Chapter 6

Step Polymerization

The step polymerization builds up the molecular weight of polymer by stepwise function. Sometimes, the polymerization involves the release of small molecule by-product, so it is also called condensation polymerization. It is the earliest polymerization technique in the synthetic polymers. In 1907, Leo Baekeland of Germany created the first completely synthetic polymer, Bakelite, by reacting phenol and formaldehyde. It is also called phenolic resin. The molecular weight of the phenolic resin builds up stepwise by removing water. The product was commercialized in 1909 by forming a company bearing his name as Bakelite until present day.

Table 6.1 lists some of the commercially important polymers prepared by step-reaction polymerization. The reaction mechanisms, kinetics of polyesters and polyamides have been thoroughly studied. Thus, we are discussing the degree of polymerization $\overline{DP}$ and the polymerization rate of step polymerization using these two polymers as examples.

6.1 Chemical Reactions and Reaction Mechanisms of Step Polymerization

The type of products formed in step polymerization is determined by the functionality of the monomers, i.e., by the average number of reactive functional groups per monomer molecule. Monofunctional monomers give only low molecular weight products. Bifunctional monomers give linear polymers. Polyfunctional monomers, with more than two functional groups per molecule, give branched or crosslinked polymers. The properties of the linear and the crosslinked polymers differ widely. The mechanism of step polymerization is discussed below according to the type of chemical reaction [2].

Table 6.1 Commercially important polymers prepared by step polymerization [1]

Polymer type	Repeating functional unit
Polyether [poly(phenylene oxide)]
Polyether (epoxy resin)
Polysulfide
Poly(alkylene polysulfide)
Polysulfone
Polyester
Polycarbonate
Polyamide
Polyurea
Polyurethane
Phenol-formaldehyde (complex network structure)
Urea-formaldehyde (complex network structure)
Melamine-formaldehyde (complex network structure)
Polyimide

6.1.1 Carbonyl Addition: Elimination Reaction Mechanism

The reaction mechanism involves the addition and elimination at the carbonyl double bond of carboxylic acids and their derivatives to form polymer as shown below:

Where R may be alkyl or aryl groups, X may be OH, OR', O-C(=O)R', or Cl; and Y may be R'O⁻, R'OH, R'NH₂, or R'COO⁻. The species in the bracket is a metastable intermediate, which can either return to the original state by eliminating Y or proceed to the final state by eliminating X. The following section provides some typical examples of polymers made by this reaction mechanism.

6.1.1.1 Direct Reaction

Polyester has been prepared by direct reaction of a dibasic acid and a glycol. A strong acid or acidic salt often serves as a catalyst. The reaction may be carried out by heating the reactants together and removing water, usually applying vacuum in the later stages.

Polyamide can be synthesized by direct reaction of dibasic acid and a diamine. The use of their salt such as hexamethylene diamine salt of adipic acid to synthesize Nylon 66 can meet stringent requirement of stoichiometric equivalent to obtain high molecular weight polymer by heating salt to above its melting point in an inert atmosphere.

6.1.1.2 Interchange

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

The alcohol by-product is easier to remove than the water, so a higher molecular weight can be achieved faster. The ester monomer also has an advantage over acid monomer on the solubility in solvent. This reaction has been used

routinely in the synthesis of polyester using ethylene glycol and dimethyl terephthalate in the industry. The other interchange reactions such as amine-amide, amine-ester, and acetal-alcohol are well-known for polymerization.

6.1.1.3 Acid Chloride or Anhydride

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:

The reaction between acid chloride and a glycol is not useful because of side reactions leading to low molecular weight products. However, the reaction of an acid chloride with a diamine is a good way to prepare polyamides. The amine is a much stronger nucleophile toward acid chloride than the alcohol, so the polymerization can be achieved quantitatively.

