

CHAPTER 11

ESTERIFICATION, POLYCONDENSATION, AND RELATED PROCESSES

CHAPTER 11 OBJECTIVES

- INTRODUCTION
- POLYESTER SYNTHESIS
 - *Transesterification*
 - *Direct Esterification*
 - *Other Esterification Reactions*
- POLYURETHANE SYNTHESIS
- POLYCARBONATE SYNTHESIS
- POLYAMIDE SYNTHESIS (NYLON)
- POLYSILOXANE (SILICONE) SYNTHESIS
- EPOXY RESINS
- GROUP TRANSFER POLYMERIZATION

INTRODUCTION

- Many of the industrial homogeneous catalytic processes produce intermediates for the synthesis of condensation polymers such as polyesters and polyamides.
- Some of the largest applications of homogeneous catalysis are in the production of intermediates having the high purity required for polymer formation.
- The selectivity of a homogeneous catalyst is a major advantage when the final product must be better than 99.9% pure.

INTRODUCTION

- Homogeneous catalysis is used in some polymerization processes.
- Soluble metal compounds are used as catalysts in most processes for the manufacture of polyesters. Similar catalysts are often used for the production of polyurethanes and polycarbonates.
- Polyamide synthesis is not usually catalyzed by metal complexes, but the topic is considered as a result of the important role of homogeneous catalysis in the production of nylon intermediates.

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POLYESTER SYNTHESIS

- The most widely used synthetic fiber is polyester - poly(ethylene terephthalate) or PET - which is sold under such familiar trade names such as Du Pont's Dacron, ICI's Terylene, or Eastman's Kodak.
- PET is also commonly encountered in the familiar plastic bottles for soft drinks, and in films such as Du Pont's Mylar® which are used for food or liquid packaging, magnetic tapes, novelty balloons, and a host of other applications.

POLYESTER SYNTHESIS

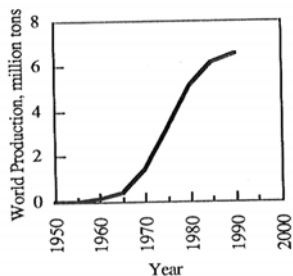


Figure 11.1 world production of polyester for the last half century.

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POLYESTER SYNTHESIS

- The major process for the production of polyester was based on dimethyl terephthalate, DMT.
- This approach involves two steps, both of which are catalyzed by soluble metal compounds.
- Transesterification of the dimethyl ester with ethylene glycol gives methanol and bis(hydroxyethyl)terephthalate, BHET.
- The hydroxyethyl ester is then heated under vacuum to drive out one equivalent of ethylene glycol forming the polyester.
- For fiber applications, it is common to add a low percentage of the sodium salt of the 5-sulfo-bis(hydroxyethyl)isophthalate as a site for dyeing the fiber.

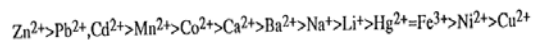
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POLYESTER SYNTHESIS

Transesterification

- The usual preparation of poly(ethylene terephthalate) uses two different catalyst systems.
- The first step in the process of Figure 11.2, the transesterification of dimethyl terephthalate with ethylene glycol, is catalyzed by a variety of metal ions.



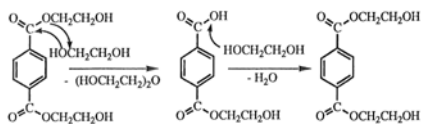
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POLYESTER SYNTHESIS

Transesterification

- It is unlikely that this is a direct dehydration of two molecules of ethylene glycol to form the ether.
- Because the benzoyl group would be a better leaving group, it is more likely that the reaction proceeds through the intermediacy of the ester:



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POLYESTER SYNTHESIS

Transesterification

- The diethylene glycol formed in this way is incorporated into the final polymer and changes the chemical and physical properties.
- In fiber applications, the diethylene glycol can act as a **dye site**, so it may even be added to the polymerization in an effort to keep its concentration constant, thereby improving dye uniformity.
- In film applications, its presence is generally minimized.
- It is common practice to add an "inhibitor" such as phosphoric acid or triphenyl phosphate before the polycondensation step.
- The inhibitor converts the metal salt to a complex phosphate that has little catalytic activity and does not interfere with the antimony-based polycondensation catalyst.

