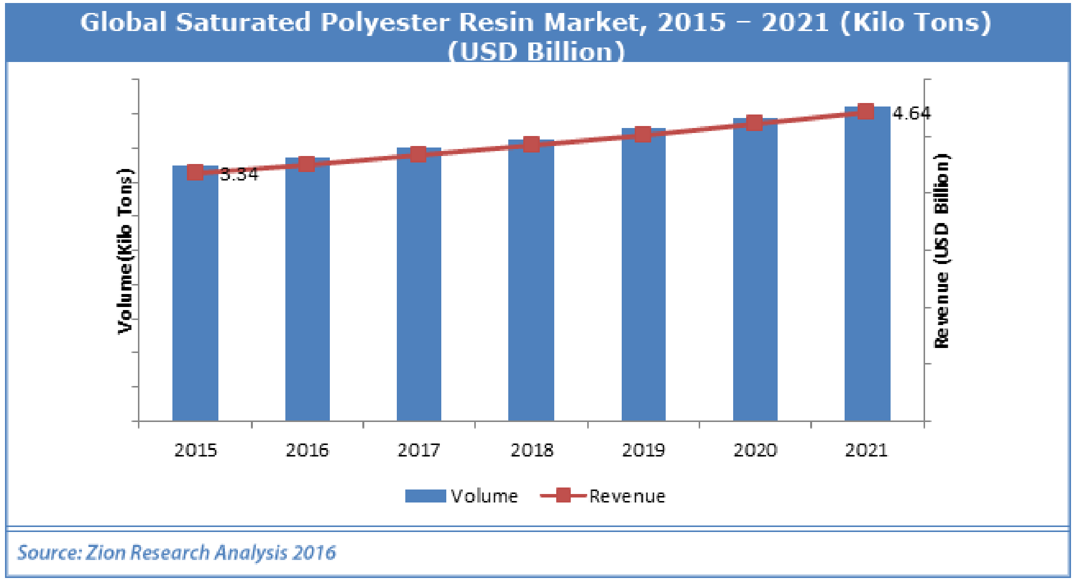
Table 4.9 A comparison of some properties of unfilled and glass reinforced resin and glass fiber

Property	*Unfilled casting*	*Glass chopped strand mat laminate (hand lay-up)*	*Glass woven cloth laminate (hand lay-up)*	*Glass fiber*
Glass content (% weight)	0	30	55	100
Specific gravity	1.2	1.37	1.7	2.54
Tensile strength (MPa)	62	140	340	3455
Flexural strength (MPa)	120	210	410	–
Compressive strength (MPa)	140	140	240	–
Impact strength (unnotched) (J/m)	110	1100	1300	–

Applications

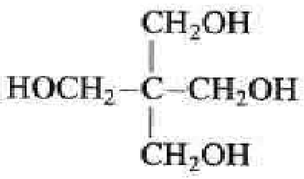
- Transportation, marine, construction, electrical, corrosion
- 50% for transportation: boat hulls, car bodies, truck cabs, public transport vehicles
- 30% for Construction: roofing, building insulation, corrosion-resistant pipes, tanks, swimming pools
- Furniture casting, simulated ornamental stone, buttons, trays, bowling balls, skis, surfboards, safety helmets, missile shells, rocket motor case
- Not good as coatings (O_2 inhibition); need UV curing

Saturated Polyester Resins (Alkyds)



Polyols


(20)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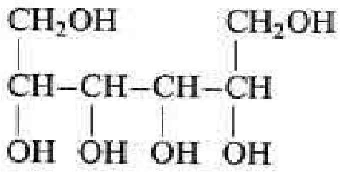
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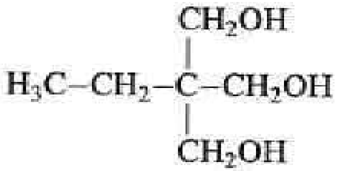
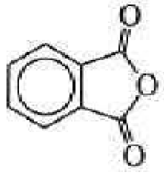

(23)

Dibasic Acids or Anhydrides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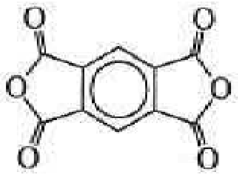
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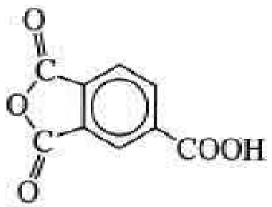
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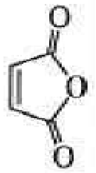
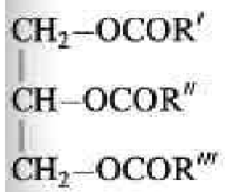

(27)

Drying Oils


(28)

$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ (29)

$CH_3(CH_2CH{=}CH)_3(CH_2)_7COOH$ (30)

$CH_3(CH_2)_3CH{=}CH{-}CH{=}CH{-}CH{=}CH(CH_2)_7COOH$ (31)

$CH_3(CH_2)_5\underset{OH}{CH}{-}CH_2{-}CH{=}CH{-}(CH_2)_7{-}CH_3$ (32)

- The amount of oil (oil length) influences the global amount of unsaturation, time of drying, and flexibility.
- Short oil alkyds (30-50% oil) and medium oil alkyds (50-70% oil) are cured at elevated temperatures (baked) to shorten the curing time; hard finishes.
- Long oil resins (70-80% oil) dry rapidly in air; flexible finishes.

