PART II

POLYMER SYNTHESIS AND MODIFICATION

3

STEP-GROWTH POLYMERIZATION

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3.1 INTRODUCTION

3.1.1 General Principles

A rational classification of polymers has been discussed for several decades. The debate began when Carothers proposed a classification according to the polymer reactivity and considered mainly two types of polymers: polymers prepared through condensation reactions (condensation polymers) and those prepared by addition reactions (addition polymers). Chapter 1 of this handbook also discusses this topic, and although there are some overlaps in the topics covered here and in Chapter 1, the two chapters can be considered complementary.

Carothers defined addition polymers as those in which the molecular formula of the monomer is identical to that of the structural unit, so that the monomer can be obtained back from the polymer by thermolysis and, vice versa, the polymer can be synthesized from the monomer by self-addition. Condensation polymers, according to Carothers, are those where the molecular formula of the monomer differs from that of the structural unit; in this case, the monomer can be obtained from the polymer by hydrolysis or an equivalent reaction, and the polymer can be synthesized from the monomer by poly-intermolecular condensation. In this type of polymerization, the elimination of simpler molecules (H_2O, HCl, NaC1, etc.) is common [1].

In 1994, the IUPAC Commission on Macromolecular Nomenclature redefined the polymerization types according to the following rules [2].

1. *Chain Polymerization*. In this case, the polymer is formed through a chain reaction in which the growth proceeds exclusively by reaction(s) between monomer(s) and reactive site(s) on the polymer chain, with regeneration of the reactive site(s) at the end of each growth step. In this kind of reactions, the polymerization is conducted by chain reaction without the formation of any small molecules.
2. *Polycondensation*. In this polymerization process, the polymers are formed through a condensation reaction between molecules of all degrees of polymerization. A condensation reaction is understood as the chemical reaction in which two functional groups (reactive groups with different chemical properties) interact to form a different functional group with the loss of a small molecule. The word "condensation" suggests a process in which two or more entities are brought "together" (from the Latin "con") to form a "dense" entity, such as in the condensation of a gas into the liquid state; this does not imply, however, that condensation reaction products have greater density than the reactants. When the two functional groups reacting are in the same molecule, the condensation is termed *intramolecular*; on the other hand, when the functional groups are in different molecules, it is termed *intermolecular condensation*.
3. *Polyaddition*. It is a polymerization reaction in which the growth of the polymer chains proceeds by addition reactions between molecules of all degrees of polymerization.

In addition to these definitions, there is another classification for the polymers that is based on the mechanism involved during the formation of the polymer chain.

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Step-growth and chain-growth polymerizations are defined by virtue of this classification, [3].

In step-growth polymerization, only one kind of reaction is involved in the formation of a polymer and the reaction proceeds step by step. The main feature of this type of reactions is that two monomers, which bear different functionalities, can react with each other, or with a polymer of any size, through the same kind of reactions. In this case, the individual polymer molecules can grow over the course of the whole process; each reaction step of a polymer molecule implies that the reactive end of a monomer or polymer encounters another species with which it can form a link. The functional group at the end of a monomer is usually assumed to have the same reactivity as that on a polymer chain of any size. The polymerizations proceed by the stepwise reaction between the functional groups of reactants as in the reactions described in Chapter 1, Section 1.2.2, of this handbook. The size of the polymer molecules increases at a relatively slow pace in polymerizations that proceed from monomer to dimer, trimer, tetramer, pentamer, and so on.

As a consequence of this mechanism, it is expected that the molecular weight grows in a slow manner at early stages of the reaction, where the reactions of oligomerization are the predominant ones. However, considering that the reactivity of the functional groups is the same during the formation of oligomers and during later stages of the reaction to form high polymer, the evolution of the average molecular weight with conversion follows the behavior shown in Figure 3.1. For this reason, a reaction with high conversion of functional groups is required to produce polymers with high molecular weight. Therefore, if polymers with high molecular weight are required, high conversions must be reached and side reactions must be avoided; in this case, the purity of the monomers plays an important role.

Many step-growth polymerizations involve an equilibrium between reactants and products, the latter comprising macromolecular species and (usually) eliminated small molecules.

The course of these polymerizations and of the distribution of the molecular weights is statistically controlled. High polymers cannot coexist with much monomer in a system in equilibrium. Step-growth polymerizations are evidently reversible and also involve interchange reactions in which terminal functional groups in a growing chain react with linking units of other molecules producing changes in the molecular weight distributions.

There are step-growth polymerization reactions in which a small molecule is not produced (e.g., the reaction between a diol and a diisocyanate); these reactions are considered irreversible and are usually very fast, leading to high degrees of polymerization.

3.1.2 Number-Average Degree of Polymerization

As mentioned before, the main characteristic of the step-growth polymerization is that it proceeds stepwise, according to the reactivity of the two functionalities involved in the formation of the new linkage. The average

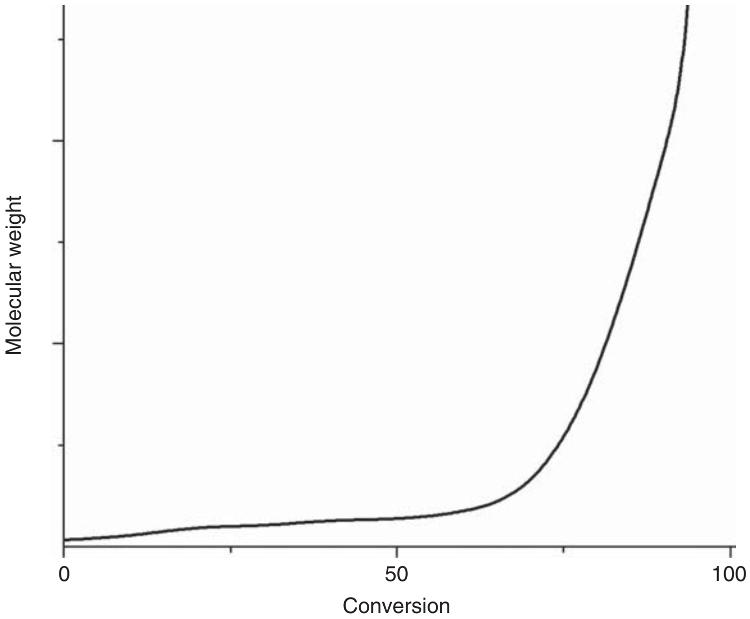


Figure 3.1 Profile of molecular weight versus conversion in a step-growth polymerization.

TABLE 3.1 Polyester Polymerization of 1,2-Ethanediol with Adipic Acid

Reagent	Reagent Concentration (% w/w)	Moles	Functionality	Equivalents
1,2-Ethanediol	99	0.99	2	1.98
Ethanol	1 (impurity in ethanediol)	0.0135	1	0.0135
1,6-Hexanedioic acid (adipic acid)	100	1	2	2
Total		2.0035		3.9935

functionality f_{av} is the average number of functional groups per monomer molecule and it is defined by Equation 3.1.

$$f_{av} \equiv \frac{\sum N_i f_i}{\sum N_i} \tag{3.1}$$

where N_i is the number of molecules of the species i and f_i is the functionality of monomeric species i. This equation is valid when the opposite functionality is present in equal concentration and in the absence of side reactions.

Consider a polymerization that forms AB links and in which $n_A < n_B$, where n_i is the number of equivalents of the functional groups of type i. In this case, the number of B equivalents that can react cannot exceed n_A, and Equation 3.1 adopts the form of Equation 3.2.

$$f_{av} = \frac{2n_A}{\sum N_i} = \frac{2n_A}{N_A + N_B} \tag{3.2}$$

The number-average degree of polymerization in the reaction mixture (X_n) is defined as the average number of structural units (or monomer units) per polymer molecule. A structural unit equals a monomer unit, that is, the residue of each monomer in the polymer. For an AB polymerization, a repeating unit is made of two structural units. This differs from what some authors term the *average degree* of polymerization (D_p, i.e., the average number of repeating units per polymer molecule). In the step-growth polymerization of a single molecule that bears two functionalities and can form a polymer, $X_n = D_p$, and when two monomers are involved, $X_n = 2D_p$, and is defined as

$$X_n = \frac{N_0}{\frac{2N_0 - N_0 p f_{av}}{2}} = \frac{2}{2 - p f_{av}} \tag{3.3}$$

where N_0 is the initial number of monomer molecules and p is the extent of reaction, which is equal to the fraction of functional groups that have reacted $0 \leq p \leq 1$. An example of the use of the number-average degree of polymerization concept is the reaction between 1,2-ethanediol with 1,6-hexanedioic acid (adipic acid). In this system, an esterification reaction takes place through the two functionalities, alcohol and acid, in the monomers and a polymer is formed. The repeating unit is $[OCH_2{-}CH_2{-}O{-}C(O){-}(CH_2)_4{-}C(0)]$, which has a molecular weight of 172 g/mol. If the monomers are in equivalent concentrations, then $f_{av} = 2$ and $X_n = 2/(2 - 2p)$. When the conversion is 90%, the number-average degree of polymerization is $X_n = 2/(2 - 2 * 0.9) = 10$ and the molecular weight is 860 g/mol. On the other hand, when the conversion is almost complete (99.5%), $X_n = 2/(2 - 2 * 0.995) = 200$ and the molecular weight is 17,200 g/mol. From this concept, the effect of conversion on molecular weight in step-growth polymerizations is clear.

Now consider the situation in which the 1,2-ethanediol monomer has a 99% (w/w) purity and contains ethanol in a concentration of 1% (w/w), as shown in Table 3.1. When 146 g of adipic acid (1 mol) is reacted with 62 g of 1,2-ethanediol (0.99 mol, considering the purity reported), at nearly complete (99.5%) conversion, the number-average degree of polymerization is $X_n = 2/(2 - 0.995 * 1.9935) = 121$ and the molecular weight obtained is 10,440 g/mol. This result clearly contrasts with the previous data found of $X_n = 200$ and molecular weight of 17,200 g/mol for the same polymerization and conversion, but with pure monomer. This example also clarifies the enormous effect of the monomers' purity on the course of a step-growth polymerization.

3.1.3 Molecular Weight Distribution

The prediction of the molecular weight distribution for a step-growth polymerization assumes that both the probability of the reaction and the reaction rate of two functional groups are independent of the sizes of the involved molecules (monomers or growing chains), as explained by Rudin [4].