6.1.1.4 Interfacial Condensation

The reaction of an acid halide with a glycol or a diamine proceeds rapidly to high molecular weight polymer if carried out at the interface between two liquid phases, each containing one of the reactants. Typically, an aqueous phase containing the diamine or glycol and an acid is layered at room temperature over an organic phase containing the acid chloride. The polymer formed at the interface can be pulled off as a continuous film or filament (Fig. 6.1). The method has been applied to the formation of polyamides, polyurethanes, polyureas, polysulfonamides, and polyphenyl esters. It is particularly useful for synthesizing polymers that are unstable at higher temperature.

A typical example is the Schotten-Baumann synthesis of polyamide from a diacid chloride dissolved in an organic solvent, and a diamine dissolved in aqueous base. The base is needed to neutralize the by-product HCl, which would otherwise react with the diamine to form amine hydrochloride. Rapid stirring to maximize the interfacial area increases the yield of polymer.

Fig. 6.1 Interfacial synthesis of polyamide

6.1.2 Carbonyl Addition: Substitution Reaction Mechanism

This reaction mechanism has been used in the synthesis of polyacetal from aldehyde and alcohol. The reaction mechanism involves first addition and then substitution at the carbonyl groups of aldehyde from alcohol to form polyacetal.

The phenolic resin made from formaldehyde and phenol is underwnt similar reaction mechanism.

6.1.3 Nucleophilic Substitution Reaction Mechanism

This reaction mechanism is used in the synthesis of epoxy resin as shown in the following:

Here, the nucleophile is bisphenol A to react with epichlorohydrin to substitute chlorine by ring closure reaction to form epoxy resin. The size of epoxy resin can be controlled by the amount of epichlorohydrin. Usually, the excess amount of epichlorohydrin is used to obtain low molecular weight liquid epoxy resin with n is equal to 0 or 1. This low molecular weight epoxy resin can be further reacted with multifunctional amine or anhydride to obtain cured thermoset epoxy resin by the following reaction:

6.1.4 Double-Bond Addition Reaction Mechanism

This reaction mechanism is typically used to synthesize polyurethane. Polyurethane is prepared by adding the hydroxyl group of polyol into the double bond of isocyanate as shown in the following. The polyol can be either polyester polyol or polyether polyol. The polyol is usually synthesized by ring opening polymerization which will be discussed in [Chap. 11](#).

6.1.5 Free-Radical Coupling

This reaction mechanism is used to synthesize arylene ether polymers, polymer containing acetylene units, and arylene alkylidene polymers as shown below:

where $[\text{O}_n]$ is an oxidizing agent.

6.1.6 Aromatic Electrophilic-Substitution Reaction Mechanism

The poly(*p*-phenylene) synthesis can be obtained by this reaction mechanism as shown in the following:

6.2 Reaction Kinetics of Step Polymerization

Linear polymers are synthesized either from difunctional monomers of the AB type or from a combination of AA and BB difunctional monomers. Network polymers are formed from monomers having functionality greater than two. Polymers retain their functionality as end groups at the completion of polymerization. A single reaction is responsible for the formation of polymer. Molecular weight increases slowly even at high levels of conversion. In 1920, Wallace Carothers proposed a Carothers equation relating $\overline{DP}$ to monomer conversion (p) as Eq. 6.11. High-yield reactions and an exact stoichiometric balance are necessary to obtain a high molecular weight linear polymer.

$$\overline{DP} = \frac{1}{1-p} \quad (6.11)$$

If the polymerization reaction is first order with respect to each functional group reactant, A and B , then the rate of reaction can be expressed by:

$$-\frac{d[A]}{dt} = k[A][B] \quad (6.12)$$

For high molecular weight polymer, we need $[A] = [B]$, then the rate of reaction becomes

$$-\frac{d[A]}{dt} = k[A]^2 \quad (6.13)$$

or, by integration,

$$\frac{1}{[A]} - \frac{1}{[A_o]} = kt \quad (6.14)$$

At any particular time, t , in the polymerization process, $\overline{DP}$ is equal to the ratio of monomer molecules present initially to the total number at that time; that is,

