4

FREE RADICAL POLYMERIZATION

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4.1 INTRODUCTION

There have been many amazing discoveries in human history. Some of them have a direct utility and others have been combined with other innovations to fit an enormous diversity of applications. Free radical polymerization (FRP) is one of these discoveries. The first papers in this area were published in the 1940s and 1950s. However, even before that, in the 1930s, the applicability of this technique rapidly propelled this method to the commercial scale for the manufacture of diverse polymers starting from oil derivatives. Nowadays, FRP is the solid foundation of many industrial processes and a source of a number of polymeric materials. Materials such as polyethylene, polystyrene, polyvinylalcohol, polyvinylacetate, polybutadienes, and other well-known commodities have significantly improved day-to-day life. However, the considerable growth of this petrochemical segment over seven decades is now in danger because of environmental issues and high oil prices. Hence, to improve profit margins and avoid reputation losses, the industry has been moving toward bioresourced polymers during the last two decades. In addition, during the mid-1990s, FRP was revitalized with the introduction of the reversible deactivation techniques—commonly known as *controlled/living RP* [1–3]—opening the possibility to form very diverse block copolymers or more complex structures, which could not be synthesized earlier by FRP techniques. The ability to manipulate and control the termination reaction is a major milestone that represents a good possibility to produce an alteration in the landscape of vinyl polymers.

The crucial feature of an FRP is an adjustable radical source, which is commonly materialized by a thermolabile substance—or initiator—that splits apart under heating to form free radicals, that is, highly reactive species with an unsatisfied electron valence pair. At the simplest, these species add to a monomer molecule to initiate propagation and turn out to be one of the end groups of a linear chain. Generally, the rate of addition of a monomer is higher if a resonance-stabilized radical is formed from a non-resonance-stabilized monomer and vice versa.

To be polymerized, vinyl monomers use the property that with the addition of each monomer, the resulting free radical maintains the same structure as that of the attacking radical and sustains the ability to add new molecules. In the formation of monomeric unit chains, the variation of entropy is negative, that is, the monomer-to-polymer conversion entails a reduction of disorder, while a compensation of the enthalpy term is observed. The alteration results in a negative variation of enthalpy; therefore, the reaction is exothermic.

The rates of addition to the unsaturated 1- and 1,1-disubsituted olefins are thought to be mainly determined by polar factors. Electron-withdrawing substituents will facilitate the addition of nucleophilic species, while electron-donating substituents will enhance the addition of electrophilic species. The addition of an initiating free radical to a monomer is called the *initiation step*, which is the first step of a chain reaction or propagation that ends through a termination reaction, in which two radicals interact in a mutually destructive reaction to form covalent bonds and cease propagation.

Generally, peroxides and azo compounds are commercially employed as initiators of a large number of monomers. The monomer and initiator industries are based on mature technologies and very few improvements centered on lower energy processes have been developed in recent years. The major worldwide players of organic peroxide initiators are Arkema, Akzo Nobel, Degussa-Huls

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AG, and Nippon Oil & Fats Co. Bulk amounts of styrene, vinylacetate, vinylchloride, ethylene, and numerous other monomers are produced worldwide by many petrochemical companies.

This chapter deals with the description of the FRP mechanism and presents a review of the latest advances in the termination reaction control.

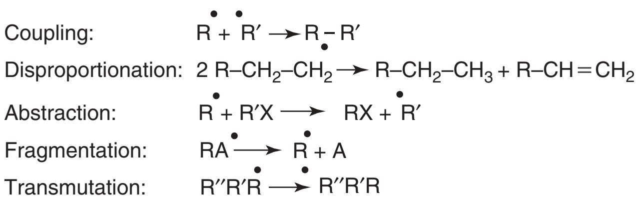
4.2 BASIC MECHANISM

The most conventional kinetic scheme of FRP includes initiation, propagation, and bimolecular termination reaction steps. Additional reactions such as chain transfer are introduced to improve the process description. Free radicals are highly reactive chemical species produced by the homolytic dissociation of covalent bonds. Such species are produced through physical (thermoexcitation, radiation) or chemical methods (oxidation–reduction, addition, etc.). Generally, their survival time is less than a second, except for those radicals highly stabilized by specific chemical groups; the hybridization state is sp^2.

Free radicals react in six different manners as illustrated in Scheme 4.1 [4, 5].

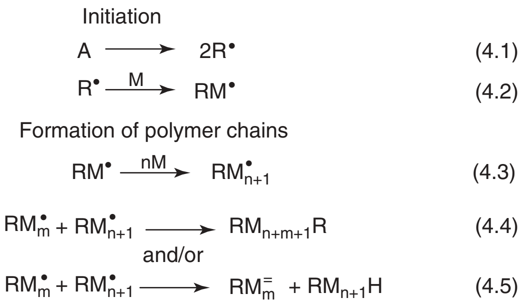
In an FRP, all these reactions are susceptible to occur, but in a concentrated monomer environment, the dominating reactions are the addition (propagation) and termination by disproportionation or coupling. The fragmentation, abstraction, and transmutation reactions are detrimental for the chain formation; however, sometimes they can be induced to regulate the degree of polymerization.

The central mechanism of chain formation involves the generation of free radicals (reaction (i)), the initiation (reaction (ii)), propagation (reaction (iii)), and termination (reactions (iv) and (v)) (Scheme 4.2). The radical generation and the first monomer *addition* to an initiating radical constitute the initiation step, whereas the successive monomer *additions* over a new free radical and the termination of chain growth by *disproportionation* and/or *coupling* actually constitute the formation of chains as represented in Scheme 4.2.



Addition:	$\dot{R} + H_2C{=}CHR_1 \longrightarrow R{-}CH_2{-}\dot{C}HR_1$
Coupling:	$\dot{R} + \dot{R}' \longrightarrow R{-}R'$
Disproportionation:	$2\ R{-}CH_2{-}\dot{C}H_2 \longrightarrow R{-}CH_2{-}CH_3 + R{-}CH{=}CH_2$
Abstraction:	$\dot{R} + R'X \longrightarrow RX + \dot{R}'$
Fragmentation:	$RA^{\bullet} \longrightarrow \dot{R} + A$
Transmutation:	$R''R'\dot{R} \longrightarrow R''\dot{R}'R$

Scheme 4.1 Free radical reactions.



Initiation

$$A \longrightarrow 2R^{\bullet} \quad (4.1)$$

$$R^{\bullet} \xrightarrow{M} RM^{\bullet} \quad (4.2)$$

Formation of polymer chains

$$RM^{\bullet} \xrightarrow{nM} RM^{\bullet}_{n+1} \quad (4.3)$$

$$RM^{\bullet}_{m} + RM^{\bullet}_{n+1} \longrightarrow RM_{n+m+1}R \quad (4.4)$$

and/or

$$RM^{\bullet}_{m} + RM^{\bullet}_{n+1} \longrightarrow RM^{=}_{m} + RM_{n+1}H \quad (4.5)$$

Scheme 4.2 Reactions induced by an initiating radical generated from the initiator A.

4.2.1 Initiation

Chemical initiation involves the decomposition of initiator molecules A to form very active primary radicals $R^{\bullet}$ capable of initiating new polymer chains. The stability of A is measured by the half-life time ($t_{1/2}$) defined in terms of its dissociation constant k_d as follows:

$$[A] = [A]_0 \exp\left(-k_d t\right) \quad (4.1)$$

or

$$\ln\frac{[A]_0}{[A]} = k_d t \quad (4.2)$$

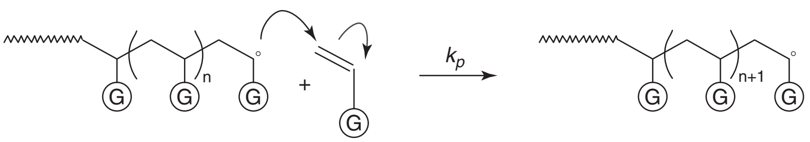
If $[A]_0/[A] = 2$, then

$$t_{1/2} = 0.693/k_d \quad (4.3)$$

Owing to the very close proximity of any two radicals generated from A, not all of them can eventually escape from their solvent "cage" to react with monomer molecules. Some radicals will either self-terminate or will react with other near-neighboring molecules before diffusing out of the cage. To account for this, an empirical initiator efficiency factor, f, which represents the fraction of all generated initiator primary radicals leading to the formation of new polymer chains, has been introduced. This parameter may have values between zero and unity. Even if the radical $R^{\bullet}$ escapes from the cage, any of the possible side reactions (reactions (ii)–(v)) can be produced, although they are minimized by the ubiquitous presence of monomer.

The concentration of initiating radicals $R^{\bullet}$ depends on [A], k_d, and f. The initiator's efficiency itself depends on the ability of $R^{\bullet}$ to add to the monomer instead of undergoing termination. Thus, the efficiency depends on the monomer concentration and the ratio k_i/k_p, where k_i is the rate constant of the initiation reaction and k_p is the rate constant of the propagation reaction.

Only some radicals $R^{\bullet}$ succeed in the initiation step to form $RM^{\bullet}$, which becomes the precursor of a polymer chain. Initiating radicals are generated from a compound



Scheme 4.3 Schematic representation of the propagation reaction.

A with kinetics governed by k_d, the rate constant of dissociation.

4.2.2 Propagation

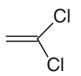
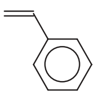
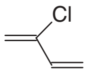
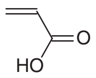
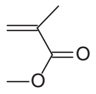
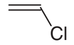
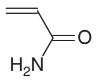
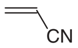
It is an addition reaction that generates the polymer chain by a series of fast successive steps of monomer addition over the propagating radical. The microstructure of the polymer, which determines its properties, is established through this reaction.