For a polymerization system involving functional groups, A, reacting with another functional group (say B), the probability of finding by random selection a growing molecule with i monomer units is given by the probability that i − 1 A groups have reacted (p^{i-1}) multiplied by the probability that the last functional group has not reacted, which is $1 - p$ (since the probabilities that a given functional group has reacted or not must add up to 1). The resulting probability is evidently $p^{i-1}(1 - p)$. Then, the probability that a randomly selected molecule will be an i-mer equals the mole fraction x_i of i-mers in the reaction mixture and is calculated as

$$x_i = (1-p)\,p^{i-1} \tag{3.4}$$

On the other hand, the total number N of molecules remaining at an extent of reaction p is

$$N = N_0\,(1-p) \tag{3.5}$$

Therefore, the number N_i of i-mer molecules is given by $Nx_i = N_0(1-p)^2p^{i-1}$, and the molecular weight of an i-mer is iM_0.

Since the total weight of all molecules equals N_0M_0 (neglecting unreacted ends), the weight fraction w_i of i-mers is

$$w_i = \frac{N_0 i M_0(1-p)^2 p^{i-1}}{N_0M_0}$$

$$w_i = i(1-p)^2 p^{i-1} \tag{3.6}$$

Equation 3.6, together with Equation 3.4, describes a random distribution of molecular sizes; this distribution is also known as the *Flory–Schulz distribution* or the *most probable distribution* [5]. Recently, Wutz and Kricheldorf [6] proposed a model describing the frequency distribution (f_i) and formulated the weight distribution (w_i) of linear chains in step-growth polymerizations considering the cyclation reaction, which is one of the most important side reactions in step-growth polymerization.

The number-average molecular weight M_n, defined as the total weight of a polymer sample divided by the total number of molecules, is given by

$$M_n = M_0X_n = \frac{M_0}{1-p} \tag{3.7}$$

where M_0 is the formula weight of the repeating unit.

3.1.4 Polymers Obtained by Step-Growth Polymerization

Step-growth polymerization is a very important method for the preparation of some of the most important engineering and specialty polymers. Polymers such as polyamides [7], poly(ethylene terephthalate) [8], polycarbonates [9], polyurethanes [10], polysiloxanes [11], polyimides [12], phenol polymers and resins, urea, and melamine-formaldehyde polymers can be obtained by step-growth polymerization through different types of reactions such as esterification, polyamidation, formylation, substitution, and hydrolysis. A detailed list of reaction types is shown in Table 3.2.

3.2 POLYMERIZATION KINETICS

Step-growth polymerizations are condensation reactions that usually occur in equilibrium, a fact that intrinsically leads to a high degree of reversibility. From the kinetic point of view, the most studied reactions are those of polyester and polyamide formation [13]. In these reactions, the value of the rate constant, k, can be considered independent of the polymer chain length, which is equivalent to assuming that the polymerization mechanism is the same throughout the entire reaction. In general, it is assumed that the polymerization is a first-order reaction with respect to the active functional groups; therefore,

$$-\frac{\mathrm{d[A]}}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}] \tag{3.8}$$

This is the case of, for example, externally catalyzed reactions. If the stoichiometric balance is exact, then Equation 3.8 can be written as

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A]^2 \tag{3.9}$$

On integration,

$$[A] = \frac{[A_0]}{1+[A_0]kt} \tag{3.10}$$

If the reaction is acid self-catalyzed, as in the case of polyesters, the reaction becomes a globally third-order reaction that can be written as

$$-\frac{\mathrm{d[A]}}{\mathrm{d}t} = k[\mathrm{A}]^2[\mathrm{B}] \tag{3.11}$$

Also, if [A] = [B] (stoichiometric concentrations), the reaction equation can be reduced to

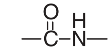
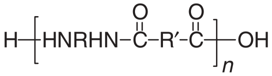
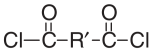
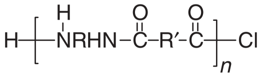
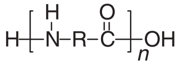
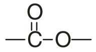
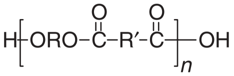
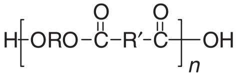
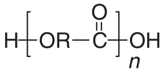
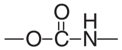
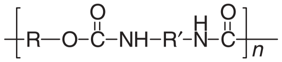
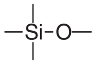
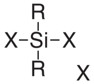
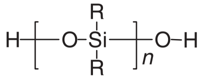
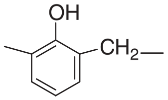
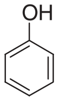
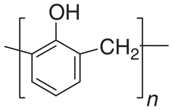
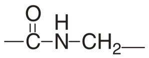
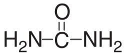
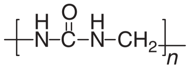
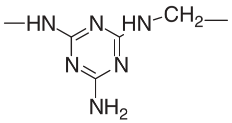
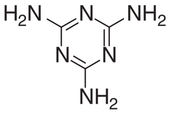
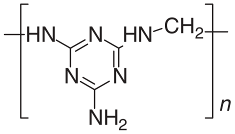
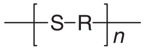
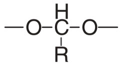
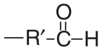
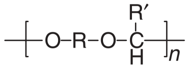
$$-\frac{\mathrm{d[A]}}{\mathrm{d}t} = k[\mathrm{A}]^3 \tag{3.12}$$

On integration,

$$[\mathrm{A}]^2 = \frac{[\mathrm{A}_0]^2}{2kt\,[\mathrm{A}_0\,]^2+1} \tag{3.13}$$

In general, the reactions for polyamide formation are seldom catalyzed. The reactions to produce thermosets, such as melamine-urea or phenol-formaldehyde, require a basic or an acidic catalyst. Some polyurethane formation reactions are catalyzed by basic reactants. Equation 3.11 applies when the rate constant of the externally catalyzed reaction (k') is much larger than that of the self-catalyzed

TABLE 3.2 Some Step-Growth Polymers and their Synthesis Reactions

Type	Interunit Linkage	Monomer	Monomer	Polymer	Small Molecule Formed
Polyamide	 $-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-$	$H_2N{-}R{-}NH_2$	$HO_2C{-}R'{-}CO_2H$	 $H{-}\left[HNRHN{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}\right]_n{-}OH$	Water
		$H_2N{-}R{-}NH_2$	 $Cl{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}Cl$	 $H{-}\left[\overset{H}{N}RHN{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}\right]_n{-}Cl$	Hydrochloric acid
		$H_2N{-}R{-}CO_2H$	None	 $H{-}\left[\overset{H}{N}{-}R{-}\overset{O}{\overset{\|}{C}}\right]_n{-}OH$	Water
Polyester	 $-\overset{O}{\overset{\|}{C}}-O-$	$HO{-}R{-}OH$	$HO_2C{-}R'{-}CO_2H$	 $H{-}\left[ORO{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}\right]_n{-}OH$	Water
		$HO{-}R{-}OH$	$R''O_2C{-}R'{-}CO_2R''$	 $H{-}\left[ORO{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}\right]_n{-}OH$	Alcohol (R″OH)
		$HO{-}R{-}CO_2H$	None	 $H{-}\left[OR{-}\overset{O}{\overset{\|}{C}}\right]_n{-}OH$	Water
Polyurethane	 $-O-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-$	$HO{-}R{-}OH$	$OCN{-}R'{-}NCO$	 $-\left[R{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R'{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}\right]_n-$	None
Polysiloxane	 $-\overset{\vert}{\underset{\vert}{Si}}-O-$	 $X{-}\overset{R}{\underset{R}{Si}}{-}X$ X = OH, Cl	—	 $H{-}\left[O{-}\overset{R}{\underset{R}{Si}}\right]_n{-}O{-}H$	Hydrochloric acid or water
Resins (phenol-formaldehyde)			CH_2O		Water
Resins (urea-formaldehyde)	 $-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-CH_2-$	 $H_2N{-}\overset{O}{\overset{\|}{C}}{-}NH_2$	CH_2O	 $-\left[\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}CH_2\right]_n-$	Water
Resin (melamine-formaldehyde)			CH_2O		Water
Polysulfide	$-S{-}R-$	$Cl{-}R{-}Cl$	Na_2S	 $-\left[S{-}R\right]_n-$	NaCl
Polyacetal	 $-O-\overset{H}{\underset{R}{C}}-O-$	$HO{-}R{-}OH$	 $-R'{-}\overset{O}{\overset{\|}{C}}{-}H$	 $-\left[O{-}R{-}O{-}\overset{R'}{\underset{H}{C}}\right]_n-$	Water

reaction (k). If this is not the case, the rate of reaction expression has to be written as

$$-\frac{d[A]}{dt} = k[A]^3 + k'[A]^2 \tag{3.14}$$

On integration,

$$k't = \frac{k}{k'}\ln\frac{[A]\,k\left(\left[A_0\right]+k'\right)}{\left(k\,[A]+k'\right)[A_0]} + \frac{1}{[A]} - \frac{1}{[A_0]} \tag{3.15}$$

This expression takes into account the values of the k' and k in the polymerization reaction.

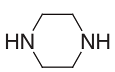
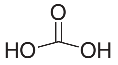
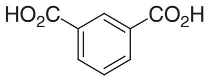
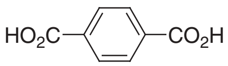
3.3 POLYAMIDES

Polyamides are polymers containing recurring amide groups (-CONH-) as integral parts of the main polymer chain. Polyamides are among the first polycondensation polymers; they were first prepared by Carothers at Dupont in 1938 [14] and were an enormous success as a substitute of natural fibers. They are prepared from hexamethylenediamine and sebacoyl chloride. Nowadays, polyamides of different types are highly appreciated due to their thermal resistance and high mechanical strength.

Polyamides can be prepared with aliphatic or aromatic monomers, either acids or amines. Aliphatic polyamides are usually hygroscopic materials, and the introduction of the aromatic ring in the monomer structure can reduce this characteristic. Water in polyamides is an important impurity when they are processed through injection molding.

Polyamides are commonly named as *Nylon* followed by two numbers, in which the first one denotes the number of carbon atoms in the diamine monomer and the second one refers to the number of carbon atoms in the diacid monomer. If a cycle is part of the polyamide, either in the amine or the acid moiety, the first letter of the cycle name must be used. In addition, if the polyamide is derived from an amino acid, only one number has to be used that describes the number of carbon atoms between the two functionalities. These rules are shown in Table 3.3.

