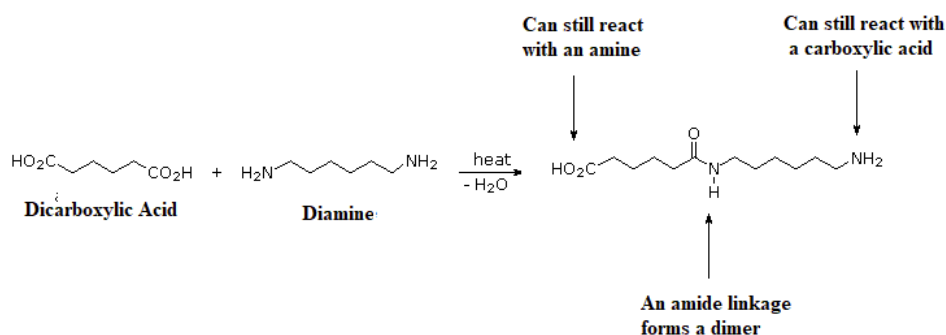
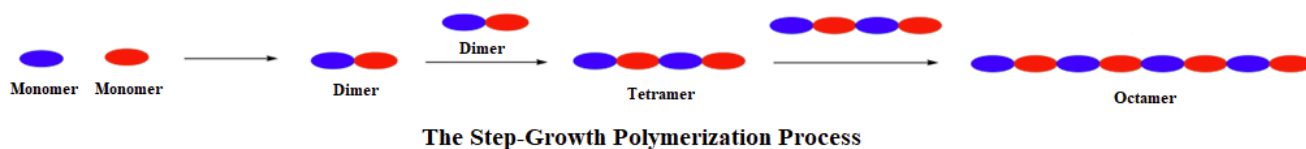


30.4: STEP-GROWTH POLYMERS

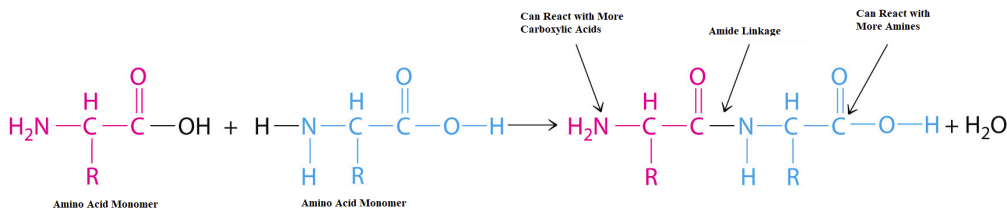
The process of step-growth polymerizations are fundamentally different than in chain-growth. In step-growth polymerizations, monomers are generally linked by a carbon-heteroatom bond (C-O & C-N) formed in non-sequential steps. Often, the reactions used to link these monomers include multiple nucleophilic acyl substitutions. Step-growth polymerizations usually use two different monomers, neither of which would undergo polymerization on its own. The two monomers are multifunctional and complementary to each other, such that each provides the other with a reactive partner. In this section, we will be focusing on monomers which are **difunctional**, meaning they contain two of the same reactive functional group. A step-growth polymerization starts with two complementary functional groups on different monomers reacting to form a dimer. Because both monomers were difunctional, each retains a reactive group and can react with additional complementary monomers.



In fact the difunctionality of the monomers, allows step-growth polymers to grow in two directions at once. First, two complementary monomers react with each other to form a dimer. Assuming that monomers react at roughly similar rates, when one end of the dimer reacts again it will likely find another dimer and form a tetramer. Then when the tetramer goes to react again it will most likely find another tetramer and form an octamer. This process is repeated allowing the polymer to grow in two directions at the same time.

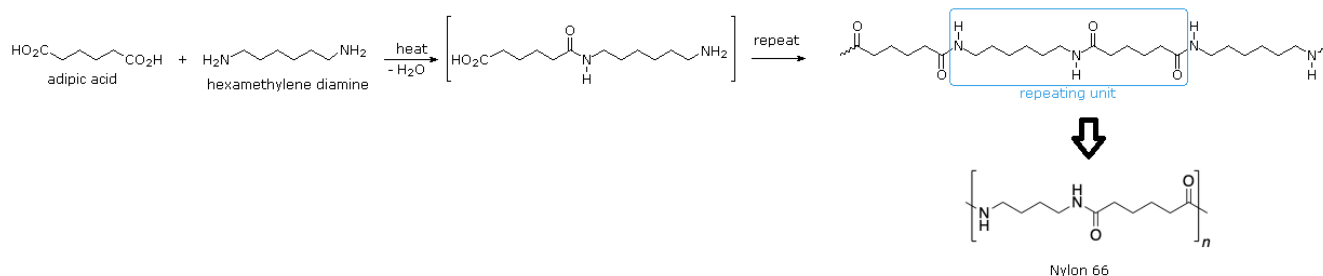


Virtually all fibers are made from some form of polymer. In particular, silk and wool are composed of a naturally occurring protein polymer. The monomers of proteins are called **amino acid residues**. These residues are connected by amide linkages which are also called **peptide bonds**. Many of the early efforts of polymer chemistry were to artificially create fibers which mimicked the properties of silk and wool.