$$\overline{DP} = \frac{[A_o]}{[A]} \quad (6.15)$$

Combining Eq. 6.15 with the Carothers equation and solving for $[A]$, one has

$$[A] = [A_o](1 - p) \quad (6.16)$$

By substitution in Eq. 6.14, one obtains

$$\frac{1}{[A_o](1 - p)} - \frac{1}{[A_o]} = kt \quad (6.17)$$

Since $\overline{DP} = 1/(1 - p)$, Eq. 6.17 can be rearranged into

$$\frac{\overline{DP}}{[A_o]} - \frac{1}{[A_o]} = kt \quad (6.18)$$

or

$$\overline{DP} = [A_o]kt + 1 \quad (6.19)$$

From initial monomer concentration $[A_o]$ and time t , we can calculate molecular weight. For the synthesis of polyester, in the absence of acid catalyst, the monomer of carboxylic acid A , assumes the role of catalyst, and the rate of reaction then becomes second order in acid, or third order overall:

$$-\frac{d[A]}{dt} = k[A]^2[B] \quad (6.20)$$

Assuming $[A]$ and $[B]$ are equal,

$$-\frac{d[A]}{dt} = k[A]^3 \quad (6.21)$$

Integration then gives

$$\frac{1}{[A]^2} - \frac{1}{[A_o]^2} = 2kt \quad (6.22)$$

Substituting for $[A]$ from Eq. 6.16 and rearranging

$$\frac{1}{[A_o]^2(1-p)^2} - \frac{1}{[A_o]^2} = 2kt \quad (6.23)$$

or

$$\frac{1}{(1-p)^2} = 2kt[A_o]^2 + 1 \quad (6.24)$$

and

$$\overline{DP}^2 = 2kt[A_o]^2 + 1 \quad (6.25)$$

For uncatalyzed polyesterification (6.25), the molecular weight increases slower than that of acid catalyzed polyesterification (6.19). The above equation deviates at both low and high levels of extent of conversion of monomers. As shown in Fig. 6.2, in the early stage, highly polar alcohol and acid are converted to much lower polarity ester. The more polar the medium, the more association through hydrogen bonding inhibits reactivity. At high conversion, water by-product is difficult to remove in high-viscosity environment (high molecular weight) that reduces the rate of conversion.

6.3 Molecular Weight Control in Step Polymerization

Three approaches have been used extensively to limit the molecular weight of polymer in step-reaction polymerization. One can quench the polymerization reaction by lowering the reaction temperature or by adding monofunctional monomer. For example, fatty acid has been added into unsaturated polyester synthesis, acetic acid added into Nylon 66 synthesis. One can also obtain low molecular weight epoxy resin by using one reactant in excess as described earlier.

When a nonstoichiometric amount of functional groups is used, the relationship between $\overline{DP}$ and reaction conversion can be quantified by a modification of the Carothers equation. We use a factor, r , representing the *stoichiometric imbalance*. For a polymerization reaction of AA and BB, when the molar equivalent of AA

Fig. 6.2 Third-order plot of the self-catalyzed polyesterification of adipic acid with diethylene glycol at 166 °C [3]

monomer (N_A^o) is different from the molar equivalent of BB monomer (N_B^o), the stoichiometric imbalance factor, r , can be expressed by:

$$r = \frac{N_A^o}{N_B^o} \quad (6.26)$$

By convention, r is always less than unity (except, when $N_A^o = N_B^o$). As before, p is the reaction conversion, which in this case represents the fraction of A groups that have reacted. Because the reaction of each A group consumes one B group, the fraction of B reacted at conversion p is equal to N_A^o , or prN_B^o . The number of unreacted groups, N_A and N_B , is then given by:

$$\begin{aligned} N_A &= (1 - p)N_A^o \quad \text{and} \\ N_B &= (1 - pr)N_B^o = (1 - pr) \frac{N_A^o}{r} \end{aligned} \quad (6.27)$$