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POLYESTER SYNTHESIS

Transesterification

- In a commercial polymerization, ethylene glycol, dimethyl terephthalate, and the metal acetate catalyst may be added continuously to a transesterification reactor that is heated to 150-200°C.
- Methanol and some glycol distill out of the mixture. The molten bis(hydroxyethyl) terephthalate that results is added to a polycondensation reactor along with the inhibitor and antimony(III) oxide which has been predissolved in glycol.

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POLYESTER SYNTHESIS

Transesterification

- Divalent metal ions are said to act as Lewis acids in the catalysis of transesterification.
- Coordination of the carbonyl group of the ester to the cation is believed to activate it to nucleophilic attack by the oxygen of an alcohol.
- The complexation and activation of dimethyl terephthalate by calcium acetate are depicted in Figure 11.3.
- When the carbonyl group coordinates to a calcium(2+) ion, electron density is transferred to the metal ion.

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POLYESTER SYNTHESIS

Transesterification

- The electron depletion of the carbonyl is most pronounced at the carbon atom.
- This effect makes the carbon especially susceptible to nucleophilic attack. The attack by a hydroxyl group is often written with a four-center transition state as shown.
- Regardless of the timing of events, the overall effect is breaking and making of C-O and O-H bonds to produce a glycol ester and free methanol.
- Dissociation of the metal ion from the carbonyl group completes the catalytic cycle.

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POLYESTER SYNTHESIS

Transesterification

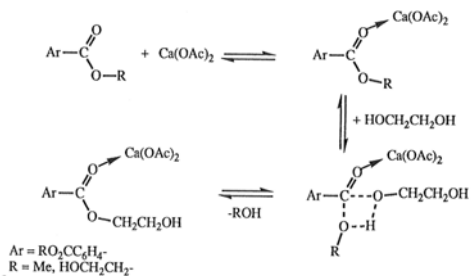


Figure 11.3 Calcium-catalyzed transesterification of aromatic esters.

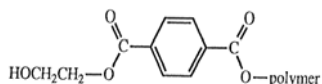
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POLYESTER SYNTHESIS

Transesterification

- The same kinds of reactions occur during the first stages in growth of the polymer chain.
- The aryl group can be a terephthalate unit at the carboxyl end of a growing polymer chain.
- Similarly, the ethylene glycol in this scheme can be replaced by a glycol-terminated chain:



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POLYESTER SYNTHESIS

Transesterification

- The mechanism of Figure 11.3 seems quite plausible for the transesterification catalyzed by divalent metal ions but is not universally accepted.
- It was proposed earlier that the metal ion reacts with ethylene glycol to form an alkoxide, for example, $[\text{Ca-OCH}_2\text{CH}_2\text{OH}]$.
- The nucleophilic alkoxide ion then attacks the carbonyl group of a coordinated ester.
- This proposal was supported by the kinetics of the transesterification catalyzed by M^{2+} ions.

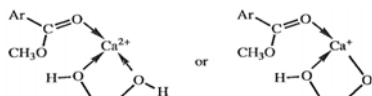
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POLYESTER SYNTHESIS

Transesterification

- The reported kinetics (first order each in glycol, ester, and catalyst) would also be consistent with the Lewis acid mechanism if the three reactants were assembled in a complex like.



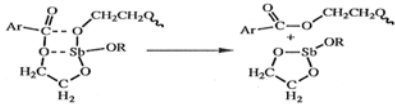
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POLYESTER SYNTHESIS

Transesterification

- The mechanism of the polycondensation reaction is also unresolved.
- In commercial practice, this final portion of the polymerization is antimony-catalyzed.
- It has been suggested that hydroxyethyl end groups of two growing polymer chains are joined to an antimony (or titanium) center as alkoxides in the intermediate:



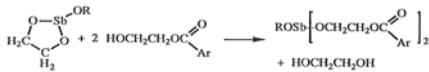
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POLYESTER SYNTHESIS