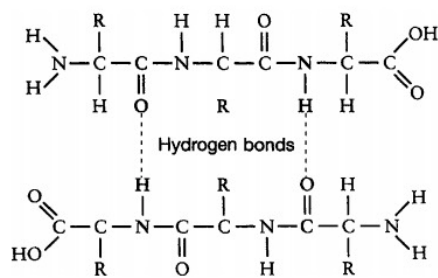


POLYAMIDES

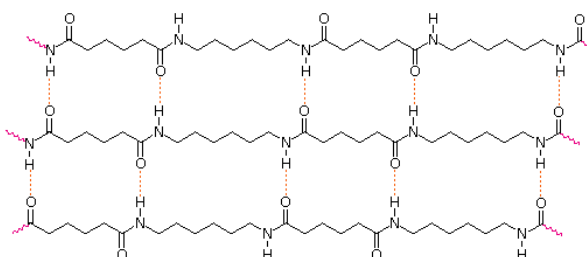
The first fully synthetic polymer fiber, nylon-6,6, was produced in 1938 by the company DuPont. The lead chemist of DuPont's work was Wallace H. Carothers, who reasoned that the properties of silk could be mimicked by constructing a polymer chain created with repeating amide bonds, just like the proteins in silk. Nylon-6,6 was created by first reacting 1,6-hexanedioic acid (adipic acid) and 1,6-hexanediamine to give a salt which was then heated creating multiple amide bonds through nucleophilic acyl substitution. The product of this particular reaction is a polyamide called nylon-6,6. The numbers of the name indicate how many carbons are contained in each monomer. The first "6" stands for the number of carbons in the diamine monomer while the second number indicated the number of carbons in the dicarboxylic acid. Simply by varying the number of carbons in each monomer, a wide variety of nylon polymers can be made.



Nylons are among the most widely used synthetic fibers—for example, they are used in ropes, sails, carpets, clothing, tires, brushes, and parachutes. Known for their high strength and abrasion resistance, nylons can be molded into blocks for use in electrical equipment, gears, bearings, and valves. The strength of nylon fibers comes, in part, from their ability to form strong hydrogen bonding intermolecular forces with each other in much the same fashion as proteins.



