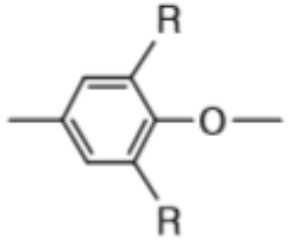
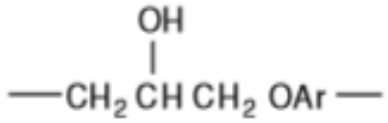
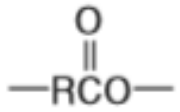
Kinetics of Condensation or Step Growth Polymerization

A condensation polymerization is a form of step-growth polymerization. In the case of a condensation reaction, two monomers combine with the loss of a small molecule, usually an alcohol, a water molecule or an acid, whereas an addition reaction involves only the rearrangement of the electrons of a double bond to form a single bond with another molecule.

A well-known example of a condensation reaction is the esterification of carboxylic acids with alcohols. If both reactants are difunctional, the condensation product is a linear polymer, and if at least one of the reactants is tri- or tetra-functional, the resulting polymer is a crosslinked polymer.

Many naturally and synthetic polymers are produced by step-growth polymerization including polyesters, polyethers, urethanes, epoxies, and polyamides (see table below).

Polymer type	Repeating functional unit
Polyether [poly(phenylene oxide)]	
Polyether (epoxy resin)	
Polysulfide	—ArS—
Poly(alkylene polysulfide)	—RS_x—
Polysulfone	—$ArSO_2$—
Polyester	
Polycarbonate	
Polyamide	

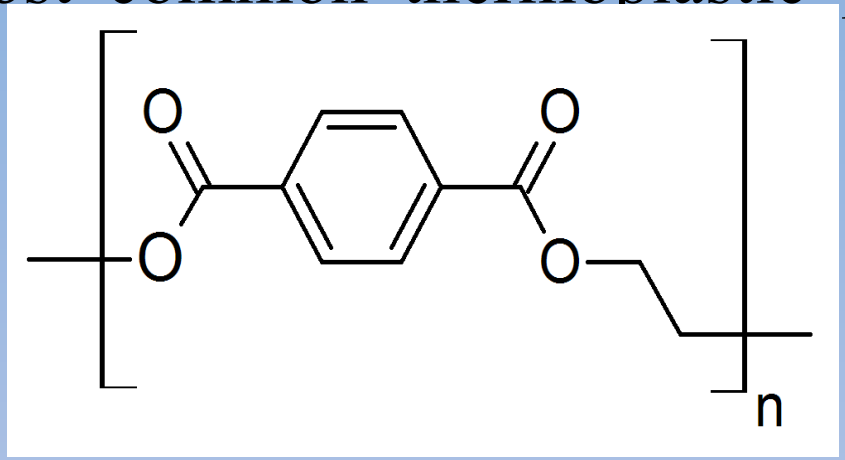
Commercially important polymers prepared by step polymerization

Functional Groups	Linkage	Polymer Type
-OH + -COOH	-C(=O)-O-	Polyester
-OH + -NCO	-O-C(=O)-NH-	Polyurethane
$-NH_2$ + -NCO	-NH-C(=O)-NH-	Polyurea
$-NH_2$ + -COOH	-NH-C(=O)-	Polyamide
-OH + -OH	-O-	Polyether

A classic step-growth condensation is the reaction between a diorganic acid and a glycol, shown below:

$$HOOC–(CH_2)_n–COOH + HO–(CH_2)_m–OH \rightarrow HOOC–(CH_2)_n–COO–(CH_2)_m–OH + H_2O$$