At this time, the number of A and B end groups is equal to $N_A + N_B$, and, because there are two end groups per molecule, the number of molecular chains, N , is given by:

$$N = \frac{1}{2}(N_A + N_B) \quad (6.28)$$

that is,

$$N = \frac{1}{2} \left[(1-p)N_A^o + (1-pr)\frac{N_A^o}{r} \right] \quad (6.29)$$

and reduces to

$$N = \frac{N_A^o}{2} \left(1 + \frac{1}{r} - 2p \right) \quad (6.30)$$

One repeating unit is formed after each reaction of A and B functional group, thus, the total number of repeating units, N_r , is given by:

$$N_r = \frac{1}{2} (N_A^o + N_B^o) \quad (6.31)$$

Since $r = N_A^o/N_B^o$,

$$N_r = \frac{1}{2} \left(N_A^o + \frac{N_A^o}{r} \right) = \frac{N_A^o}{2} \left(\frac{r+1}{r} \right) \quad (6.32)$$

The average degree of polymerization is equal to the number of monomeric units divided by the number of chains; that is,

$$\overline{DP} = \frac{N_r}{N} = \frac{(N_A^o/2)[(r+1)/r]}{(N_A^o/2)[1 + (1/r) - 2p]} \quad (6.33)$$

and reduces to

$$\overline{DP} = \frac{1+r}{r+1-2rp} \quad (6.34)$$

From Eq. 6.34, at given the stoichiometric imbalance factor, r , one can calculate the extent of reaction necessary to achieve a given degree of polymerization. If $r = 1$, the relationship reduces to

$$\overline{DP} = \frac{1}{1-p} \quad (6.35)$$

which becomes, the Carothers equation. When monomer A is completely used up in the polymerization (i.e., when $p = 1$), the equation becomes

$$\overline{DP} = \frac{1 + r}{1 - r} \quad (6.36)$$

If monofunctional reagent is added to control the molecular weight of polyester, the imbalance factor r (Eq. 6.26) needs to be redefined as r' as the following:

$$r' = \frac{N_A^o}{N_B^o + 2N_B^o} \quad (6.37)$$

where N_B^o , is the number of monofunctional B groups. The factor 2 takes into account the fact that each monofunctional B' molecule is equally as effective as one excess BB monomer in limiting the molecular weight.

6.4 Molecular Weight Distribution

Using statistical methods derived by Paul Flory, the molecular weight distribution in step polymerization can be related to the reaction conversion. One needs to determine the probability of finding a chain containing x monomer units and a single unreacted A or B group at time t for a polymerization reaction of AA and BB. The probability that $x-1$ of A or B has reacted is p^{x-1} , where p is the reaction conversion, defined previously as

$$p = \frac{N_o - N}{N_o} \quad (6.38)$$

The probability of finding an unreacted group is $1 - p$. The probability of finding a molecule containing x units and an unreacted A or B group is then $p^{x-1}(1 - p)$. If the total number of molecules present at time t is N , then the fraction that contains x units, N_x is given by:

$$N_x = Np^{x-1}(1 - p) \quad (6.39)$$

Knowing that $N/N_o = 1 - p$ (Carothers equation), one can rewrite the expression for N_x as the following:

$$N_x = N_o(1 - p)^2 p^{x-1} \quad (6.40)$$

where N_o is the number of monomer units present initially. The above relationship can be plotted and shown in Fig. 6.3.

The figure shows, even at 99 % conversion, monomer still represents the most abundant species present. This is misleading. One can have a more reasonable picture expressing the molecular weight distribution in terms of the weight

Fig. 6.3 Mole fraction distribution in linear step polymerization [1]

fraction. The molecular weight can be expressed by the weight fraction as shown in the following equations:

$$w_x = \frac{xN_xM_o}{N_oM_o} = \frac{xN_x}{N_o} \quad (6.41)$$

where M_o is the mass of the repeating unit, substituting the expression of N_x , one obtains

$$w_x = x(1-p)^2p^{x-1} \quad (6.42)$$

Figure 6.4 shows the plot of w_x versus x at four levels of conversion. Both figures confirm that high degrees of polymerization can be achieved by very high conversion.