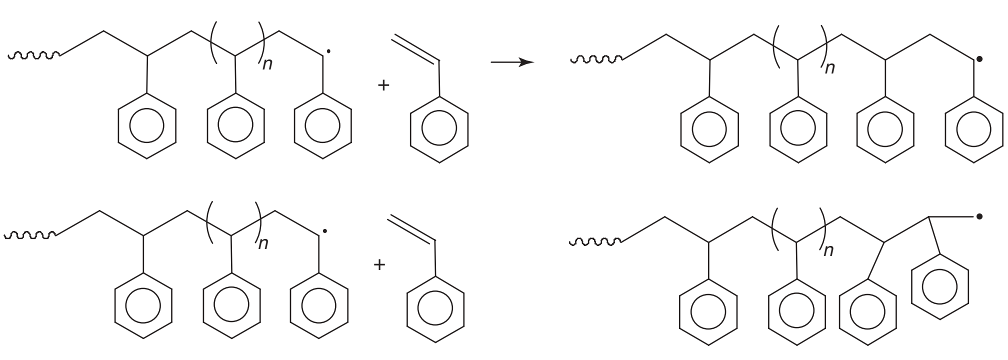
The addition of a monomer unit results in a radical structurally similar to the radical before the addition; therefore, there is no alteration in the stability of the growing radical. The group substituent (G in Scheme 4.3) has an effect on the stability of both the double bond and the resulting radical. An increase in the stabilizing effect of G produces a reduction of k_p, the rate constant of the propagation reaction, as indicated in Table 4.1. To simplify the mathematical treatment of the kinetics in the radical polymerization, it is assumed that k_p is independent of the size of the propagating radical. Nevertheless, it is known that the diffusivity of species affects the rate constant, a fact that is more evident at low molecular weights (MWs).

Given that the propagation involves the addition of unsymmetrical alkenes, regioselectivity is an important issue. As a general rule, is less-substituted carbon is more preferred to produce a bond. However, the more-substituted carbon is not totally discriminated. Thus, for a given monomer, different modes of bonding are observed and their percentages depend on the nature of substituent G. For a substituent providing a strong stabilization to the end-free radical, the regioselectivity increases, that is, the head-to-tail addition (Scheme 4.4) is predominant in comparison with the head-to-head addition.

For conjugated dienes such as butadiene, the delocalization of the radical induces the formation of species with the unpaired electron in carbon 2 or carbon 4 at the last monomer unit in the propagating chain. Such species can then add the next butadiene unit by carbon 1 or carbon 4 forming additions called 1–2 or 1–4, respectively. In the case of monosubstituted dienes, such as isoprene or chloroprene, additions 3–4 can also occur depending on

TABLE 4.1 Propagation Rate Constants of Some Monomers at 25 °C

Monomer	Chemical Structure	k_p (l/(mol s))
Vinylidene chloride		9
Styrene		35
Chloroprene		228
Acrylic acid		650
Methyl methacrylate		1,010
Vinyl chloride		3,200
Acrylamide		18,000
Acrylonitrile		28,000



Scheme 4.4 Head-to-tail and head-to-head (bottom) additions.

the regioselectivity of the monomer. As an example, in the polymerization of butadiene, 1–4 additions account for 80% of the total additions.

In FRP, the monomer addition is practically not stereoselective, as at the moment of the monomer additions, there is no preferred conformation of the radical. Therefore, there is no regular conformation of monomer units in the polymer chain. The sp^2 hybridization in the carbon atoms of a double bond and the resulting π bond favor a planar arrangement of the two carbon atoms and the four immediate ligand atoms. On the other hand, the geometry of alkyl radicals is considered to be a shallow pyramid, somewhere between sp^2 and sp^3 hybridization; the energy required to invert the pyramid is very small. In practice, one can usually think of alkyl radicals as if they were sp^2 hybridized and then their conformation is undefined at the moment of the radical addition over the planar double bond. Only the steric hindrance or electrostatic forces slightly affect the orientation of the monomer substituent and the resulting polymer is atactic, that is, it does have a random spatial orientation of substituent G. The formation of isotactic or syndiotactic polymers is not possible via radical polymerization.

4.2.3 Termination

Termination is also a fundamental reaction. Since the rate constants of this reaction are very high ($k_t = 1 \times 10^7$ to 1×10^8 l/(mol s)), the very low concentration of propagating chains is critical for the radical to survive some seconds or fractions of a second before the encounter with another radical species. A propagating chain can be deactivated through one of several possible reactions to become a polymer molecule. Termination is generally associated with reactions involving coupling and disproportionation processes, but a propagating radical can also participate in abstraction reactions resulting in growth deactivation; this type of reaction is called *chain transfer*.

The formation of polystyrene chains initiated by radicals generated by thermolysis of AIBN (2,2′ azobisisobutyronitrile) can be quoted as an example. The 2-cyanoprop-2-yl radical adds to styrene, opening the π bond to form a new carbon-centered radical. This new species rapidly add to another styrene molecule and chain growth is produced by the successive additions of new styrene in a repetitive process occurring at very high rates. The active center is thus continuously relocated at the end of the growing polystyrenyl chain. This propagation stops when two radical species encounter each other and recombine to form a larger chain or disproportionate resulting in two inactive polystyrene chains. Termination rate is diffusion controlled, which means that its speed is determined by how fast the molecules move.

The speed of movement mainly depends on the molecule size and some other related factors, such as the number of obstacles around the polymer and the temperature of the system. In fact, this is the origin of the complexity of the termination reaction.

There is no precise method for the measurement of the termination rate. Major difficulties in rate constant (k_t) determination arise from the diffusion control of this reaction. Termination rate may depend on segmental and translation diffusion (and reaction diffusion) of radical species occurring in an increasingly viscous medium that change with monomer conversion. In other words, because of the decrease of the diffusion coefficient with molecular size, the termination rate coefficient is lower at higher chain lengths.

The size or MW is self-regulated by the termination reaction and the inherent side reactions. Externally, MW can be also adjusted by the reaction conditions. An increase of temperature causes faster AIBN decomposition, resulting in a lower MW because more chains are created; on the contrary, higher pressure increases the propagation and inhibits the termination resulting in higher MW. The increase of the AIBN concentration has a similar effect to that of the increase of temperature.

4.3 OTHER FREE RADICAL REACTIONS

4.3.1 Chain Transfer to Small Species

A propagating chain (live species) can also terminate via chain transfer reaction to a small molecule. This will lead to termination of the propagating chain, along with the generation of a radical on the small molecule that can initiate another propagating chain. This is schematically represented in Scheme 4.5, where $P_n{}^\bullet$ is a propagating chain having n number of units, TA is a small molecule to which the activity is being transferred, D_n is dead polymer having n number of units, and $A^\bullet$ is the radical resulting from the activation of the small molecule. In the process, the atom or species T is transferred to the growing chain and is incorporated in the dead polymer molecule. Usually, the net effect of the chain transfer is negligible on the polymerization rate, since there is no net creation or destruction of radicals (their *nature* of them changes but *not* their *number*), but it causes a decrease in MW. However, other effects may occur depending on the relative values of k_{trTA} and k_{iA} with respect to k_p. The units of the rate coefficients are liter per mole per second or cubic meter

$$P_n{}^\bullet + \mathrm{TA} \xrightarrow{k_{trTA}} D_n + \mathrm{A}^\bullet$$

$$\mathrm{A}\bullet + M \xrightarrow{k_{iA}} P_1\bullet$$

Scheme 4.5 Simplified mechanism of chain transfer to a small species TA.

per mole per second. It is common practice to report the ratio of the transfer rate coefficient to the propagation rate coefficient, and this quantity is denoted as transfer constant $C_{\mathrm{trTA}} = k_{\mathrm{trTA}}/k_{\mathrm{p}}$; it is defined to measure the ability of each substance to produce a chain transfer reaction.

The small species TA can be a monomer (M), a solvent (S), a chain transfer agent (CTA), an initiator (I), or an impurity (X) in the system. Chain transfer reactions occur spontaneously because of the inherent reactivity of free radicals; however, such reactions can be also induced by adding a CTA having a high proclivity to react with growing chains. A chain transfer agent is a species specifically added to the system to control the MW. In the following, the characteristics of the chain transfer reaction to specific species are considered.

4.3.2 Chain Transfer to Monomer

This reaction is generally described by the simple scheme shown above (Scheme 4.5) with TA being monomer and T (the transferred atom) being H; therefore the rate of C_{M} is k_{trM} [P][M], where [P] is the total concentration of propagating chains. However, Moad and Solomon [5] consider that this mechanism is reasonable for monomers having aliphatic labile hydrogens (such as methyl methacrylate, vinyl acetate, and allyl monomers), but it is not likely to occur for monomers having only vinylic or aromatic protons (such as styrene or vinyl chloride), due to the difficulty of breaking the strong C–H bond in these cases. The details of the exact mechanisms for these monomers remain to be of a speculative character. Table 4.2 lists C_{M} values for some common monomers. In the absence of other transfer reactions, chain transfer to monomer will impose an upper limit to the maximum MW achievable in the polymerization of the corresponding monomer. This does not mean that this reaction will in general be the controlling step determining the MW; indeed bimolecular termination usually plays this role. However, there are monomers for which C_{M} is so high (e.g., vinyl chloride) that transfer to monomer becomes the controlling factor. High values of transfer constants to monomer are associated with high reactivity of the propagating radical.