Transesterification

- Ligand exchange within the coordination sphere of antimony forms a new ester link which couples the two growing polymer chains.
- The oilier product is an antimony salt of ethylene glycol which can release ethylene glycol by reaction with other hydroxyethyl groups:



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POLYESTER SYNTHESIS

Transesterification

- This mechanism is speculative, but it seems consistent with the kinetic data available.
- The polycondensation reaction is also catalyzed by other metals whose activity is reported to be in the order:

Ti>Sn>Sb>Mn>Zn>Pb

- The influence of temperature varies for each of the catalysts, indicating differing mechanisms of activity and deactivation.
- Catalysts such as Mn, Zn, and Pb typically used for the transesterification step are very active in media having both a high and a low hydroxyl content, but they are easily poisoned by very small amounts of carboxylic end groups.

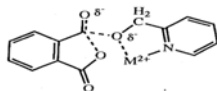
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POLYESTER SYNTHESIS

Transesterification

- Antimony trioxide, which is typically used in the polycondensation step, is insensitive to the presence of acidic carboxylic end groups, but its activity is inversely proportional to the hydroxyl group concentration.
- Thus ethylene glycol must be removed rapidly.
- The importance of the chelation shown in the intermediates sketched above is highlighted by studies of the hydrolysis of pyridylmethyl hydrogen phthalates.
- Divalent metal ions such as Ni^{2+} , Co^{2+} and Zn^{2+} are very good catalysts for the reaction.



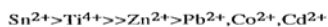
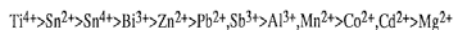
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POLYESTER SYNTHESIS

Direct Esterification

- The change from dimethyl terephthalate to terephthalic acid as a starting material for polyester production requires a change in catalyst.
- The divalent metal salts usually used as transesterification catalysts have little activity in the esterification of a carboxylic acid with an alcohol.
- Extensive screening of potential catalysts for esterification has led to the ordering of activities for reaction of ethylene glycol with benzoic acid to form hydroxyethyl benzoate, and for reaction of ethylene glycol with terephthalic acid to form bis(hydroxyethyl) terephthalate.



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POLYESTER SYNTHESIS

Direct Esterification

- The tin compounds that have good activity in direct esterification include tin(II) oxide and oxalate and organotin(IV) compounds such as dialkyltin(IV) oxides and carboxylates.
- The titanium catalysts are typically titanium(IV) alkoxides.

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POLYESTER SYNTHESIS

Direct Esterification

- A slurry of terephthalic acid in excess ethylene glycol is fed continuously to a reactor along with titanium(IV) tetraisopropoxide.
- The hot (250-300°C) reaction mixture which contains bis(hydroxyethyl) terephthalate and low molecular weight polymer dissolves the terephthalic acid and permits esterification to proceed in a relatively homogeneous medium.
- Continuous distillation removes some excess glycol and the water as it is formed.

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POLYESTER SYNTHESIS

Direct Esterification

- The insolubility of terephthalic acid has impeded mechanistic studies on polyester synthesis by direct esterification.
- As an alternative, kinetic studies have been done on the reactions of benzoic acid, isophthalic acid, and substituted isophthalic acids with ethylene glycol.
- Once benzoic acid is added to one end of the ethylene glycol, the remaining OH group is more active toward esterification.
- Tin(II) and titanium(IV) show similar kinetic dependencies, although the order of the reaction varies with the acid that is being esterified.

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POLYESTER SYNTHESIS

Direct Esterification

- Since the rate depends on the concentrations of acid, glycol, and catalyst, it appears that all three components must be assembled in a reactive complex such as $(ArCO_2)_xM(OCH_2CH_2OH)_y$.
- The role of such a complex in esterification of benzoic acids is illustrated in the catalytic cycle of Figure 11.4.
- Dimethyltin oxide is normally all oligomer, but much of its chemistry is that expected from the hypothetical monomer, $Me_2Sn=O$.
- The initial reaction within the catalytic cycle is the addition of the alcohol O-H to form a hydroxy-alkoxy derivative.

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POLYESTER SYNTHESIS

Direct Esterification

- Esterification of this compound with the arenecarboxylic acid generates the proposed $(ArCOO)M(OCH_2CH_2OH)$ intermediate.
- Intramolecular nucleophilic attack on the carbonyl group by the alkoxide ligand produces ester and Me_2SnO to complete the cycle.
- This mechanism seems quite plausible for the direct esterification, but much additional work is required to establish it conclusively.