TABLE 3.3 Codes to be Used with the Different Polyamides in the Nylon Nomenclature

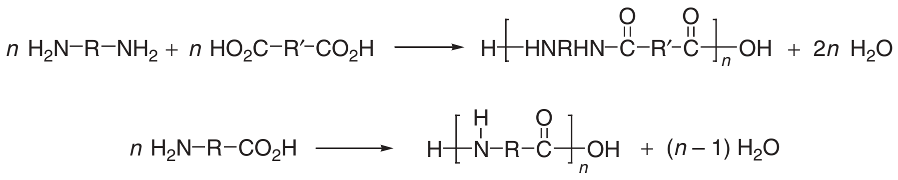
	Structure	Code
Diamine		
Hydrazine	H_2NNH_2	0
Ethylenediamine	$H_2N{-}CH_2CH_2{\cdot}NH_2$	2
Hexamethylenediamine	$H_2N{-}(CH_2)_6{-}NH_2$	6
1,8-Octanediamine	$H_2N{-}(CH_2)_8{-}NH_2$	8
Piperazine		Pip
Diacids		
Carbonic acid		1
Oxalic	$HO_2C{-}CO_2H$	2
Glutaric acid	$HO_2C{-}(CH_2)_3{-}CO_2H$	5
Adipic acid	$HO_2C{-}(CH_2)_4{-}CO_2H$	6
Suberic acid	$HO_2C{-}(CH_2)_6{-}CO_2H$	8
Isophthalic acid		I
Terephthalic acid		T

3.3.1 Polyamidation

Most polyamides are prepared by a direct amidation reaction between diacids and diamines, and numerous combinations of monomers are possible. This reaction is accompanied by the elimination of water, and the amount of water released can serve as a measure of the extent of the reaction. In addition to this, the intramolecular reaction of the amino acids can also produce a polyamide (Fig. 3.2).

The reaction path involves acid–base reaction between the monomers or the amino acid, generating the carboxylic ammonium salt, followed by loss of water, generating the amide linkage. It has been reported that this reaction can be accelerated by the use of microwave energy [15] (Fig. 3.3).

The amidation is also possible through the use of diesters instead of diacids, generating polyamides and alcohols. The use of diamides of low molecular weight in reaction with a diacid monomer also produces polyamides and acid as a by-product.



$$n\,H_2N{-}R{-}NH_2 + n\,HO_2C{-}R'{-}CO_2H \longrightarrow H\left[HNRHN{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}\right]_n OH + 2n\,H_2O$$

$$n\,H_2N{-}R{-}CO_2H \longrightarrow H\left[\overset{H}{\overset{|}{N}}{-}R{-}\overset{O}{\overset{\|}{C}}\right]_n OH + (n-1)\,H_2O$$

Figure 3.2 Polyamidation of amino acids or diacids and diamines.

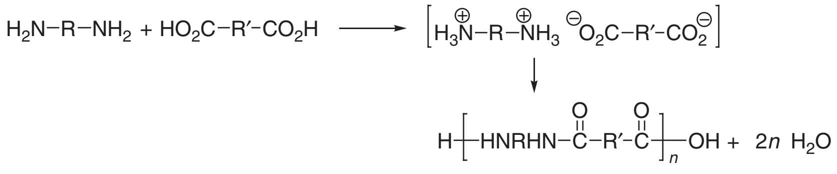


Figure 3.3 Reaction path of the amidation reaction.

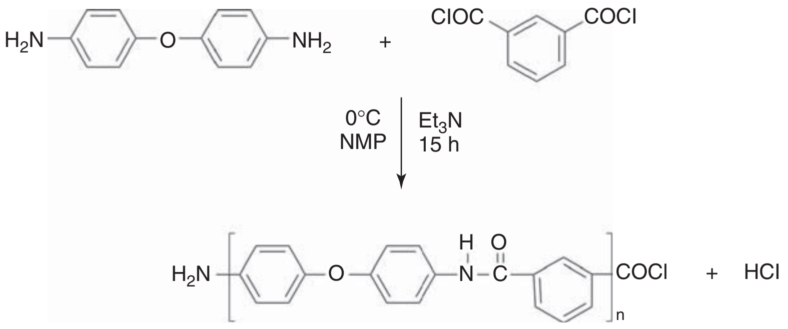


Figure 3.4 Interfacial polyamidation of terephthalic chloride.

The reaction of diamines with diacid chlorides produces at least two types of polymerization. The first type is an interfacial polymerization in which the diamine is dissolved in water and the diacid chloride is in the organic phase. This reaction can be improved by the addition of an inorganic base to the aqueous solution or by the inclusion of a surfactant; the reaction will take place in the interface. The second type is a polymerization in solution in which both diamine and diacid chloride are dissolved in an organic solvent. With this method, a high molecular weight polyamide can be prepared.

One example is the reaction between aromatic polyether isophthalic amine and terephthalic chloride [16] at a low temperature generating a polyamide, as discussed later (Fig. 3.4).

The resulting polyamides also have high molecular weight and the monomer reactants are carefully kept in stoichiometric amounts.

The polyamides can be prepared by ring-opening reaction of the correspondent lactam; according to its mechanism, this reaction cannot be properly considered as a step-growth polymerization.

3.3.2 Aromatic Polyamides

Aromatic polyamides totally built (or at least 85%) from adjacent-to-aromatic-monomer links are called *aramids*. It was long recognized that highly favorable properties might be obtained with a polyamide that is made entirely of aromatic rings directly connected to the amide links. These properties would result from the stiffness and stability of the rings and the complete absence of aliphatic content. Owing to the unique properties that aromatic rings impart to a macromolecule of this kind, poly(*p*-phenylene terephthalamide), better known as *Kevlar*, has become one of the most famous of the specialty polymers. However, one of the main problems in making such polymers is to maintain them in a liquid state, necessary for forming. This and other obstacles have been overcome by researchers who proposed different polymerization processes for their synthesis. Among the type of reactions that is commonly used for their preparation, the first one was developed by Yamasaki [17], and involves the use of triphenyl phosphate and pyridine in an aprotic solvent, such as *N*-methylpyrrolidinone (NMP) or dimethylformamide (DMF). A typical example of this reaction would be the preparation of polyhexafluoro isopropylidene isophthalamide or the preparation of a poly(fluorenylidene) isophthalamide as described in the scheme of Figure 3.5.

Using this method, a number of poly-isophthalamides with trifunctional monomers [18] or poly-trimethyl and *tert*-butylhydroquinone aromatic polyamides can be prepared [19]. Another interesting example of the use of Yamasaki's reaction is the preparation of organosoluble aromatic polyamides containing phosphorus [20] or the preparation of polyamides with a diamantane moiety embedded in the structure of the principal chain [21].

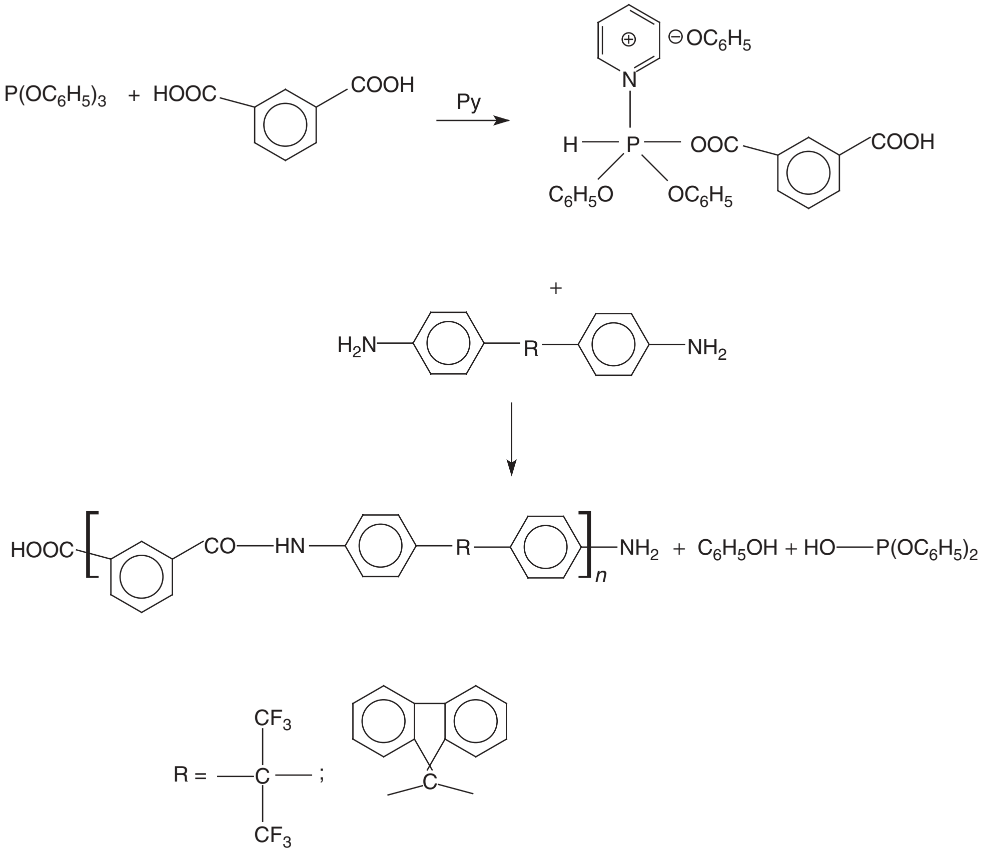


Figure 3.5 Preparation of polyaromatic amides.

3.4 POLYIMIDES

The progress of modern science and technology would not have been possible without polyimide materials; polyimides have had a significant impact on the development of various fields of science and technology. Polyimides have found applications as films, fibers, foams, membranes, plastics, composites, glues, adhesives, and coatings and are widely used for the fabrication and coating of various structures, units, and parts operating under extreme temperature conditions. One of the fields in which the use of polyamides is crucial is membrane technology, specifically in applications of gas processing technology and energy storage.

Polyimides can be prepared through several step-growth processes. One of the most common methods used for this purpose is the reaction of dianhydrides with diamines (Fig. 3.6). The first product obtained is poly(amic acid), which has the advantage of being soluble in organic solvents (normally aprotic polar solvents are used, such as dimethyl sulfoxide, DMF, dimethylacetamide, and NMP). The solution of poly(amic acid) can easily be manipulated or processed. The acid can then be cycled thermally, generating the polyamide, which is insoluble in most of the common organic solvents.

In addition, other preparation methods of polyimides use bis(methylol imide) in reaction with diamines, diisocyanates, or dinitrile compounds, according to the scheme shown in Figure 3.7.

3.5 POLYESTERS

3.5.1 Polyesters from Diacids

The polycondensation of difunctional oligomers leads to the preparation of well-defined polymer structures. Monomers in this type of reactions must be soluble in the reaction mixture and stable when the reaction is carried out in the melt, which is the case for some aromatic polymers prepared by polycondensation [22]. As previously described, polycondensation can occur with monomers bearing the same or a different functional group at both ends of the molecule. When one of the reactive functional groups is a hydroxyl moiety, several types of materials can be prepared, such as polyethers, polyesters, and polyurethanes, independently if they are used to form homopolymers, copolymers, or hyperbranched polymers.