TABLE 4.2 Values of Chain Transfer to Monomer Constant C_{M} for Some Common Monomers

Monomer	Temperature (°C)	$C_{\mathrm{M}} \times 10^4$
Acrylonitrile	60	0.26–1.02
Butyl acrylate	60	0.333–1.05
Ethylene	60	0.4–4.2
Methyl methacrylate	60	0.07–0.18
Styrene	60	0.07–1.37
	70	0.6–2.0
Vinyl acetate	60	1.75–2.8
Vinyl chloride	50	8.5
	60	12.3

All values are taken from Reference [6] except for vinyl chloride [7].

4.3.3 Chain Transfer to Initiator

Values for chain transfer constants to initiator are listed in Table 4.3. Note that these values are generally larger than those of transfer to monomer; however, the effect of this reaction is attenuated by the fact that the initiator is present in very small amount with respect to the monomer, as the rate of transfer to initiator is k_{trI} [P][I].

4.3.4 Chain Transfer to Solvent and Chain Transfer Agents

When polymerization takes place in a solvent, it is important to be aware of possible chain transfer to solvent reactions. On the other hand, there are many instances, especially in industrial processes, in which it is convenient to include in the polymerization recipe some species (called *chain transfer agent*) that have a

TABLE 4.3 Values of Chain Transfer to Initiator Constant C_{M} for Some Common Polymerization Systems

		C_{I}		
Initiator	Temperature (°C)	Styrene	Methyl Methacrylate	Vinyl Acetate
AIBN (2,2′ azobisisobutyronitrile)	60	0–0.16	0	—
Benzoyl peroxide	60	—	0–0.02	0.032–0.15
	70	0–0.18	—	—
	80	0.13–0.813	—	—
Lauroyl peroxide	60	—	—	0.10
	70	0–0.024	—	—
Palmytoil peroxide	60	—	0.10–0.17	0–0.16
	70	0.142	—	—
Tert-butyl peroxide	70	0.031	—	—
	80	0.0022–0.0033	—	—

All values are taken from Reference [6].

TABLE 4.4 Values of Chain Transfer to the Solvent or CTA constant C_S/C_{CTA} for Some Common Polymerization Systems

		C_S		
Solvent or CTA	Temperature (°C)	Ethylene	Methyl methacrylate	Styrene
Acetone	60	—	0.195	0.32–4.1
	80	—	0.225–0.275	—
	130	160–168	—	—
1-Butanethiol	60	—	0.66–0.67	21.0–25
	70	—	—	15.0
	80	—	—	17.0
	130	5.8	—	—
Carbon tetrachloride	60	—	0.42–20.11	69–148
	70	—	1.74	—
	80	—	2.4–24.4	133
	140	1,600–180,000	—	—
Chloroform	60	—	0.454–1.77	0.41–3.4
	80	—	1.129–1.9	0.50–0.916
	140	3,210–37,600	—	—
Ethyl benzene	60	—	0.766	0.67–2.7
	80	—	1.311–2.1	1.07–1.113
	100	—	—	1.38–2.33
Hexane	100	—	—	0.9
	130	68	—	—
	189	225	—	—
Propane	130	27–31	—	—
Toluene	60	—	0.17–0.45	0.105–2.05
	70	—	0.561	—
	80	—	0.292–0.91	0.15–0.813
	100	—	—	0.53–0.8
	130	130–180	—	—
1-Dodecanethiol	60	—	0.7	—
	70	—	0.55	0.69–19
	80	—	0.42	—
	90	—	0.33	1.3
	100	—	—	13.0
	110	—	—	26.0

All values are taken from Reference [6].

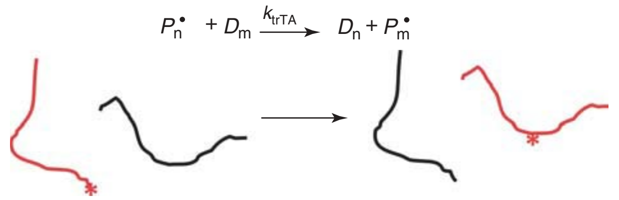
high chain transfer constant in order to lower the MW of the polymer being formed. Among many different substances used for that purpose, thiols are by far the most popular chain transfer agents. Evidently, depending on the nature of T, the chain transfer reaction occurs at different rates. The addition of a CTA is rather common in, for example, emulsion polymerization, in which the compartmentalized nature of the reaction tends to produce very high MW polymer due to the relative isolation of the propagating radicals in very small particles. The rates of reaction of chain transfer to a solvent and to a CTA are conceptually the same: k_{trS} [P][S] and k_{trCTA} [P][CTA], respectively. The values of chain transfer constants to solvent and to CTAs are usually reported in one table, as they lie in a continuum going from low values for solvents to rather high values for CTAs (see Table 4.4 for illustrative values).

4.3.5 Chain Transfer to Impurities

Impurities can also act as chain transfer agents. In some instances, as in the production of low density polyethylene via high pressure radical polymerization, impurities and/or the so-called inerts (methane, ethane, and propane), which come as impurities in the ethylene, are used as effective chain transfer agents to lower the MW of the polymer.

4.3.6 Chain Transfer to Polymer

The mechanism of Scheme 4.5 can also occur when the TA species is not a small molecule, but an inactive or a dead polymer instead. In this case, it is convenient to rewrite the reaction mechanism for clarity (Scheme 4.6).



$$P_n^\bullet + D_m \xrightarrow{k_{trTA}} D_n + P_m^\bullet$$

Scheme 4.6 Simplified mechanism of chain transfer to a small species TA.

Evidence suggests that the mechanism proceeds by hydrogen abstraction, but this has been proved only for a few monomers [5]. However, since the hydrogen abstraction on the inactive chain D_m can occur at any monomeric unit along the chain, the free radical left in the reactivated chain will most likely give rise to a branch (unless the activation occurs at a chain end), once that monomer propagates from the just activated site. The mechanism represented in Scheme 4.6 corresponds to the intermolecular chain transfer, which involves two independent polymer chains (one active and the other dead); it is also possible that intramolecular chain transfer occurs (also called *backbiting*), in which the hydrogen abstraction occurs in the same active chain, a few carbons (about five) before the active end of the growing polymer. Intermolecular transfer will give rise to long branches, while intramolecular transfer will be the origin of short branches. Both short and long branches have a profound influence in the physical and rheological properties of the polymer formed.

The experimental determination of the chain transfer to polymer constant is difficult, as it does not necessarily result in a decrease of the MW of the polymer. Therefore, there is a large spread of values reported in the literature for this constant [6]. Since it involves hydrogen abstraction, the activation energy of chain transfer to polymer is relatively high (compared to propagation) and it is reported in the range of 9000 cal/mol in the case of ethylene [8]. Reaction conditions that favor transfer to polymer are high temperatures and high conversions (due to the high concentration of dead polymer present).

4.3.7 Backbiting

Recent studies convincingly proved the existence of mid-chain radicals (MCRs) and the secondary reactions that are responsible for the formation of MCRs during the polymerization process [9]. For instance, the polymerization of butyl acrylate (BA), and in general of the acrylate monomer family, proceeds with the presence of two radicals: a chain-end (secondary) radical and an MCR (tertiary and significantly less reactive) that are predominantly formed by the backbiting process, an intramolecular transfer to polymer, that produces short-chain branches.

The MCRs can also be formed by intermolecular chain transfer to polymer (leading to long-chain branches), but its contribution is small.

Backbiting generates a tertiary (mid-chain) radical, R_t, by abstraction of a hydrogen atom from an acrylate unit on the backbone of the secondary (chain-end) radical R_s, most likely via the formation of a six-membered ring, as shown in Scheme 4.7 for BA. Subsequent addition of monomer to R_t creates a short-chain branch (SCB) in the polymer and leads to re-formation of a chain-end radical. The propagation rate coefficient for monomer addition to the MCR, k_{pt}, is significantly lower than that for addition to the secondary chain end [10].

4.3.8 Inhibition

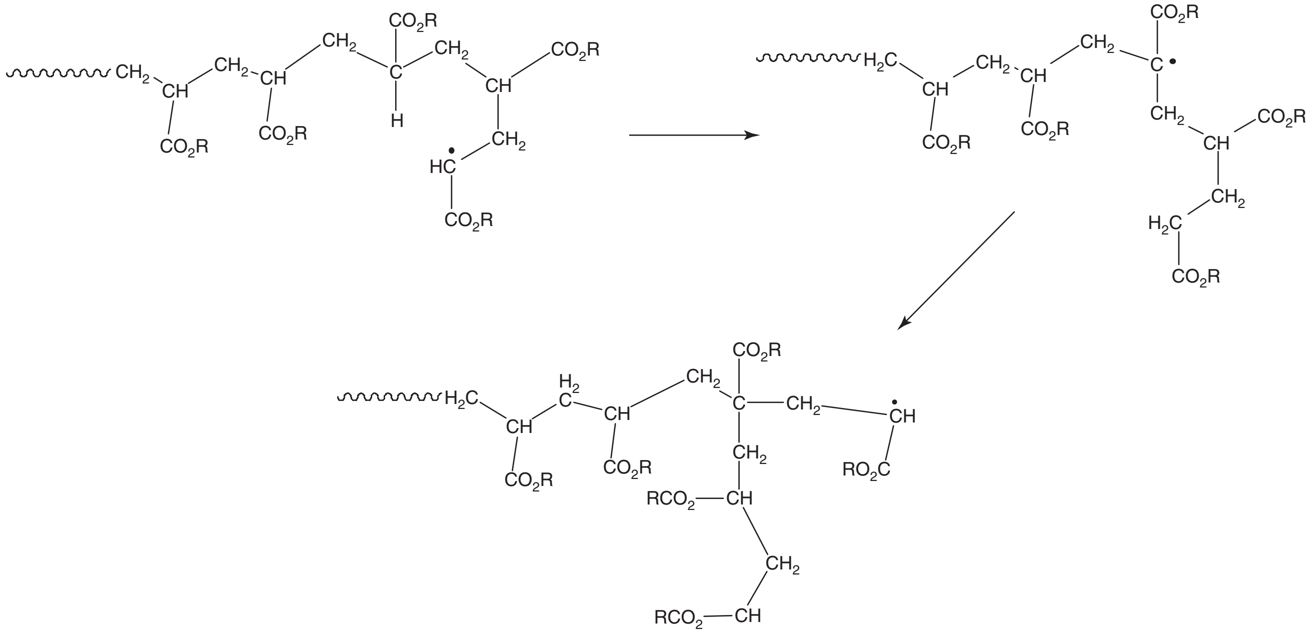
An inhibitor is used to completely stop the conversion of monomer to polymer produced by accidental initiation during storage. To induce the inhibition, some stable radicals are mixed with the monomer. Such radicals are incapable for initiation the polymerization, but they are very effective in combining with any propagating radical. Diphenylpicrylhydrazyl and tetramethylpiperidinyloxy (TEMPO) are two examples of radicals used to inhibit the radical polymerization. The chemical reactions of the inhibition produced by these compounds are shown in Scheme 4.8.