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POLYESTER SYNTHESIS

Direct Esterification

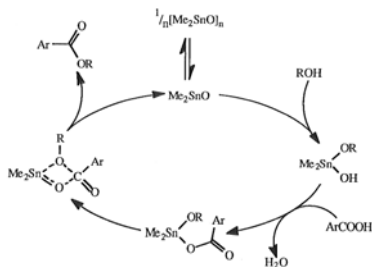


Figure 11.4 Tin-catalyzed esterification of benzoic acid. Dimethyl tin oxide is polymeric; the mononuclear species shown in this diagram are not meant to imply the nuclearity of the catalytically active species.

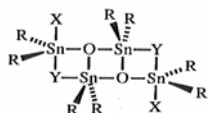
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POLYESTER SYNTHESIS

Direct Esterification

- Catalysts based upon ladder-tetramer $Sn_4R_8O_2X_2Y_2$ (combinations of $X = Cl, NCS$; $Y = Cl, OH, NCS$) have been employed quite successfully in esterification and transesterification reactions.
- It is felt that the tetramer stays intact during catalysis and two metal sites are involved during the catalytic step.



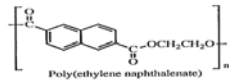
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POLYESTER SYNTHESIS

Other Esterification Reactions

- The transesterification and direct esterification processes discussed above serve to illustrate the general principles involved in most metal-catalyzed esterification and transesterification reactions.
- These catalysts are also applied to a number of lower- volume polymers and chemicals.
- Du Pont and Teijin have introduced a polyester film based upon ethylene glycol and 2,6-naphthalenedicarboxylate for food packaging, magnetic tapes, and high- performance electrical applications.
- Advantages include higher transparency and better resistance to permeation of oxygen and moisture.

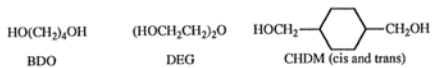


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POLYESTER SYNTHESIS

Other Esterification Reactions

- While most of the polymers discussed to this point involve ethylene glycol, other glycols or diols are also employed in polymer synthesis.
- Terephthalate polyesters are synthesized from 1,4-butanediol (BDO), diethyleneglycol (DEG), or cyclohexanedimethanol (CHDM).
- The butanediol product finds wide use as a high-performance elastomer in applications such as tires on small vehicles and protective joint "boots" for front-wheel drive cars.
- Terephthalate esters of DEG and CHDM find use in more limited specialty applications.



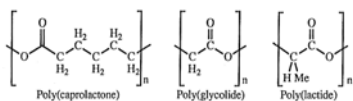
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POLYESTER SYNTHESIS

Other Esterification Reactions

- Tributyltin(IV) catalysts are effective for the ring-opening polymerization of ϵ -caprolactone in solution or bulk.
- The polymers can be taken to high molecular weight, but there are also commercial applications for lower molecular weight species.
- The related species, poly(glycolide), poly(lactide), and their copolymers have been commercialized for bone screws and other high-value medical applications.



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POLYESTER SYNTHESIS

Other Esterification Reactions

- Polyglycolides and polylactides are synthesized by ring-opening of their cyclic dimer esters using tin catalysts in solution or in the melt, but many other metal-based catalysts are also effective.
- The choice of metal for the catalyst can have a pronounced effect upon the rate of polymerization and also the subsequent thermal stability of the polymer.
- Because of their biological origin, lactide dimers can be obtained as the enantiomerically pure d,d-, l,l-, or racemic d,l-species, thus providing stereochemically "labeled" starting materials.

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POLYESTER SYNTHESIS

Other Esterification Reactions

- There is a substantial industry based upon the esterification and transesterification of organics.
- Phthalic acid esters of long-chain alcohols derived from oxo synthesis or ethylene oligomerization are used as plasticizers. They are often synthesized from the convenient anhydride.
- The mechanism of the titanium- catalyzed reaction has been explored, and the proximity of the two carboxylate groups has an influence on the course of the reaction.
- The degree of hydrolysis of titanium catalysts can have a pronounced effect on the catalyst activity.