Fig. 6.4 Weight fraction distribution in linear step polymerization [1]

To determine the polydispersity index ($\bar{M}_w/\bar{M}_n$) at a given conversion, one needs to define $\bar{M}_w$ and $\bar{M}_n$ in terms of p . Given that $\bar{M}_n$ is the product of $\overline{DP}$ and M_o , and $\overline{DP} = 1/(1 - p)$, one can write

$$\bar{M}_n = \frac{M_o}{1 - p} \quad (6.43)$$

For $\bar{M}_w$, one can have the following expression:

$$\bar{M}_w = \sum w_x M_x \quad (6.44)$$

and rewrite it for x units as

$$\bar{M}_w = \sum w_x x M_o \quad (6.45)$$

Substituting the expression for w_x above, one obtains

$$\bar{M}_w = M_o(1 - p)^2 \sum x^2 p^{x-1} \quad (6.46)$$

The series $\sum x^2 p^{x-1}$ reduces to $(1 + p)/(1 - p)^3$; therefore,

$$\bar{M}_w = \frac{M_o(1 + p)}{1 - p} \quad (6.47)$$

Then, one can have the polydispersity index as the following:

$$\frac{\bar{M}_w}{\bar{M}_n} = 1 + p \quad (6.48)$$

6.5 Network Formation from Step Polymerization

If monomers contain functionality greater than two are used in the step polymerization, then chain branching and crosslinking are resulted. The crosslinked polymer exhibits superior physical and chemical properties as compared with linear polymer. If the reaction is carried to a high enough conversion, gelation occurs. *Gel point* is a sudden increase in viscosity during the polymerization, polymer liquid changes into solid gel. When the gelation occurs in the reactor, it is very difficult to take the gel out of the reactor. Special attention needs to pay during the polymerization using multifunctional monomers. It is desirable to be able to predict the gel point from manufacturing point of view. When the monomers with different functionality are used in the correct amount, the gelation of the polymerization can be controlled as shown in the following equations.

Given that

$$p = \frac{N_o - N}{N_o} \quad (6.49)$$

where N_o and N are the number of monomer molecules initially and at conversion p , respectively, then the number of functional groups that have reacted is $2(N_o - N)$. The number of functional groups initially is $N_o f_{av}$. Thus,

$$p = \frac{2(N_o - N)}{N_o f_{av}} \quad (6.50)$$

Since $\overline{DP} = N_o/N$, the above expression may be rewritten as:

$$p = \frac{2}{f_{av}} - \frac{2}{\overline{DP} f_{av}} \quad (6.51)$$

By rearranging Eq. 6.51, one can obtain the number average degree of polymerization as

$$\bar{X}_n = \frac{1}{1 - f_{av}p/2} \quad (6.52)$$

and the weight-average (degree of polymerization) by

$$\bar{X}_w = xW_x = \frac{1 + p}{1 - (f_{av} - 1)p} \quad (6.53)$$

At the gel point, the weight-average degree of polymerization becomes infinite. As may be seen in Fig. 6.5, where both averages are plotted against p . The very large values of $\bar{X}_w/\bar{X}_n$ near the gel point illustrate the extreme breadth of the distributions.

It is assumed that gelation occurs when $\overline{DP}$ becomes infinite, at which point the second term of Eq. (6.51) becomes zero. Then

$$p_c = \frac{2}{f_{av}} \quad (6.54)$$

where p_c denotes the *critical reaction conversion* at which gelation occurs.

