1

FREE RADICAL AND CONDENSATION POLYMERIZATIONS

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1.1 INTRODUCTION

Polymers are macromolecules composed of many monomeric repeat units and they can be synthetic or naturally occurring. While nature has long utilized polymers (DNA, proteins, starch, etc.) as part of life's machinery, the history of synthetic polymers is barely 100 years old. In this sense, man-made macromolecules have made incredible progress in the past century. While synthetic polymers still lag behind natural polymers in many areas of performance, they excel in many others; it is the unique properties shared by synthetic and natural macromolecules alike that have driven the explosion of polymer use in human civilization. It was Herman Staudinger who first reported that polymers were in fact many monomeric units connected by covalent bonds. Only later we learned that the various noncovalent interactions (i.e., entanglements, attractive or repulsive forces, multivalency) between these large molecules are what give them the outstanding physical properties that have led to their emergence.

In recent years, the uses of synthetic polymers have expanded from making simple objects to much more complex applications such as targeted drug delivery systems and flexible solar cells. In any case, the application for the polymer is driven by its physical and chemical properties, notably bulk properties such as tensile strength, elasticity, and clarity. The structure of the monomer largely determines the chemical properties of the polymer, as well as other important measurable quantities, such as the glass transition temperature, crystallinity, and solubility. While some important determinants of properties, such as crystallinity, can be affected by polymer processing, it is the polymerization itself that determines other critical variables such as the molecular weight, polydispersity, chain topology, and tacticity. The importance of these variables cannot be overstated. For example, a low-molecular-weight stereo-irregular polypropylene will behave nothing like a high-molecular-weight stereo-regular version of the same polymer. Thus, it is easy to see the critical importance the polymerization has in determining the properties and therefore the potential applications of synthetic polymers. It is therefore essential to understand the polymerization mechanisms, the balance between thermodynamics and kinetics, and the effect that exogenous factors (i.e., temperature, solvent, and pressure) can have on both.

1.1.1 Structural Features of Polymer Backbone

1.1.1.1 ***Tacticity*** Tacticity is a measure of the stereochemical configuration of adjacent stereocenters along the polymer backbone. It can be an important determinant of polymer properties because long-range microscopic order (i.e., crystallinity) is difficult to attain if there is short-range molecular disorder. Changes in tacticity can affect the melting point, degree of crystallinity, mechanical properties, and solubility of a given polymer. Tacticity is particularly important for a, a′-substituted ethylene monomers (e.g., propylene, styrene, methyl methacrylate). For a polymer to have tacticity, it is a requirement that a does not equal a′ because otherwise the carbon in question would not be a stereocenter. The tacticity is determined

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during the polymerization and is unaffected by the bond rotations that occur for chains in solution. The simplest way to visually represent tacticity is to use a Natta projection, as shown in Figures 1.1–1.3 using poly (propylene) as a representative example.

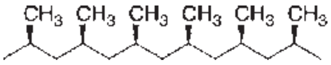


FIGURE 1.1 Isotactic polypropylene.

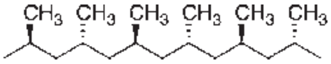


FIGURE 1.2 Syndiotactic polypropylene.

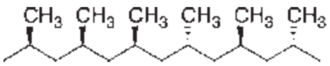


FIGURE 1.3 Atactic polypropylene.

An isotactic chain is one in which all of the substituents lie in the same plane (i.e., they have the same stereochemistry). Isotactic polymers are typically semicrystalline and often adopt a helical configuration. Polypropylene made by Ziegler–Natta catalysis is an isotactic polymer.

A syndiotactic chain is the one where the stereochemical configuration between adjacent stereocenters alternates.

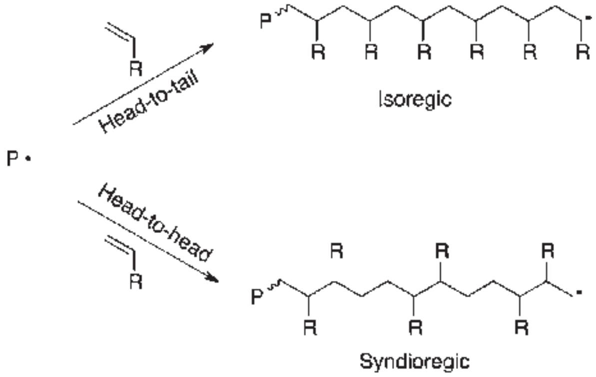
An atactic chain lacks any stereochemical order along the chain, which leads to completely amorphous polymers.

1.1.1.2 ***Composition*** Copolymer composition influences a number of quantities, including the glass transition temperature. One commercially relevant example of this effect is with Eastman's copolymer Tritan™, which has been replacing polycarbonate in a number of applications due to concerns over bisphenol-A's (BPA's) health effects. Tritan™ can be considered poly(ethylene terephthalate) (PET), where a percentage of the ethylene glycol is replaced by 2,2,4,4-tetramethyl-1,3-cyclobutane diol (TMCBDO). In the case of beverage containers, T_g must be greater than 100 °C so they can be safely cleaned in a dishwasher or autoclave. The T_g of Tritan is engineered to be ~110 °C by tuning the relative incorporation of the ethylene glycol (low T_g) and TMCBDO (T_g-increasing) diol monomers.

Altering the glass transition temperature is by no means the only reason to include comonomers in a polymerization. In designing copolymers with specialized applications, comonomers can be included for specific functions, or as sites for further functionalization or initiation of a secondary polymerization (e.g., to make graft copolymers in a graft-from approach). In more broadly used commercial polymers, comonomers can be included to alter different properties, including swelling in particular solvents, stability, viscosity, or to induce self-assembly (e.g., styrene-butadiene-styrene rubbers where styrene domains within the butadiene matrix provide mechanical integrity). While block copolymers produced in sequential polymerizations are not confronted with the problem of unequal reactivity, monomers often have different reactivities within a polymerization. Such discrepancies lead to differences between the composition of monomer feed and the composition of the final polymer.

1.1.1.3 ***Sequence*** The difference in reactivity between comonomers affects the composition and also alters the placement of the monomer units along the chain. In the case of living polymerization, sequential monomer addition leads to the formation of block copolymers. However, when a random copolymer is targeted, reactivity differences can lead to nonrandom distribution of monomer units. If the incorporation of a comonomer B is intended to disrupt crystallinity of poly(A), uninterrupted sequences of A can lead to domains of crystallinity. For example, block copolymers of ethylene–propylene are highly crystalline, while random copolymers are completely amorphous.

1.1.1.4 ***Regioselectivity*** The issue of regioselectivity is most relevant here to vinyl monomers undergoing free radical polymerization, but also applies to other polymerization mechanisms discussed (particularly the synthesis of conducting polymers, which often entails the use of monomers bearing alkyl chains designed to improve solubility). The example of 1-substituted ethylene derivatives (e.g., styrene) is shown in Scheme 1.1. When a propagating chain adds a monomer unit, the radical can add to either C^1 or C^2. If each successive addition occurs in the same fashion, the result is an isoregic chain, typically referred to as a head-to-tail arrangement.



SCHEME 1.1 Regioselectivity in free radical polymerization.

The alternate configuration is achieved when each successive monomer addition alternates between C^1 and C^2 additions, giving a syndioregic chain, commonly called a head-to-head arrangement. For free radical polymerizations, isoregic addition is overwhelmingly favored. This is due jointly to resonance and/or inductive stabilization of the resulting radical, which favors head-to-tail addition, and steric constriction around the R group, which discourages head-to-head addition.

1.1.2 The Chain Length Distribution

It is evident that the molecular weight of a polymer chain determines important properties such as viscosity and mechanical strength. Because synthetic polymers do not have a single chain length *i* and are instead polydisperse, any measure of molecular weight is an average. The chain length distribution is typically characterized by the first three moments of the distribution, where the *k*th moment is described as follows:

$$\mu^{(k)} = \sum_{P=1}^{\infty} P^k \cdot \chi_{\mathrm{P}} \tag{1.1}$$

where P is the length of an individual polymer chain and χ_{P} is the number of chains of length P.

The weighted degrees of polymerization are defined as the ratio of successive moments, as seen in Equations 1.2 through 1.4:

$$dp_{\mathrm{n}} = \overline{P_{\mathrm{n}}} = \frac{\mu^1}{\mu^0} = \frac{\sum_{P=1}^{\infty} P \cdot \chi_{\mathrm{P}}}{\sum_{P=1}^{\infty} \chi_{\mathrm{P}}} \tag{1.2}$$

$$dp_{\mathrm{w}} = \overline{P_{\mathrm{w}}} = \frac{\mu^2}{\mu^1} = \frac{\sum_{P=1}^{\infty} P^2 \cdot \chi_{\mathrm{P}}}{\sum_{P=1}^{\infty} P \cdot \chi_{\mathrm{P}}} \tag{1.3}$$

$$dp_{\mathrm{z}} = \overline{P_{\mathrm{z}}} = \frac{\mu^3}{\mu^2} = \frac{\sum_{P=1}^{\infty} P^3 \cdot \chi_{\mathrm{P}}}{\sum_{P=1}^{\infty} P^2 \cdot \chi_{\mathrm{P}}} \tag{1.4}$$

The number-average degree of polymerization is the number of polymerized units divided by the number of polymer chains, obtained by end-group analysis (e.g., NMR). The weight-average degree of polymerization determines most important properties of a polymer:

$$\mathrm{PDI} = \frac{dp_{\mathrm{w}}}{dp_{\mathrm{n}}} = \frac{\mu^{(2)}\mu^{(0)}}{\mu^{(1)}\mu^{(1)}} \tag{1.5}$$

The polydispersity of a polymer sample is described by the polydispersity index (PDI), which is a ratio of the weight-average and number-average degrees of polymerization. For monodisperse polymers, such as a proteins, the PDI will equal 1, while synthetic polymers have PDIs that can approach 1, or conversely go to values higher than 10.

1.1.3 Polymerization Mechanisms

It is useful in the classification of polymerizations to define several mechanisms of polymer growth, each one with distinctive and defining features. In the context of this chapter, three mechanisms are considered: step growth, chain growth, and “living” polymerization. Carothers initially classified polymers into condensation and addition, and while these terms are often used interchangeably with step and chain polymerizations, it must be stressed that this is not entirely accurate.

Step polymerization indicates a mechanism of growth where monomers combine with each other to form dimers, the dimers combine with each other or other monomer units to form tetramers or trimers, respectively, the process continuing until polymer is formed. While each coupling step in a step polymerization is often accompanied by the elimination of a small molecule (e.g., water), making it a condensation polymerization, this is not always the case (e.g., isocyanates and alcohols reacting to make polyurethanes). Furthermore, not all polymerizations in which a condensate is formed follow a stepwise mechanism.

Step polymerization leads to high-molecular-weight polymer when monomer conversion is very high (see Table 1.1). In comparison, the chain growth mechanism immediately leads to high-molecular-weight polymer regardless of monomer conversion. In this case, there is an active chain end, which adds monomer units one by one until the chain is rendered inactive by termination or transfer. In a normal chain growth process, a chain lifetime is short compared to the polymerization process, new chains being constantly initiated and terminated.

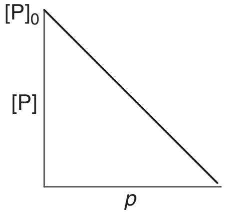
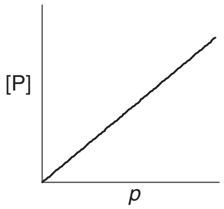
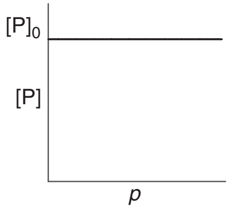
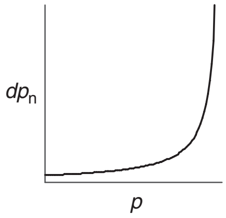
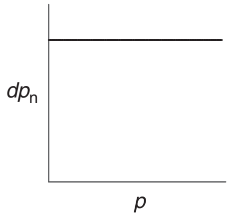
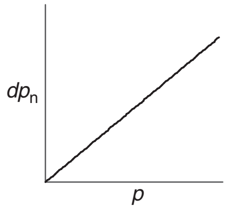
Living polymerization is a chainwise mechanism where transfer and termination reactions have been eliminated. Therefore, all polymer chains are active throughout the entire polymerization and grow at similar rates. A major consequence of living polymerization is that PDIs are much lower (≤1.1) than for the usual chainwise mechanism. Table 1.1 highlights some salient features of each mechanism.

1.2 FREE RADICAL POLYMERIZATION

Free radical polymerization is a globally important method for the production of polymers, both academic and industrial. In fact, free radical polymerization is used to produce a significant percentage of the polymers made worldwide, including 45% of manufactured plastics and 40% of synthetic rubber, which amounts to 100 and 4.6 million tons, respectively.