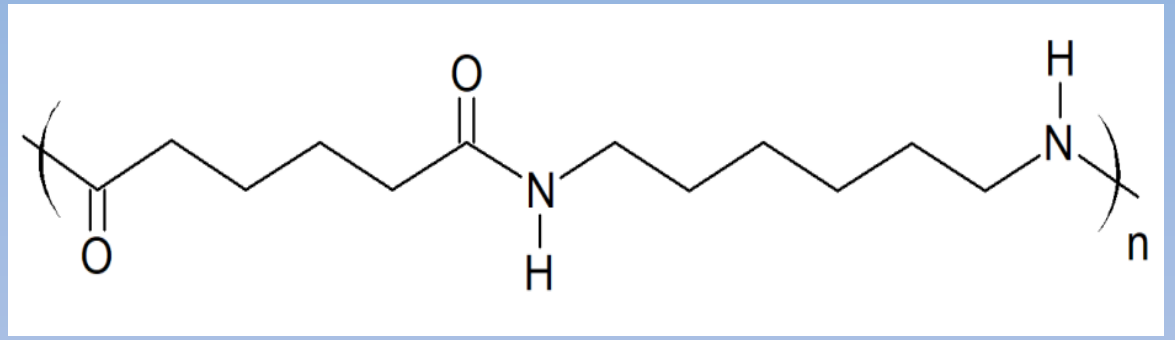
The resulting polymer is called a polyester. The by-product water is removed from the reaction system because it is reactive with ester linkages to reverse the reaction. One of the most common thermoplastic polyesters is poly(ethylene terephthalate)(PET) :



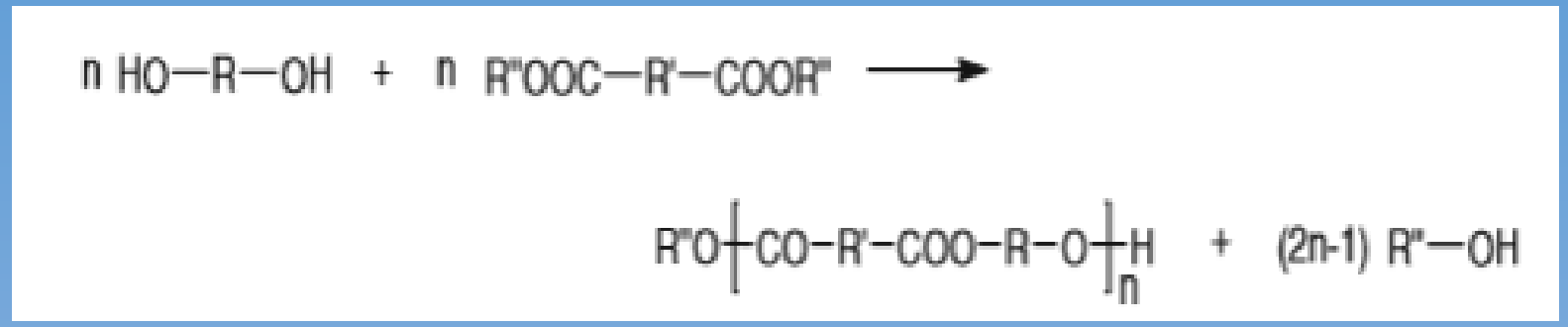
Other important condensation reaction is amidization. For example, polyamides, very common condensation polymers, can be produced by reacting diamides with dicarboxylic acids:

$$\mathbf{HOOC–(CH_2)_4–COOH + H_2N–(CH_2)_6–NH_2 \rightarrow [–HNOC–(CH_2)_4–CONH–(CH_2)_6–]}$$