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POLYESTER SYNTHESIS

Other Esterification Reactions

- Esters are widely used as fragrances, and there is a major industry built upon their synthesis.
- Esters are also employed in medicinals. Long-chain esters of aliphatic diacids are used as high-performance synthetic lubricants in demanding applications such as turbojet engines.
- While conventional strong-acid catalysis is most commonly used in the synthesis of these low-volume, high-value products, titanate catalysis has been explored.
- Chiral titanium catalysts can even be used to carry out stereoselective esterifications on α -arylcarboxylic acid derivatives and intermediates for insecticides.

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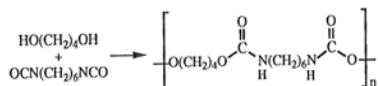
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POLYURETHANE SYNTHESIS

- The diversity of applications of polyurethanes (a urethane is an N- and O-substituted derivative of carbamic acid) is very impressive.
- They range from upholstery foams to rigid structural resins, from durable flooring and automotive finishes to designer fibers like Du Pont's Lycra spandex, and from rubbers to quick-bonding adhesives.
- They are prepared by reaction of diisocyanates with dihydroxy compounds.
- A simple example is the synthesis of Perlon-U, the first commercial polyurethane resin:

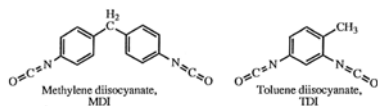


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POLYURETHANE SYNTHESIS

- This is a good example of an aliphatic polyurethane, but most modern polyurethanes are prepared from aromatic diisocyanates such as MDI or TDI in combination with diols such as ethylene or propylene glycol, polyether diols, aliphatic polyesterdiols, or siliconediols.
- As in other condensation polymers, high-purity monomers are required to achieve the molecular weights required for desirable physical properties.
- Polyester diols mentioned above also find application in specialty applications.

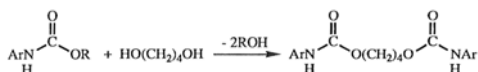


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POLYURETHANE SYNTHESIS

- Polyurethanes can also be prepared from simple carbamic esters by catalytic transesterification.
- This polymerization process is much less common than the isocyanate-based process, but it finds some use in the synthesis of plasticizers.



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POLYURETHANE SYNTHESIS

- The reaction of an aromatic diisocyanate with a glycol occurs readily and no catalyst is required.
- However, catalysts are used to accelerate polyurethane formation in most commercial processes.
- For aliphatic isocyanates, catalysts are required. The most common catalysts are tertiary amines, but metal complexes are also widely used.
- The most commonly used metal catalysts are tin derivatives, although titanium tetraalkoxides are very effective with both isocyanates and carbamic esters.
- Polyurethane formation is also catalyzed by many of the other metal compounds that are used for polyester production.

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POLYURETHANE SYNTHESIS

- Polyurethanes are used in many different ways - fibers, coatings, adhesives - but one of the largest uses is in the preparation of foams.
- The polymerization is carried out in the presence of a "blowing agent" which releases a gas such as N_2 or CO_2 or a fluorocarbon. The gas forms bubbles in the viscous prepolymer.
- The foam structure is retained after the polymer attains high molecular weight and becomes solid.
- Trifunctional reactants such as triols provide crosslinks for rigidity. The process is illustrated by a patent in which a nonvolatile amine and tin(II) octoate are used as cocatalysts to produce both flexible and rigid foams.

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POLYURETHANE SYNTHESIS

- A mixture of the polyalcohol (a propylene oxide adduct of glycerin), the catalysts, the blowing agent, and a trace of water are vigorously stirred while 2,4-toluenediisocyanate is added.
- The foaming mixture is poured into a heated box and cured at 100-105°C for one hour in order to produce a cube of polyurethane foam.
- The rigidity of the foam depends on the number of polymer crosslinks provided by the alcohol component.