Despite its widespread use, gaining a full understanding of the polymerization process is not a straightforward task. Free radical polymerization is controlled by a number of

TABLE 1.1 Distinctions between Stepwise, Chainwise and Living Polymerization

Characteristic	Stepwise	Chainwise	"Living"
Number and type of reactions	Only one: reaction between two (usually dissimilar) functional groups	Initiation Propagation Termination Also: Transfer Inhibition	Initiation Propagation
Convention as to what is considered polymer	All species considered to be polymer	Unreacted monomer is distinct from polymer	Unreacted monomer is distinct from polymer
Polymer concentration with conversion p			
Degree of polymerization with conversion p			

different processes, each of which has its own kinetics and thermodynamics. If each of these individual processes is fully understood and its rate coefficient determined, the kinetics of the overall polymerization can be determined and the full molecular weight distribution can be accurately predicted. A major complicating factor is that all these processes are closely related to each other, making it challenging to separate and determine kinetic rate coefficients. However, much effort has been devoted to study the processes that constitute a free radical polymerization and modern experimental techniques have improved their understanding.

This section will focus on the kinetics of free radical polymerization, but will also address the effect of kinetics on molecular weight distributions of commonly used monomers. This chapter will not address controlled free radical polymerization (CRP) since it is covered at length in Chapter 2.

1.2.1 Initiation

Initiation is the process by which radicals are formed and then subsequently initiate polymerization by reacting with a monomer molecule. The prerequisite step is for an initiator molecule to decompose into a radical species. While not always the case, the most common scenario is for an initiator molecule to decompose into two radical species:

$$\text{Initiator} \xrightarrow[h\nu,\,\Delta]{k_\text{d}} \text{I}_1^\bullet + \text{I}_2^\bullet \tag{1.6}$$

Initiator decomposition can be triggered in a variety of ways. The most common method for industrial free radical polymerization is thermal initiation (typically using azo or peroxy initiating species), while photoinitiation is more popular for laboratory scale kinetic studies. In either case, Equation 1.6 describes the decomposition of initiator into two radical species, which may or may not have equal reactivities, depending on the choice of initiator [1, 2]. The concentration of initiator can then be calculated by:

$$-\frac{d[\text{I}]}{d\text{t}} = k_\text{d}[\text{I}] \tag{1.7}$$

An important consideration is that initiator decomposition is not equivalent to chain initiation because of the various side reactions that can take place before reaction of the radical species with a monomer unit. To achieve initiation of a growing polymer chain, the radical species must escape the solvent cage [3] before undergoing deleterious side reactions that reduce chain initiation efficiency. The quantity f represents the fraction of produced radicals that can initiate polymerization, typically between 0.5 and 0.8 for most free radical polymerization initiators. Odian has demonstrated, using benzoyl peroxide as initiator, that initiating radicals can undergo side reactions which decrease the initiator efficiency, f, before escaping the solvent cage [4].

The first-order rate law, R_d, for the production of radicals that can initiate polymerization is conveyed by Equation 1.8. The f term accounts for all of the various inefficiencies in initiating polymerization:

$$R_d = \frac{d[\mathrm{I}^\bullet]}{dt} = -2f\frac{d[\mathrm{I}]}{dt} = 2fk_d[\mathrm{I}] \tag{1.8}$$

This leads directly to the concentration of initiator molecules as a function of time:

$$[\mathrm{I}] = [\mathrm{I}]_0 e^{-k_d t} \tag{1.9}$$

Another complication is that for many initiators, decomposition leads to two radicals of different structures and reactivities [1, 2]. The difference in reactivities between the radicals produced in an unsymmetrical decomposition is addressed in the following equations:

$$\mathrm{I}^\bullet_{(1)} + M \xrightarrow{k_i^{(1)}} \mathrm{R}_1^\bullet \tag{1.10}$$

$$\mathrm{I}^\bullet_{(2)} + M \xrightarrow{k_i^{(2)}} \mathrm{R}_1^\bullet \tag{1.11}$$

This means that in the case of unsymmetrical decomposition of initiator into two radicals with differing reactivity, the expression for the overall rate of initiator is actually a composite of two different reactions (Eq. 1.12). However, for the sake of simplicity, the two different initiation rate coefficients will be combined into an average rate constant to give the overall rate of initiation, R_i:

$$R_i = \frac{d[\mathrm{R}^\bullet]}{dt} = -\frac{d[\mathrm{I}_1^\bullet]}{dt} - \frac{d[\mathrm{I}_2^\bullet]}{dt} \tag{1.12}$$

$$R_i = k_i^{(1)}[\mathrm{M}]\left[\mathrm{I}^\bullet_{(1)}\right] + k_i^{(2)}[\mathrm{M}]\left[\mathrm{I}^\bullet_{(2)}\right] \tag{1.13}$$

$$R_i = k_i[\mathrm{M}][\mathrm{I}^\bullet], \quad \text{where } k_i = \frac{k_i^{(1)} + k_i^{(2)}}{2} \tag{1.14}$$

1.2.1.1 ***Thermal Initiation*** Thermal initiators are very common and typically decay following a first-order rate law, as shown in Equation 1.9. Most common thermal initiators are peroxides or diazo compounds, such as azobisisobutyronitrile (AIBN) [5]. Initiators are chosen so that at polymerization temperature, decomposition is slow with typical values for k_d ranging from 10^{-6} to 10^{-4} s^{-1}. Commonly, the rate at which a thermal initiator decomposes is reported as the temperature at which the half-life (Eq. 1.15) is equal to 10 h:

$$t_{1/2} = \frac{\ln 2}{k_d} \tag{1.15}$$

Table 1.2 shows temperature for a 10 h half-life for several common thermal initiators. Their slow decomposition allows initiators concentration to be considered constant over the course of polymerization, particularly when compared to the average lifetime of an active chain.

TABLE 1.2 Decomposition Rate and 10 h $t_{1/2}$ for Common Thermal Initiators

Initiator	Solvent	10 h Half-life °C
4,4-Azobis(4-cyanovaleric acid)	Water	69
2,2′-Azobisisobutyronitrile (AIBN)	Toluene	65
tert-Amyl peroxybenzoate	Benzene	99
Benzoyl Peroxide	Benzene	70
tert-Butyl peracetate	Benzene	100
tert-Butyl peroxide	Benzene	125
Dicumyl peroxide	Benzene	115
Peracetic acid	Toluene	135
Potassium persulfate	Water	60

1.2.1.2 ***Photoinitiation*** Photoinitiation [6] takes advantage of initiators that can form radical species upon UV irradiation. Unlike thermal initiation, which produces a relatively small supply of radicals throughout the course of a polymerization, photoinitiation can provide a burst of radicals when desired. This makes photoinitiation an ideal candidate for kinetic experiments or surface-initiated polymerization because the production of radicals is limited to the area that is irradiated at the time of irradiation. Furthermore, the concentration of radicals, ρ, produced by a given number of photons can be easily calculated as follows:

$$\rho = 2\Phi\frac{n_{\mathrm{abs}}}{V} \tag{1.16}$$

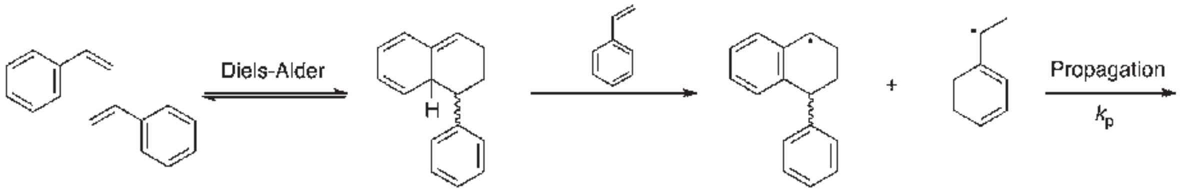
where Φ is the primary quantum yield, n_{abs} is the number of absorbed photons, and V is the irradiated volume.

Rearrangement of Beer's law and combination with Equation 1.16 gives a final expression for the concentration of radicals produced by an irradiation event:

$$\rho = 2\Phi\frac{(E_{\mathrm{tot}}/E_\lambda)\cdot(1-10^{-\varepsilon bc})}{V} \tag{1.17}$$

1.2.1.3 ***Self-Initiation*** A free radical polymerization can be started by self-initiation of the monomer species. In fact, true self-initiation is very rare and some of the cases reported in the literature are actually due to oxygen producing peroxide species that can act as initiators, or other impurities that lead to radical formation [7].

One monomer that is known to self-initiate, even at high purity is styrene [8–10]. As shown in Scheme 1.2, styrene undergoes a Diels–Alder reaction to give a styrene dimer. This dimer can then react with another styrene monomer to give a styrene radical or $\mathrm{R}_1^\bullet$. Significantly, the activation energy for the self-initiation is rather large.



SCHEME 1.2 Initiation mechanism in the auto-polymerization of styrene. With permission from Odian G. *Principles of Polymerization*. 4th ed. © 2004 Hoboken (NJ): John Wiley & Sons, Inc.

The half-life for 50% monomer conversion is only 4 h at 127 °C, but it is 400 days at 29 °C.

1.2.2 Propagation

Propagation is the step most closely associated with the actual polymerization reaction as it is the addition of a monomer unit to the propagating macroradical. Writing a rate law for the propagation reaction is somewhat complicated by the fact that the rate of propagation is chain length-independent [11–16]. For example, for the polymerization of methyl methacrylate at 60 °C, the first propagation step is 16 times faster than the long chain propagation reaction.

This can be accounted for by a simple summation of the propagation for each chain length *i*:

$$-\frac{dM}{dt} = \sum_i k_p^i [R_i][M] \tag{1.18}$$

where k_p^i is the propagation rate constant for a macroradical with chain length *i* and $[R_i]$ is the concentration of polymers with chain length *i*.

It is important to review the stringent requirements that lead to successful propagation. For a typical free radical polymerization, a successful propagation reaction can be expected to occur with frequency of $10^3\,s^{-1}$, while the collision frequency in a liquid near room temperature is much higher: $10^{12}\,s^{-1}$. Given the high monomer concentration in a polymerization, this effectively means that only one in every 10^9 collision events leads to a successful propagation step [17] (i.e., addition of one monomer molecule to the growing macroradical). These values highlight the fine balance between the reactivity and stability of the propagating macroradical. The radical must be reactive enough to produce a polymer in a matter of seconds but also must be stable enough to survive the 10^9 nonproductive collisions that occur for every successful propagation reaction.

Furthermore, there is a fine balance between the reactivity of the monomer and the stability of the macroradical, quantities typically inversely related. For example, styrene is a very reactive monomer but produces a more stable (i.e., less reactive) chain end in the form of a resonance-stabilized secondary benzyl radical. The other extreme would be ethane, which is a very nonreactive monomer that leads to an extremely reactive primary radical chain end.

The kinetic rate coefficient for propagation, k_p, is chain length and monomer concentration dependent. Solvent choice normally does not have a significant effect on k_p [18–20], although this is not the case when ionic liquids are used as solvents [21–23]. However, the dependence of k_p on monomer concentration is not nearly as significant as dependence on pressure. Free radical polymerizations have large negative activation volumes (Eq. 1.14), meaning that at higher pressures the rate of propagation increases [24–26]:

$$\frac{d\ln k}{dP} = -\frac{\Delta V}{RT} \tag{1.19}$$

1.2.3 Transfer

Transfer reactions involve the transfer of the radical from a growing polymer chain to another molecule, T, typically by the donation of a hydrogen atom to the macroradical, $R_i^\bullet$, to produce an inactive polymer chain, P_i, and another radical $T^\cdot$:

$$-\frac{dT}{dt} = k_{tr}[R^\bullet][T] \tag{1.20}$$

Each molecule involved in radical transfer reactions is characterized by a transfer constant, *C*, which is a ratio of the rate constant for transfer and the rate constant for propagation:

$$C = \frac{k_{tr}}{k_p} \tag{1.21}$$

Both monomer and solvent can act as transfer agents; often chain transfer agents (CTAs) are intentionally added to polymerization reactions. While such a transfer reaction renders the propagating chain inactive and thus affects the molecular weight of the chain, it does not affect the kinetic chain, which is a measure of how long a given radical persists. Thus, in most cases, transfer reactions do not affect the rate of polymerization but do alter the molecular weight distribution.