It is worth mentioning that these radicals are very effective at low temperature, but at temperatures above 100 °C, these reactions are reversible. Some other compounds, such as phenols, quinones or hydroxyquinones, or even molecular oxygen, are also employed to inhibit the polymerization; the mechanism of action of these compounds involves the transformation of the propagating radical to an oxygen-centered radical that is unable to initiate polymerization. The case of quinones is shown in Scheme 4.9.

4.4 KINETICS AND POLYMERIZATION RATE

In its simplest and essential form, the mechanism of FRP involves the steps of initiation (radical generation), propagation, and bimolecular termination. The corresponding reaction rates for the three steps are denoted by R_i, R_p, and R_t, respectively. To derive a rate expression, for the sake of generality, the simplified mechanism and expressions in columns 2 and 3 of Table 4.5 are considered first; later a more detailed mechanism (column 4 of Table 4.5), specific for chemical initiation and involving termination by disproportionation and combination, is analyzed.

In FRP, the progress of the reaction is measured in terms of conversion of monomer into polymer (this is different

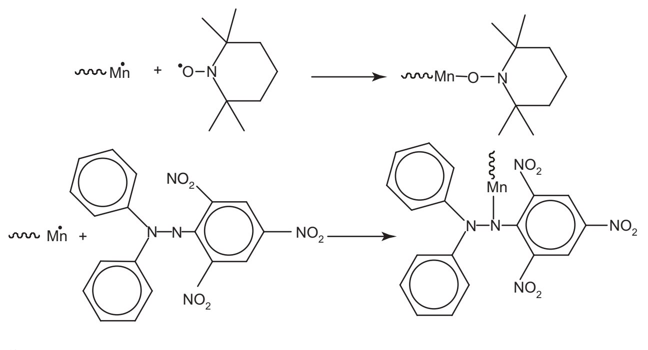


Scheme 4.7 Backbiting reaction or intramolecular transfer to polymer.

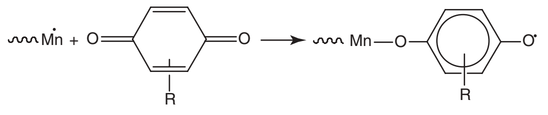
TABLE 4.5 Simple Kinetic Mechanism for Free Radical Polymerization

Reaction step	Simplified Mechanism	Rate Expression	Detailed Mechanism for Chemical Initiation
Initiation	None specified	R_i	$I \xrightarrow{k_\mathrm{d}} 2R$ $R + M \xrightarrow{k_\mathrm{i}} P_1$
Propagation	$P + M \xrightarrow{k_\mathrm{p}} P$	$R_\mathrm{p} = k_\mathrm{p}[\mathrm{M}][\mathrm{P}]$	$P_n + M \xrightarrow{k_\mathrm{p}} P_{n+1}$
Termination	$P + P \xrightarrow{k_\mathrm{t}} D$	$R_\mathrm{t} = k_\mathrm{t}[\mathrm{P}]^2$	$P_n + P_m \xrightarrow{k_\mathrm{td}} D_n + D_m$ $P_n + P_m \xrightarrow{k_\mathrm{tc}} D_{n+m}$

P, M, and D are the growing radicals, monomer, and dead polymer, respectively. I and R are the chemical initiator and primary radicals, respectively. When included, the subindex in polymeric species (P and D) represents chain length.



Scheme 4.8 Schematic representation of inhibition reactions with TEMPO and with diphenylpicrylhydrazyl.



Scheme 4.9 Schematic representation of inhibition reactions with quinones.

from the polycondensation case, in which the conversion is measured in terms of reacted functional groups). It is assumed that, independently of the initiation method used, most of the monomer is consumed by the propagation reaction (this is the so-called long chain hypothesis or LCH); therefore, the rate of polymerization is defined as

$$R_\mathrm{p} = -\frac{\mathrm{d[M]}}{\mathrm{d}t} = k_\mathrm{p}\,[\mathrm{M}]\,[\mathrm{P}] \tag{4.4}$$

with units of liter per mole per second. The experimental measurement of [P] is difficult[1] given the low concentrations of growing radicals in a typical polymerization; therefore, it is convenient to write this quantity in terms

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[1] Electron spin resonance (ESR), also called *electron paramagnetic resonance* (*EPR*), can be used to experimentally measure [P] [72].

of other species that are easier to measure. To do this, a differential mass balance on [P] is written:

$$\frac{d[P]}{dt} = R_i - k_t[P]^2 \tag{4.5}$$

The growing radicals are very reactive intermediate species that conform to what in chemical kinetics is called a *quasi-steady state* (QSS) or *stationary state hypothesis* [11, 12]. This means that the rate of formation and consumption of that species become nearly equal in a very short timescale; as a consequence, the absolute value of the derivative becomes very small and negligible compared with the derivatives of other species in the system (e.g., d[M]/dt) and for practical purposes can be approximated as zero. Note, however, that this does not imply constancy of the value of [P], as sometimes interpreted by some authors, but this will be more clear later. By making the QSS approximation in Equation 4.5

$$R_i - k_t[P]^2 \approx 0 \tag{4.6}$$

and

$$[P] = \left(\frac{R_i}{k_t}\right)^{1/2} \tag{4.7}$$

Equation 4.7 is a general expression for the QSS concentration of growing radicals in a FRP. Other features related to the QSS are noticeable from this expression. (a) The high reactivity of the growing radicals is reflected in a rather high value of k_t (in the order of 10^7–10^8 l/(mol s)), which is also consistent with a rather low value of the QSS concentration of [P] (typical values are 10^{-7} to 10^{-9} mol/l) as this concentration is inversely proportional to the value of k_t. (b) Since R_i and k_t may change during the course of a polymerization (as they usually do), the value of [P] will not be constant; it will change following the changes in the "slow" variables of the system (initiator and monomer concentration, kinetic coefficients, etc.) instead.[2] Finally, in writing expressions 4.6 and 4.7, the convention that a single radical has been consumed by the termination reaction (instead of the other convention in which two radicals are consumed) has been used. It has been recently noted that the convention used here is the correct one [13], according to the rules of formulation of kinetic rate equations. Nonetheless, the reader should be aware that both conventions are still amply used in the technical literature.

When a specific type of initiation is used, the expression for R_i will be more detailed. The fourth column in Table 4.5 includes the kinetic mechanism for the commonly used initiation via a chemical initiator (such as a peroxide or an azo compound). In that case, the effective rate of generation of polymeric radicals is given by the second initiation step. The resulting expression is

$$R_i = k_i[R][M] \tag{4.8}$$

Again, it is desirable to write the rate expression without explicitly including the concentration of primary radicals R, which is difficult to measure. A differential balance for the primary radicals, followed by the application of the QSS, results in

$$\frac{d[R]}{dt} = 2fk_d[I] - k_i[R][M] \approx 0 \tag{4.9}$$

which, combined with Equation (4.8), results in

$$R_i = 2fk_d[I] \tag{4.10}$$

The factor f, called *initiator efficiency*, takes into account that not all the primary radicals R effectively initiate polymer chains; some can be lost due to the so-called cage effect. This implies secondary reactions of the radicals within a "cage" of solvent surrounding the initiator [5] (the effect can be more pronounced at high conversions/viscosities due to diffusion limitations). The values of f usually lie in the range 0.3–0.8.

The resulting expressions for the reaction rate are then

$$R_p = k_p[M]\left(\frac{R_i}{k_t}\right)^{1/2} \tag{4.11}$$

$$R_p = k_p[M]\left(\frac{2fk_d[I]}{k_t}\right)^{1/2} \tag{4.12}$$

for any R_i or for chemical initiation, respectively.

4.4.1 Variations of k_p and k_t with Length and Conversion: Autoacceleration

In the above derivations, the values of k_p and k_t have been implicitly considered as constants independent of the reaction medium and of the chain length of the polymeric chains involved in the reactions. For propagation, it is known that this is true only to a first approximation, since there is increasing evidence that the value of k_p should be greater for the first few propagation steps, when the chain

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[2] The apparent paradox of a zero derivative for [P] with the simultaneous possibility of a changing value for the same quantity is cleared by noting that the time derivative of [P] is not really zero; it is very small instead, compared with the derivatives of other "slow" species in the system. In dynamic terms, the time for [P] to reach a QSS value (e.g., from the start of a polymerization when [P] = 0) is extremely short (in the order of a second) compared with the characteristic time of a polymerization (minutes or hours). Seen from the point of view of the polymerization timescale, the value of [P] is instantaneously and continuously adjusted (and therefore always at a QSS value) to reflect the slow changes occurring for the slow species in the reaction system.

length of the growing chain is in the single-digit range, than for longer chains (length > 20) [5]. In addition, it is well established that the termination among radicals is a diffusion-controlled process, which may be affected by the reaction medium (polymer concentration, temperature) and the lengths of the individual chains reacting; therefore, the value of k_t is not really constant.