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POLYURETHANE SYNTHESIS

- The mechanism of catalytic polyurethane production may be analogous to that of polyester production.
- Lewis acidic M^{2+} salts can activate the isocyanate function by coordination to oxygen as in transesterification.
- Organotin compounds act through alkoxide and carbamate intermediates as shown in Figure 11.5.
- Coordination of the isocyanate to the tin activates the C=N group to intramolecular nucleophilic attack by alkoxide to form a tin carbamate.
- Alcoholysis of the Sn-N bond liberates the carbamate-containing polymer and regenerates the tin alkoxide for another cycle of reaction.
- For reactions with glycols, intermolecular hydrogen bonding may play a role in the reaction.

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POLYURETHANE SYNTHESIS

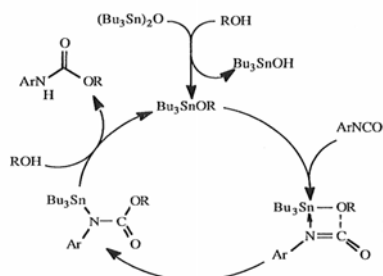


Figure 11.5 Tin-catalyzed addition of alcohols to isocyanates to yield carbamates.

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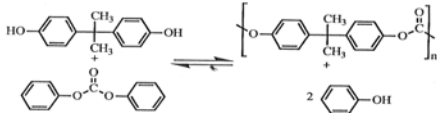
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POLYCARBONATE SYNTHESIS

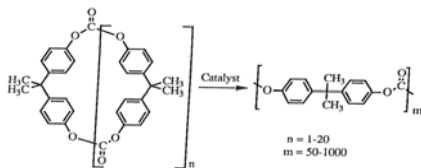
- The original synthesis of polycarbonates was by transesterification of aromatic diesters of carbonic acid with dihydroxydiaryls such as bisphenol-A in the presence of basic catalysts.
- The reaction is also catalyzed by $Ti(OBu)_4$, much like the polyesterifications.
- To achieve the high molecular weights necessary for desired properties, the equilibrium is shifted by distilling off the phenol at high temperature.
- This process was largely displaced by reaction of the sodium salt of bisphenol-A directly with phosgene.



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POLYCARBONATE SYNTHESIS

- General Electric has developed a synthesis based upon macrocyclic monomers which are polymerized by ring-opening polymerization using basic catalysts such as phenyl lithium, lithium phenoxide, tetrabutylammonium tetraphenylborate, and other strong anions.
- The polymerization can also be accomplished using β -diketonate complexes of a variety of metals including Al, Fe, Ce, and Ti.



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POLYCARBONATE SYNTHESIS

- There are many advantages to this new synthesis. At equilibrium, almost no cyclics remain.
- Since no byproducts are formed in the reaction, the final molecular weight is determined solely by monomer purity and the level of initiator used.
- The molecular weights of 2-400,000 typically achieved are significantly higher than those obtained in conventional polymerizations.
- Because the melt viscosities of the cyclics are much lower than the polymers, composites, crosslinking, copolymerizations, and extruder polymerizations can now be considered.

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POLYAMIDE SYNTHESIS (NYLON)

- The most widely used polyamide in the United States is poly(hexamethyleneadiPamide), usually known as nylon-6,6.
- The numerical designation indicates that it is prepared from a six-carbon diamine and a six-carbon dicarboxylic acid.
- Second behind nylon-6,6 and equal on a worldwide scale is nylon-6, which is made by the ring-opening polymerization of ϵ -caprolactam.
- The largest outlet for both polymers is in the production of fibers for carpets, hosiery, and other applications.
- The polymers are also used as engineering plastics.

POLYAMIDE SYNTHESIS (NYLON)

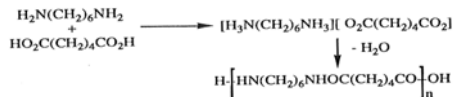
- There is a growing use of nylon-6,12 and nylon-12,12 for more demanding applications because their changes in physical dimensions upon exposure to humidity are reduced because of the higher aliphatic content.
- Nylon-12,T, where T stands for terephthalic acid, is also under investigation.
- Nylon-46 is produced in Europe and Japan for its improved properties at higher temperatures.