There are a number of different possible cases for transfer reactions, the relative rates of propagation, k_p, transfer, k_{tr}, and reinitiation, $k_{re\text{-}in}$, determining the effects of the transfer reactions on the overall rate of polymerization, as well as on the molecular weight distribution [17]. The first case is when k_p is much greater than k_{tr} and $k_{re\text{-}in}$ is much greater than k_{tr}, which is considered normal chain transfer. In this scenario, because there is a relatively low amount of chain transfer and the small molecule radical formed quickly reinitiates polymerization, normal chain transfer does not affect the overall rate of polymerization, R_p, but leads to a decrease in the molecular weight. The next case is where k_p is much smaller than k_{tr}, but comparable to $k_{re\text{-}in}$. This type of transfer leads to a high percentage of active radicals existing on the transfer agent, T, but again does not decrease the overall rate of polymerization. It does drastically decrease the molecular weight of the resulting polymers, leading to telomerization, or the production of mostly dimers and trimers. The third case of chain transfer is when propagation is much faster than transfer ($k_p >> k_{tr}$), but reinitiation is slow relative to propagation ($k_{re\text{-}in} < k_p$). Here, both the rate of polymerization and the molecular weight decrease, but not enough that the polymerization would be completely stopped; this is called retardation [27, 28]. Finally, there is the case of inhibition [27, 28], which occurs when the rate of transfer is much higher than propagation ($k_{tr} >> k_p$) and reinitiation is slower than propagation ($k_{re\text{-}in} < k_p$). Inhibition occurs when the transfer agent efficiently traps radicals and the resultant transfer radical is very stable. Examples of radical inhibitors include BHT, nitrobenzene, and diphenyl picryl hydrazyl (DPPH), which are useful for preventing autopolymerization of vinyl monomers stored over long periods of time.

Radical transfer could greatly complicate the kinetics of polymerization, particularly because a wide variety of molecules can act as transfer agents, including but not limited to monomer, solvent, initiator, polymer [29], and added CTAs. Even molecular oxygen can be a radical transfer agent [30], which, if present in significant amounts, acts as an inhibitor in most free radical polymerizations. While the possibilities for transfer seem endless, careful planning of the reaction conditions can control most transfer reactions. For example, a decrease in temperature will generally lower the transfer constant C for all species. Furthermore, a judicious choice of initiator or simply a decrease in initiator concentration can significantly reduce transfer to the initiating species. The only species to which transfer cannot be avoided is the monomer, which in fact is often a limiting factor for the molecular weight. Table 1.3 lists the values for the monomer transfer constant, C_M, for various common monomers. Another important transfer reaction is to the solvent, which can be problematic because of the high solvent concentrations used in industrial polymerizations (Table 1.2).

TABLE 1.3 Transfer Constants to Monomers, $C_M \times 10^4$

Monomers	T (°C)	$C_M \times 10^4$
Methyl methacrylate	0	0.128
	60	0.18
	120	0.58
Acrylonitrile	60	0.26
Styrene	0	0.108
	60	0.75
	117	1.40
Methyl acrylate	60	0.036
Ethylene	60	0.40
Methacrylamide	60	10×10^5
Vinyl acetate	60	1.75

Despite the tendency for radical transfer reactions to slow polymerization kinetics, decrease or limit molecular weight, and complicate the kinetic picture of a given polymerization, the transfer process can also be very useful for the process engineer. For example, a simple way to achieve lower molecular weight polymers is to increase the initiator concentration. As consequence, the rate of polymerization would increase, which could, on the other hand, lead to the loss of control and exothermicity. The addition of a CTA can regulate molecular weight without affecting the rate of polymerization, avoiding the associated problems. Furthermore, if CTAs chosen have high chain transfer constants, they can be used in relatively low concentrations.

1.2.4 Termination

Termination is probably the most complex step in the free radical process, owing to the fact that k_t depends on monomer conversion, pressure, temperature, system viscosity, and the chain length of the terminating macroradicals [31, 32]. The complexity of termination is manifested in the widely spread k_t values found in the literature for any given system [33, 34]:

$$-\frac{d[\mathrm{R}^{\bullet}]}{dt} = \sum_{i}\sum_{i} 2k_{\mathrm{t}}^{\mathrm{i,j}}[\mathrm{R}_{\mathrm{i}}^{\bullet}][\mathrm{R}_{\mathrm{j}}^{\bullet}] \qquad (1.22)$$

There are different modes of termination: combination and disproportionation. Active chains terminated by disproportionation will have the same molecular weight, where one of the chains will have an unsaturation and the other will be fully saturated. When chains are terminated by combination, because two propagating chains combine, the number of chains decreases by one, and the resultant molecular weight is the sum of the two macroradicals, thereby increasing the final molecular weight distribution.

The relative contribution of each mode of termination is described by δ in the following equation:

$$\delta = \frac{k_{\mathrm{t,d}}}{k_{\mathrm{t,d}} + k_{\mathrm{t,c}}} \tag{1.23}$$

Disproportionation is generally favored slightly over combination at increased temperatures, but other factors such as monomer choice can have a greater impact on δ.

Looking at the rate and activation energy for termination in comparison with the other steps in a polymerization, it might seem surprising that polymers can be produced at all. The rate constant for termination is always very high and the activation energy for the chemical reaction can be considered 0 [35]. Indeed, the reason that termination is not the dominating reaction in a given polymerization is because two propagating macroradicals (i.e., polymer chain ends) must first find each other before they can react. To better understand chain termination, the process can be broken into three stages [36–38]:

1. Translational diffusion of the macroradical coils toward each other within the reaction medium.
2. Segmental diffusion of the chains ends toward each other, putting them in a position to react.
3. The chemical reaction between the two radicals that leads to termination.

As it is always the case, the slowest process will be the rate-determining step. Because the chemical reaction rate is very high (on the order of 10^{10} l mol^{-1} s^{-1}), the rate-determining step will always be either translational (i.e., center-of-mass) diffusion or segmental diffusion [39]. At low conversion, segmental diffusion is the rate-limiting step, while at high conversion, center-of-mass diffusion controls the rate of termination. This phenomenon occurs because at high conversion the polymer chains become entangled and translational diffusion becomes difficult. Polymer chains must undergo translational diffusion by reptation, significantly slowing this mode of diffusion. At very high conversion (>80%), diffusion can actually be controlled by reaction of monomer [40] (i.e., the position of the chain end moves by addition of a monomer unit). However, the case of reaction-controlled diffusion will not be treated in great detail here.

Because both rate-controlling termination processes are diffusion controlled, it should follow that both processes will be chain length dependent. However, segmental diffusion and translational diffusion show very different dependencies on molecular weight. A facile way to envision this is to consider a macroscopic termination rate constant, k_{t}, which is a weighted summation of the microscopic termination reactions. The molecular weight dependence of this macroscopic rate constant is described in Equation 1.24. The value for α is empirically known for both translation diffusion and segmental diffusion:

$$\langle k_{\mathrm{t}} \rangle = k_{\mathrm{t}}^{0} \cdot \overline{P}^{-\alpha} \tag{1.24}$$

For translational diffusion, α is between 0.5 and 0.6, depending on the solvent quality, while segmental diffusion shows much less of a molecular dependence, with $\alpha \sim 0.16$ [41–46].

While the chain length dependence of termination was discussed earlier, the reality is that termination is much more strongly dependent on pressure [47, 48] than on chain length. The large negative activation volumes typical for termination describe this effect. Because increased pressure not only decreases the rate of termination but also increases k_{p}, pressure can lead to a marked increase in the final molecular weight.

1.2.5 Rate of Polymerization

The overall rate of polymerization is determined by the contributions of the various processes discussed in the aforementioned sections: initiation, propagation, transfer, and termination. It is instructive to separate a polymerization into different regimes and to understand their kinetics. Thus, at the beginning of the polymerization, when the concentration of radicals is increasing (this phase lasts only a few seconds [49]), a stationary phase is observed, where the concentration of radicals can be considered constant; dead-end polymerization [50, 51] occurs if the initiator is completely consumed before monomer conversion is complete. The latter scenario can be easily avoided by carefully choosing the concentration and type of initiator (half-life time, $t_{1/2}$), so that the polymerization can be completed before the initiator is consumed.

1.2.5.1 ***Stationary Polymerization*** The most classic kinetic treatment for the rate of polymerization is the quasi steady-state polymerization, which assumes a constant free radical polymerization throughout the course of the polymerization [52]:

$$\frac{d[\mathrm{R}^{\bullet}]}{dt} = 0 \tag{1.25}$$

A number of assumptions are made to derive the overall rate of polymerization, R_{p}, in a straightforward way. These assumptions are as follows:

1. The concentration of initiator-derived radicals remains constant throughout the polymerization.
2. Instantaneous establishment of a steady-state free radical concentration.
3. Chain length and conversion-independent rate coefficients, k_{t} and k_{p}.

4. Monomer is only consumed by chain propagation (which allows the loss of monomer to be directly associated with R_p).
5. All reactions are irreversible.

The central tenet of the steady-state (or stationary) polymerization is that the concentration of radicals is constant. It closely follows that the rate of formation of radicals must equal the rate of radical termination.

Combining Equations 1.8 and 1.22 gives the following:

$$2fk_\mathrm{d}[\mathrm{I}] = 2k_\mathrm{t}[\mathrm{R}_\mathrm{i}^\bullet][\mathrm{R}_\mathrm{j}^\bullet] \tag{1.26}$$

$$2fk_\mathrm{d}[\mathrm{I}] = 2k_\mathrm{t}[\mathrm{R}^\bullet]^2 \tag{1.27}$$

The right half of the equation can be simplified using assumption 3 to give $[\mathrm{R}^\bullet]^2$ instead, because there is no need to distinguish between different chain lengths of the macroradicals. Furthermore, when Equation 1.17, which describes the disappearance of monomer, is simplified by assumption 3, it can be directly correlated with the rate of polymerization:

$$R_\mathrm{p} = -\frac{d[\mathrm{M}]}{dt} = k_\mathrm{p}[\mathrm{M}][\mathrm{R}^\bullet] \tag{1.28}$$

By solving for $[\mathrm{R}^\bullet]^2$ in Equation 1.27, and substituting into Equation 1.28, an expression for the rate of polymerization is obtained. Integration of Equation 1.28 with respect to time and combination of the various rate constants into a single empirical rate constant, k_obs, give an expression for the rate of polymerization, in terms of monomer conversion, p:

$$k_\mathrm{obs}t = \ln\left(\frac{1}{1-p}\right), \quad \text{where } k_\mathrm{obs} = k_\mathrm{p}\left(f\frac{k_\mathrm{d}}{k_\mathrm{t}}[\mathrm{I}]\right)^{0.5} \tag{1.29}$$

1.2.6 The Chain Length Distribution

The chain length distribution for a given monomer determines numerous properties of the resulting polymer; therefore, understanding how different polymerization parameters affect the distribution is of paramount importance. Here, the focus is on calculating the chain length distribution rather than the molecular weight distribution, even though molecular weights are reported often.

The chain length distribution can easily be converted to a molecular weight distribution considering that a chain of length *i* has a molecular weight of *i* times the mass of the repeat unit plus the mass of the two end-groups. In the case of unknown end-groups (e.g., polymers initiated by benzoyl peroxide, which can initiate through a number of different radical species), it may be difficult to calculate the exact mass of the polymer chain. Fortunately, the mass of the end-groups becomes insignificant for longer polymers.

Typically, the chain length distribution is characterized by the moments of the distribution. It is also possible to gain an understanding of the distribution by focusing on the microscopic distribution. By knowing the concentration of every macroradical species, one can build a picture of the entire distribution.

For example, Equation 1.30 shows the solution for the rate of change in concentration of macroradicals with chain length *i*; that is, the production by addition of one monomer unit from macroradicals of length $i - 1$, subtracted by the combined loss through transfer and termination reactions, or the addition of another monomer unit to make a macroradical of chain length $i+1$. However, solving this set of differential equations becomes increasingly complex mathematically:

$$\frac{d[R_i^\bullet]}{d\mathrm{t}} = k_\mathrm{p}^{i-1}[\mathrm{M}][R_{i-1}^\bullet] - \left(k_\mathrm{p}^{i}[\mathrm{M}] + k_\mathrm{tr}^{M}[\mathrm{M}] + k_\mathrm{tr}^{T}[\mathrm{T}] + 2\sum_{j=1}^{\infty} k_\mathrm{t}^{i,j}[R_j^\bullet]\right)[R_j^\bullet] \tag{1.30}$$

An alternate starting point involves the use of the kinetic chain length, defined as the total number of monomer units added divided the total number of initiation steps:

$$\text{Kinetic chain length } \nu = \frac{\text{total number of polymerized units}}{\text{total number of initiation steps}} = \frac{\int_0^t (d[\mathrm{M}]/dt)\,dt}{\int_0^t (d[\mathrm{I}^\bullet]/dt)\,dt} \tag{1.31}$$