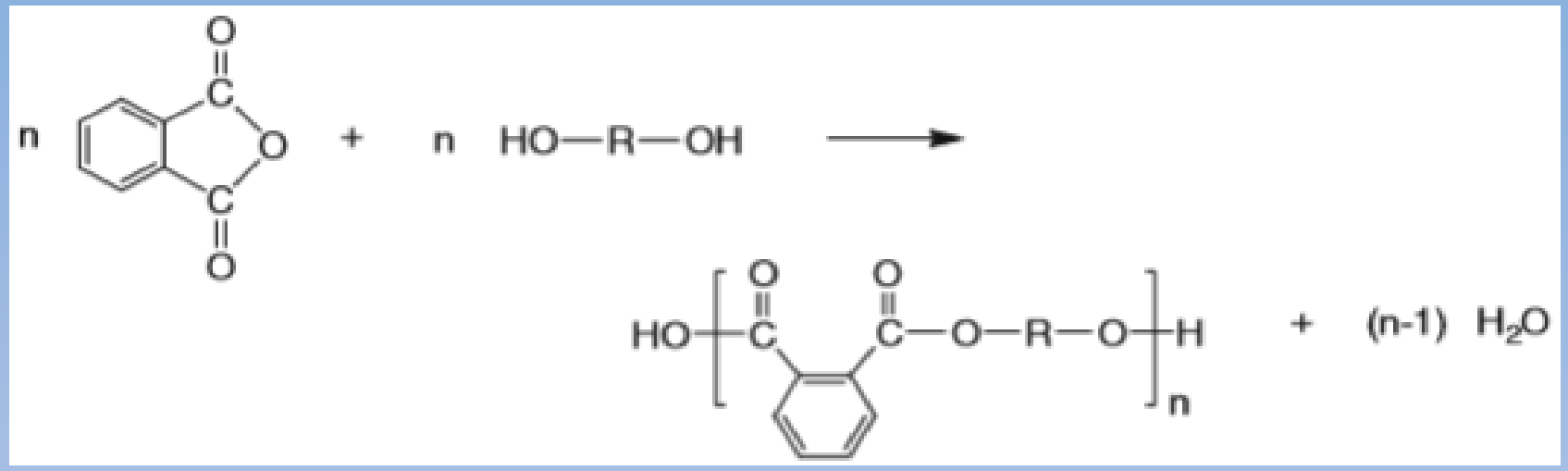
In this example the product is poly(hexamethylene adipamide), also known as Nylon 6,6 which is one of the most common thermoplastic polyamides. Its chemical structure is shown below



The ester exchange has been used to synthesize polyester using a glycol and ester as the following:



Either acid chloride or anhydride can be reacted with a glycol or an amine to give a polymer. The anhydride reaction is widely used to form an alkyd resin from phthalic anhydride and a glycol:



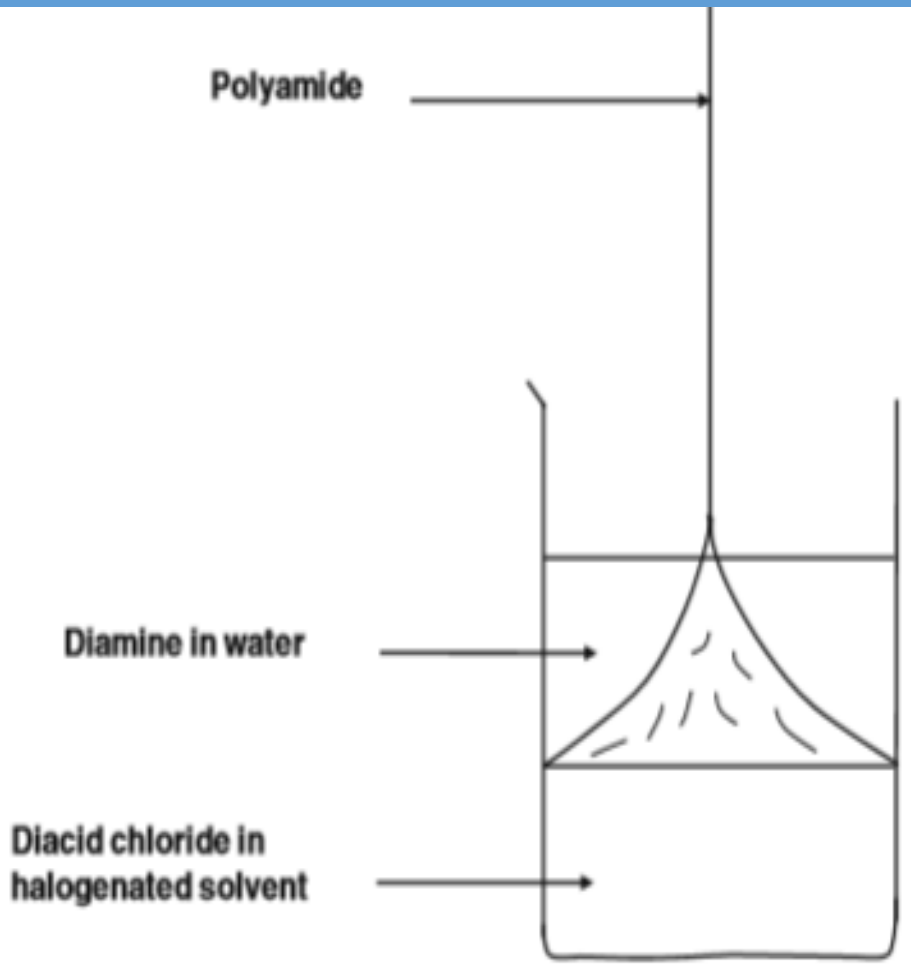
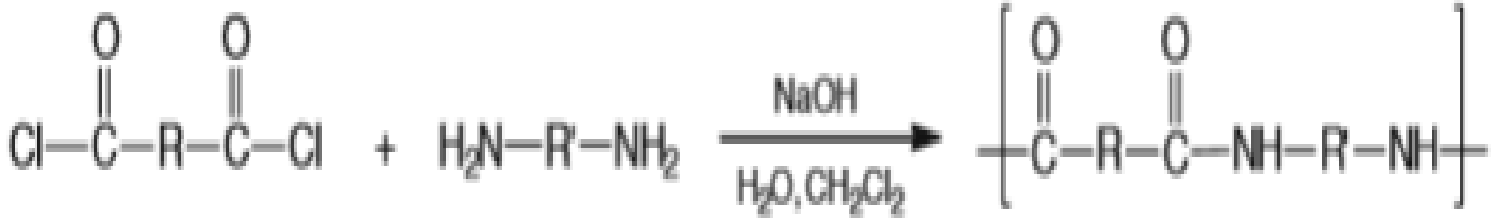
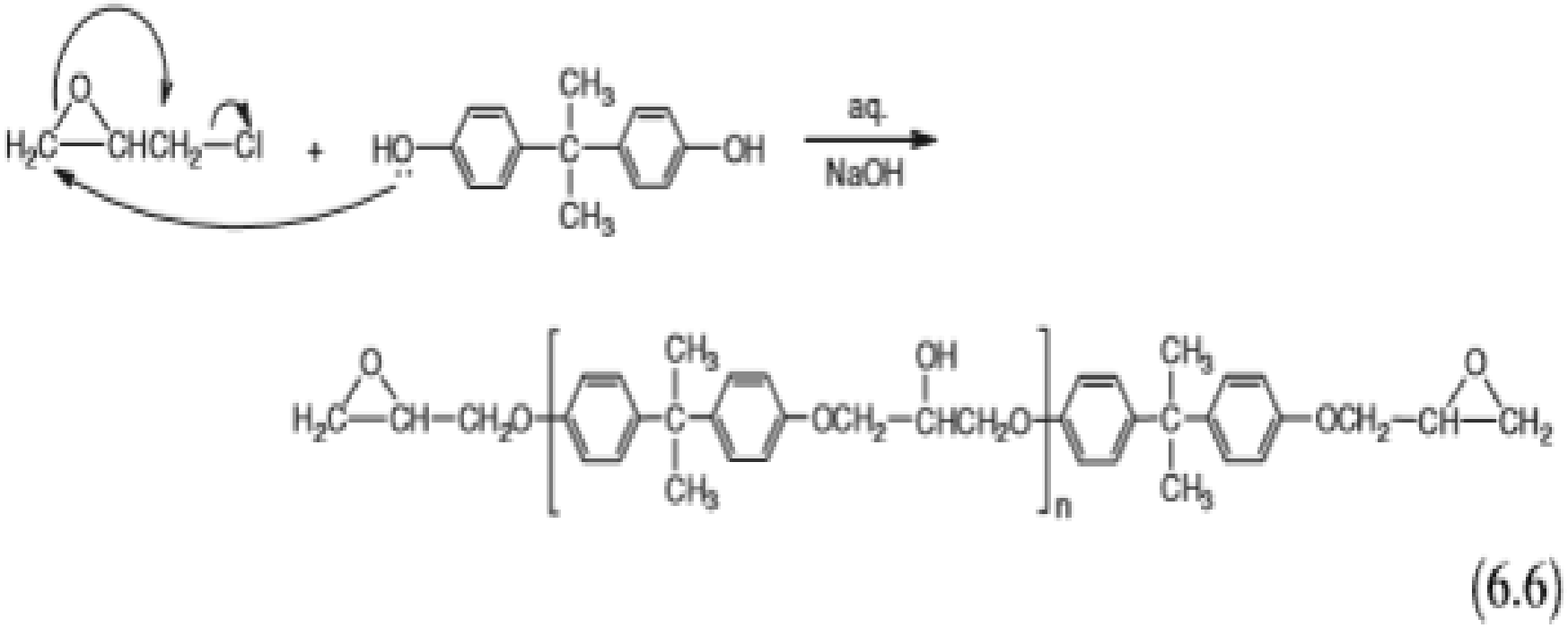