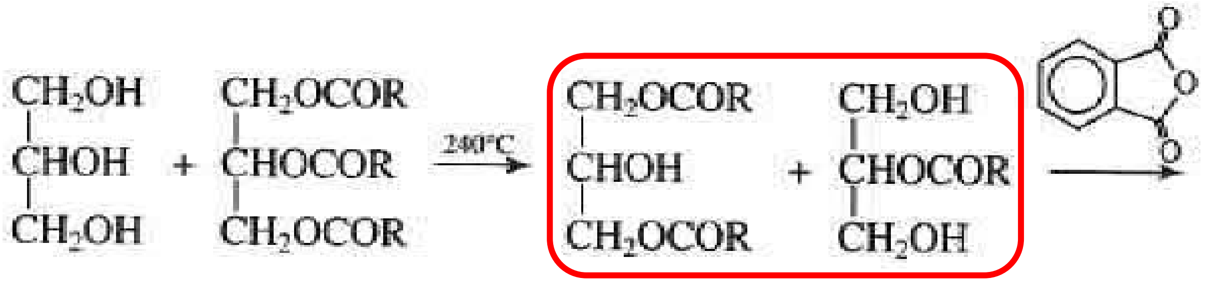
Synthesis and Curing

Cannot mix drying oil with glycerol and diacids – immiscible and phase separate!

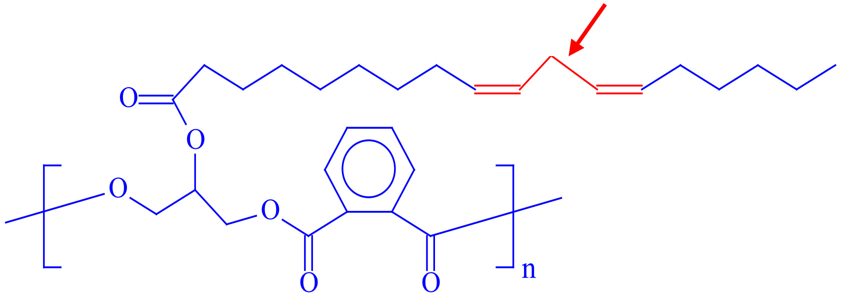
(a) Fatty Acid Process

- Saponification to obtain 'split oils' w/ 1 or 2 unsaturated esters (see red box below)
- Split oil is mixed with glycerol and phthalic anhydride
- Polycondensation by heating at 200-240°C under an inert gas flow or azeotropic distillation to remove H_2O