The kinetic chain deviates from dp_n because of transfer reactions and termination by combination but remains a good starting place. In the absence of all transfer reactions and for termination occurring exclusively by disproportionation, the kinetic chain length will equal dp_n. In the analogous case (no transfer reactions) where combination is the only termination method, dp_n will equal twice the kinetic chain length. The relation between the kinetic chain length and dp_n when there is no chain transfer is shown in Equation 1.32:

$$dp_\mathrm{n} = \left(\frac{2}{1+\delta}\right)\nu \tag{1.32}$$

A more useful simplification is to assume a steady-state polymerization, which means that the radical concentration (and the monomer and initiator concentrations) and the relevant rate constants will remain constant over the course of the polymerization. By adopting a steady-state model, one can substitute the rate of polymerization R_p (Eq. 1.26) and the rate of dissociation R_d (Eq. 1.23) into Equation 1.31 to give an expression for the kinetic chain length [53, 54]:

$$\nu = \frac{R_p}{R_d} = \frac{k_p[R^\bullet][M]}{2fk_d[I]} \tag{1.33}$$

In the steady-state model, the simplified expression for $[R^\bullet]$ can be substituted to give an expression for the kinetic chain length in terms of only rate constants and concentrations, which can be controlled by the polymerization engineer:

$$[R^\bullet] = \left(\frac{fk_d[I]}{k_t}\right)^{0.5} \tag{1.34}$$

$$\nu = \frac{R_p}{R_d} = \frac{k_p k_t^{0.5}[M]}{2(k_d f[I])^{0.5}} \tag{1.35}$$

While Equation 1.35, in combination with Equation 1.32, can give the number-average degree of polymerization, it is important not to ignore the role of the transfer reactions. Even in the case where transfer to initiator and solvent is nonexistent (presumably by careful initiator choice and a solvent-free polymerization), transfer to monomer can never be avoided entirely. Another way to approach the problem is to consider the simplest definition of dp_n; that is, the total number of polymerized monomers units divided by one-half the number of chain ends. Here, it is worth considering the number of chain ends produced by each of the processes [17]. Neither propagation nor termination by combination produce any chain ends ($n=0$), while both initiation and termination by disproportionation produce one chain end ($n=1$), and transfer reactions actually create two chain ends ($n=2$). The steady-state approximation again allows the absolute number of each of these processes to be substituted by the overall rate of each:

$$dp_n = \frac{R_p}{\frac{1}{2}(R_i + R_{t,d} + R_{tr})} \tag{1.36}$$

Among the distinct processes involved in the polymerization, termination by combination is noticeably absent in Equation 1.36, since combination contributes to neither the total number of polymerized monomer units nor the total number of chain ends in the final molecular weight distribution. Recalling the rate law for each of the processes in Equation 1.36 for a stationary polymerization and subsequently inverting the entire equation leads to a very useful relationship, which can be substantially simplified to give Equation 1.41.

$$R_i = 2fk_d[I] = 2(k_{t,d} + k_{t,c})[R^\bullet]^2 \tag{1.37}$$

$$R_p = k_p[M][R^\bullet] \tag{1.38}$$

$$R_{t,d} = 2k_{t,d}[R^\bullet]^2 \tag{1.39}$$

$$R_{tr} = k_{tr}^{M}[M] + \sum_b k_{tr}^{T_b}[T_b][R^\bullet] \tag{1.40}$$

$$\frac{1}{dp_n} = \frac{2k_{t,d} + k_{t,c}}{k_p^2[M]^2} R_p + \frac{k_{tr}^{M}}{k_p} + \sum_b \frac{k_{tr}^{T_b}}{k_p} \cdot \frac{[T_b]}{[M]} \tag{1.41}$$

The summation of the last term in Equation 1.41 accounts for transfer to b different types of species, which typically include solvents, initiators, polymer chains, and any added CTA. Transfer to the monomer is separate from the summation because it cannot be avoided and, thus, must always be considered.

It is normal practice to provide a chain transfer constant (Eq. 1.21) for each of the different types of species that can accommodate transfer reactions:

$$C_M = \frac{k_{tr}^{M}}{k_p}; C_s = \frac{k_{tr}^{S}}{k_p}; C_I = \frac{k_{tr}^{I}}{k_p}; C_P = \frac{k_{tr}^{P}}{k_p}; C_T = \frac{k_{tr}^{T}}{k_p} \tag{1.42}$$

If each of these transfer reaction replaces the summation in Equation 1.41, the following relationship to the inverse of the number-average degree of polymerization is obtained:

$$\frac{1}{dp_n} = \frac{2k_{t,d} + k_{t,c}}{k_p^2[M]^2} R_p + C_M + C_S\frac{[S]}{[M]} + C_I\frac{[I]}{[M]} + C_P\frac{[P]}{[M]} + C_T\frac{[T]}{[M]} \tag{1.43}$$

If one considers an idealized case, where there is no transfer to the solvent (solvent-free polymerization), initiator, or polymer (e.g., in a low conversion regime), and there is no added transfer agent, Equation 1.41 can be further simplified:

$$\frac{1}{dp_n} = \frac{(1+\delta)k_t}{k_p^2[M]^2} R_p + C_M \tag{1.44}$$

Equation 1.44 gives an important relationship between molecular weight and the transfer reaction to monomer. Even in the extreme case where termination becomes completely nonexistent (Eq. 1.45), the maximum attainable molecular weight is still limited by the transfer reaction to the monomer:

$$\lim_{k_t \to 0} \frac{1}{dp_n} = C_M \therefore dp_n^{\max} = C_M^{-1} \tag{1.45}$$

For example, consider the polymerization of styrene performed at 100 °C. The transfer constant for styrene at this temperature is 2×10^{-4}; therefore, the maximum attainable degree of polymerization is 5000 even in the complete absence of any termination reactions. The same polymerization performed at 0 °C, at which the C_{sty} has a value of 1×10^{-5}, can lead to a degree of polymerization as high as 100,000.

The previous analysis allows determination of dp_n using the kinetic parameters in a steady-state polymerization; however, a complete characterization of the molecular weight distribution requires the first three moments of the chain length distribution (to provide M_n, M_w, and PDI). A statistical approach to analyze the inactive polymer chains can be used to calculate these quantities.

A generic polymer chain of length i is produced through $i - 1$ propagation reactions, after which the chain becomes inactive by termination (by disproportionation) or transfer. One can start by defining the probability of propagation, q, as shown in Equation 1.46:

$$q = \frac{R_p}{R_p + R_{tr} + R_t} \tag{1.46}$$

Next, the probability (or mole fraction χ) of forming a polymer chain of any given length can be derived. One simply calculates the probability of $i - 1$ propagation reactions, multiplied by the probability of any reaction that is not propagation:

$$\chi_{i,disp} = q^{i-1}(1-q) \tag{1.47}$$

Recalling the expressions for each of the moments of the chain length distribution (Eqs. 1.2–1.4), and substituting for χ from Equation 1.47, a series of easily solvable summations for each of these quantities is obtained:

$$\mu^{(0)} = \sum_{i=1}^{\infty} \chi_{i,disp} = \sum_{i=1}^{\infty} q^{i-1}(1-q) = -\frac{1-q}{q-1} = 1 \tag{1.48}$$

$$\mu^{(1)} = \sum_{i=1}^{\infty} i \cdot \chi_{i,disp} = \sum_{i=1}^{\infty} i \cdot q^{i-1}(1-q) = -\frac{1}{q-1} = (1-q)^{-1} \tag{1.49}$$

$$\begin{aligned} \mu^{(2)} &= \sum_{i=1}^{\infty} i^2 \cdot \chi_{i,disp} = \sum_{i=1}^{\infty} i^2 \cdot q^{i-1}(1-q) \\ &= \frac{q^2+q}{(q-1)^2 q} = (1+q)(1-q)^2 \end{aligned} \tag{1.50}$$

From each of these moments, various important quantities such as the number-average and weight-average degrees of polymerization (dp_n and dp_w, respectively), and the PDI can be computed:

$$\mathrm{PDI} = \frac{dp_w}{dp_n} = \frac{\mu^{(2)}\mu^{(0)}}{\mu^{(1)}\mu^{(1)}} = 1 + q \tag{1.51}$$

Using the results for the moments from this approach, the PDI is computed in Equation 1.51. Because q is the probability of propagation compared to chain inactivation events, the value for q must be very close to 1 for a polymer of any appreciable length to be produced. This finding shows that the PDI for a steady-state free radical polymerization terminated exclusively by disproportionation should be ~2.

Termination by combination complicates the situation slightly because an additional probability must be considered. In this case, chains of length n and m, respectively, with a combined chain length i, must first each be made and then combine to form the inactive polymer with length i. Because there are different combinations of chains with lengths n and m that can combine to form i, a summation must be done to calculate the mole fraction χ_i:

$$\chi_{i,comb} = \sum_{n=1}^{i-1} q^{n-1}(1-q)q^{m-1}(1-q) = (i-1) \cdot q^{i-2}(1-q)^2 \tag{1.52}$$

In the same way as it was derived for termination by disproportionation, χ is inserted into the expression for each of the moments of the chain length distribution. Again, these summations can be solved to give expressions for the first three moments:

$$\mu^{(0)} = \sum_{i=1}^{\infty} \chi_{i,comb} = \sum_{i=1}^{\infty} (i-1)(1-q)^2 q^{i-2} = 1 \tag{1.53}$$

$$\begin{aligned} \mu^{(1)} &= \sum_{i=1}^{\infty} i \cdot \chi_{i,comb} = \sum_{i=1}^{\infty} i \cdot (i-1)(1-q)^2 q^{i-2} \\ &= -\frac{2}{q-1} = 2(1-q)^{-1} \end{aligned} \tag{1.54}$$

$$\begin{aligned} \mu^{(2)} &= \sum_{i=1}^{\infty} i^2 \cdot \chi_{i,comb} = \sum_{i=1}^{\infty} i^2 \cdot (i-1)(q-1)^2 q^{i-2} \\ &= \frac{2(q^3 + 2q^2)}{(q-1)^2 q^2} \\ &= (2q+4)(1-q)^{-2} \end{aligned} \tag{1.55}$$

The PDI can be computed in the same manner, which equals $1 + q/2$; and again, because q must be around 1, the polydispersity for a free radical polymerization in a stationary polymerization terminated exclusively by combination should equal 1.5. The polydispersity is lower in the case of termination purely by combination, due to the statistically random coupling of chains of different lengths:

$$\mathrm{PDI} = \frac{dp_\mathrm{w}}{dp_\mathrm{n}} = \frac{\mu^{(2)}\mu^{(0)}}{\mu^{(1)}\mu^{(1)}} = \frac{(4+2q)(1-q)^{-2}}{4(1-q)^{-2}} = 1 + \frac{q}{2} \tag{1.56}$$

1.2.7 Exceptions and Special Cases

The previous sections address the kinetics for each of the processes involved in free radical polymerization, as well as the overall polymerization process. A steady-state approximation was used to determine the overall rate of polymerization and the chain length distribution. Practically, there are many exceptions to these approximations, including nonstationary polymerization and dead-end polymerization [50, 51], which are treated in more detail elsewhere.

There is also the case of reaction-controlled diffusion (briefly discussed in Section 1.2.4), closely associated with the Trommsdorff effect [55, 56], which leads to the loss of control even under isothermal conditions because the slow diffusion of radicals drastically decreases the rate of termination. This subsequently increases the concentration of radicals, as well as the rate of propagation relative to termination. Under these circumstances, polydispersity can increase significantly, easily reaching PDIs in excess of 10. In fact, the solutions found for polydispersity in a steady-state system in Section 1.2.7 generally underestimate the PDI values expected by a polymerization engineer due to various effects at high conversion and other deviations from steady-state conditions. It has also been recently shown that nanoconfinement of a free radical polymerization can actually lower the polydispersity [57–59].

Over the past two decades, new methodologies have been developed, which combine attributes of living polymerization and free radical polymerization, resulting in what is termed CRP [60]. It has become very attractive recently, due to its ability to polymerize a wide variety of monomers with low polydispersities and well-defined end-groups in a highly reproducible fashion. It encompasses a variety of techniques including but not limited to atom transfer radical polymerization (ATRP) [61, 62], reversible addition-fragmentation chain transfer (RAFT) [63], and nitroxide-mediated polymerization (NMP) [64, 65].

In a simplistic view, the control is achieved by using a reversible capping moiety which serves to render an actively growing polymer chain a nonreactive species (i.e., not a radical) for the majority of its time in the reaction mixture. This means that only a small fraction of the active polymer chains exist as macroradicals undergoing propagation reactions at any given time, most of them being in a reversibly dormant state. This mechanism allows all the polymer chains to grow at approximately the same rate (i.e., much slower, taking hours or days instead of seconds), while drastically reducing the concentration of radicals and, thus, the associated side reactions.

1.3 CONDENSATION POLYMERIZATION

Condensation polymerization is defined as the polymerization where each addition of a monomer unit is accompanied by the elimination of a small molecule. It is used to synthesize some of the most important commodity polymers, including polyesters, polyamides, and polycarbonate.

Condensation polymerization also has a special place in polymer science history. The first truly synthetic polymer, Bakelite, was developed in 1907, as the condensation product of phenol and formaldehyde [66]. Meanwhile, Wallace Carothers pioneered polyester synthesis in the 1930s at Dupont and developed a series of mathematical equations to describe the kinetics, stoichiometry, and molecular weight distribution of condensation polymerizations.