A phenomenon that has a particularly significant effect in the value of k_t and has been studied for many years is the so-called gel effect, which is also known as *Trommsdorff* or *Norrish–Smith effect* [14, 15]. This consists in an autoacceleration of the reaction rate as the conversion increases, and it is due to an effective decrease in the termination rate as the growing radicals encounter more difficulty in diffusing in the increasingly viscous medium. As the value of k_t decreases by several orders of magnitude in the course of the polymerization as a consequence of this phenomenon, the concentration of growing radicals [P] increases, as well as the polymerization rate (Eq. 4.7, 4.11, and 4.12). A broadening of the molecular weight distribution (MWD) simultaneously occurs. The gel effect is a complex phenomenon and it is mainly determined by translational (center of mass) and segmental diffusion (internal movement or rearrangement of the polymer coil) [16], although other motion mechanisms can also have an influence on it, for example, reptation and reaction-diffusion (chain-end motion by monomer addition at the reactive end). Experimental evidence for the gel effect usually takes the form of a rise in the slope of a plot of monomer conversion versus time. At low conversion, the slope is nearly constant. At intermediate levels of conversion, the magnitude of which depends on the monomer and other factors, the polymerization rate begins to increase to a much higher level, resulting in a steeper slope.

The quantitative modeling of this phenomenon has been addressed by many authors, but the problem is rather complex, and so far no single model is generally accepted. Most of the modeling studies have used styrene and methyl methacrylate polymerization experimental data for comparison, as in these systems the presence of the gel effect is quite clear. For several other systems, the extent of the effect has not been clearly assessed. It has been argued that the diffusion-controlled termination is present from the very start of the polymerization [17]; however, the sharp autoacceleration of the reaction rate (or gel effect onset) occurs at some moderate-to-medium conversion (20–80% depending on the system) and this point is expected to be correlated with the polymer concentration needed for chain entanglement [18]. Early attempts at modeling this phenomenon were mostly empirical or semi-empirical [19–26], in which the values of the propagation and termination constants were written as a function of some system parameters such as viscosity, conversion, temperature, or free volume. For example, see the models of Friis and Hamielec [21] (temperature and conversion), Marten and Hamielec [20], and Ross and Laurence [22] (temperature and free volume). Other models were based on more fundamental concepts [17, 27–29], for example, reptation [29], or in the division of growing radicals into two classes: one below the critical length for chain entanglement and one above this limit [30–32].

Some reviews on previous gel effect models or on the concepts on which they are based have also been published [33–36].

For the systems in which this phenomenon is clearly present, its effects on reaction rate and process control can be significant, and so this has important practical consequences for the design of polymerization reactors and processes, especially in bulk polymerization. When solvents are used, the effect is attenuated and/or its onset is retarded to higher conversions, and so at high dilutions, the effect can be very mild or insignificant. In addition, the use of chain transfer agents will diminish the MW of the polymer formed, lowering the viscosity of the reaction medium and therefore retarding or attenuating the effect [36].

At very high conversions, the reaction medium becomes a glassy matrix, and the diffusion is very slow. At this stage, the controlling mechanism for termination is reaction-diffusion, and so the value of the termination constant becomes controlled by the propagation step. The propagation itself may become controlled by diffusion at very high conversions (which is called *glass effect*), but this effect must be separated from the lowering in the initiator efficiency, which also occurs at high conversion due to diffusion limitations. In the case of the bulk polymerization of styrene, the glass effect occurs at monomer conversions roughly above 70–90% where even diffusion of styrene is impeded. A consequence of this phenomenon is the freezing of the reaction mixture at conversions about 95% for styrene.

4.5 MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION

The random character of the events defining the length of each polymeric chain will lead to a distribution of MWs instead of a unique MW as in the case of small molecules. However, in the case where all chains terminate by bimolecular termination, a number average MW can be easily obtained by making the following quotient:

$$M_n = \frac{R_p}{R_i = R_t} M_0 = \frac{k_p[\mathrm{M}][\mathrm{P}]}{k_t[\mathrm{P}]^2} M_0 = \frac{k_p[\mathrm{M}]}{\left(2k_t f k_d[\mathrm{I}]\right)^{1/2}} M_0 \tag{4.13}$$

which represents the ratio of the number of events of chain growth per event of chain initiation for the case of termination by disproportionation (one dead chain per each

TABLE 4.6 Kinetic Scheme for Detailed MWD

Step	Reaction	Rate constant
Initiation	$I \xrightarrow{fk_\mathrm{d}} 2R^\bullet$	k_d
First propagation	$R^\bullet + M \xrightarrow{k_\mathrm{i}} P_1^\bullet$	k_i
Propagation	$P_r^\bullet + M \xrightarrow{k_\mathrm{p}} P_{r+1}^\bullet, \quad r \geq 1$	k_p
Transfer to monomer	$P_r^\bullet + M \xrightarrow{k_\mathrm{trM}} P_1^\bullet + D_r, \quad r \geq 1$	k_trM
Transfer to solvent	$P_r^\bullet + S \xrightarrow{k_\mathrm{trS}} P_1^\bullet + D_r, \quad r \geq 1$	k_trS
Termination by combination	$P_n^\bullet + P_m^\bullet \xrightarrow{k_\mathrm{tc}} D_{n+m}, \quad n, m \geq 1$	k_tc
Termination by Disproportionation	$P_n^\bullet + P_m^\bullet \xrightarrow{k_\mathrm{td}} D_n + D_m, \quad n, m \geq 1$	k_td

$R^\bullet$, $P_r^\bullet$ are primary radicals and length-r growing radicals, respectively. *I, M, S,* and D_r are initiator, monomer, solvent, and length-r dead polymer, respectively.

initiated chain).When termination by combination occurs instead, the above expression must be multiplied by two.

When other termination reactions are also allowed (transfer to initiator, monomer, and solvent), the above expression must be modified, ending up in

$$M_\mathrm{n} = \frac{R_\mathrm{p}}{R_\mathrm{t} + k_\mathrm{trM}[\mathrm{P}][\mathrm{M}] + k_\mathrm{trS}[\mathrm{P}][\mathrm{S}] + k_\mathrm{trI}[\mathrm{P}][\mathrm{I}]} M_0 \quad (4.14)$$

or

$$\frac{1}{M_\mathrm{n}} = \frac{1}{M_0}\left[\frac{k_\mathrm{t} R_\mathrm{p}}{k_\mathrm{p}^2\,[\mathrm{M}]^2} + C_\mathrm{M} + C_\mathrm{S}\frac{[\mathrm{S}]}{[\mathrm{M}]} + C_\mathrm{I}\frac{[\mathrm{I}]}{[\mathrm{M}]}\right] \quad (4.15)$$

Equation 4.15 is the Mayo equation and can be used for experimental determination of some of the transfer constants (C_M, C_S, C_I).

4.5.1 Full Molecular Weight Distribution

The full MWD can be obtained either by probabilistic arguments [4] or by a kinetic approach. Flory showed that the form of the MWD in FRP is the same as in condensation polymerization (the most probable or Flory–Schulz distribution), when termination occurs by disproportionation or transfer to a small molecule; however, in a free radical mechanism, it represents only the distribution obtained at a given instant of the polymerization or under constant reaction conditions (as those occurring, e.g., in a continuous tank reactor operating at steady state). According to Flory, letting p represent the probability of a growing chain continuing to grow instead of terminating:

$$p = \frac{R_\mathrm{p}}{R_\mathrm{p} + R_\mathrm{td} + R_\mathrm{trS}} \quad (4.16)$$

where R_i represent reaction rates with i = p, propagation, i = td, termination by disproportionation, and i = trS, transfer to solvent S; hence, only the last two mechanisms are considered for chain termination (Table 4.6). The probability that a terminated polymer chain has exactly x monomer units is given by

$$n_x = (1-p)\,p^{x-1} \quad (4.17)$$

This also represents the number fraction of polymer chains having x monomer units.

If N_0 is the number of monomer moles in polymer chains, $N = N_0(1-p)$ is the number of polymer moles, since $(1-p)$ represents the probability of termination of a chain. Therefore, the number of moles of polymer having x monomer units is

$$N_x = N_0\,(1-p)^2\,p^{x-1} \quad (4.18)$$

And the weight fraction w_x of polymer moles having x monomer units is xN_x/N_0 or

$$w_x = x\,(1-p)^2\,p^{x-1} \quad (4.19)$$

For termination by combination, a sharper distribution results, but a general derivation including various types of termination is more easily obtained using kinetic instead of probabilistic arguments. In the kinetic approach, differential rate expressions are written for each polymer species and the QSS approximation is used. The derivation is based on the kinetic scheme listed in Table 4.6.