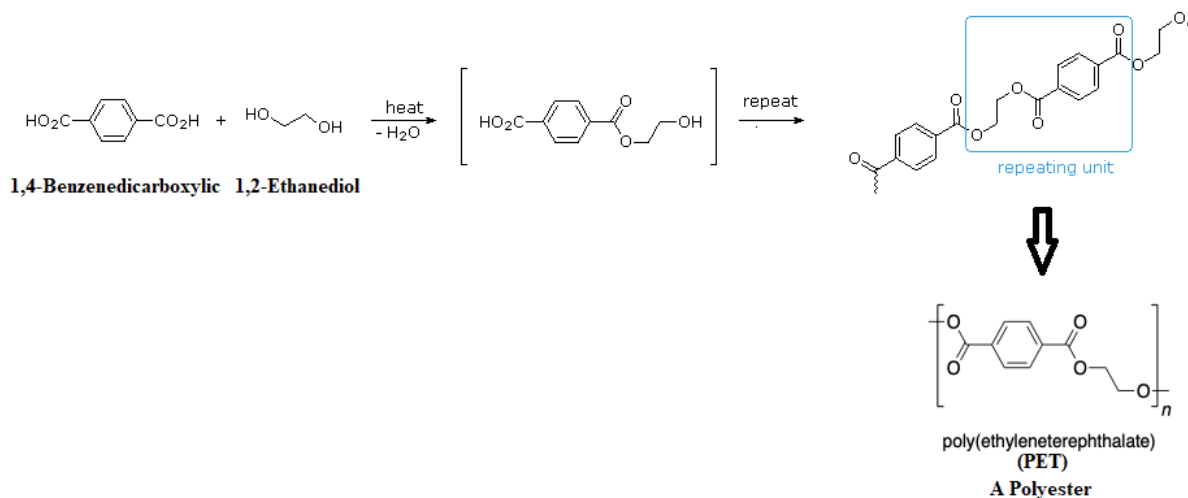
The Hydrogen Bonding between Proteins



The Hydrogen Bonding between Nylon Polyamides

POLYESTERS

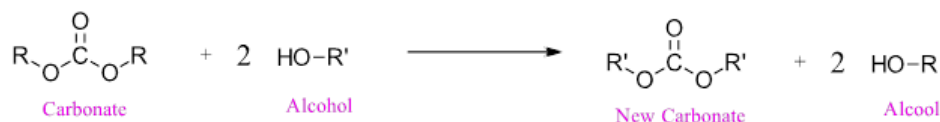
Esterification, via nucleophilic acyl substitutions, can also be used to form the primary linkages in step-growth polymers. A polyester is typically produced when a dicarboxylic acid and a diol are reacted together. After the initial reaction, the ester product contains a free (unreacted) carboxyl group at one end and a free alcohol group at the other. Further esterification using a step-growth polymerization, produces a polyester. The most important polyester, polyethylene terephthalate (PET), is made from the reaction of 1,4-benzenedicarboxylic (terephthalic acid) and 1,2-ethanediol (ethylene glycol) monomers.



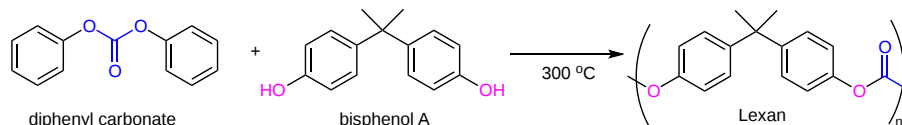
Polyester molecules make excellent fibers and are used in many fabrics. A knitted polyester tube, which is biologically inert, can be used in surgery to repair or replace diseased sections of blood vessels. PET is used to make bottles for soda and other beverages. It is also formed into films called Mylar. When magnetically coated, Mylar tape is used in audio- and videocassettes.

POLYCARBONATES

Beyond carboxylic acid derivatives, virtually any reaction which involves reactive species on two different molecules can be used to perform a step-growth polymerization. A variation involves using a monomer containing a carbonate functional group ($-\text{O}-(\text{C}=\text{O})-\text{O}-$). A carbonate acts like a double ester and can undergo a type of double transesterification reaction with two alcohols to form a new carbonate containing compound.



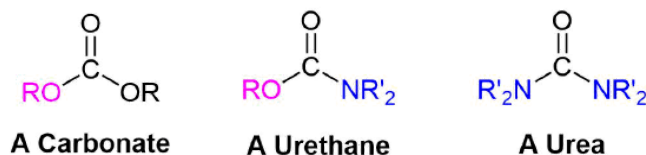
In effect, a carbonate is difunctional and can be reacted with a diol to form polymers containing repeated carbonate groups in their structure called polycarbonates. An example of a polycarbonate is the polymer, Lexan, which is created when diphenyl carbonate and bisphenol A (a diol) are reacted together.



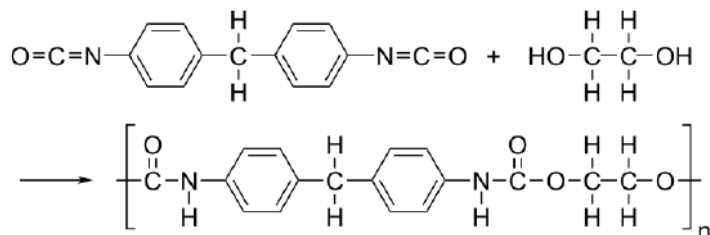
Bisphenol (BPA), primarily used to make polycarbonate, is one of the highest-volume chemicals produced in the world, with over six billion pounds made each year. Because polycarbonate is used to make plastic bottles, the lining for food cans, and the lining for beverage cans there has been much concern about trace amounts of BPA leaching from the containers and being ingested. A study conducted in 2003 and 2004 by the Center for Disease Control and Prevention found trace amounts BPA in the tissues of 93% of people in the United States. Consequently, this has led to many beverage companies switching to non-polycarbonate polymers.

POLYURETHANE

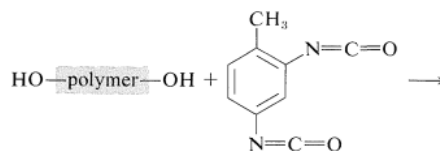
A urethane is a functional group similar to a carbonate and a urea. A urethane has an $-\text{OR}$ and a $-\text{NR}_2$ group attached to the carbonyl carbon.