Carothers categorized polymerizations into condensation and addition mechanisms [67], where a step-growth mechanism was synonymous with condensation polymerization. However, not all condensation polymerizations follow a step-growth mechanism. In particular, recent advancements have coerced condensation polymerizations to follow chainwise, and even "living" mechanisms. Nonetheless, the step-growth mechanism is still most common for condensation polymers, particularly among industrially relevant materials. The kinetic treatment will thus focus on the step-growth mechanism, with a separate section devoted to cases of living polycondensation.

1.3.1 Linear AB Step Polymerization

A wide variety of chemistries can be utilized to synthesize condensation polymers, typically producing polymers containing heteroatoms along the backbone. The truly distinctive feature of a stepwise mechanism is the reaction of functional groups from species of any size.

Flory advanced the understanding of step polymerization by postulating that such reactions were strictly random, meaning that reaction rates are independent of chain length [68, 69]. In this case, the problem becomes mathematically simple and probability can be used to compute the molecular weight distribution.

It is useful to start the kinetic analysis with an idealized case, which avoids complications that arise due to unequal stoichiometry, chain length-dependent reactivity, monofunctional impurities, cyclization, and reversible polymerization. The model addressed here is a linear AB step polymerization.

Any reaction in an AB step polymerization can be denoted as shown in Equation 1.57, where A represents one reactive group and B represents the complementary group:

$$(\mathrm{AB})_n + (\mathrm{AB})_m \rightarrow (\mathrm{AB})_{n+m} \tag{1.57}$$

In the case of Nylon-11, a bioplastic derived from castor beans and one of the few industrially relevant AB-derived condensation polymers, A represents the carboxylic acid while B represents the amine in the monomer 1-aminoundecanoic acid:

$$\frac{d[\mathrm{A}]}{dt} = \frac{d[\mathrm{B}]}{dt} = -k[\mathrm{A}][\mathrm{B}] \tag{1.58}$$

One starts by defining the rate constant for the polymerization in Equation 1.58. The choice of an AB system requires that the initial concentration of each monomer, $[\mathrm{A}_0]$ and $[\mathrm{B}_0]$ be equal at time zero, and the chemistry of amidation dictates that the rate of disappearance of each monomer also be equal.

As summarized in Table 1.1, it is recalled that in a stepwise mechanism, all species are treated as polymer, leading directly to Equation 1.59:

$$\frac{d[\mathrm{P}]}{dt} = -k[\mathrm{P}]^2 \tag{1.59}$$

With the condition that [P] equals $[\mathrm{P}_0]$ at time zero, Equation 1.59 has the following solution:

$$[\mathrm{P}] = \frac{[\mathrm{P}_0]}{1 + kt[\mathrm{P}_0]} \tag{1.60}$$

In this notation, P_i is a species with chain length i, meaning that monomer is denoted as P_1.

An expression for the rate of disappearance of the monomer species is written in Equation 1.61. Of some importance is the factor of 2, which is included because of the two indistinguishable reactions that lead to consumption of monomer (i.e., P_1 can be consumed either by the reaction of its amine with the carboxylic acid of P_i or by the reaction of its carboxylic acid with the amine of P_i):

$$\frac{d[\mathrm{P}_1]}{dt} = -2k[\mathrm{P}_1][\mathrm{P}] \tag{1.61}$$

To compute the entire molecular weight distribution, the rate of evolution of each species has to be known. Because a species with chain length i can be formed in $i - 1$ different ways, a summation must be used in the production term:

$$\frac{d[\mathrm{P}_i]}{dt} = k\sum_{j=1}^{i-1}[\mathrm{P}_j][\mathrm{P}_{i-j}] - 2k[\mathrm{P}_i][\mathrm{P}] \tag{1.62}$$

From here, it is evident that there is a set of infinite differential equations to be solved. The simplest way to confront this problem is to sequentially solve each differential equation and look for a pattern to emerge. This is possible because each successive solution depends on the previous solutions (i.e., larger species are derived from the combination of smaller species).

Substituting the expression for [P] from Equation 1.60 into the rate of disappearance of monomer $[\mathrm{P}_1]$ gives the following:

$$\frac{d[\mathrm{P}_1]}{dt} = -2k[\mathrm{P}_1][\mathrm{P}] = -2k[\mathrm{P}_1][\mathrm{P}_0]\cdot\frac{1}{1 + kt[\mathrm{P}_0]} \tag{1.63}$$

Note that the product term is unnecessary for monomeric species. The differential equation is easily separated and solved to give the solution for the concentration of monomer:

$$[\mathrm{P}_1] = [\mathrm{P}_0]\left(\frac{1}{1 + kt[\mathrm{P}_0]}\right)^2 \tag{1.64}$$

The next step is to write an expression for the evolution of dimer, which can only be produced by the reaction of two monomeric species with each other.

$[\mathrm{P}_1]$ is substituted with the solution from Equation 1.64, while the value for [P] is still taken from Equation 1.60:

$$\frac{d[\mathrm{P}_2]}{dt} = k[P_1]^2 - 2k[\mathrm{P}_2][\mathrm{P}] = k[\mathrm{P}_0]^2\left(\frac{1}{1 + kt[\mathrm{P}_0]}\right)^4 - 2k[\mathrm{P}_2][\mathrm{P}_0]\cdot\frac{1}{1 + kt[\mathrm{P}_0]} \tag{1.65}$$

The solution for this previous differential equation is more complex. With the condition that at time zero $[\mathrm{P}_2] = 0$, the solution can be found by using the variation of constants method [70]:

$$[\mathrm{P}_2] = [\mathrm{P}_0]\left(\frac{1}{1 + kt[\mathrm{P}_0]}\right)^2\left(\frac{kt[\mathrm{P}_0]}{1 + kt[\mathrm{P}_0]}\right) \tag{1.66}$$

In the same manner, an expression is written for the evolution of trimer, produced by the reaction of dimer with monomer:

$$\begin{aligned}\frac{d[\mathrm{P}_3]}{dt} &= k[\mathrm{P}_1][\mathrm{P}_2] - 2k[\mathrm{P}_3][\mathrm{P}] \\ &= k[\mathrm{P}_0]^2\left(\frac{1}{1 + kt[\mathrm{P}_0]}\right)^4\left(\frac{kt[\mathrm{P}_0]}{1 + kt[\mathrm{P}_0]}\right) \\ &\quad - 2k[\mathrm{P}_3][\mathrm{P}_0]\cdot\left(\frac{1}{1 + kt[\mathrm{P}_0]}\right)\end{aligned} \tag{1.67}$$

Under the initial condition, $[P_3]=0$, the following solution is obtained:

$$[P_3]=[P_0]\left(\frac{1}{1+kt[P_0]}\right)^2\left(\frac{kt[P_0]}{1+kt[P_0]}\right)^2 \tag{1.68}$$

Based on the aforementioned expressions, a general solution for the concentration of any given species $[P_i]$ can be postulated:

$$[P_i]=[P_0]\left(\frac{1}{1+kt[P_0]}\right)^2\left(\frac{kt[P_0]}{1+kt[P_0]}\right)^{i-1} \tag{1.69}$$

One can prove this by induction, starting with the assumption that this form is true for $[P_{i-1}]$ and inserting it into the kinetic equation for $[P_i]$:

$$\frac{d[P_i]}{dt}=(i-1)k[P_0]^2\left(\frac{1}{1+kt[P_0]}\right)^4\left(\frac{kt[P_0]}{1+kt[P_0]}\right)^{i-2} - 2k[P_i][P_0]\left(\frac{1}{1+kt[P_0]}\right) \tag{1.70}$$

Since the solution to the homogenous equation is always the same, Equation 1.70 can be simplified:

$$[P_i]=[P_0]\left(\frac{1}{1+kt[P_0]}\right)^2\int_0^t(i-1)\left(\frac{kt[P_0]}{1+kt[P_0]}\right)^{i-2}\left(\frac{1}{1+kt[P_0]}\right)^2 k[P_0]dt \tag{1.71}$$

The equation can then be integrated, giving the result postulated for the general form. Then, since this form was shown to be true for 1, 2, 3, and $i-1$, the validity of the general form is proven:

$$[P_i]=[P_0]\left(\frac{1}{1+kt[P_0]}\right)^2\left(\frac{kt[P_0]}{1+kt[P_0]}\right)^{i-1} \tag{1.72}$$

The general result for the concentration of P_i can be simplified by creating a simple expression for the conversion, p, of functional groups, derived from Equation 1.60:

$$p=\frac{[A]_0-[A]}{[A]_0}=\frac{[B]_0-[B]}{[B]_0}=\frac{[P]_0-[P]}{[P]_0}=\frac{kt[P_0]}{1+kt[P_0]} \tag{1.73}$$

which can be used to derive a simplified expression for $[P_i]$:

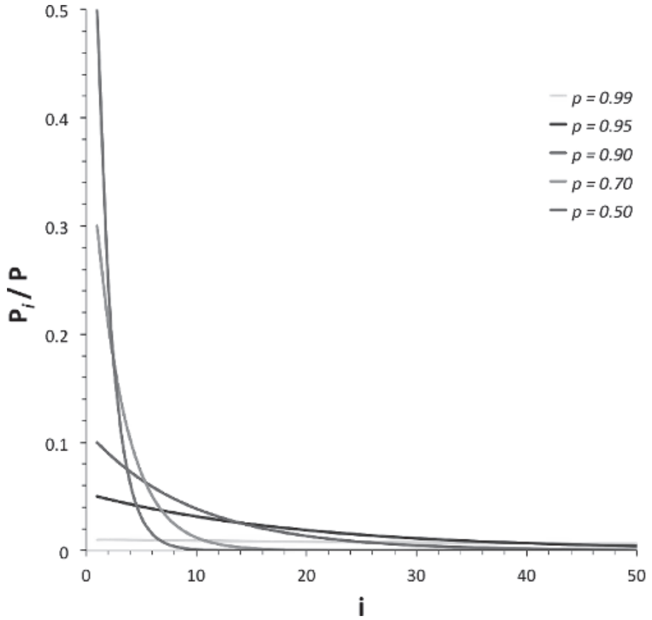


FIGURE 1.4 Geometric chain length distribution at different conversions. (*See insert for color representation of the figure.*)

$$[P_i]=[P_0](1-p)^2\cdot p^{i-1} \tag{1.74}$$

The aforementioned expression is the geometric distribution or the Flory–Schulz distribution. The results can be illustrated by plotting the mole fraction of chain length for different values of conversion, p.

Figure 1.4 shows the chain length distribution for a geometric distribution for different values of p, while Figure 1.5 shows the corresponding molecular weight distribution (without taking into account the mass loss due to the condensate).

While the entire chain length distribution is shown in Figure 1.4 and Figure 1.5, polymer size is usually characterized by the moments of the distribution, as described in Section 1.1.2. From the results computed for the geometric chain distribution, one can solve for the moments in a straightforward way. By combining Equation 1.1 with 1.74, an expression for each of the first three moments can be written as follows:

$$\mu_0=\sum_{i=1}^{\infty}[P_i]=[P_0]\sum_{i=1}^{\infty}(1-p)^2\cdot p^{i-1}=[P_0](1-p)^2\sum_{j=0}^{\infty}p^j \tag{1.75}$$

$$\begin{aligned}\mu_1&=\sum_{i=1}^{\infty}i\cdot[P_i]=[P_0](1-p)^2\sum_{i=1}^{\infty}i\cdot p^{i-1}\\&=[P_0](1-p)^2\sum_{j=0}^{\infty}(j+1)\cdot p^j\end{aligned} \tag{1.76}$$

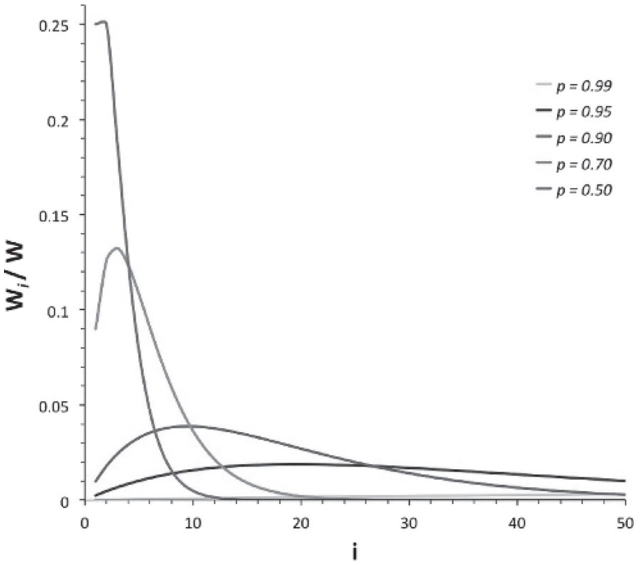


FIGURE 1.5 Geometric molecular weight distribution at different conversions. (*See insert for color representation of the figure.*)

$$\mu_2 = \sum_{i=1}^{\infty} i^2 \cdot [\mathrm{P}_i] = [\mathrm{P}_0](1-p)^2 \sum_{i=1}^{\infty} i^2 \cdot p^{i-1} \\ = [\mathrm{P}_0](1-p)^2 \sum_{j=0}^{\infty} (j+1)^2 \cdot p^j \tag{1.77}$$

While the conversion p can approach 1, it will never reach unity. Because p is always less than 1, each of the aforementioned summations converges to give the results for each of the moments as follows [71]:

$$\mu_0 = [\mathrm{P}_0](1-p) \tag{1.78}$$

$$\mu_1 = [\mathrm{P}_0] \tag{1.79}$$

$$\mu_2 = [\mathrm{P}_0] \cdot \frac{(1+p)}{(1-p)} \tag{1.80}$$

Next, the number-average and weight-average degrees of polymerization and the PDI can be computed:

$$dp_{\mathrm{n}} = \frac{\mu_1}{\mu_0} = \frac{1}{(1-p)} \tag{1.81}$$

$$dp_{\mathrm{w}} = \frac{\mu_2}{\mu_1} = \frac{1+p}{1-p} \tag{1.82}$$

$$\mathrm{PDI} = \frac{\mu_2 \mu_0}{\mu_1 \mu_1} = 1+p \tag{1.83}$$

Equation 1.81 is also known as the Carothers equation, which offers an expression for dp_{n} in terms of functional group conversion. Carothers equation clearly proves that high molecular weight can be achieved in a stepwise polymerization only by reaching very high conversion. Also, the polydispersity will approach 2 because conversion p must be close to 1 for a polymerization to attain any significant molecular weight.