Block copolymers can be prepared by polycondensation of difunctional oligomers (which are previously prepared

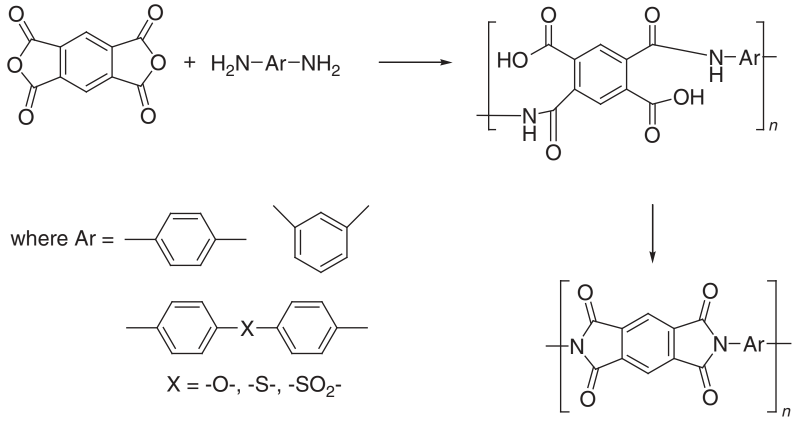


Figure 3.6 Synthesis of polyimides by the reaction of diacid anhydrides and diamines.

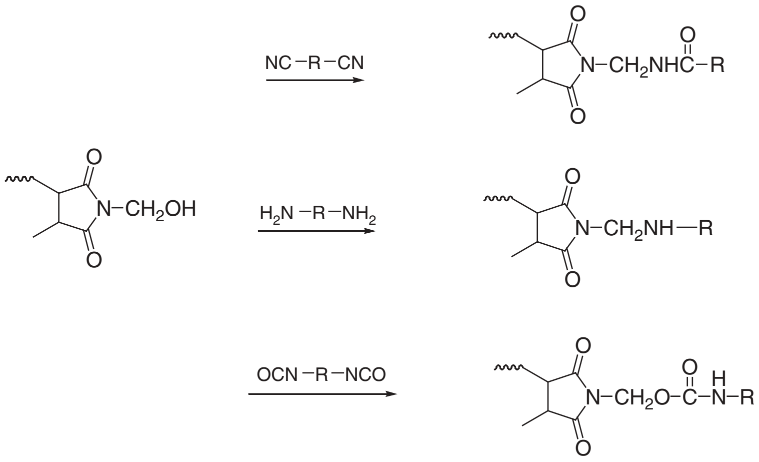


Figure 3.7 Preparation of polyimides with the use of bis(methylol imide).

by polycondensation or polyaddition reactions), reacting as precursors of each block. They can also be prepared by the coupling of different difunctional oligomers, usually no more than two, since otherwise structures that are complex and difficult to handle can be obtained.

Efforts aimed at the synthesis of highly branched polymers have followed two major pathways: one directed toward the synthesis of the desired structures by stepwise growth polymerization and another one that uses one-pot or "click" polymerization of difunctional monomers.

In addition, there has been an increasing interest in new synthetic methods for the preparation of well-defined polymers with controlled chain-end functional groups [23], such as telechelic polymers, which are characterized by the presence of reactive functional groups placed at both chain ends. These materials can then be used as precursors in the synthesis of block copolymers, as modifiers of the thermal and mechanical properties of condensation polymers, as precursors in the preparation of polymer networks, and as compatibilizers in polymer blends [24].

3.5.2 Polyethers

The simplest method to prepare a polyether oligomer by condensation reactions is by the use of hydroxyl functionalized monomers, as described in Figure 3.8.

Polycondensation reactions have also been used to develop an efficient and versatile "one-step" method for the preparation of some polymers by "click processes," which has been applied for the synthesis of telechelic polymers [25].

Alkene-functionalized linear polymers, such as the polyether-thioether described in Figure 3.9, was prepared by thiol-ene click step-growth polymerization using a fast, efficient, and green approach for the synthesis of macromonomers with a variety of functionalities.

Synthesis of polyethers by polycondensation of alcohols can also be performed by the classical interfacial reaction between functionalized monomers. By this procedure, an organotin polyether was synthesized in a rapid (15 s) and high yield reaction (>80%) [26].

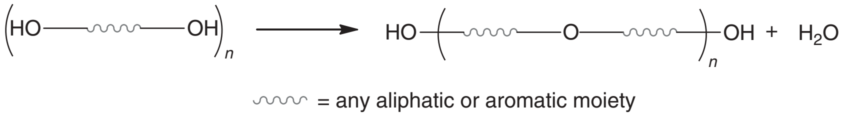


Figure 3.8 General representation of a polycondensation reaction in alcohols.

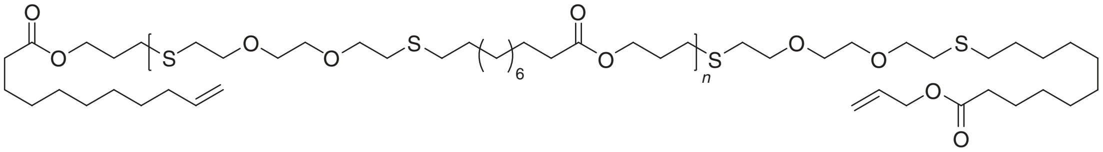


Figure 3.9 Polyether-thioether based on undecanoic acid synthesized by a two-step click condensation process.

3.5.3 Polyesters

Polyesters are among the most widely used fibers in the world today. Generally, they can also be prepared by step-growth polymerization involving the condensation reaction between diols and carboxylic acids or its derivatives, which has been extensively studied. Functionalization in polyesters is usually achieved using a prefunctional monomer such as maleic acid, or any other monomer bearing a double bond, thus providing a large amount of possibilities for combinations between monomers and polymerization techniques [27].

All polymerization reactions can be categorized into two different types: chain- and step-growth polymerization, which are incompatible in terms of monomer structure, experimental conditions, reaction rates, etc. In the past years, research concerning step-growth polymerization has been oriented to the preparation of new polyester materials by the combination of condensation and free radical techniques [28], as shown in Figure 3.10.

Another example that uses the same synthetic strategy is the synthesis of aliphatic polyesters bearing pendant alkyne groups. These polyesters can be successfully prepared by step-growth polymerization of different building blocks, such as adipic and succinic acid, in combination with an acetylene-based diol, examples of which are 2-methyl-2-propargyl-1,3-propanediol, 1,4-butanediol, and the most common ethylene glycol. Alkyne groups can survive the high reaction temperatures (200°C) in the presence of a radical inhibitor. Subsequently, the alkyne groups are reacted by a "click" cycloaddition reaction to obtain a functionalized polyester based on poly(ethylene succinate) and poly(butylene adipate) [29].

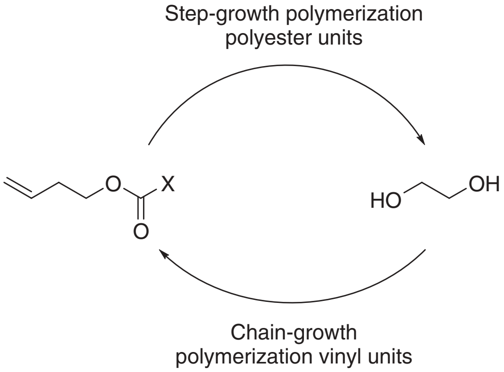


Figure 3.10 Polymerization of bifunctional monomers by step-growth and chain polymerizations.

On the other hand, owing to the rising demand for specialty polymers with novel properties and characteristics designed for specific applications, hyperbranched polymers have attracted much investigation in the past decades [30]. The growing strategy uses the symmetrical nature of the molecules to construct macromolecules functionalized at each end [31].

Recently, the synthesis of seed oil-modified polyester with a hyperbranched polyether core was reported [32]. This methodology involved the preparation of a carboxyl-terminated prepolymer from the monoglyceride of the oil, which was condensed with phthalic and maleic anhydrides.

Also, 10,11-undecanoic acid in the presence of a quaternary ammonium or phosphonium bromide as initiator undergoes polymerization via ring opening of the epoxide group with the carboxylic acid moiety to yield a hydroxyl-functionalized aliphatic polyester [33].

3.5.4 Polyurethanes

Polyurethanes are widely used in several important applications including foams, elastomers, coatings, and adhesives. They result from the reaction between an alcohol and an isocyanate, and from this reaction, hyperbranched polymers can also be prepared from AB_2 monomers having both functional groups in the proper ratio. The high reactivity of isocyanates, even in self-condensation, can lead to the formation of dimer or carbamates by reaction with

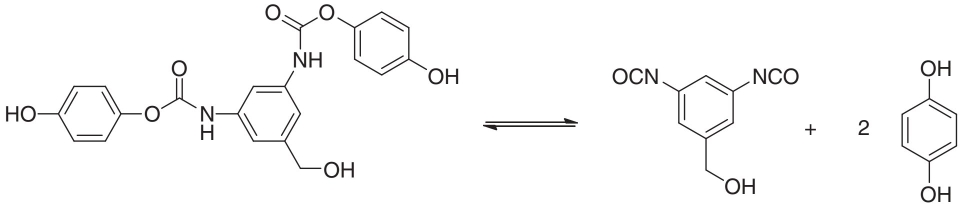


Figure 3.11 Step-growth polymerization reaction between an isocyanate and an aromatic alcohol.

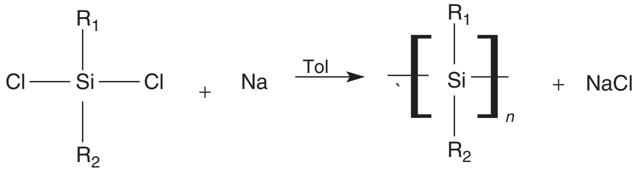


Figure 3.12 General condensation reaction for polysilane preparation. Tol, toluene.

an alcohol molecule. This requires the protection of the isocyanate moiety during storage.

Figure 3.11 shows the preparation of polyurethane by the reaction between an isocyanate molecule and an aromatic alcohol [34].