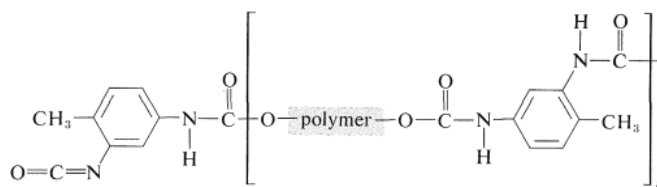


Polyurethane (PUR and PU) is a polymer composed of organic units joined by carbamate (urethane) links. Polyurethanes are produced by reacting an isocyanate containing two or more isocyanate groups per molecule ($\text{R}-(\text{N}=\text{C}=\text{O})_n$) with a polyol containing on average two or more hydroxyl groups per molecule ($\text{R}'-(\text{OH})_n$) in the presence of a catalyst or by activation with ultraviolet light.



The very widely used polyurethane foams can be considered to be either block polymers or copolymers. The essential ingredients are a diisocyanate and a diol. The diisocyanate most used is 2,4-diisocyanato-1-methylbenzene, and the diol can be a polyether or a polyester with hydroxyl end groups. The isocyanate groups react with the hydroxyl end groups to form initially an addition polymer, which has polycarbamate (polyurethane) links, and isocyanate end groups:

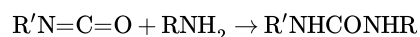




A foam is formed by addition of the proper amount of water. The water reacts with the isocyanate end groups to form carbamic acids which decarboxylate to give amine groups:









The carbon dioxide evolved is the foaming agent, and the amino groups formed at the same time extend the polymer chains by reacting with the residual isocyanate end groups to form urea linkages:



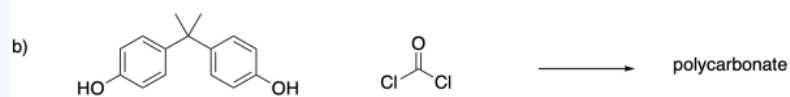
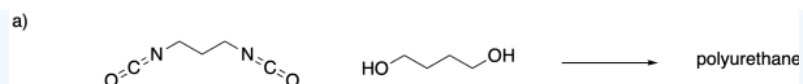
Polyurethanes are used in the manufacture of high-resilience foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires (such as roller coaster, escalator, shopping cart, elevator, and skateboard wheels), automotive suspension bushings, electrical potting compounds, high performance adhesives, surface coatings and surface sealants, synthetic fibers (e.g., Spandex), carpet underlay, hard-plastic parts (e.g., for electronic instruments), condoms,^[1] and hoses.

Common Step Growth Polymers

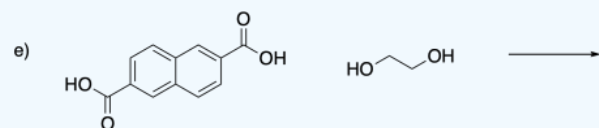
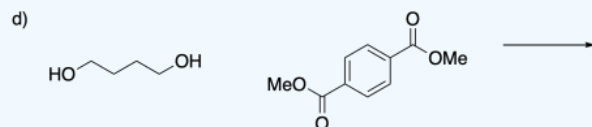
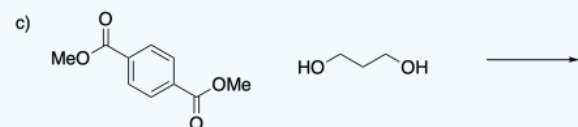
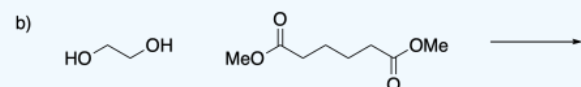
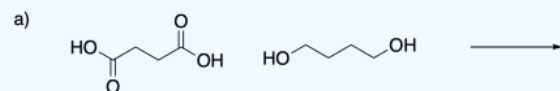
Formula	Type	Components	T _g °C	T _m °C
$\sim[CO(CH_2)_4CO-OCH_2CH_2O]_n\sim$	polyester	HO ₂ C-(CH ₂) ₄ -CO ₂ H	< 0	50
		HO-CH ₂ CH ₂ -OH		
	polyester Dacron, Mylar	para HO ₂ C-C ₆ H ₄ -CO ₂ H	70	265
		HO-CH ₂ CH ₂ -OH		
	polyester	meta HO ₂ C-C ₆ H ₄ -CO ₂ H	50	240
		HO-CH ₂ CH ₂ -OH		
	polycarbonate Lexan	(HO-C ₆ H ₄) ₂ C(CH ₃) ₂	150	267
		(Bisphenol A)		
		X ₂ C=O (X = OCH ₃ or Cl)		
$\sim[CO(CH_2)_4CO-NH(CH_2)_6NH]_n\sim$	polyamide Nylon 66	HO ₂ C-(CH ₂) ₄ -CO ₂ H	45	265
		H ₂ N-(CH ₂) ₆ -NH ₂		
$\sim[CO(CH_2)_5NH]_n\sim$	polyamide Nylon 6 Perlon		53	223
	polyamide Kevlar	para HO ₂ C-C ₆ H ₄ -CO ₂ H	---	500
		para H ₂ N-C ₆ H ₄ -NH ₂		
	polyamide Nomex	meta HO ₂ C-C ₆ H ₄ -CO ₂ H	273	390
		meta H ₂ N-C ₆ H ₄ -NH ₂		