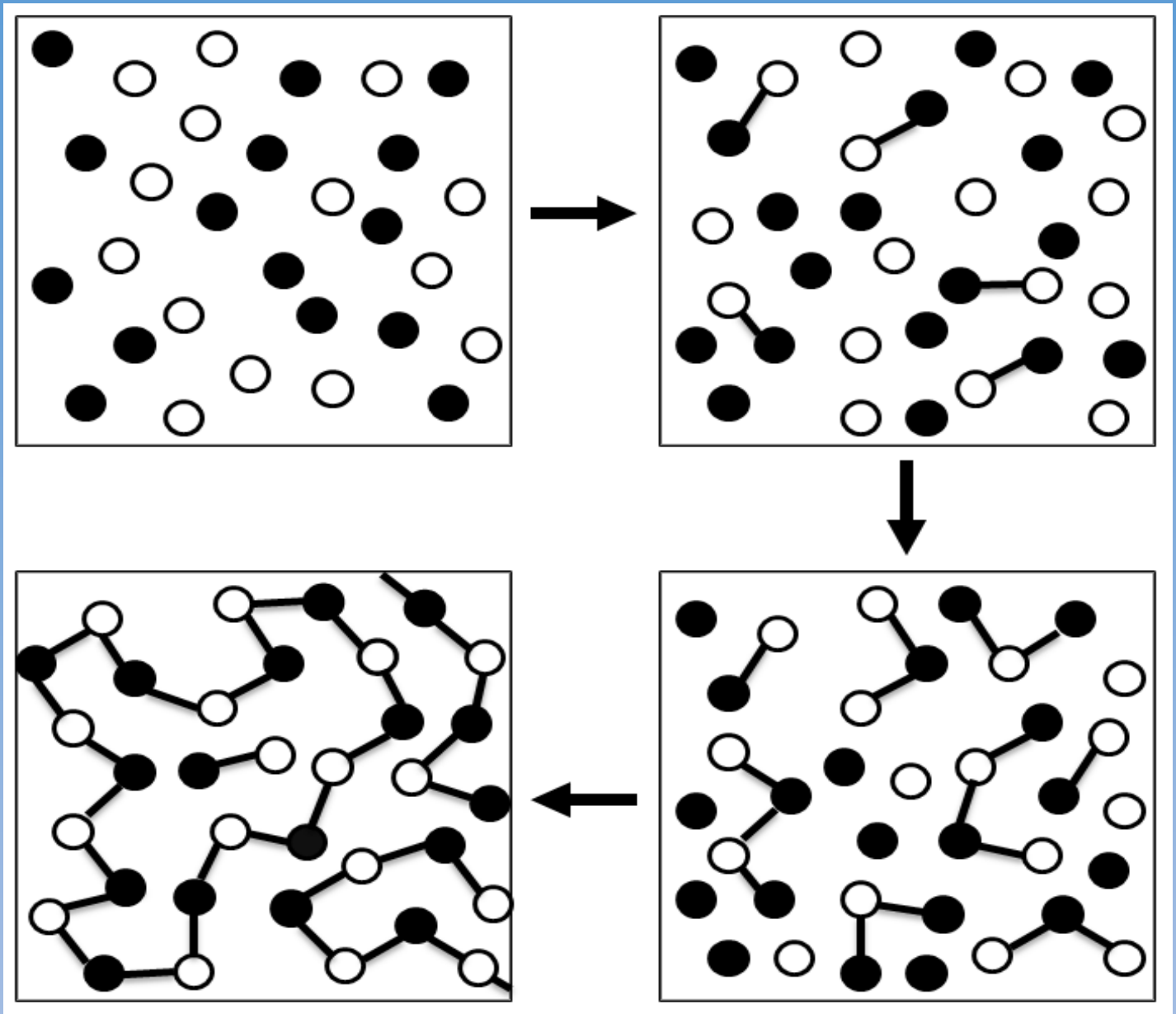
Fig. 6.1 Interfacial synthesis of polyamide