1.3.2 Linear Step AA–BB Polymerization: Stoichiometric Imbalance

Despite the fact that the AB type of polymerization serves as a useful model for deriving the Carothers equation and gaining a basic understanding of step polymerization kinetics, most industrially relevant stepwise polymers are made using an AA–BB system. While this naturally simplifies monomer synthesis, it introduces a complicating factor into account, that of stoichiometry. In an AB system, perfect stoichiometry is assured. This does not hold for AA–BB systems, imbalances in stoichiometry leading to serious consequences for the molecular weight distribution, namely a severe reduction in molecular weight. While reaction engineers have many tools at their disposal for assuring the desired stoichiometry, it is still important to determine the results of unbalanced concentration of monomers:

$$r = \frac{[\mathrm{A}]_0}{[\mathrm{B}]_0} = \frac{p_{\mathrm{B}}}{p_{\mathrm{A}}} \le 1 \tag{1.84}$$

There are a number of ways to approach this problem. Assuming a system where B is the monomer in excess (described by Eq. 1.84), Flory's approach can be taken. If the chains are termed by their end-groups (i.e., AA-$(\mathrm{AABB})_n$-AA is an "odd-A" chain, AA-$(\mathrm{AABB})_n$-BB is an "even" chain, and BB-$(\mathrm{AABB})_n$-BB is an "odd-B" chain), the rate of evolution of each type of chain at length i can be determined, bearing in mind that at high conversion both "odd-A" and "even" chains will disappear. There are multiple statistical approaches to this problem, including those described by Case [72], Miller [73], and Lowry [74]. The results of these analyses are briefly presented in the following, other sources for a more rigorous mathematical treatment being available [70].

The number-average degree of polymerization is given by Equation 1.85 in terms of conversion and stoichiometric imbalance. In a situation where $r = 1$ (i.e., perfect stoichiometry), this equation simplifies to Carothers equation (Eq. 1.81).

$$dp_{\mathrm{n}} = \frac{1+r}{1+r-2rp} \tag{1.85}$$

To address the question of how stoichiometric unbalance limits molecular weight, the effect at the limit where conversion p is equal 1 should be considered. The following equations give the expressions for the number-average and weight-average degrees of polymerization, and the PDI at full conversion:

$$dp_{\mathrm{n}} = \frac{1+r}{1-r} \tag{1.86}$$

$$dp_{\mathrm{w}} = \frac{1+r}{1-r} + \frac{4r}{1-r^2} \tag{1.87}$$

$$\mathrm{PDI} = 1 + \frac{4r}{(1+r)^2} \tag{1.88}$$

Carothers equation indicates that at full conversion, infinite molecular weight will be attained. However, in the case of 0.01% excess of monomer B ($r \cong 0.9999$), the number-average degree of polymerization will be 20,000. If that excess of monomer B rises to 1%, dp_{n} at full conversion will be only 201. This clearly proves the extreme limiting effect on the molecular weight of even a slight excess of one reagent. To avoid these problems, reaction engineers have designed a range of strategies for gaining the desired stoichiometry, including what amounts to a titration between carboxylic acids and amines in the synthesis of polyamides and the creation of a quasi-A_2 monomer from an AA–BB system during the synthesis of polyesters (see Section 1.3.4 for more details). One can see that the polydispersity is a monotonically decreasing function of the stoichiometric ratio r, where the PDI is equal to 2 in the case of perfect stoichiometry and is equal to 1 when $r = 1$ (i.e., only monomer is present because no reaction is possible). While it may seem that stoichiometric unbalance is entirely negative, it can be used intentionally with positive effects.

For example, consider a polyamide (e.g., nylon-6,6, see Section 1.3.4.3) made by starting with perfect stoichiometry and polymerized to a conversion of 99%. This polymer has a dp_{n} of 100, with a mixture of "odd-A," "even," and "odd-B" chains. Because the end-groups are still potentially reactive, if the polymer is subjected to heating, further amidation reactions are possible. This would change the molecular weight and potentially alter the mechanical properties of the polymer. Alternatively, a dp_{n} of 100 can be achieved by starting with a 2 mol% excess of B ($r \cong 0.98$) and reacting until nearly complete conversion is achieved. At full conversion, all the chains will be "odd-B" (i.e., all of the chain ends would be terminated by amines). In this scenario, additional heating will not alter the molecular weight distribution since no further amidation reactions can take place.

1.3.3 Effect of Monofunctional Monomer

The presence of monofunctional monomer has a similar effect as unequal stoichiometry on the molecular weight distribution in a stepwise polymerization. There are two scenarios where monofunctional monomer must be considered. The first case is when the monofunctional monomer is an impurity, which will deleteriously limit the molecular weight; this is particularly problematic when high molecular polymer is desired. A monofunctional monomer can also be added to act as a chain stopper, thereby limiting the molecular weight and resulting in nonreactive chain ends, as discussed at the end of the previous section. Regardless of the intent, the effect on the molecular weight distribution is the same.

The stoichiometric ratio r' is defined in Equation 1.89 (a different variable was chosen to distinguish from the case of unequal stoichiometry):

$$r' = \frac{[\mathrm{P}]_0}{[\mathrm{P}]_0 + [\mathrm{P}_{\mathrm{mono}}]_0} \tag{1.89}$$

The expressions for dp_{n} and dp_{w} are similar to those found in Section 1.3.2. The molecular weight is limited not only by the conversion p but also by the relative amount of monofunctional agent present in the system:

$$dp_{\mathrm{n}} = \frac{1}{1-r'p} \tag{1.90}$$

$$dp_{\mathrm{w}} = \frac{1+r'p}{1-r'p} \tag{1.91}$$

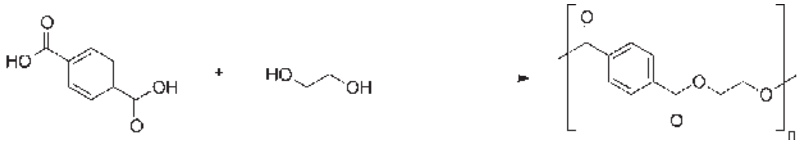
1.3.4 Common Condensation Polymers Made by a Stepwise Mechanism

The previous sections describe the kinetics of a stepwise polymerization, which can be implemented using a wide array of different functional groups. This is unlike the case of the free radical polymerization, where the propagation step is always due to a radical adding across a carbon–carbon double bond.

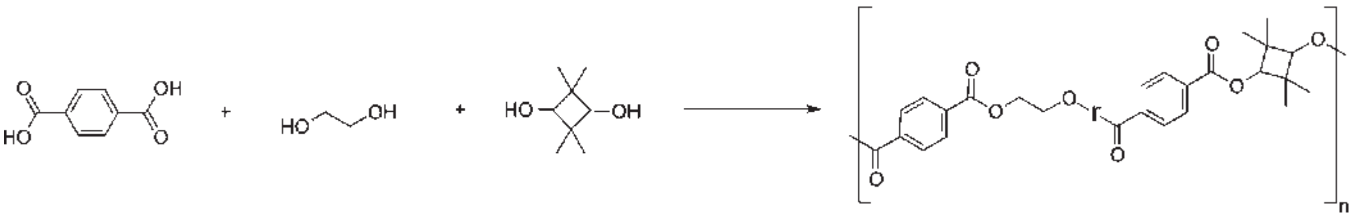
Due to the wide variety of different chemistries employed to make condensation polymers by a stepwise process, a brief overview of some of the more common polymers made by this mechanism is given in the following subsections.

1.3.4.1 ***Polyesters*** Polyesters, polymers that contain an ester bond in the backbone of their repeating unit, are the most widely produced type of condensation polymer. In fact, PET (Scheme 1.3) is the third most highly produced commodity polymer in the world, trailing only polyethylene and polypropylene.

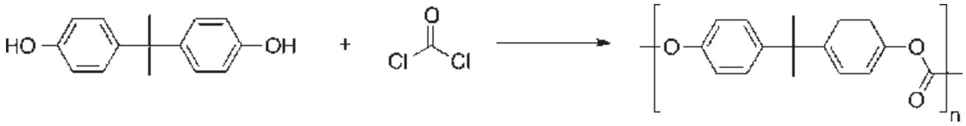
Polyethylene terephthalate, commonly referred as polyester, can be made by several slightly differing routes. In the terephthalic acid process, ethylene glycol is reacted with terephthalic acid at temperatures above 200 °C, which drives the reaction forward by removal of water. An alternative process utilizes ester exchange to reach high molecular weights.



SCHEME 1.3 Poly(ethylene terephthalate) via the terephthalic acid approach.



SCHEME 1.4 Copolymerization of terephthalic acid with ethylene glycol and TMCBDO to produce Tritan™ copolymer.



SCHEME 1.5 Reaction of bisphenol-A (BPA) with phosgene to make polycarbonate.

An initial esterification reaction occurs between an excess of ethylene glycol with dimethylterephthalate under basic catalysis at 150 °C. Removal of methanol by distillation drives the formation of bishydroxyethyl terephthalate, which can be considered an A_2 monomer. A secondary transesterification step performed at 280 °C drives polymer formation via ester exchange, which is pushed toward high molecular weight by removal of ethylene glycol via distillation.

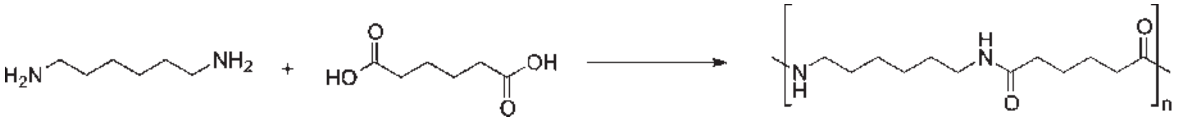
Another polyester becoming increasingly important in the marketplace is Eastman's Tritan™ copolymer (Scheme 1.4), which has replaced polycarbonate in a variety of commercial products. Tritan™ is a modified PET copolymer, where a portion of the ethylene glycol is replaced by 2,2,4,4-tetramethyl-1,3-diol (TMCBDO).

The TMCBDO monomer imparts a higher glass transition temperature and improved mechanical properties, including resistance to crazing and efficient dissipation of applied stresses, while its diastereomeric impurity helps to prevent crystallinity and to keep Tritan amorphous, leading to improved clarity. While the real industrial feat may be the large-scale production of TMCBDO, which is made via a ketene intermediate, the interesting feature in the scope of this book is a step A_2–B_2, B_2' polymerization, where the two B_2 monomers have different reactivities (in fact, the *trans*- and *cis*-isomers of TMCBDO may also have different reactivities, but this has not been studied in detail to this point). As discussed in Section 1.1.2, the differing reactivity ratios could lead to gradient or blocky copolymers. However, in the case of polyesterification, ester exchange reactions can serve to scramble the sequence and lead to a random distribution of monomer units even for unequal reactivities.