Fig. 6.5 Weight- and number-average degree of polymerization as a function of p for a trifunctional step polymerization [2]

The following are two examples of gel point calculation for equivalent amounts of acid and alcohol functional groups. Their chemical structures are shown in the following:

1

2

3

4

1. For an equimolar mixture of phthalic anhydride (**1**, $f = 2$), trimellitic acid (**2**, $f = 3$), ethylene glycol (**3**, $f = 2$), and glycerol (**4**, $f = 3$), one can calculate f_{av} and p_c as

$$f_{av} = (2 + 3 + 2 + 3)/4 = 2.5$$

$$p_c = 2/2.5 = 80\%$$

If only difunctional monomers are in the mixture, then

$$\overline{DP} = 1/(1 - p_c) = 1/(1 - 0.8) = 50$$

2. For a mixture of 3 mol of **1** and 2 mol of **4**, the f_{av} and p_c as

$$f_{av} = [(3 \times 2) + (2 \times 3)]/5 = 2.4$$

$$p_c = 2/f_{av} = 2/2.4 = 83\%$$

In real case, such mixture gels at about 77 % conversion. The discrepancy arises primarily from the greater contribution of high molecular weight fraction.

In terms of critical gel point for nonequivalent amount of acid and alcohol, we can derive the following relationship. A mixture consisting of three monomers A, B, C; A and C have the same functional groups but different functionality, B contains a different functional group and in excess. Then the average functionality is given by:

$$f_{av} = \frac{2rf_A f_B f_C}{f_A f_C + r\rho f_A f_B + r(1 - \rho)f_B f_C} \quad (6.55)$$

where the constants r and ρ are given by:

$$r = \frac{N_A f_A + N_C f_C}{N_B f_B} \quad (6.56)$$

and

$$\rho = \frac{N_C f_C}{N_A f_A + N_C f_C} \quad (6.57)$$

The critical conversion, p_c , then refers to the extent of reaction of the A groups only.

Statistical methods have also been developed that predict gelation at a lower level of conversion than that predicted by the Carothers equation. For the case of f_A and f_B each equivalent to 2, and $f_C > 2$, the method will derive p_c as the following:

$$p_c = \frac{1}{[r + r\rho(f - 2)]^{1/2}} \quad (6.58)$$

where f is the functionality of C. Experimental value of p_c fall between the values calculated by the statistical and nonstatistical method.

6.6 Step Copolymerization

A copolymer is defined in step polymerization as one having more than one kind of repeating unit. Thus, a polyester **5** prepared from terephthalic acid and ethylene glycol is a homopolymer, but a polyester **6** made with a 1:1:2 mixture of terephthalic acid, isophthalic acid, and ethylene glycol is a copolymer. In synthesizing copolymers such as **6**, the distribution of monomer units is random because the two dicarboxylic acids have virtually equal reactivity.

Alternating step copolymers can also be synthesized. Consider the hypothetical case of two different monomers, AA and BB, both of which react with monomer CC. A 1:1:2 mixture of AA, BB, and CC yields a random copolymer. If, however, AA is first reacted with CC, then the product is reacted with BB, an alternating copolymer is formed. This is shown schematically in Eq. 6.59. Figure 6.6 illustrates an example of synthesis of polyurethane elastomers using this approach.

Fig. 6.6 Synthesis of elastomeric polyurethane

Step polymers are true telechelic polymers, so one can easily prepare block copolymers by linking homopolymers together through co-reactive functional groups. As shown in Eq. 6.60, the AB block copolymer of polyether and polyurethane can be synthesized by reacting hydroxyl-terminated polyether with isocyanate-terminated polyurethane. The AB block copolymer of polyester and polyamide can be obtained by reacting an acid chloride-terminated polyester with an amine-terminated polyamide as shown in Eq. 6.61. Alternatively, one could react an isocyanate-terminated polyurethane with two equivalents of hydroxyl-terminated polyester to form an ABA block copolymer as shown in Eq. 6.62.

6.7 Techniques of Step Polymerization

Four step polymerization techniques have been developed for synthetic polymers: (a) homogeneous bulk polymerization, (b) homogeneous solution polymerization, (c) heterogeneous interfacial polymerization, and (d) heterogeneous phase-transfer catalyzed polymerization. For homogeneous bulk polymerization, it has the advantage of providing a product free of contaminants other than by products or side reactions. The major disadvantage is that high viscosities necessitate the use of elevated temperature and inert atmosphere (avoid oxidative decomposition). For homogeneous solution polymerization, it minimizes the high-viscosity problem and can assist in removal of by-product by azeotropic distillation. The major disadvantage of the process is the necessary removal of the solvent.