The final and general result is given by the following expression [37]:

$$w_x = (\tau+\beta)\left\{\tau + \frac{1}{2}\beta\,(\tau+\beta)\,(x-1)\right\} x\varphi^{x+1} \quad (4.20)$$

where

$$\varphi = \frac{1}{1 + \tau + \beta} \tag{4.21}$$

$$\tau = \frac{k_{\mathrm{td}}\,[\mathrm{P}] + k_{\mathrm{trM}}\,[\mathrm{M}] + k_{\mathrm{trS}}\,[\mathrm{S}]}{k_{\mathrm{p}}\,[\mathrm{M}]} \tag{4.22}$$

$$\beta = \frac{k_{\mathrm{tc}}\,[\mathrm{P}]}{k_{\mathrm{p}}\,[\mathrm{M}]} \tag{4.23}$$

[P] can be calculated by the expression at QSS (Eq. 4.7). Equation 4.20 is a convenient general form of the instantaneous weight MWD for the mechanism listed in Table 4.6. The reader must be aware that the real distribution obtained from a reaction running up to moderate or high conversions will be the addition of many instantaneous distributions that may differ from each other due to the continuously changing conditions (e.g., in a batch reactor), which will affect the concentrations of monomer, initiator, and so on and can even affect the rate coefficients (gel effect). To obtain the final MWD, an integration procedure adding the differential contributions at each reaction moment should be performed [38].

From distribution expressions such as Equation 4.17, 4.19, or 4.20, the instantaneous number and weight average MW, as well as the instantaneous polydispersity, can be obtained. The moments of the distributions are most useful as intermediate quantities for these calculations and they are defined as (see also Chapter 1)

$$\mu_s = \sum_{i=1}^{\infty} x^s n_x,\ \lambda_s = \sum_{x=1}^{\infty} x^s w_x;\ s = 0, 1, 2, \ldots \tag{4.24}$$

μ_s and λ_s are the s-moments of the number chain length distribution (NCLD) and weight chain length distribution (WCLD), respectively. The number average (M_{n}) and weight average (M_{w}) MWs are then given by

$$M_n = \frac{\mu_1}{\mu_0} M_0 \tag{4.25}$$

$$M_{\mathrm{w}} = \frac{\mu_2}{\mu_1} M_0 = \frac{\lambda_1}{\lambda_0} M_0 \tag{4.26}$$

and the polydispersity index (PDI) [3] is simply given by the ratio PDI $= M_{\mathrm{w}}/M_n$

Closed expressions can be obtained for M_{n}, M_{w}, and PDI, depending on the specific reaction mechanisms taken into account. For example, for the distribution given by Equation 4.17 (termination only by disproportionation or transfer to solvent), the evaluation of moments and summations in Equations 4.24–4.26[4] leads to the following expressions:

$$M_{\mathrm{n}} = \frac{M_0}{(1 - p)} \tag{4.27}$$

$$M_{\mathrm{w}} = M_0 \frac{(1 + p)}{(1 - p)} \tag{4.28}$$

$$\mathrm{PDI} = 1 + p \tag{4.29}$$

4.6 EXPERIMENTAL DETERMINATION OF RATE CONSTANTS

Up to the 1980s, the determination of k_{p} and k_{t} was carried out mainly by the rotating sector method [39]. However, since the late 1980s, given the advances in pulsed laser techniques and size exclusion chromatography, as well as the IUPAC recommendations for the search of a more reliable and reproducible method for the measurement of rate constants of polymerization, *pulsed laser polymerization* (PLP) has become the preferred method for the measurement of these two kinetic constants [40]. In this method, a reaction mixture of monomer and photoinitiator is radiated by a pulsed laser beam. Each laser flash (≈1 ns pulse) generates radicals that initiate the polymerization during the illuminated period, while no radicals are formed during dark periods (≈1 s). All the radicals formed during an illuminated period grow approximately at the same rate, since all of them are started at approximately the same time; hence, they generate a narrow MWD. After a dark period of length t_0, the next laser pulse generates another burst of radicals, some of which annihilate most of the growing radicals still active and initiated during the previous pulse, which terminate with approximately the same chain length L_0 (generated during the time interval t_0 between light periods). As some of the radicals survive the next pulse, after several cycles (illuminated–dark), the concentration of radicals with lengths $2L_0$, $3L_0$, and so on increases with each pulse. In the end, a final, well-defined MWD is obtained, with peaks at L_0 and at its multiples. The chain length $L_{0,n}$ of a radical that has grown by n periods (pulses) is related with k_{p} as $L_{0,n} = nk_{\mathrm{p}}\ [\mathrm{M}]\ t_0$. From this and experimental measurements of $L_{0,n}$ (via SEC), [M], and for a known t_0, k_{p}can be estimated. The measurement of $k_{\mathrm{t}}/k_{\mathrm{p}}$ can be done by similar techniques. A detailed description of the technique can be found elsewhere (40c).

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[3] Although the term *polydispersity* or *polydispersity index* is widely used, its use is now discouraged by IUPAC. The term *dispersity* is recommended instead [73].

[4] The following identities are useful for the evaluation of summations appearing in moment expressions:

$$\sum_{x=1}^{\infty} xp^{x-1} = \frac{1}{(1-p)^2};\ \sum_{x=1}^{\infty} x^2 p^{x-1} = \frac{(1+p)}{(1-p)^3};\ \sum_{x=1}^{\infty} x^3 p^{x-1} = \frac{\left(1+4p+p^2\right)}{(1-p)^4}$$

4.7 THERMODYNAMICS OF POLYMERIZATION

The thermodynamics of polymerization has been reviewed by several authors [41–43].

The propagation reaction of alkenes implies the formation of a σ-bond from a π-bond and this makes the enthalpy of propagation (ΔH) negative (exothermic and favorable). On the other hand, the entropy of propagation (ΔS) is negative and unfavorable (the polymer chain represents a more ordered state than the unbound monomer molecules); however, the absolute value of ΔH is dominant. Therefore, the resulting ΔG ($\Delta G = \Delta H - T\Delta S$) is negative and favorable. Table 4.7 lists values of the enthalpies of polymerization for some common monomers. Most values fall in the range of 50–120 kJ/mol. There is some scattering in the data reported by different authors, and this scattering is attributed to the effect of the physical state of the monomer and the polymer. Note also that, from the point of view of polymerization process engineering, the values of ΔH on a mass basis, instead of molar, are of more significance, since differences in exothermicity among different polymerization systems tend to be more pronounced in this way (see, e.g., the high value corresponding to ethylene polymerization on mass basis).

The propagation step is potentially reversible and, owing to entropic effects, the depropagation reaction will be favored by higher temperatures. The equilibrium temperature at which the propagation and depropagation rates are equal is known as the ceiling temperature, or T_c. Most common monomers show negligible depropagation rates at typical polymerization temperatures, but some with alkyl substituents in the α-position, such as α-methyl styrene, will show lower T_c.

TABLE 4.7 Heat of Polymerization of Some Common Monomers in Different Units

Monomer	ΔH_p (kJ/mol)	ΔH_p (kcal/mol)	ΔH_p (cal/g)	T (°C)
Butadiene	73	17.5	323	25
Isoprene	75	17.9	263	25
Ethylene	101.5	24.3	866	25
Acrylonitrile	76.5	18.3	345	74.5
Methacrylic acid	64.5	15.4	179	25
Methyl methacrylate	55.6	13.4	134	74.5
	56	13.4	134	130
Acrylic acid	67	16.0	222	74.5
Methyl acrylate	78	18.7	217	76.8
	81.8	19.6	227	80
Ethyl acrylate	78	18.7	187	74.5
	80.7	19.3	193	90
Butyl acrylate	78	18.7	146	74.5
Styrene	70	16.7	160	25
	73	17.5	168	127
Vinyl chloride	71–111.5	17–27	272–432	25
	96	23	368	74.5
Vinyl acetate	88	21.1	245	74.5

Using the notation and kinetic scheme of Table 4.5 and adding to it the depropagation reaction:

$$P \xrightarrow{k_{rev}} P + M \tag{4.30}$$

The equilibrium is reached when $k_p[\mathrm{P}][\mathrm{M}] = k_{rev}[\mathrm{P}]$ and the equilibrium constant is given by

$$K = \frac{k_p}{k_{rev}} = \frac{1}{[\mathrm{M_c}]} \tag{4.31}$$

From thermodynamic relationships $\Delta G = \Delta G^\circ + RT \ln K$ and at equilibrium $\Delta G = 0$, so

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = RT \ln[\mathrm{M_c}] \tag{4.32}$$

Therefore,

$$\ln[\mathrm{M_c}] = \frac{\Delta H^\circ}{(RT_c)} - \frac{\Delta S^\circ}{R} \tag{4.33}$$

and

$$T_c = \frac{\Delta H^\circ}{\Delta S^\circ + RT \ln[\mathrm{M_c}]} \tag{4.34}$$

From Equation 4.34 it is concluded that T_c increases with larger $[\mathrm{M_c}]$ (negative ΔH) and there is not a single value for T_c. Usually, the reported values of T_c are for pure monomers and therefore they represent the maximum value for that monomer. In general, at higher temperatures, the depropagation becomes increasingly important in relation to the forward propagation reaction. Equation 4.34 also implies that in a solution polymerization at a given temperature T (which must be initiated with a monomer concentration larger than the $[\mathrm{M_c}]$ corresponding to T), the monomer is consumed and its concentration decreases until it possibly reaches the $[\mathrm{M_c}]$ corresponding to T, where the reaction will stop.

4.7.1 Floor Temperature

Most monomers exhibit an exothermic polymerization reaction (negative and large ΔH) with a small but negative entropy change. In that case, they have a ceiling temperature as described in the previous section. However, a few exceptional monomers (e.g., cyclic sulfur) exhibit a very small ΔH (either positive or negative) with a positive entropy change. In these cases, the polymerization will have a floor temperature T_f below which the polymerization does not proceed.