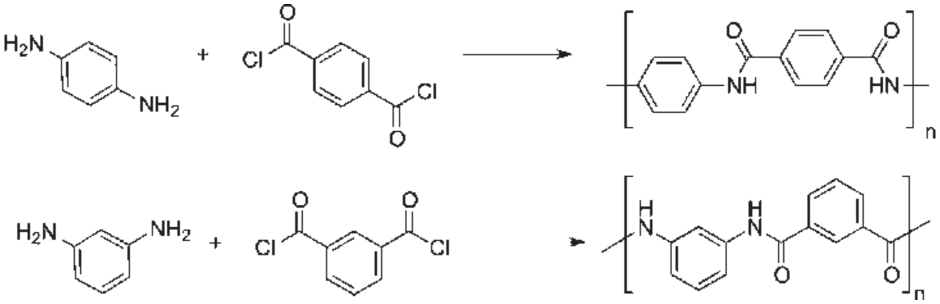
1.3.4.2 ***Polycarbonate*** Polycarbonate (Scheme 1.5) is produced by the reaction of BPA with phosgene; it is the leaching of endocrine-disrupting BPA that has lead to its replacement in food and beverage containers. Nonetheless, polycarbonate is still used extensively as a building material, in data storage, and as bullet-resistant glass. In this reaction, the condensate is hydrochloric acid. Polycarbonate, despite its BPA-related problems, is a durable plastic that is flame retardant, heat resistant, and a good electrical insulator.

1.3.4.3 ***Polyamides*** Polyamides are polymers containing amide bonds along the polymer backbone synthesized by the reaction of amine with carboxylic acid (or derivatives thereof, e.g., methyl ester, acyl halide). Proteins are polyamides made by a biosynthetic polycondensation, each having a specific sequence and monodisperse molecular weight distribution. Synthetic polyamides are not nearly as complex as their biological counterparts, but still have excellent properties. In particular, the hydrogen-bonding nature of the amide bond leads to high melting points and semicrystalline behavior, desirable traits for synthetic fibers.

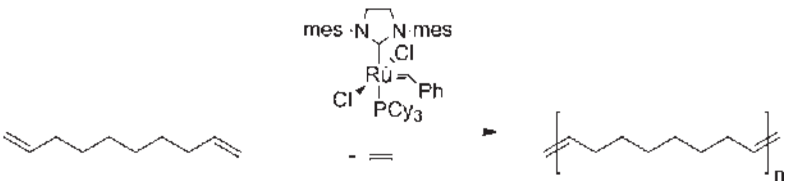
The best-known class of polyamides is nylon. First discovered by Carothers in 1935, nylon-6,6 is produced by the condensation reaction between 1,6-hexanediamine and



SCHEME 1.6 Reaction of 1,6-hexanediamine with adipic acid gives nylon-6,6.



SCHEME 1.7 Polymerization of aryl amine with terephthaloyl chloride to give the *p*-aramid Kevlar and the *m*-aramid Nomex, respectively.



SCHEME 1.8 ADMET polymerization of 1,9-decadiene by Grubbs' second generation catalyst.

adipic acid (Scheme 1.6). It has a melting point of 265 °C and has been used as a fiber for a variety of applications, including in parachutes during World War II in the midst of worldwide silk shortages. A similar polymer, nylon-6, is made by the ring-opening polymerization of caprolactam, which is not a polycondensation reaction.

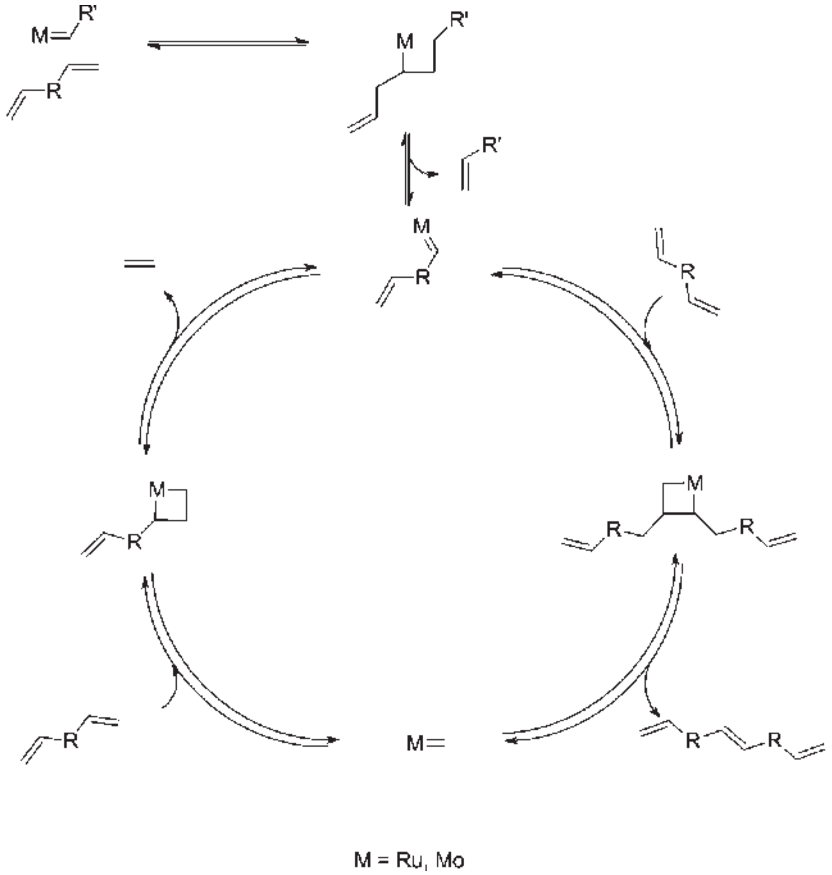
Polyamides can also be made by the reaction of amines with acyl halides, where the condensate is hydrochloric acid. This process is used to make aromatic polyamides, notably Kevlar and Nomex (Scheme 1.7). The reaction of *p*-phenylenediamine with terephthaloyl chloride results in the high performance *p*-aramid Kevlar. While Kevlar is expensive because processing requires the use of anhydrous sulfuric acid as solvent, its outstanding mechanical and thermal properties led to its use in demanding applications, including personal armor, bicycle tires, and racing sails.

When the corresponding *meta* monomers are used, the resulting polymer is Nomex. Nomex is more easily processed than Kevlar and since its fibers have excellent fire retardant properties, it is the material of choice for protective equipment for firefighters, fighter pilots, and racecar drivers.

1.3.4.4 ***ADMET*** Whereas this Section might be more appropriately titled "polyolefins" to match more closely with the previous subsections, the polymerization process itself is more notable than the products.

Acyclic diene metathesis (ADMET) [75] is the process by which a transition metal catalyst leads to a stepwise condensation polymerization of diene monomers, characterized by loss of gaseous ethylene and the production of linear polyolefins containing regular unsaturations along the polymer backbone (Scheme 1.8). In fact, many of the polymeric structures accessible by ADMET can be made by alternate mechanisms (e.g., 1,4-polybutadiene made by ADMET polymerization of 1,6-hexadiene is more commonly made by the anionic polymerization of 1,4-butadiene).

Nonetheless, ADMET is a versatile technique that allows the incorporation of a wide variety of functional groups into the resultant polymers. Scheme 1.9 shows the catalytic cycle of ADMET, controlled by the metathesis catalyst, which can be either ruthenium- [76, 77] or molybdenum-based [78, 79]. While the kinetics are controlled by the catalyst (there is no reaction in its absence), it still follows the kinetic picture described in Section 1.3.2. This is because the catalyst is removed from the chain end after each successful alkene metathesis reaction (i.e., coupling) and the olefin with which it subsequently reacts is statistically random.



SCHEME 1.9 Generally accepted ADMET mechanism.

Acyclic diene metathesis polymerizations are often pushed to high molecular weight by solid-state reaction under high vacuum, while reaction under ethylene pressure causes depolymerization.

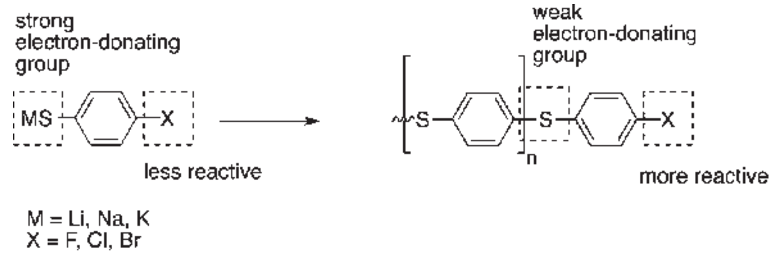
1.3.4.5 ***Conjugated Polymers*** For the past 20 years, conjugated polymers have been made by polycondensation using Stille [80, 81] and Suzuki [82, 83] couplings. The Stille coupling reacts stannanes and aryl halides to form new carbon–carbon bonds [84], while the Suzuki coupling makes carbon–carbon bonds by coupling of boronic acids (or esters) and aryl halides [85, 86]. For Suzuki coupling, either an A_2–B_2 or AB system can be used. Even though using an AB monomer can help eliminate stoichiometric imbalance, A_2–B_2 systems are generally favored because it is simpler to synthesize the monomers. Stille couplings can run into problems with stoichiometry caused by the reduction of the Pd(II) catalyst to Pd(0) by the organotin monomer, and when homocoupling of the ditin monomer occurs. Because of these issues, oftentimes the catalyst and organotin monomer concentrations may be varied from equimolar to maintain proper stoichiometry.

A vast array of aromatic monomers has been polymerized by these techniques, including substituted benzenes, thiophenes, fused thiophenes, pyrroles, pyrazines, ethylene and acetylene derivatives, and many more complex ring structures. More recently, techniques have been developed allowing chainwise and even "living" polymerization of many of the same basic monomer units using different mechanisms.

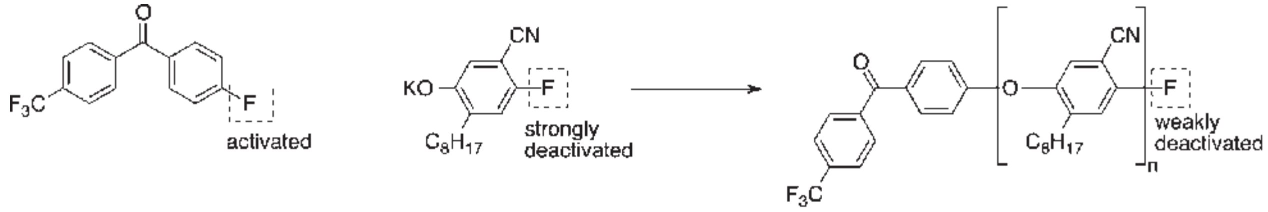
1.3.5 Living Polycondensation

The previous sections have focused on condensation polymerizations following a stepwise growth mechanism. However, a number of strategies have emerged which facilitate condensation polymerizations that would otherwise follow a stepwise growth mechanism to propagate via a chainwise or "living" mechanism. In fact, because condensation polymerization is defined only as a polymerization that releases a small molecule during each growth step, there are well-known condensation polymerizations that do not follow a stepwise mechanism under any circumstance.

The ring-opening polymerization of N-carboxyanhydride (NCA) monomers to give poly(peptides) proceeds via a chainwise or "living" growth mechanism and has been studied in great detail over the past 15 years. This polymerization has been performed under a variety of conditions, including anionic [87],



SCHEME 1.10 Polymeric aryl halide is more reactive than monomeric aryl halide.



SCHEME 1.11 Potassium alkoxide strongly deactivates monomeric aryl fluoride relative to the polymeric aryl fluoride.

activated-monomer, and transition metal catalyzed [88], and in all cases the addition of one monomer unit is accompanied by the release of carbon dioxide. However, NCAs are not multifunctional monomers and cannot produce polymer via a stepwise mechanism and thus, reactions of this type will not be considered in this Section. The focus is on systems that can grow based on a stepwise mechanism, but on which strategies that alter the kinetic parameters were rather used to confer a chainwise or "living" behavior [89, 90].One of the most important assumptions made by Flory and Carothers was that of equal and random reactivity (i.e., chain length-independent) between any of the functional groups in the system. It is this assumption that leads to the growth kinetics and molecular weight distributions seen in stepwise polymerization.

One can start by considering Equation 1.62, which describes the rate of evolution for a polymer of chain length *i*. Equation 1.62 is rewritten in a way that separates the addition of a monomer unit, or P_1, from the addition of any other species, with k'' representing the rate for monomer addition and k' representing the rate constant for additions of species with $i \geq 2$:

$$\frac{d[\mathrm{P}_i]}{dt} = k'\sum_{j=2}^{i-2}[\mathrm{P}_\mathrm{j}][\mathrm{P}_{i-\mathrm{j}}] + k''[\mathrm{P}_1][\mathrm{P}_{i-1}] - 2k'[\mathrm{P}_i]\cdot\left([\mathrm{P}]-[\mathrm{P}_1]\right) - 2k''[\mathrm{P}_i][P_1] \qquad (1.92)$$

If Carothers's assumption that reactivity is equal and random reactivity holds, Equation 1.92 still equals the general form for step polymerization written in Equation 1.62. However, if a chemical system is designed such that $k'' >> k'$, Equation 1.92 can be rewritten in a simpler form, which now resembles the rate of evolution for a chainwise system (see Eq. 1.33).