For heterogeneous interfacial polymerization, the reaction involves solutions of the two monomers in separate, immiscible solvents. When the two solutions are brought into contact, polymer is formed at the interface. Some examples have been discussed in [Sect. 6.1.1.4](#). Interfacial polymerization differs significantly from bulk or solution polymerization. The reaction goes rapidly at low temperature. The diffusion of monomer to the interface is a rate determining step. Monomer reacts with the growing chains at the interface more rapidly than it diffuses through the polymer film to initiate new chain (similar to chain polymerization) hence molecular weights tend to be significantly higher. Thus, an exact stoichiometric balance is not necessary. High cost of acid chlorides and the usage of large volumes of solvent make the interfacial method prohibitively expensive for many polymers relative to bulk or solution processes.

For heterogeneous phase-transfer catalyzed polymerization [1], the method involves an aqueous phase and an organic phase, each containing one of monomers. It is also an interfacial technique. Quaternary ammonium salt transports a nucleophilic monomer from the aqueous phase to the organic phase. Its nucleophilicity is greatly enhanced because of reduced solvation effects. *Phase-transfer catalysis* (PTC), although commonly employed in organic synthesis, has limited application in polymerization reactions. The polymer **9** can be synthesized by the reaction of α,α' -dichloro-*p*-xylene **7** and *t*-butyl cyanoacetate **8** using benzyltriethylammonium chloride (Eq. 6.63). In this case, an anion derived from **8** by reaction with NaOH is transported to the benzene solution as the soluble benzyltriethylammonium salt, where it reacts rapidly with **7** by nucleophilic displacement. Polymer is formed because **8** contains two active hydrogens.

6.8 Synthesis of Dendritic Polymers (Dendrimers)

Dendrimers [1] are defined by their three component parts: A central core, an interior dendritic structure, and an exterior surface. Their macromolecular dimensions are easily controlled by the number of the repeating level of the synthesis steps. Dendrimers are more soluble than linear polymers because of their high surface functionality. The surface functionality has potential application in target drug delivery and molecular sensors. Their viscosity is usually lower than that of linear polymer because no chain entanglement. They are useful for rheology modifiers. Supramolecular assemblies may be constructed by incorporating guest molecules among the interior branches of the dendrimer. Thus, they are useful for drug delivery systems, controlled release of agricultural chemicals. Figure 6.7 shows the size prospective of dendrimers as compared with other matters. The size of dendrimer can be precisely controlled by stepwise polymerization as discussed by two following synthetic methods.

6.8.1 Divergent Method

For the synthesis of polyamidoamine (PAMAM), NH_3 is used as core. In first generation: NH_3 is added to methylacrylate via Michael addition, the resultant triester **10** is then reacted with excess 1,2-ethanediamine to form amide-amine **11**. Each new generation results from a repetition of the two-step reaction sequence as shown below:

Fig. 6.7 Size comparisons of different matters

For generations 2 and 3, they are schematically shown in Fig. 6.8. With each new generation, the number of surface functional group doubles, reaching 3072 by the 10th generation. It is called starburst polymer.

6.8.2 Convergent System

Figures 6.9 and 6.10 show the convergent synthesis of a polyether dendrimer. The branching unit, 3,5-dihydroxybenzyl alcohol **13**, is first reacted with the benzylic bromide **12** to yield **14** in the presence of base. The alcohol group of **14** is then converted to bromide, and reacted again with **12** (Fig. 6.9). The steps are repeated until the desired segment size is reached. The polyether dendrimer is then assembled by condensing a benzylic bromide-terminated segment with a polyfunctional phenol (Fig. 6.10).