Hyperbranched polyurethanes have also been synthesized by step-growth polymerization reactions such as the reaction between 3,5-diaminobenzoic acid and 2-hydroxypropyl[3, 5-bis{(benzoxycarbonyl)imino}]benzyl ether to prepare an AB_2-type blocked isocyanate monomer functionalized with an ester group [35]. Several years earlier, Barmar et al. had reported the preparation of a polyurethane-based thickener starting from an ethoxylated urethane prepolymer that was reacted with polyethylene glycol and dicyclohexylmethane diisocyanate [36].

3.6 INORGANIC CONDENSATION POLYMERS

3.6.1 Polysilanes

Polysilanes, which are only slightly different from polysiloxanes, are a class of interesting inorganic polymers that, depending on the molecular weight and lateral substitutions on the silane atom, could be useful as photoinitiators or UV photoresists because of the presence of a σ-bond along the chain [37]. The condensation reaction commonly used for polysilane preparation is the denominated Wurtz reaction that proceeds by the coupling of organodichlorosilanes with sodium metal under toluene reflux, as depicted schematically in Figure 3.12.

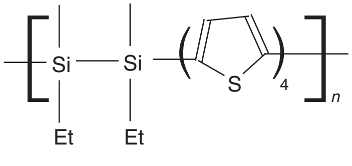


Figure 3.13 Structure of poly(disilanylene-oligothienylene).

In a complete and extensive review by Miller and Milch [38], it is indicated that sodium is favored over lithium because Li tends to undergo oligomerization. Potassium tends to promote degradation and cyclation instead of the formation of linear polymers. Gauthier and Worsfold [39] investigated the effect of phase-transfer catalyst, crown ethers, quaternary ammonium salts, and cryptands to increase the stability and repeatability of the final polysilane (see also Chapter 30 in this handbook).They found an increased reproducibility and better molecular weight distribution of the polymer produced and a certain dependence of the molecular weight upon the concentration of the crown ether. The effect was attributed to the presence of anionic species involved in the polymerization process.

In order to produce polysilanes with controlled optical properties, the substituents have to be picked up properly; thus, poly(alkyl(methoxyphenyl)silane) homo and copolymers are reported by Nakashima and Fujiki [40], who found that poly(alkyl(alkoxyphenyl)silane) with methyl, ethyl and n-hexyl moieties showed a typical absorption peak around 340–360 nm attributed to the delocalized σ-conjugation.

Other combinations, such as doped poly(disilanylene-oligothienylene)s, have been prepared [41] (Fig. 3.13), that are photoconducting when irradiated with visible light at 480 nm.

There are also reports on the optical properties of poly[(octamethyltetrasilylene)methylene] [42], a periodic polycarbosilane, in the presence of crown ethers. A large study on the effect of the substituents R_1 and R_2 in polysilanes and their effect on the different UV radiation absorptions was carried out by Herzog and West [43], who synthesized phenylalkyldicholorosilanes with n-propyl, n-hexyl, n-octyl, and p-Me$O$$C_6H_4SiHexCl_2$ using the Wurtz reaction. They describe changes in the absorption of UV radiation depending on the alkyl substitution, as well as the presence of halogen atoms. More recently, Reuss and Frey [44] described a strategy to obtain multihydroxy-functional polysilanes using an acetal-protecting group that

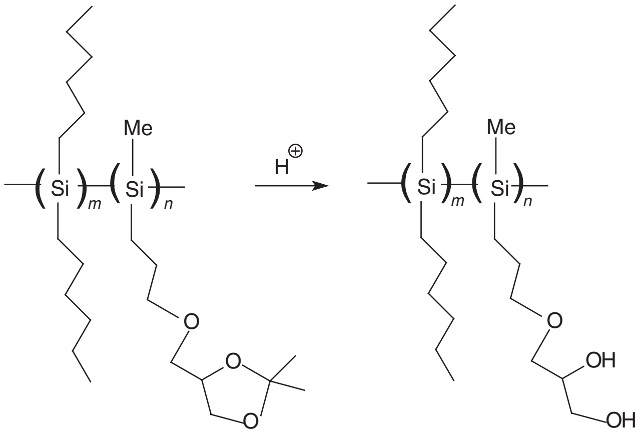


Figure 3.14 Preparation of copolysilane PHDS-*co*-GMS.

is achieved by the coupling of dichloro(3-(2,2-dimethyl -1,3-dioxolane-4-yloxy)propyl)methylsilane and poly[di-n-hexylsilane-co-(isopropylidene glyceryl propyl ether) methylsilane] (P(DHS-co-IMS)), eliminating at the end the dioxol moiety by protonation to form the hydroxyl groups, poly[di-n-hexylsilane-co-(glyceryl propyl ether)methylsilane] (P(DHS-*co*-GMS) (Fig. 3.14).

3.6.2 Polyphosphazenes

Polyphosphazenes are inorganic polymers in which the backbone consists of alternating P and N atoms with two lateral groups. Polyphosphazene monomers are prepared by a condensation reaction involving phosphorus pentachloride and ammonia. The reaction takes place in a stepwise process by elimination of the hydrogen chloride to form the cyclic chlorophosphazene monomer that undergoes ring-opening polymerization (Fig. 3.15).

Similar processes are followed for the preparation of cyclic arylphosphazenes that have a similar tendency to form cyclic phosphazenes [45].

On the other hand, Wisian-Neilson and Neilson [46–48] report a condensation method that leads to the formation of polyphosphazenes. In this route, $NH-(Si-(CH_3)_3)_2$ is reacted in the presence of *n*-butyllithium and PCl_3 to form the dichloride phosphazene using the Grignard reactant, as depicted in Figure 3.16

It is reported that this polydimethyl phosphazene can lead to exchange reactions with Li to produce anionic species that could be reacted with organic or organometallic halides to produce pending alkyl polyphosphazenes.

3.7 DENDRIMERS

The use of monomers with functionality larger than two allows the formation of tridimensional structures by step-growth polymerization. In particular, the use of monomers with the general formula A_xB_y could generate several architectures such as hyperbranched, dendrimers, and star polymers. Each architecture will have different physical and chemical properties. In particular, dendrimers are regularly branched polymers that can be produced by the divergent approach or the convergent approach [49]. In the divergent approach, the dendrimer grows

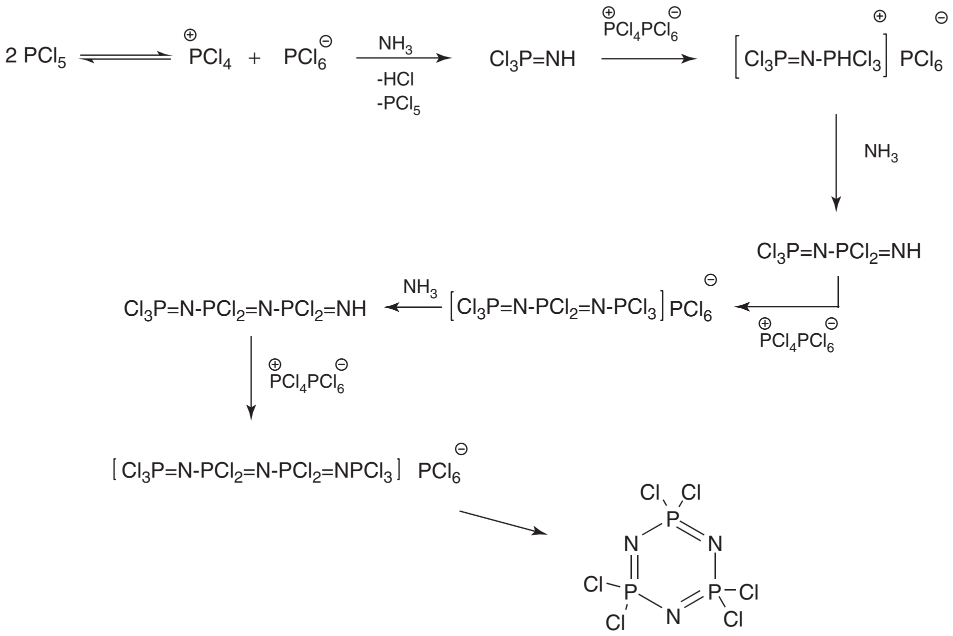


Figure 3.15 Schematic of phosphazene monomer preparation.

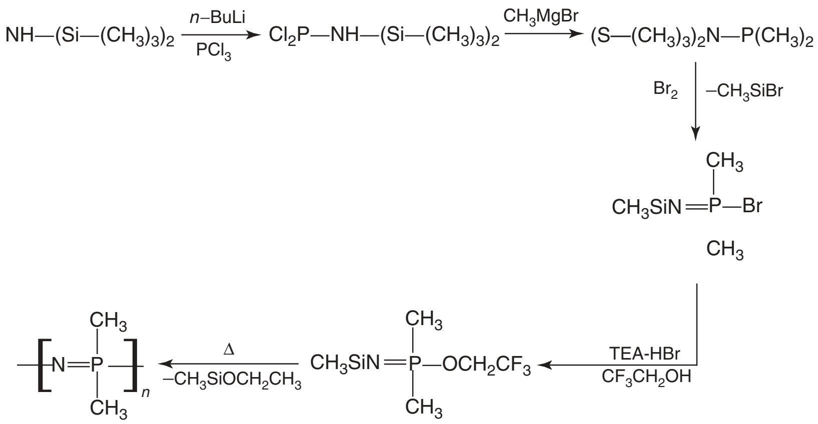


Figure 3.16 Preparation of polydimethyl phosphazene by a stepwise reaction.

from the center and spreads radially out in layers, each of them built by a stepwise reaction. In the convergent approach the dendrimer production starts at the end with the so-called surface functional groups coupled to AB_y building blocks, which allows the preparation of a larger dendron, and the process is repeated to increase the size of the dendrons. At the end, the dendrons are attached to a multifunctional core molecule to produce dendrimers [50]. Examples of AB_y monomer used, for example, in polyesters, are those where A and B are -COOH and -OH groups, respectively, or in some cases their derivatives such as -COCl, $\text{-O}-(CH_2)_2-\text{OH}$, $\text{-O}-Si(CH_3)_3$, or CH_3COO-. A recent example of a dendrimer formation is the synthesis of 3,5-bis(hydroxymethyl)benzylbromide dendrimer unit reported by Kathiresan et al. [51]. They described the divergent approach using a CB_2 branching unit to form the dendrimer, as depicted in Figure 3.17.

This approach is used in several instances to control the arms, molecular weight, and crystallinity of the resulting polymer [52]. The convergent approach is illustrated elsewhere [53, 54]. This subject is not reviewed here in detail because a whole chapter of this handbook (Chapter 30) is dedicated to it.