? EXERCISE 30.4.1

1) The following difunctional monomers would undergo polymerization together. Show the product that results.

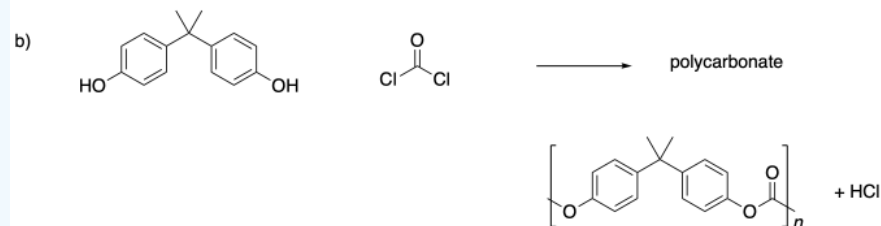
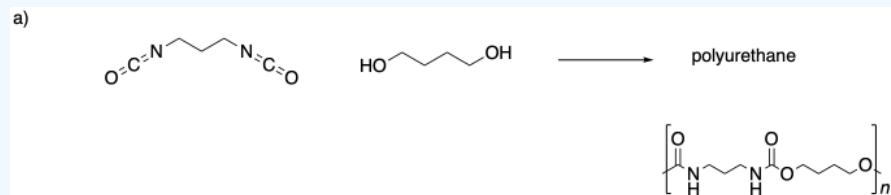


2) Provide structures of the polyesters made from the monomers as indicated.

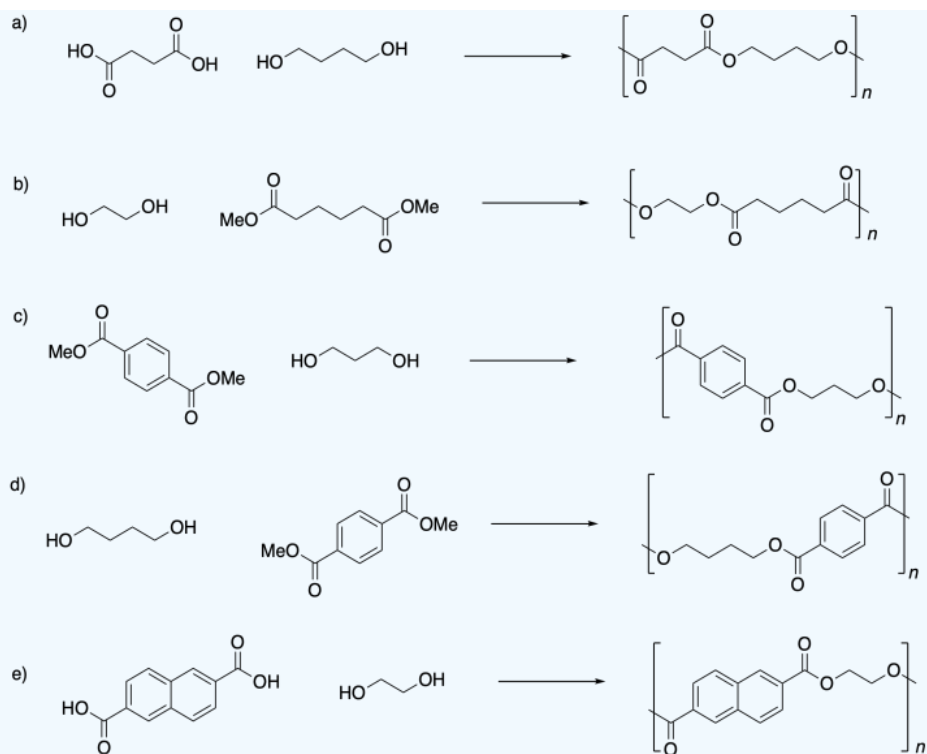


Answer

1)



2)



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