Fig. 6.8 Formation of second and third generation of PAMAM dendrimer. Reaction sequence: (1) excess $\text{CH}_2=\text{CHCO}_2\text{CH}_3$ and (2) excess $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ [1]

Fig. 6.9 Formation of polyether dendritic segment [1]

Fig. 6.10 Convergent synthesis of a dendrimer from dendritic segments [1]

6.8.3 Molecular Weight of Dendrimer

The size of dendrimer is self limited because of steric congestion. Dendrimers with molecular weights in the hundreds of thousands have been achieved. Their molecular dimensions lie in the nanometer range, so they are called nanomaterials.

6.9 Hyperbranched Copolymer

The hyperbranched aromatic copolymer can be synthesized by Suzuki coupling reaction. The reaction was first reported in 1979 by Akira Suzuki, the reaction couples aromatic boronic acids to aromatic halides [4]. The reaction relies on a palladium catalyst such as tetrakis(triphenylphosphine)palladium(0) to take in part of the transformation. This reaction has been extensively used in the synthesis of donor–acceptor of alternating conjugated copolymer for polymer solar cell application [5]. The 2010 Nobel Prize in Chemistry was awarded in part to Suzuki for his discovery and development of this very versatile mild reaction to link aromatic molecule together.

For example, a conjugated alternate copolymers constituted of triphenylamine and phenylene units can be obtained by palladium catalyzed coupling of tris(*p*-bromophenyl)amine **15** and benzene-1,4-diboronic acid **16** (Fig. 6.11) [6]. Amine **15** and acid **16** are trifunctional (B_3) and difunctional (A_2) monomers, respectively. Hyperbranched polymers can be prepared through intermediate AB_2 monomers formed from B_3 and A_2 monomers. The copolymer (**17**) was soluble in organic solvents such as chloroform and tetrahydrofuran. GPC indicated that it had an average molecular weight of 5,400.

Fig. 6.11 Example of synthetic route of hyperbranched copolymer

6.10 Problems

1. Considering the reaction conditions for bulk polycondensations, suggest reasons other than those given in the chapter for deviations in the plots of $\overline{\text{DP}}$ versus t for polyesters.

2. To what percent conversion should a batch of 11-amino undecanoic acid be processed to yield polyamide having a number average molecular weight of 2.5×10^4 ?
3. Rate constants for polyesterification of adipic acid and 1,10-decanediol at 161°C are $0.0012 (\text{eq/kg})^2/\text{min}$ (uncatalyzed) and $0.079 (\text{eq/kg})/\text{min}$ (catalyzed). How long would it take to prepare a polyester of number average molecular weight 15,000 (bulk processing) under each set of condition? (Assume equimolar amounts of each reactant and 2 equivalents per mole, and that bulk mass remains constant.) What would the polydispersity index be for the polymer?
4. If 5 mol % excess diol was used in the previous problem, what number average molecular weight would be obtained if the reaction was carried to the same conversion?
5. Using the Carothers relationship, please calculate the percent conversion at the gel point for (a) 3:1:3 and (b) 1:1:2 molar ratio of phthalic anhydride, trimellitic acid, and glycerol.
6. Calculate $\bar{X}_n$ and $\bar{X}_w$ for an equal molar mixture of a diacid and a glycol at the following extent of reactions: 0.500, 0.750, 0.950, 0.980, 0.990, and 0.995.
7. A polyester, made with an equivalent amount of terephthalic acid and ethylene glycol, the molecular weight of the polyester was controlled at $\bar{X}_n = 100$ by adding methanol. (a) How much methanol is required? (b) Calculate $\bar{X}_w$ and the weight and number fractions of monomer in the resulting polymer, (c) If the glycerol was added instead of methanol. Will the mixture gel if the reaction is carried to completion?
8. Explain why aliphatic polyamides but not aliphatic polyesters can be prepared by interfacial polymerization.
9. Write equations illustrating the synthesis of (a) an alternating copolyamide from isophthaloyl chloride, terephthaloyl chloride, and m-diaminobenzene, and (b) an ABA block copolymer of poly(11-undecanoamide) (A) with the polyamide (B) formed in (a).
10. Please propose the reaction mechanism of Suzuki coupling reaction for the formation of diphenyl (hint: review Ref. [7]).

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