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POLYAMIDE SYNTHESIS (NYLON)

- The usual preparation of nylons from diamines and diacids begins with the reaction of the two components to form a salt - thus guaranteeing balanced stoichiometry.
- In the polymerization step, the salt is heated under vacuum to expel water and form the amide bonds:



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POLYAMIDE SYNTHESIS (NYLON)

- In contrast to adipic acid, which is made by similar processes by most producers, 1,6-hexanediamine is manufactured by several different processes though each goes through adiponitrile as an intermediate.
- The dinitrile is hydrogenated smoothly to the diamine with a heterogeneous catalyst.
- The oldest route is reaction of adipic acid with ammonia to give ammonium adipate that dehydrates to form adiponitrile when it is heated strongly.
- Electrolytic reductive dimerization of acrylonitrile to adiponitrile is widely practiced and is especially competitive on a smaller scale.

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POLYAMIDE SYNTHESIS (NYLON)

- The synthesis of nylon-6 from ϵ -caprolactam does not require the salt-forming step because the acid and amine function are combined into a single cyclic molecule, thereby assuring balance of the two functionalities.
- However, the polymerization is an equilibrium between polymer and monomer
- The monomer is only slightly less stable than polymer, so there is an appreciable equilibrium concentration.
- The uncatalyzed polymerization of pure monomer proceeds very slowly at temperatures as high as 250°C, and monomer becomes more favored at these higher temperatures.

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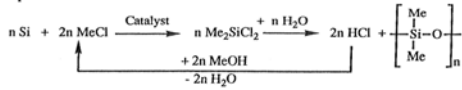
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- GROUP TRANSFER POLYMERIZATION

POLYSILOXANE (SILICONE) SYNTHESIS

- The silicon-oxygen bond is one of the most stable bonds in nature and, as a result, it confers a great deal of stability to the siloxane ($-\text{SiR}_2-\text{O}$)_x backbone of silicones.
- The physical properties of silicones, which range from mobile fluids to elastomers and highly crosslinked resins, are retained over a wide range of temperatures and conditions.
- They also have unique surface properties and low toxicity.
- These features make them useful in applications such as protective coatings, sealants, medical implants, hydraulic oils, and water-repellants.

POLYSILOXANE (SILICONE) SYNTHESIS

- The process for making methyl silicones starts with the addition of two equivalents of methyl chloride to silicon metal.
- The resulting dimethyl silicon dichloride is hydrolyzed with one equivalent of water yielding the desired Si-O-Si linkages and two equivalents of HCl.



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POLYSILOXANE (SILICONE) SYNTHESIS

- The HCl is recycled by reaction with methanol to give methyl chloride; thus the overall reaction is methanol plus silicon to give silicone and water.
- Cyclic oligomers are the simplest of the useful products obtained. Linear polymers are obtained by incorporating Me_2SiCl or other monochlorides into the hydrolytic reaction, thereby controlling end-group functionality and molecular weight.
- The RSiCl_2 molecules provide branching points in the polymer to further adjust the desired properties.

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POLYSILOXANE (SILICONE) SYNTHESIS

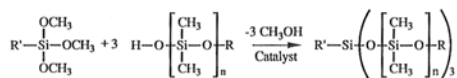
- In the 1960s, silicone elastomers that could undergo room-temperature vulcanization (RTV), that is, cure or crosslink in situ without application of heat, were introduced.
- These products quickly became an appreciable fraction of the entire industry.
- Single-component RTV elastomers based upon an acetate cure are most familiar to consumers as bathtub caulks.
- Of the four commercially important curing processes to form silicone rubbers, three - the one- and two-component condensation cures and the silane/olefin-addition cure - utilize metallic catalysts.
- The fourth is a peroxide-induced, free-radical cure and is not covered here.

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POLYSILOXANE (SILICONE) SYNTHESIS

- The condensation cure is used for most RTV silicone rubbers, as well as most solvent-borne silicone resins.
- The reaction is much like esterification or transesterification if silicon methoxides are considered to be esters of silicic acid.
- In one form, a trialkoxy silicon alkyl is reacted with three silanol-terminated polysiloxanes to yield a branch or crosslink in the $(-\text{SiR}_2-\text{O}-)_x$ backbone.