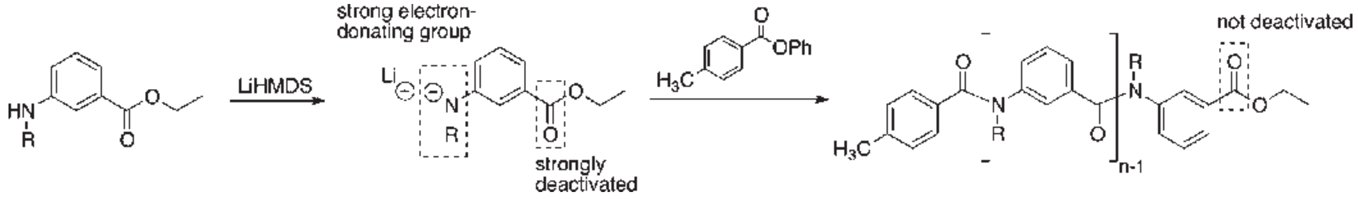
$$\frac{d[\mathrm{P}_i]}{dt} = k''[\mathrm{P}_1][\mathrm{P}_{i-1}] - 2k''[\mathrm{P}_i][\mathrm{P}_1] \qquad (1.93)$$

Efforts to influence condensation polymerizations to follow a "living" mechanism must favor the addition of monomer units to active chains over all other possible reactions. In other words, a chemical system must be designed such that k'' is much greater than k'. In some ways, compelling polycondensation to demonstrate "living" behavior is simpler than for free radical polymerizations because condensation polymerization is not affected by the various transfer and termination processes that plague free radical chemistry.

A successful method in creating conditions for living polycondensation takes the advantage of differing substituent effects to activate the polymer chain end relative to the monomer. With this approach, aromatic monomers have great use due to their propensity to be strongly activated or deactivated by substituents on the ring.

Early work performed by Lenz et al. in the 1960s demonstrated this approach by using electrophilic aromatic substitution to produce poly(phenylene sulfide) [91] (Scheme 1.10). In this case, an aryl halide is the electrophile, which is substituted by the metal thiophenoxide nucleophile. In the monomer, the metal sulfide is a strong electron-donating group, which deactivates the *para* position where electrophilic substitution must take place. Conversely, the polymer chain end is only weakly deactivated by the sulfide bond, rendering the polymeric aryl halide more reactive than the monomeric aryl halide. Unfortunately, Lenz was unable to characterize molecular weight distribution due to the insolubility of the resultant polymers.

Later work by Yokozawa et al. took advantage of the same principal to produce aromatic polyethers with PDIs < 1.1 [92]. In this case, the aryl fluoride was again strongly deactivated in the monomer by the electronic donating *p*-phenoxide (Scheme 1.11), while the chain end was only weakly deactivated by the ether bond *para* to the



SCHEME 1.12 Inductively deactivated monomer in transamidation condensation polymerization.

chain-end aryl fluoride. Taking this concept a step further, the authors polymerized the deactivated monomer in the presence of 4-fluoro-4′-trifluoromethylbenzophenone, the aryl halide of which is activated. This molecule is much more reactive to electrophilic substitution than the monomer, it is effectively an initiator and leads to polymers with controlled molecular weight distributions and well-defined chain ends.

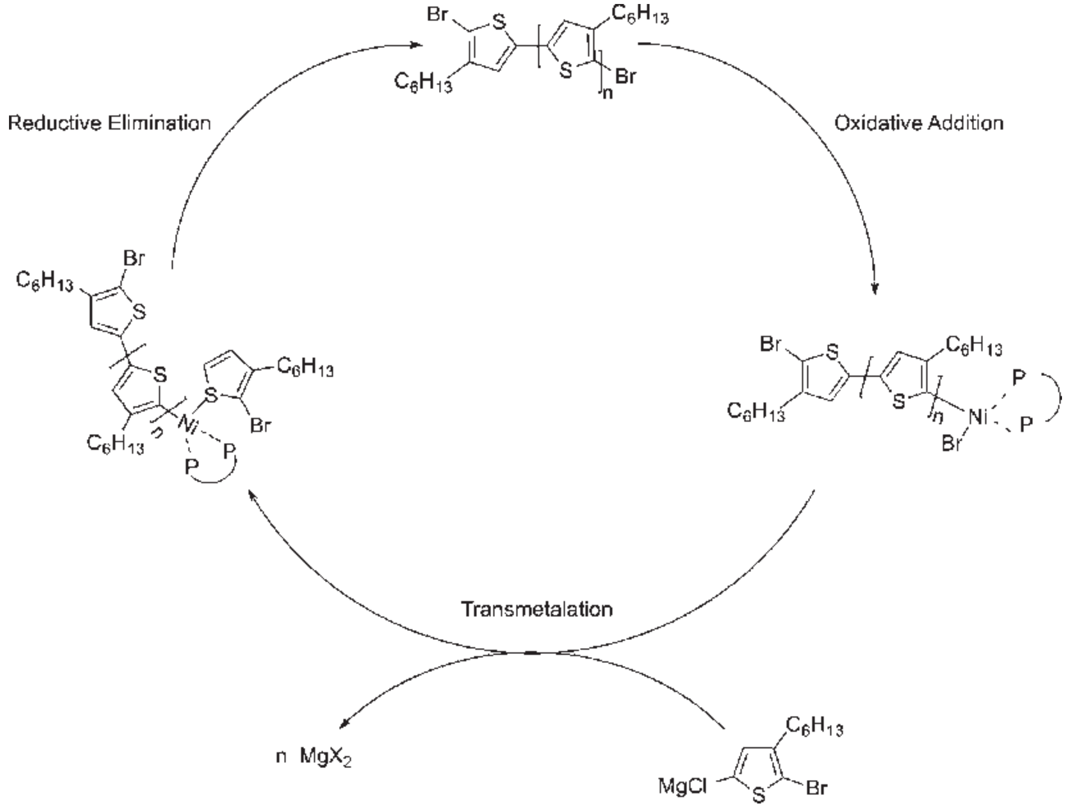
A similar strategy of monomer deactivation through an aromatic group has been used to successfully polymerize *m*-substituted monomers in a controlled fashion by using the inductive effect. An example is the transamidation of benzoate monomers to give poly(*m*-benzamides) [93]. The carbonyl of the monomer ester is strongly deactivated by the lithium amide in the *m*-position, discouraging its transamidation (Scheme 1.12). 4-Methylbenzoate was employed as an initiator, which is activated at the carbonyl by the *p*-methyl group. The resultant chain end is much more reactive to amidation than the monomer, which again results in a situation where $k'' >> k'$, leading to polymers with narrow molecular weight distributions.

Another method to activate the polymer relative to the monomer is to transfer a catalyst to the chain end. Catalyst-transfer living polycondensation has had an enormous impact in the field of conjugated polymers, providing facile routes to relatively monodisperse polythiophenes [94–97], polyphenylenes [98], polypyrroles [99], and polyfluorenes [100, 101] all made in a living fashion. Conjugated polymers have attracted great interest [102] due to their applications in organic optoelectronic devices including photovoltaics [103, 104], light-emitting diodes [105], organic field-effect transistors [106], and nonlinear optical devices. These applications highlight the importance of living polycondensation because conjugated polymers made by stepwise growth (e.g., Suzuki, Stille couplings) lack consistent molecular weight distributions and well-defined end-groups, leading to batch-to-batch variations that can affect materials performance.

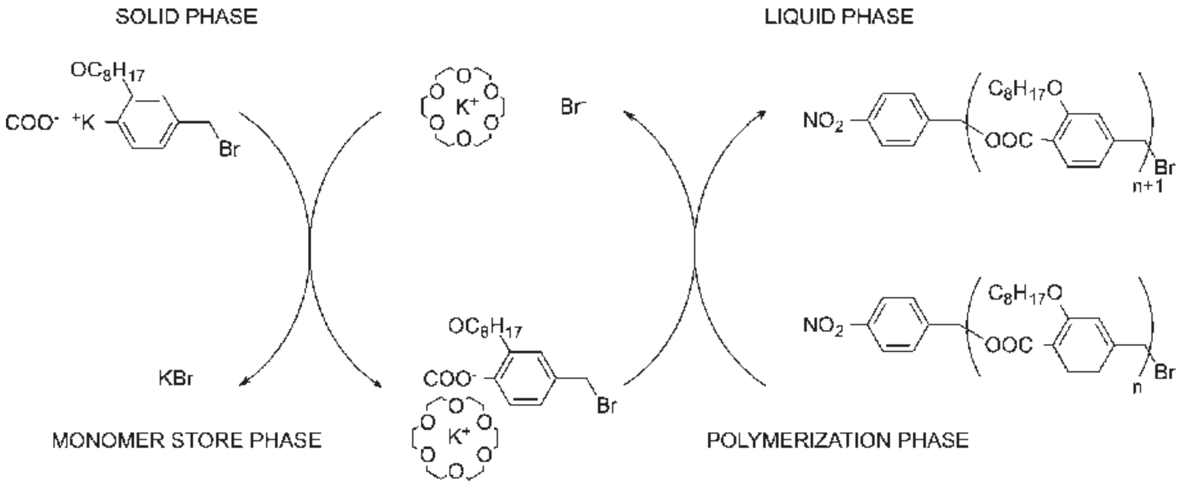
One of the most highly researched conjugated polymers is poly(3-alkylthiophene) (underivatized polythiophene is insoluble). In a synthetic method developed by McCullough [94, 96] and further modified by Yokozawa [95, 97], Kumada catalyst-transfer polycondensation (KCTP), also commonly known as Grignard metathesis polymerization (GRIM), is a nickel-catalyzed organometallic polycondensation that allows access to regioregular poly(3-alkylthiophene) and block copolymers thereof. While KCTP is affected by termination, as proved by the existence of maximum attainable molecular weights, in the same time, it exhibits a living behavior and consistently leads to polymers with PDIs ≤ 1.1. The initiating species are formed via transmetalation of two monomer molecules to produce the bis-organonickel compound. As shown in Scheme 1.13, the catalytic cycle during propagation involves transmetalation with a monomer unit, reductive elimination of the catalyst to add one unit to the propagating chain, and oxidative addition to reform the active Ni(0) species at the active chain end. The key step in this process is the ability of the nickel catalyst to reductively eliminate and subsequently reinsert into the terminal C–Br bond without diffusing into the reaction mixture (as compared to ADMET), thus, resulting in one polymer chain produced for each molecule of nickel catalyst (i.e., the molecular weight is inversely proportional to the catalyst loading).

Beyond its success in polymerizing thiophene derivatives, KCTP has been adapted not only to polymerize a variety of other monomers via a living chainwise growth mechanism, but also to produce an array of polymeric architectures. In particular, KCTP is capable of producing block copolymers by successive addition of monomer: a hallmark of living polymerization. Iovu et al. reported the synthesis of the first all-thiophene block copolymer by successive polymerization of 3-hexylthiophene and 3-dodedecylthiophene [94]. Subsequently, block copolymers comprising entirely of different conjugated polymers have been synthesized, including polymers containing pyrroles [99], phenylenes [99], fluorenes [101], thiophenes, and seleophenes [107]. Catalyst-transfer polycondensation has also been applied to a grafting-from strategy to synthesize brush copolymers [108]. as well as surface-initiated polymerization to produce mechanically robust polymer-coated objects [109, 110].

An attractive approach to controlled polycondensation developed by Yokoyama takes advantage of a biphasic system using phase-transfer catalysis (scheme 1.14) [111, 112]. The authors begin by dispersing the solid monomer, potassium-4-bromomethyl-2-*n*-octyloxybenzoate, in a nonsolvent. They also dissolved an initiator, 4-nitrobenzylbromide, into the liquid phase. By using 18-crown-6 as a phase transfer



SCHEME 1.13 Catalytic cycle for Kumada catalyst-transfer polymerization of poly(3-hexylthiophene).



SCHEME 1.14 Schematic showing phase-transfer catalysis polycondensation.

catalyst, a small amount of the monomer is solubilized into the liquid phase, where it can react with the initiator (and later, the polymer chain end) to form a *p*-nitrobenzyl ester. A key factor in this approach is careful choice of the molar equivalents of the initiator and phase transfer agent, so that only a small monomer is allowed in solution at any time, suppressing self-condensation. However, if the concentration of the crown ether is too low, only small amounts of monomer will enter the reactive liquid phase and homogenous growth of the polymer chains will not be possible. Therefore, accurately balancing solubility is critical. If the monomer is too soluble, the self-condensation reaction will not be sufficiently suppressed. On the other hand, the polymer chains have to be soluble in order to achieve significant molecular weight. Certainly, the fine balance of these parameters calls into question its versatility with other molecular systems. Nonetheless, it provides a rather simple way in which a stepwise mechanism can be converted to chainwise or even "living" polymerization.

1.4 CONCLUSIONS

Free radical and condensation polymerization reactions allow the synthesis of some of the world's most important commodity polymers, as well as cutting edge materials in research laboratories across the globe. Furthermore, recent advances in controlled polymerization techniques have offered the possibility to change the growth mechanism to a "living" polymerization in both cases. The kinetics and resulting molecular weight distributions for each polymerization have been discussed.

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