4.8 CONTROLLED RADICAL POLYMERIZATION

The year 1994 can be considered as the starting year of a revolutionary change in the field of chemistry of FRP, due to the advent of the techniques generically called *controlled/living radical polymerization* (CRP) [44, 45]. Recently, the term *reversible deactivation radical polymerization* has been recommended by the IUPAC [46] instead of other terms; however, in this section, we adhere to the older notation that is still in common use. These new techniques preserve the robustness of traditional FRP (tolerance to impurities and water) and its versatility in terms of range of monomers, reaction conditions, and types of industrial processes [47]. On the other hand, CRP techniques can produce polymers with a precisely controlled architecture and composition that had never been produced before: polymers with narrow MW distributions; block, gradient, and graft copolymers; and hybrid materials in which well-controlled organic polymers are chemically linked to inorganic materials, among others [1, 47, 48]. These materials cannot be produced via traditional FRP and some of them were produced before by using techniques that require extremely clean conditions (such as anionic polymerizations) and that lead to costly industrial processes, when feasible. In summary, CRP combines some of the best features of traditional FRP (robustness and versatility) and of true living polymerizations (such as anionic), with the capability of the latter of producing precisely controlled architectures.

The term *control* in CRP refers to the capability of producing a polymer with low polydispersity and with a prespecified MW. On the other hand, the term *livingness* refers to the potential of a chain to be extended by the addition of extra monomer (of the same or different chemical nature) after a first batch of monomer has been exhausted.

CRP is one of the most rapidly expanding areas of chemistry and polymer science due to the effectiveness already demonstrated by these techniques and their enormous potential for the synthesis of a broad variety of polymeric or polymer-related materials. The degree of control of the molecular architecture that can be achieved with these techniques is the driving force that has led many groups interested in the synthesis of materials with specific functionality, properties, or structures, to work in this field. The number of publications in this field (papers and patents) has seen an exponential increase in the last decade and it is estimated that in a single year (2005) more than a thousand publications were brought out [47].

The mechanism of all CRP techniques is based on a dynamic equilibrium between very small concentrations of propagating radicals and dormant species (Fig. 4.1), which can be reactivated by virtue of this equilibrium [48, 2]. A key factor for achieving good control (low polydispersities and good MW prediction) is a fast exchange between dormant and active species; however, it is possible for some of these processes to exhibit livingness, even in the absence of good control, when the exchange is not sufficiently fast. Since irreversible termination between radicals is always present, CRP is never completely living. In FRP, all the chains terminate; however, in CRP there is a large concentration of polymer chains (10^{-1} M, as opposed to 10^{-3} M, in FRP) and out of them only a small percentage (around 1%) are terminated chains, while the vast majority are dormant chains [47].

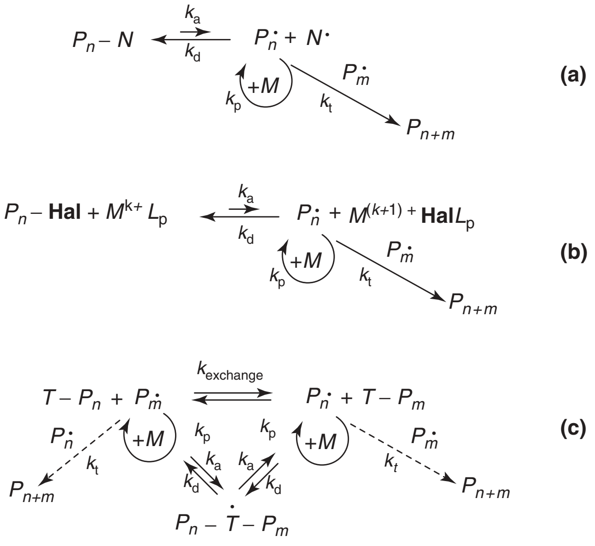


Figure 4.1 Controlled radical polymerization mechanisms via (a) NMRP, (b) ATRP, and (c) RAFT.

There are several techniques for performing CRP, but the most popular and successful ones so far are as follows: stable free radical (SFR) or nitroxide-mediated radical polymerization (NMRP) [44, 45, 49], atom transfer radical polymerization (ATRP) [50, 51], and degenerative transfer techniques, including particularly reversible addition-fragmentation transfer (RAFT) polymerization [3]. These are examined in some detail in the following sections.

In general, CRP techniques are based on either an SFR that exhibits the persistent radical effect (PRE) [52–55] (e.g., N in NMRP), an inactive species $M^{(k+1)+}$ HalLp in ATRP (which acts as a persistent radical), or, as in the RAFT case, a highly active chain transfer agent ($T - R$) (refer to Fig. 4.1 for notation).

4.8.1 Stable Free Radical Polymerization (SFRP) or Nitroxide-Mediated Radical Polymerization (NMRP)

NMRP (also called *NMP*, *nitroxide-mediated polymerization*) or SFRP (stable free radical polymerization) was first disclosed by Solomon et al. from CSIRO (Commonwealth Scientific Industrial Research Organization) in 1984. Their patent [49] describing a unimolecular process in which an alkoxyamine thermally breaks and produces both an initiating radical and a nitroxide radical that will control the polymerization (Scheme 4.10a) was an important landmark; however, this process required the previous synthesis of the alkoxyamine and had little diffusion. Ten years later, Georges et al. at Xerox published a couple of patents [44] disclosing the bimolecular process that, from the point of view of industrial application, was simpler to implement than the monomolecular process. In the second case, a stable (nitroxide) radical (e.g., TEMPO, 2,2,6,6 tetramethylpiperidine *N*-oxyl) and a radical initiator are added to the polymerization recipe to achieve a controlled polymerization (Scheme 4.10b).

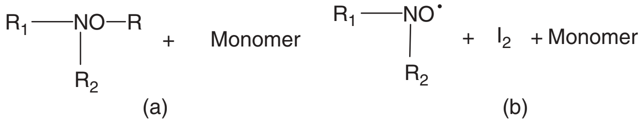
Conceptually, both processes are similar, because in the bimolecular process an alkoxyamine is formed *in situ*. The mechanism for both processes is represented by Scheme 4.11. The steps in the scheme occur in addition to the regular steps in FRP listed in Table 4.5.

The kinetic analysis of NMRP using the concept of PRE was made by Fischer [52–55]; nitroxide radicals do not terminate between themselves as propagating radicals do; hence, during a polymerization, some propagating radicals will terminate between themselves, decreasing their concentration, while the nitroxide radical concentration will remain nearly constant or will increase to satisfy the quasi-equilibrium:

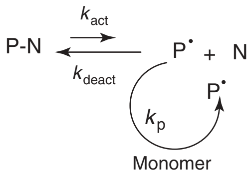
$$k_{\mathrm{act}}\,[\mathrm{P-N}] \approx k_{\mathrm{deact}}\,[\mathrm{P}]\,[\mathrm{N}] \tag{4.35}$$

where the dots have been removed from the radicals for simplicity of notation. The polymerization in the presence of nitroxide will proceed near the equilibrium given by

$$K_{\mathrm{eq}} = \frac{k_{\mathrm{act}}}{k_{\mathrm{deact}}} = \frac{[\mathrm{P}]\,[\mathrm{N}]}{[\mathrm{P-N}]} \tag{4.36}$$



Scheme 4.10 (a) Monomolecular process using an alkoxyamine as an initiator and a controller; and (b) bimolecular process using a nitroxide radical as a controller and radical initiator (I_2) to generate radicals.



Scheme 4.11 Reversible activation–deactivation of the growing radical P• with the nitroxide radical N•.

which is highly biased toward the dormant polymer. Typical values for the equilibrium constant are in the range 10^{-7}–10^{-12} M, strongly depending on the chemical structure of the nitroxide radical. A significant number of nitroxide structures have been synthesized and reported in the literature (2, 58, 59); a small sample of these is shown in Figure 4.2. Fischer [52, 53] recognized three regimes in the kinetics of a monomolecular NMP. In the first regime (which lasts only for a period in the order of a fraction of a second or seconds), living and persistent radicals appear in equal concentrations as the alkoxyamine decomposes. In the intermediate state, the quasi-equilibrium in Equation 4.35 is established.

Finally, at long reaction times, a steady state of the persistent radical is reached. Fischer [52–55] and Fukuda [2, 56] first developed kinetic equations that describe the evolution of the nitroxide radicals with reaction time t. These equations were later refined by Tang et al. to take into account the variation of the alkoxyamine initiator with time, not considered before [57], resulting in

$$\frac{I_0^2}{I_0 - N} + 2I_0 \ln \frac{I_0 - N}{I_0} - \left(I_0 - N\right) = 2k_{\mathrm{t}}K_{\mathrm{eq}}^2 t \tag{4.37}$$

where k_{t} is the termination constant and I_0 is the initial alkoxyamine concentration. This is an approximated expression based on the assumptions that $|\mathrm{d}N/\mathrm{d}t| \gg |\mathrm{d}P/\mathrm{d}t|$ and quasi-equilibrium (Eq. 4.35). In their analysis, Tang et al. identified three periods that differ slightly from those described by Fischer. The quasi-equilibrium (Eq. 4.35) is the third period in this last analysis, and this is preceded by a pre-equilibrium (similar to the first regime of Fischer) and a transition period (not identified by Fischer). In this study, an equation was also derived for the monomer conversion in terms of the nitroxide concentration (N) at time t:

$$l\mathrm{n}\left(\frac{M_0}{M}\right) = \frac{k_{\mathrm{p}}}{2k_{\mathrm{t}}K_{\mathrm{eq}}}\left(I_0 l\mathrm{n}\left\{\frac{I_0}{I_0 - N}\right\} - N\right) \tag{4.38}$$

k_{p}, M, and M_0 are the propagation constant, monomer concentration, and initial monomer concentration, respectively. The degree of polymerization DP_n is simply calculated by

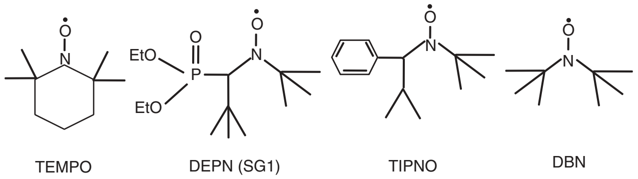


Figure 4.2 Some common nitroxide radicals and their acronyms.