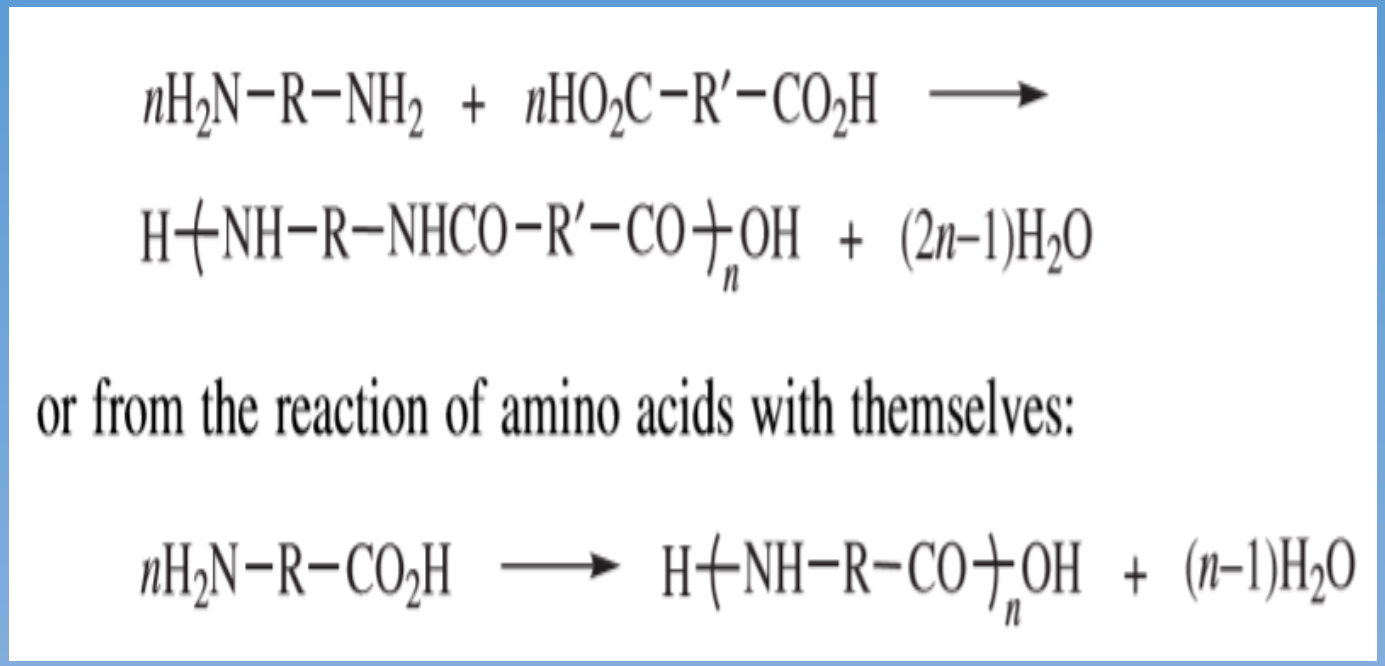




(6.6)

Nucleophilic Substitution Reaction Mechanism





The two groups of reactions can be represented in a general manner by the equations