3.8 THERMOSET POLYCONDENSATION POLYMERS

This section focuses on polycondensation reactions to synthesize thermoset polymers. Specific condensation chemistries are studied here; a more extensive treatment of the subject of thermoset polymers can be found in Chapter 28 of this handbook.

The most common applications of these materials are as paints and coatings. However, their uses are extremely diversified and include boat and marine construction materials, automotive and aircraft bodies, luggage, furnishing, appliances, textiles, and packaging. Owing to their industrial applications, these materials are commonly known as *resins*. The resin industry is quite mature and is predominantly characterized by well-known and established products, applications, and processes [55, 56]. However, the synthesis of these resins requires a different approach because of their differences in chemical composition. Polyester, epoxy, alkydic, and phenolic resins are among the crosslinking polymers that are more commonly synthesized by a stepwise reaction.

3.8.1 Polyester Resins

In general, polyester resins are synthesized by the reaction between carboxylic acids and alcohols, with three or more reactive groups. Recently, unsaturated polyesters were incorporated in various ways to produce terminal, pendant, and internal double bonds [57–59]. In the case of unsaturated polyesters, maleic anhydride is most commonly used to produce internal unsaturation. The double bond present on unsaturated polyester reacts with a vinyl monomer, mainly styrene, resulting in a 3D crosslinked structure. This structure acts as a thermoset. The crosslinking is initiated through an exothermic reaction involving an organic peroxide, such as methyl ethyl ketone peroxide or benzoyl peroxide (Fig. 3.18).

3.8.2 Epoxy Resins

Epoxy resins are among the most important of the high performance thermosetting polymers and have been widely used as structural adhesives and matrix for fiber composites. Epoxy resins are characterized by the presence of epoxide groups before cure, and they may also contain aliphatic, aromatic, or heterocyclic structures in the backbone. The epoxy group can react with amines, phenols, mercaptans,

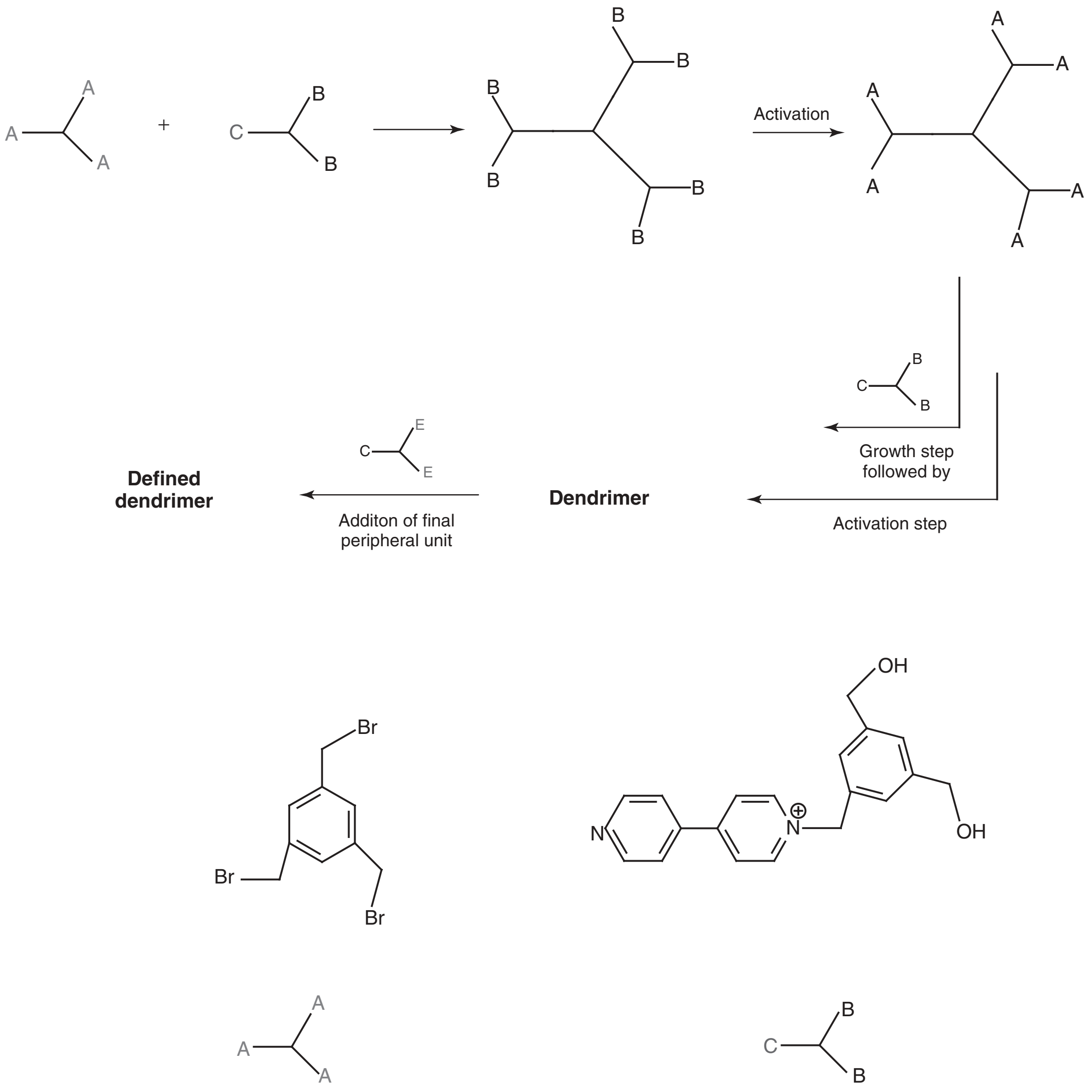


Figure 3.17 Dendrimer prepared by the divergent approach.

isocyanates, anhydrides, or acids as the first step (Fig. 3.19). Usually, aliphatic and aromatic diamines are widely used as curing agents [60].

3.8.3 Alkyd Resins

Alkyd resins are based on polymeric resins developed in the 1920s. The first alkyd resins sold commercially under the name *Glyptal* were made by the General Electric Company (Fig. 3.20). Alkyd resins are a class of polyesters synthesized by condensation between an alcohol and an acid or anhydride. Actually, the anhydride is modified with a monofunctional acid, most commonly C_{18} fatty acid, which can be obtained from vegetable oil (rubber seed oil (RSO) or palm oil) [61–63]. The major advantage of the alkyd resins is their components (fatty acids and triglyceride derivatives), which are obtained from low cost renewable resources.

The synthesis of alkyd resins using vegetable oils proceeds in two stages. For example, pentaerythritol, the tetraol of choice and mainly responsible for the degree of branching of the alkyd [64], and a vegetable oil are reacted to form an ester by transesterification. Then, a slight excess of phthalic anhydride is added to obtain a crosslinked alkyd resin (Fig. 3.21) [65]. Both reactions are monitored by acidity and viscosity measurements [66].

3.8.4 Phenolic Resins

Phenolic resins are a generic name given to a wide range of crosslinked polymers produced by phenol and formaldehyde. There are two types of phenolic resins, Resol and Novolac. The type of resin being made depends on the pH of the catalyst and the ratio of phenol to formaldehyde.

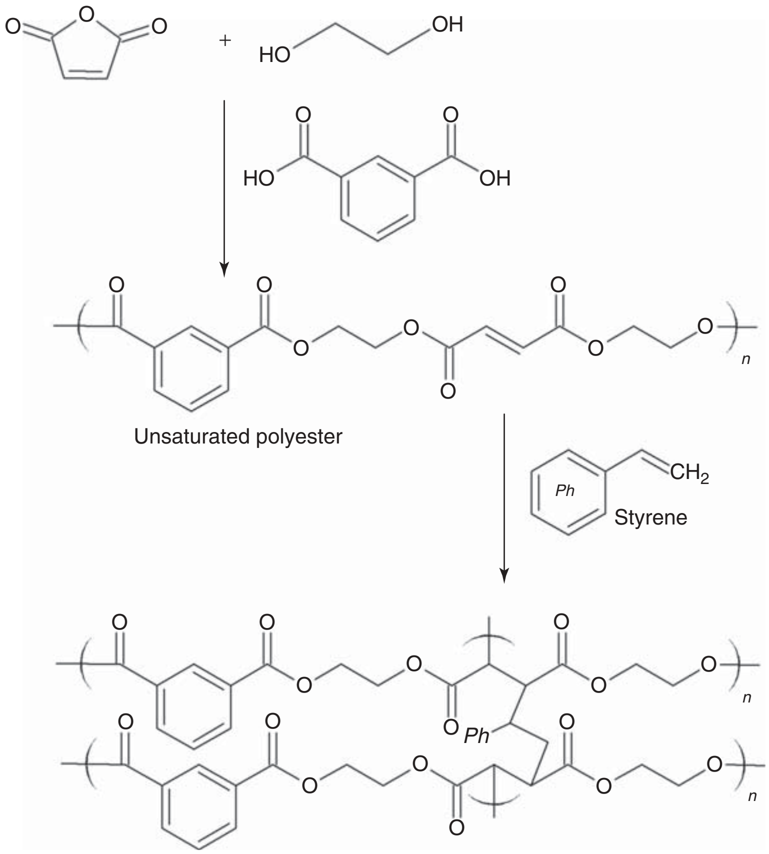


Figure 3.18 Synthesis of unsaturated polyester resin.

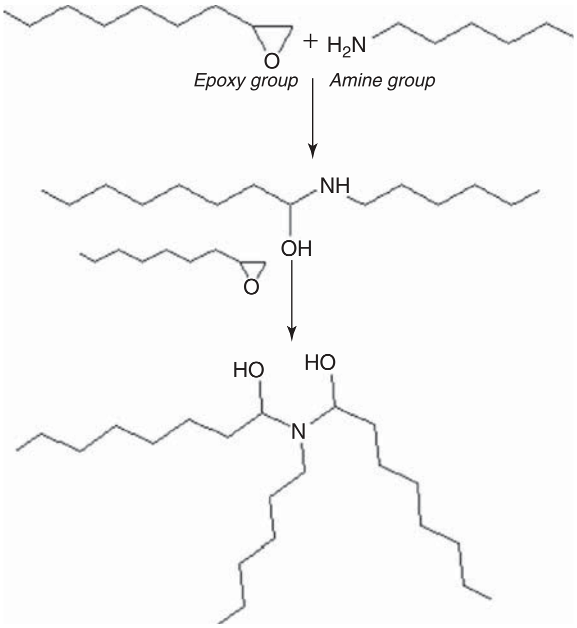


Figure 3.19 Crosslinking polymers using epoxy-amine-cured reactions.