(b) Alcoholysis Process



R = unsaturated side chains



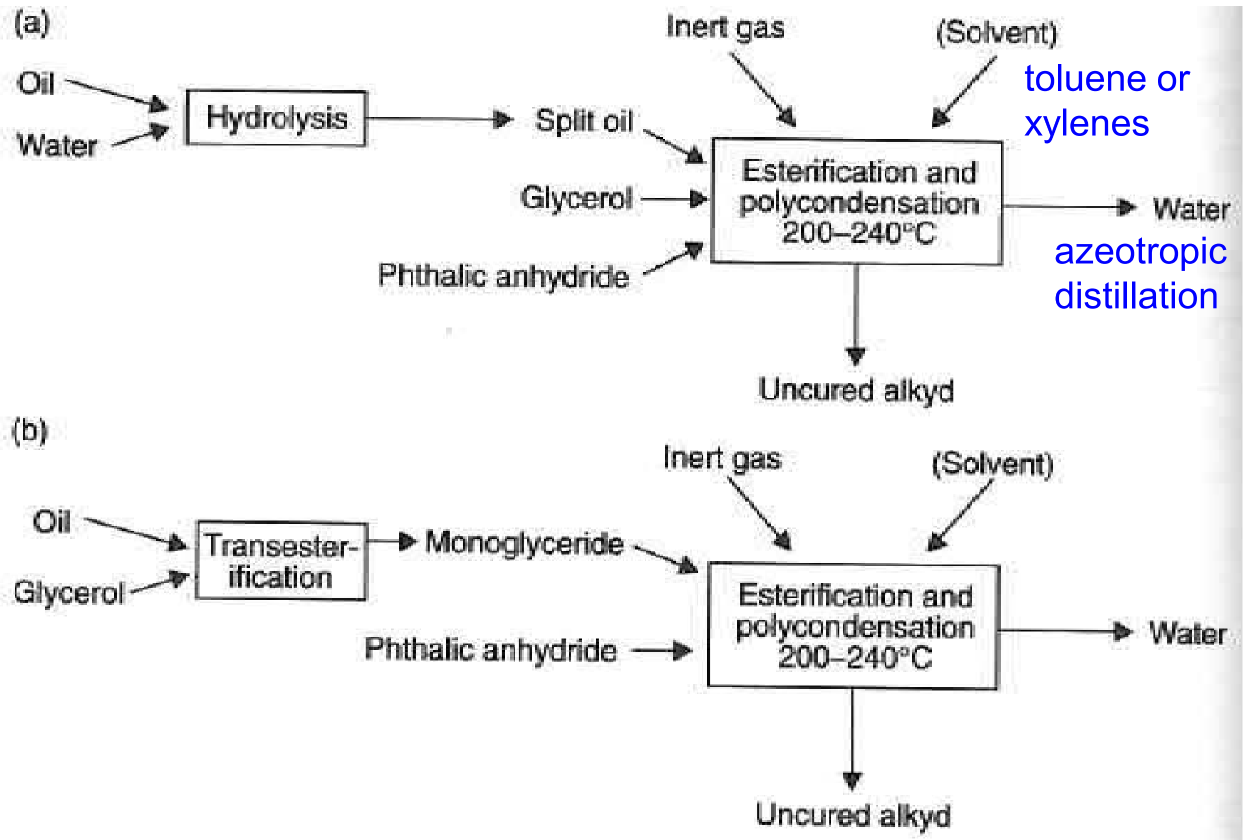


Figure 4.8 Preparation processes for alkyd resins: (a) fatty acid process; (b) alcoholysis process.

Uncured alkyd polyester is non-crosslinked.

Alkyd Paint Formulation

(a) Solvent-based or Water-based

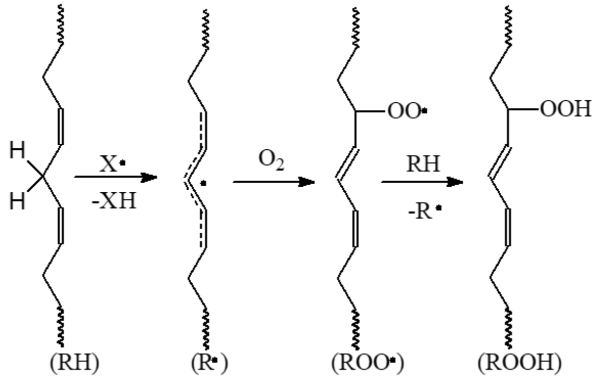
- Aromatic solvents (toluene/xylene) for short oil alkyds
- Aliphatic solvents or aromatic-aliphatic mixtures for medium and long alkyds
- Alkyd paints can be made into emulsions

(b) Catalyst or Drier

- Hydrocarbon-soluble organic salt of cobalt, lead or manganese such as naphthenates or octoates
- To speed up the formation of a solid film of coating

Crosslinking Mechanism for Alkyd Paint

Polymeric hydroperoxide formation by O_2 in air



X• is some impurity radical generated in the system by either UV or other ways

Hydroperoxide to generate radicals

$$Co^{2+} + ROOH \longrightarrow Co^{3+} + RO\bullet + OH^-$$

$$Co^{3+} + ROOH \longrightarrow Co^{2+} + ROO\bullet + H^+$$

Haber-Weiss cycle

$\xrightarrow{\text{alkyd}}$ crosslinked paint

Formulation for alkyd paints using cottonseed oil and standard soybean oil alkyds and octoate driers

Ingredients	Long oil alkyd paint formula (g)	Short oil alkyd paint formula (g)	Standard soya alkyd paint formula (g)
(mineral oil) White spirit	16.50	16.50	16.50
Cottonseed oil/standard soya alkyds	50.22	50.22	50.22
Calcium drier	0.60	0.45	0.80
Cobalt drier	0.65	0.58	0.50
~~Lead drier~~	~~1.50~~	~~1.16~~	~~2.70~~
Titanium (IV) oxide	16.55	16.55	16.55
Calcium carbonate	6.00	6.00	6.00
Formalin	2.03	2.03	2.03
Total	93.06	93.03	94.71

(lead drier is not used anymore)

(c) Modifiers

- Silicone modification for heat and water resistance
- Chorinated rubber for flame retardancy