Equation 4.39:

$$\mathrm{DP}_n = \frac{[\mathrm{M}]_0\, x}{I_0} \tag{4.39}$$

where x is monomer conversion and the subindex 0 refers to initial conditions.

Numerous polymers and copolymers have been synthesized using NMP techniques. See, for example, the reviews by Hawker [58, 59]. Graft copolymers and hybrid materials synthesized by NMP are reviewed in Chapter 10.

4.8.2 Atom Transfer Radical Polymerization (ATRP)

The basic concept of ATRP was simultaneously and independently disclosed by Matyjaszewski [50] and Sawamoto [51]. In ATRP, the dormant species, P_n-Hal (Fig. 4.1b), is formed by the reaction between propagating species $P_n^\bullet$ and halogen atoms (Hal) [53], as illustrated in mechanism (b) of Figure 4.1. Ingredients included in an ATRP recipe are as follows: an initiator (usually an alkyl halide), an organometallic complex that acts as a catalyst or an activator, formed by a metal halide and a ligand, as well as the monomer. The metal is of the transition type (M^{k+}), which can expand its coordination sphere and increase its oxidation number (k). The halogen from the dormant species reversibly binds to the metal complex (M^{k+}/Lp) increasing its oxidation state by one unit ($M^{(k+1)+}\mathrm{Hal}/Lp$) and producing propagating radicals ($P_n\cdot$) with an activation constant k_a. The oxidized state of the metallic complex, also known as *metalloradical*, plays the role of persistent radical [53], which does not propagate or finish. Meanwhile, the propagating radicals may terminate irreversibly or continue their propagation in the presence of monomer. Copper metal complexes were the first ones used extensively, but others have also been tested [53], such as Fe, Ni, Re, Rh, Ru, and Pd (among others) in the ATRP of a widespread variety of monomers. The ligands are nitrogen based, the common ones being bidentatebipyridyl ligands. Since poor solubility of the complex in the reaction media may be an issue, bipyridyl ligands possessing long alkyl chains are preferred. Other ligands exhibit better solubility when forming the complex, for example, TMEDA (tetramethylethylenediamine) and PMDETA (N,N,N',N',N''-pentamethyldiethylenetriamine) [5].

The kinetics of ATRP has been studied and summarized by Matyjaszewski [60]. Assuming fast equilibrium, complete initiation, and neglecting termination, the total concentration of propagating radicals, [P], is given by

$$[\mathrm{P}] = \frac{k_\mathrm{a}}{k_\mathrm{d}}\ \frac{[\mathrm{P}_n - \mathrm{Hal}][\mathrm{M}^k]}{[\mathrm{M}^{k+1}\mathrm{Hal}]} \tag{4.40}$$

and the polymerization rate R_p is [60]

$$R_\mathrm{p} = k_\mathrm{p}[\mathrm{P}][\mathrm{M}] = k_\mathrm{p}\ \frac{k_\mathrm{a}}{k_\mathrm{d}}[\mathrm{M}]\frac{[\mathrm{P}_n - \mathrm{Hal}][M^k]}{[\mathrm{M}^{k+1}\mathrm{Hal}]} \tag{4.41}$$

In Equation 4.41, the concentration of dormant species $[\mathrm{P}_n - \mathrm{Hal}]$ can be replaced by the initial initiator concentration $[\mathrm{R} - \mathrm{Hal}]_0$ under the assumption of complete initiation.

The degree of polymerization DP_n can be simply calculated by Equation 4.42 [60]:

$$\mathrm{DP}_n = \frac{[\mathrm{M}]_0 x}{[\mathrm{R} - \mathrm{Hal}]_0} \tag{4.42}$$

where x is the monomer conversion. Finally, the MW dispersity, Đ, is given by [60]

$$Đ = \frac{\overline{M_\mathrm{W}}}{\overline{M_\mathrm{n}}} = 1 + \frac{k_\mathrm{p}[\mathrm{R} - \mathrm{Hal}]_0}{k_\mathrm{d}[\mathrm{M}^{k+1}\mathrm{Hal}]}\ \left|\frac{2}{x} - 1\right| \tag{4.43}$$

Following the development of the original ATRP, the group of Matyjaszewski invented modified versions of the procedure. Reverse ATRP [61] was created to avoid some of the problems of this process when it is taken to an industrial scale or performed in aqueous dispersions, as the components of this recipe are less sensitive to air and moisture. In this version, the transition metal is added to the system in its higher oxidation state, and the catalyst or activator $M^k Lp$ is generated *in situ* by the decomposition of a conventional free radical initiator. Simultaneous reverse and normal atom transfer radical polymerization (SR/N ATRP) [62] is another modality of the process that allows for the use of more active (and sensitive) catalyst systems. The activator generated by electron transfer or AGET-ATRP process [63] is similar to SR/N ATRP, but instead of using a free radical initiator, it uses a reducing agent to generate the activator from the higher oxidation state of the metal complex. Looking for the ways to reduce the concentration of metal used in the ATRP procedure, ARGET (activator regenerated by electron transfer) ATRP [64] was proposed; in this case, proper reducing agents are used that continuously regenerate the activator from the metal in its higher oxidation state present in species formed by irreversible termination, thus allowing for a net reduction of the metal concentration in the system. Finally, ICAR (initiator for continuous activator regeneration) ATRP [65] is similar to ARGET, but it uses a traditional free radical initiator to compensate for the loss of M^k activator, which is consumed by the termination reactions at these low concentrations of catalysts. A review of the multiple applications of polymer synthesis using ATRP techniques has been presented by Matyjaszewski and Xia [66].

4.8.3 Reversible Addition–Fragmentation Chain Transfer Polymerization (RAFT)

RAFT is a variant of a degenerative transfer [67]. It requires a careful election of the RAFT agent (T-R) depending on the monomer to polymerize (see mechanism (c), Fig. 4.1). Dithioesters, dithiocarbamates, tri-thiocarbonates, and xanthates are examples of some RAFT agents that have been successfully used as transfer agents to produce novel polymeric topologies with high MW and narrow polydispersity [68]. The exchange reactions can be very fast, providing good control in these systems due to the presence of highly active transfer agents [53].

The kinetic mechanism was first proposed by the CSIRO group in its seminal 1998 paper [3] and is schematically represented by the lower path in scheme of Figure 4.1c (the higher path with the k_{exchange} kinetic constant is rather a representation of all degenerative transfer processes). The representation of the figure corresponds to the core equilibrium. Before that, a similar equilibrium is first established with the RAFT chain transfer agent T-R instead of the species T-P_n (see left side of Fig. 4.1c) and with primary radicals from a radical initiator instead of the polymeric radical T-P_{m}•. Moad and Barner-Kowollik have reviewed the kinetics of the process [69]. The degree of polymerization and MWD dispersity (under negligible contributions of bimolecular termination and external initiation, as well as uniform transfer activity throughout the whole reaction) are given by [69]

$$\mathrm{DP}_n = \frac{[\mathrm{M}]_0 x}{[T - R]_0 + df(I_0 - 1)} \tag{4.44}$$

$$Đ = 1 + \frac{1}{\mathrm{DP}_n} + \left|\frac{2 - x}{x}\right| \frac{1}{C_{\mathrm{tr}}} \tag{4.45}$$

where d is the number of chains produced in a bimolecular termination reaction, f is the initiator efficiency, and C_{tr} is the chain transfer constant. To obtain the number average MW, one must multiply expression (Eq. 4.43) by $(M_0 + M_{\mathrm{T-R}})$ (where the terms are the MWs of the monomer and the CTA, respectively). C_{tr} can be estimated experimentally using Equation 4.45 or, in some conditions [69], from the approximated expression (Eq. 4.46):

$$\frac{\mathrm{d}[\mathrm{T} - \mathrm{R}]}{\mathrm{d}[\mathrm{M}]} \approx C_{\mathrm{tr}} \frac{\mathrm{d}[\text{T-R}]}{\mathrm{d}[\mathrm{M}]} \tag{4.46}$$

Common RAFT chain transfer agents (T-R) are of the thiocarbonylthio type, RSC(Z) = S, in which the chemical nature of the groups Z and R are key to effective control of the reaction. The group Z must provide stability to the intermediate radical $\mathrm{P}_n - \dot{T} - \mathrm{P}_m$ (Fig. 4.1c), while the salient group R must reinitiate a chain readily with the monomer. A careful selection of the CTA must be done depending on the monomer or monomers to be polymerized. The CSIRO group has published a number of excellent reviews on the fundamentals and practical application of the RAFT technique for the synthesis of a variety of polymeric structures [68–71]. A current challenge in this field is the discovery of an universal CTA able to polymerize a vast number of monomer families.

4.8.4 Outlook of CRP Techniques

All the CRP techniques have advantages and drawbacks; some of these techniques will be more suitable for some applications than others. In general terms, SFRP or NMP is perhaps the simplest from the chemical point of view and it is rather robust, but it requires relatively high temperatures and it works better with styrenics. Milder reaction conditions are needed for ATRP and RAFT polymerizations, and these two techniques work better with a larger number of monomers than NMRP, does although in both cases a final step of metal (ATRP) or color (RAFT) removal from the polymer may be necessary. In terms of the number of reported applications/publications, ATRP is the leading technique, followed by RAFT, and then NMRP, but a further expansion, maturity, and eventual extended industrial application of all of them are expected.

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