Novolac is made under acidic conditions, and the ratio of phenol to formaldehyde used ranges from 1.49 to 1.72, whereas Resol resins are synthesized in a basic medium using a ratio of phenol to formaldehyde in the range of 1.0 to 0.33 [54, 67, 68]. A synthetic route for both resins is shown in Figure 3.22.

3.9 CONTROLLED MOLECULAR WEIGHT CONDENSATION POLYMERS

Traditionally, a nonstoichoimetric polycondensation method is used to control the number-average molecular weight of a condensation polymer [69–71]. This method assumes that no side reactions take place and that the average degree of polycondensation X_n (number of monomer units in the oligomer) at conversion p of the functional groups A and B is given by Carother's equation [72]. Generally, two dissimilar reactive difunctional monomers are used to synthesize telechelic oligomers, which have the same end-group functionality that the monomer used in excess (Fig. 3.23).

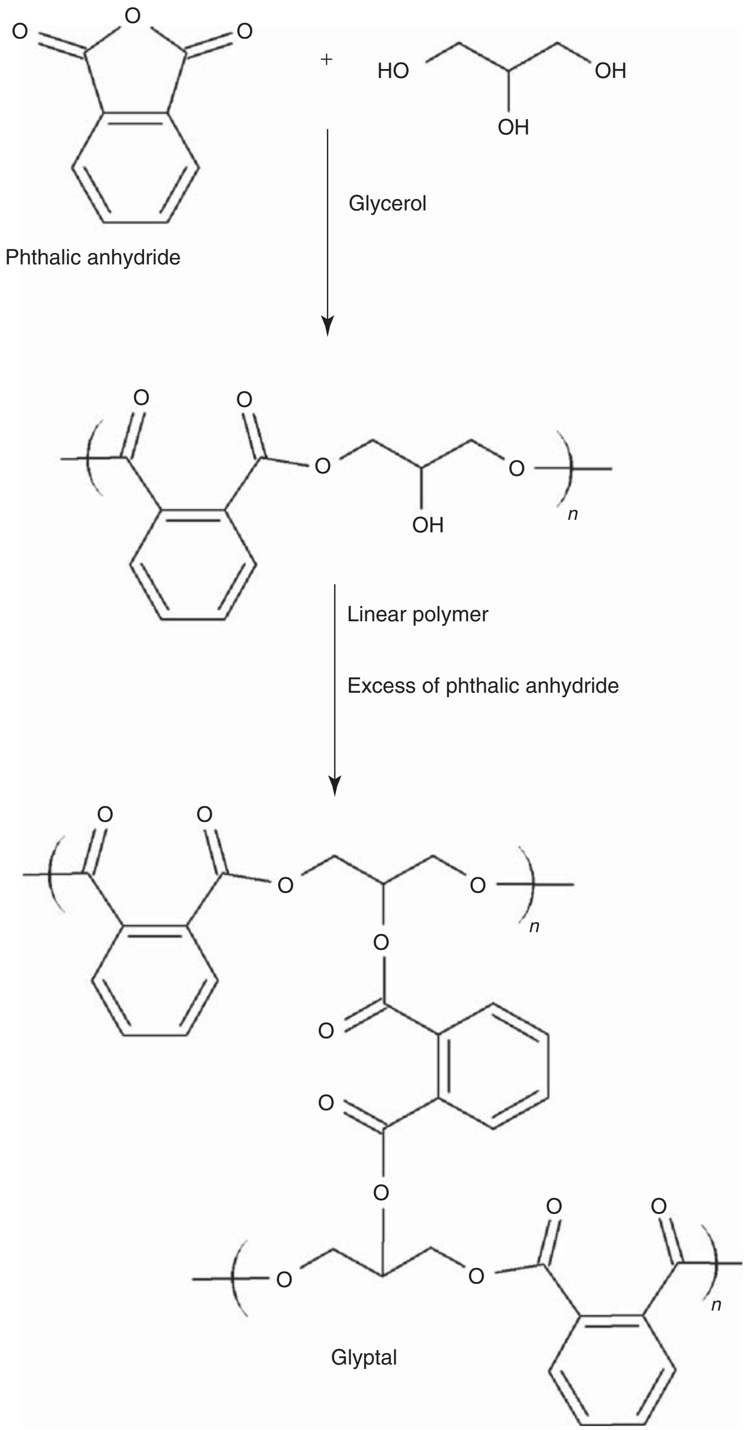


Figure 3.20 Schematic representation of the synthesis of Glyptal.

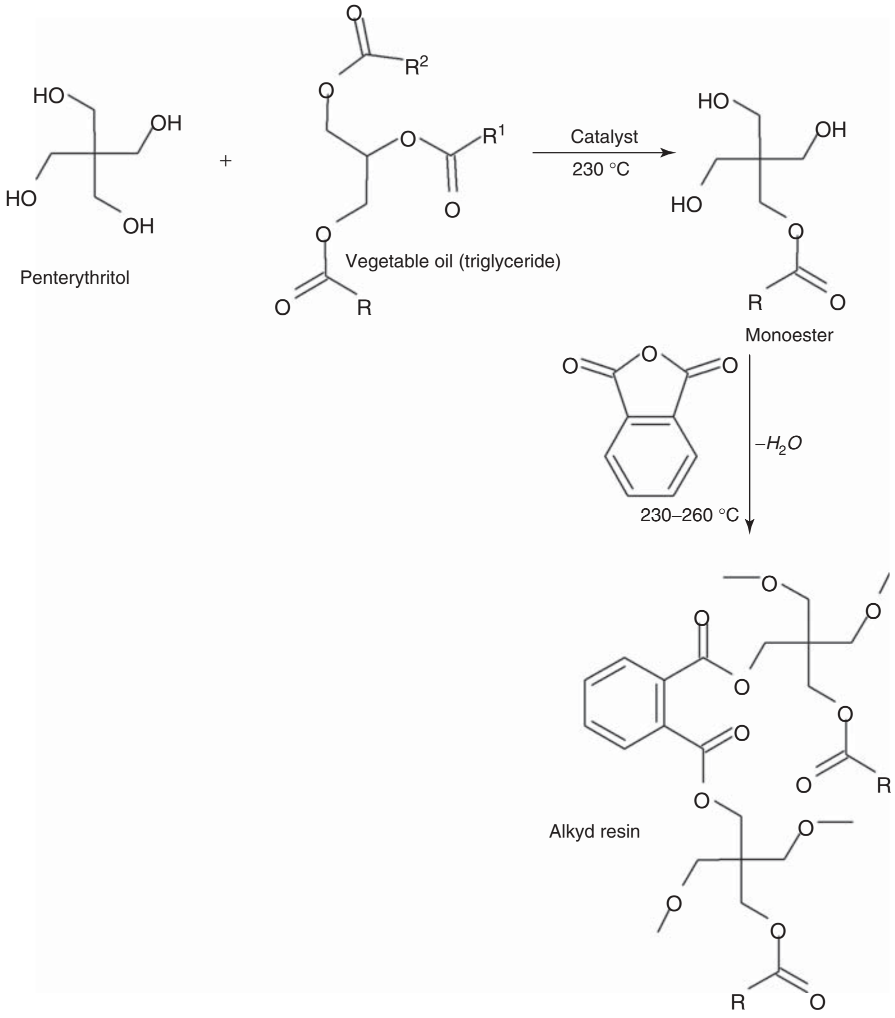


Figure 3.21 Schematic representation of alkyd resins preparation.

Recently, well-defined condensation polymers have been synthesized via substituent effect-assisted chain-growth condensation polymerization, in which the polymer-propagating ends are more reactive than the monomers because of resonance or inductive effects between the functional groups of the terminal monomer units. Figure 3.24 shows a schematic illustration of this concept in the polymerization of AB-type monomers. In this monomer, the substituent effect of the A site diminishes the reactivity of the B site, suppressing undesired step-growth polymerization between monomers. When the monomer reacts with an initiator that has a reactive site, the substituent reactivity has a change. If the substituent effect is to enhance the reactivity of the formed bond of the polymer end group, the next monomer will react selectively with the polymer-propagating end [73].

3.9.1 Solid-Phase Synthesis

Solid-phase synthesis has been used in the preparation of well-defined polymers enabling the convergence between synthetic organic chemistry and polymer chemistry. Solid-phase synthesis has the following advantages over solution-phase methods: ease of purification, speed, and easier sequencing and control of the monomers [74]. A more complete report on techniques, supports, linkers, and reaction types on solid-phase syntheses is given by Zaragoza-Dörwald [75]. In general, this procedure can be realized using

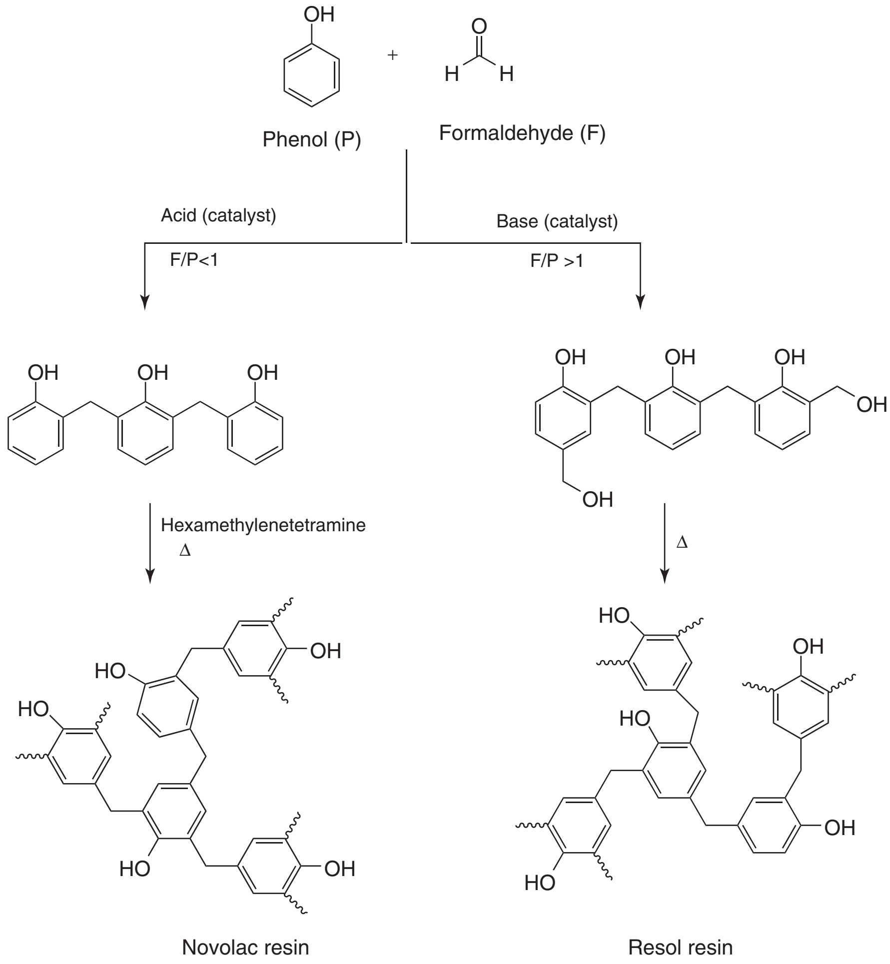
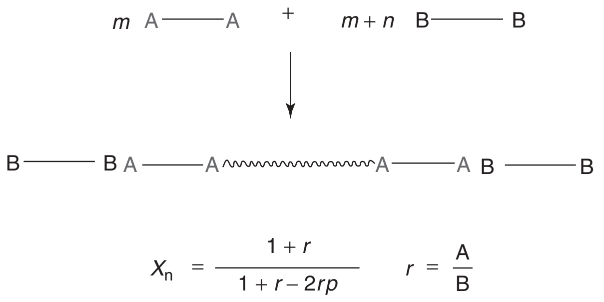


Figure 3.22 Synthetic route for phenolic resins.



$$X_n = \frac{1+r}{1+r-2rp} \qquad r = \frac{A}{B}$$

Figure 3.23 Carother's equation and synthesis of telechelic oligomers by a nonstoichoimetric polycondensation method.