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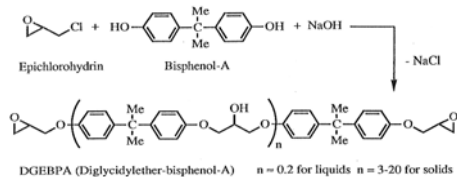
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EPOXY RESINS

- Epoxy resins are characterized by their good adhesion to a variety of substrates, high stability to chemicals, temperature, and corrosion, and good electrical and mechanical properties.
- The most important epoxy resins are based upon the product of the reaction of epichlorohydrin with bisphenol-A.



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EPOXY RESINS

- Anhydride-cured systems usually rely upon a direct, uncatalyzed reaction, but the desire to increase the rate of cure while leaving the storage-life of the resin unaffected has led to the discovery of "latent accelerators" for the reaction.
- The complex $\text{BF}_3 \cdot \text{NH}_2\text{Et}$ is effective for this application, but has an adverse effect on electrical properties.
- Transition metal β -diketonates catalyze the reaction and have no effect on the electrical or mechanical properties.

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EPOXY RESINS

- The $\text{Co}(\text{acac})_3$ -catalyzed curing reaction follows first-order kinetics, but surprisingly, it is 0.25 order in catalyst.
- A variety of chromium compounds exhibited excellent latent catalytic properties in the curing of bisphenol-A epoxy resins with 1-methyltetrahydrophthalic anhydride.
- Catalyst residues in a copper-catalyzed isomethyltetrahydrophthalic anhydride system catalyze the oxidative thermal degradation of the resulting epoxy polymer.

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GROUP TRANSFER POLYMERIZATION

- Free-radical polymerization has been the standard method of preparation of poly(methyl methacrylate) polymers.
- It is a relatively inexpensive and simple procedure to get high molecular weight homopolymer.
- The method is equally effective for random copolymerization of mixed methacrylates.
- If one desires homopolymers having a low or narrow molecular weight or copolymers with customized sequences of the comonomers, one must use anionic or group transfer polymerization (GTP).
- Generally, anionic polymerization uses hindered lithium alkyl compounds as initiators and the polymerizations are carried out at -60°C .

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GROUP TRANSFER POLYMERIZATION

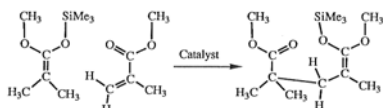
- Group transfer polymerization is initiated by the Michael addition of a silylketene acetal to an α,β -unsaturated ketone.
- In the illustration for methylmethacrylate, the addition results in a new silyl ketene acetal which can undergo further additions.
- The polymerization is living, the molecular weight distribution approaches one, all of the initiating groups are consumed, and initiation is fast relative to propagation.
- The polymerization requires a catalyst to function. The original catalyst was TAS bifluoride [tris(dimethylamino)sulfonium bifluoride], but tetrabutylammonium fluoride trihydrate is also effective.

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GROUP TRANSFER POLYMERIZATION

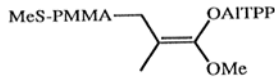
- The waters of hydration do not need to be removed. Though less effective, tetrabutylammonium carboxylates or bicarboxylates are the preferred catalysts because of availability and reproducibility.
- All of these catalysts operate by coordinating to and activating the silicon group for transfer, Lewis acids such as ZnBr_2 or HgI_2 are also effective catalysts, though they operate by a completely different mechanism.
- Rather than activate silicon, most of the Lewis acids activate the incoming methacrylate by coordination to the carbonyl oxygen atom.



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GROUP TRANSFER POLYMERIZATION

- A form of GTP in which the transferring group is an aluminum tetraphenylporphyrin results in a polymerization which has been termed "immortal" because of its robust nature.
- Polymerization of methyl methacrylate initiated with AlTPP(SMe) gives a polymer which is terminated on one end with a methyl sulfide group and on the other with an aluminum porphyrin.
- This system has been used to make a variety of interesting copolymers.

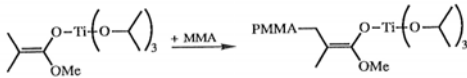


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GROUP TRANSFER POLYMERIZATION

- A living polymerization of methacrylates can also be initiated using tri(isopropoxy)titanium enolates.



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