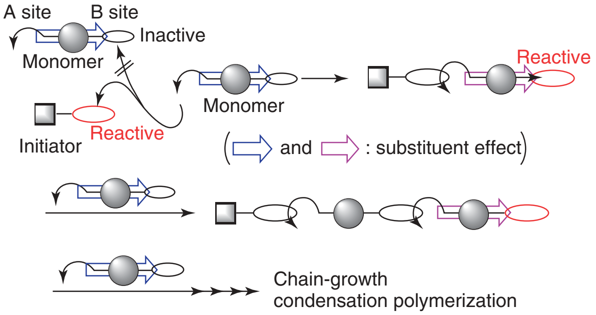


Figure 3.24 Scheme of chain-growth condensation polymerization. *Source*: Reprinted with permission from Yokoyama A, Yokozawa T. *Macromolecules* 2007;40:4093 [73]. Copyright 2007 American Chemical Society. (*See insert for the color representation of the figure*.)

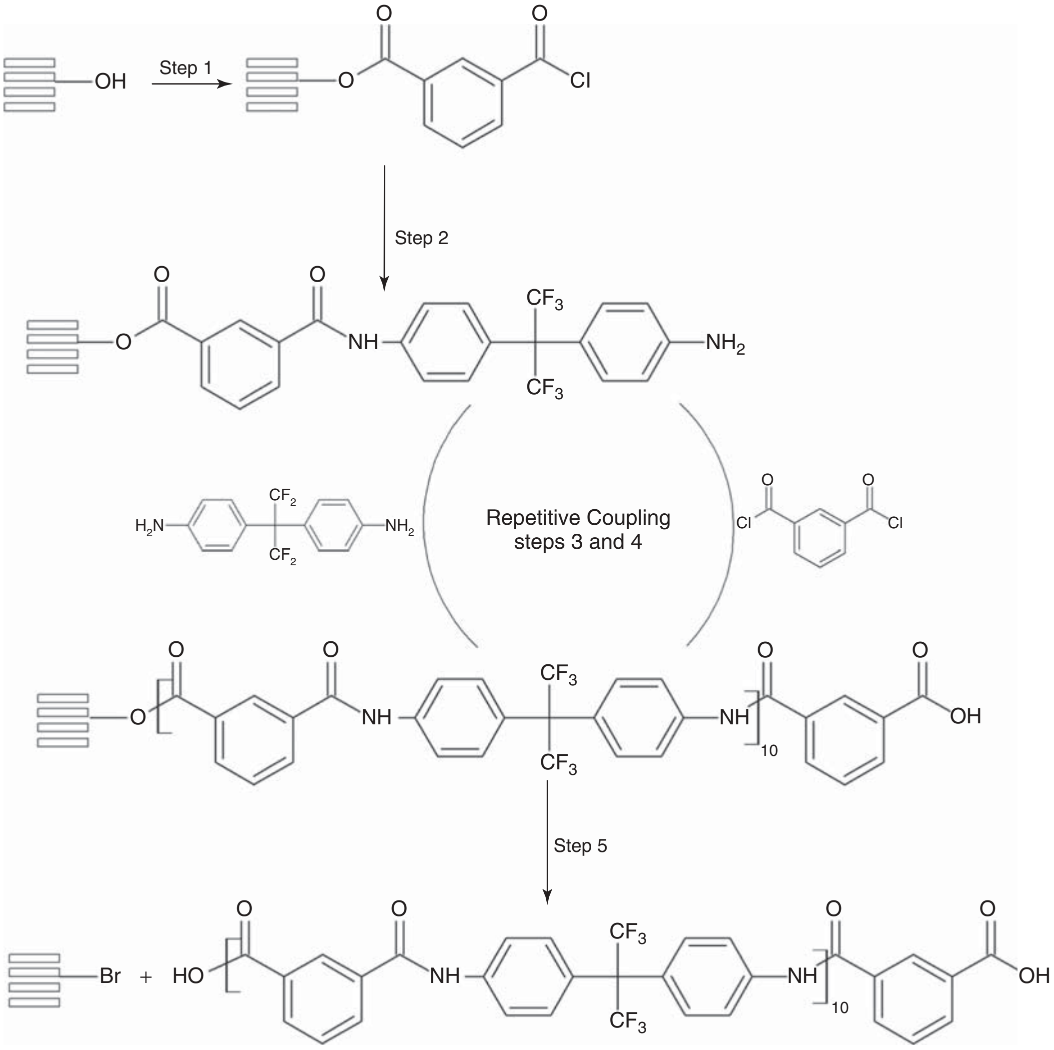


Figure 3.25 Solid-phase synthesis of aromatic oligoamides. *Source*: Reproduced with permission from Santiago-García JL, Aguilar-Vega M. *Eur Polym J* 2009;45:3210 [79]. Copyright 2009 Elsevier Ltd.

condensation monomers with different or equal functionalities [76–79]. Figure 3.25 shows a representative example of the synthesis of aromatic oligoamides using the solid-phase synthesis on SynPhase Lanterns as supports. This procedure shares most features of the key elements of solid-phase peptide synthesis described by Merrifield [80].

3.9.2 Use of Macromonomers in Condensation Reactions

Macromolecular monomers, called *macromonomers* or *macromers*, are a relatively new category of functionalized polymer materials having a molecular weight range of $10^3–10^4$ and possessing one or more reactive polymerizable end groups [81] of those described in Table 3.2. The most intensively studied macromers consist of telechelic polymers that can be used as crosslinkers, chain extenders, and precursors for block and graft copolymers, and their synthesis and modifications have been studied in detail and covered by several authors [82, 83]. One of the most often used methods to synthesize telechelic polymers is polycondensation using Carother's equation, described earlier. Figure 3.26 shows the synthesis of HFATERT-*b*-DBFISO block copolyaramides using different-size macromers [71, 84], via a condensation reaction between diacid and diamino end groups on the HFATERT and DBFISO oligomers. On the other hand, AB_2 macromonomers can be used for the synthesis of polymer with dendritic and hyperbranched structures, DendriMacs and HyperMacs, respectively [85].

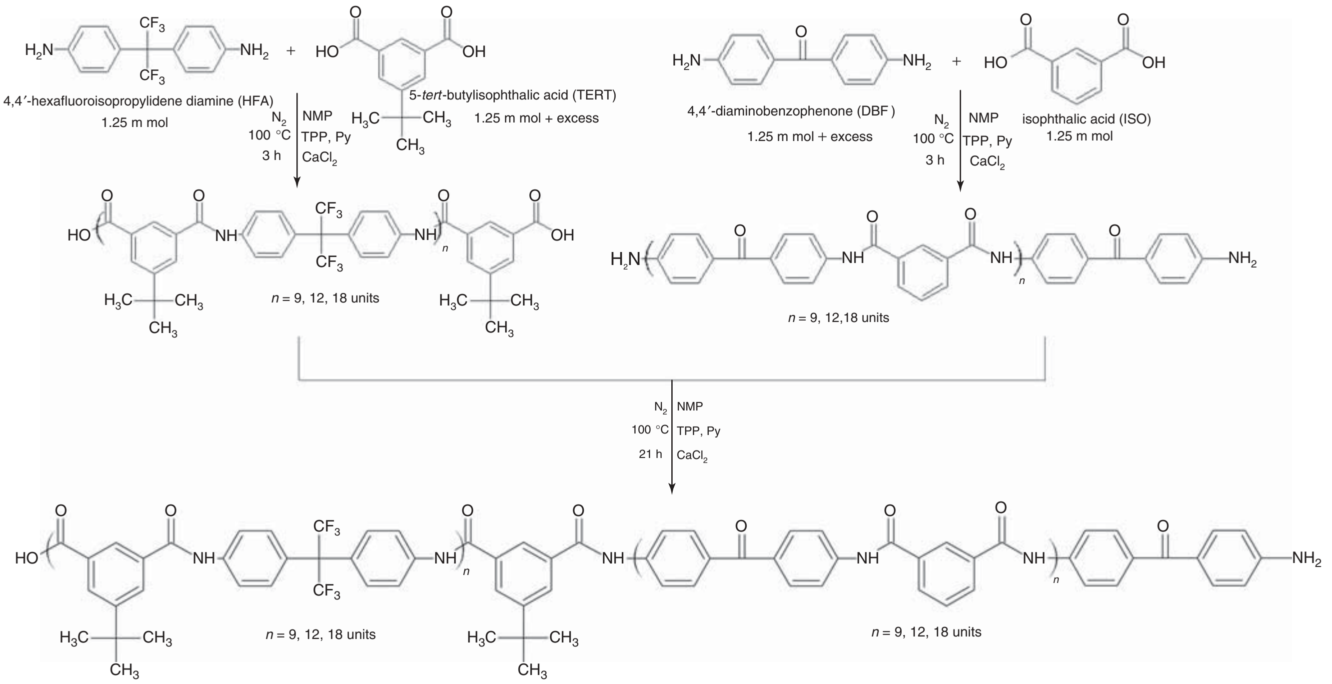


Figure 3.26 Synthesis of HFATERT-*b*-DBFISO rigid block copolyaramides by polycondensation of macromers.

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