POLYMER SYNTHESIS AND INDUSTRIAL POLYMERIZATION

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1 Introduction to and Definition of Polymer Technology

Introduction. Among the remarkable technological developments of the 20th century, the synthesis of polymers could very well be ranked in the top five along with synthetic fertilizers, nuclear power, aerospace technology, and the transistor in its impact on modern society. Synthetic polymer products are an integral part of modern life; indeed, an increasing larger fraction of the materials in the cars we drive, the computers we work with, the furniture we sit on, the clothes we wear, and the floors or carpets we walk on are made of polymers.

Polymers are produced in both heterogeneous and homogeneous catalytic processes which consume well over half the output of the organic chemical industry. Approximately fifteen of the top fifty chemicals produced in the U.S. are monomers used primarily in the production of high-volume polymers. U.S. production levels of thermosets, thermoplastics, elastomers, and fibers in 1995 were 3.4, 28, 1.0, and 4.5 million metric tons (mt) respectively; thermoplastics accounted for 77% of these polymers. Six thermoplastics: polyethylene (PE), polypropylene (PP), polystyrene, styrene copolymers, polyvinyl chloride (PVC), and polyester, accounted for 87% of thermoplastic production. Global production of polymers in 1996 was about 98 million mt.

Polymers Defined and Classified. A *polymer* is a macromolecule consisting of chains composed of *mers* or *monomer residues* joined together with covalent bonds. A *monomer* is a small molecule or one of a pair of small molecules incorporated into a polymer as it is synthesized. Polymers may be classified based on their thermal processing behavior, flexibility, structure, and polymerization mechanism. Polymers that can be heat-softened for processing are called *thermoplastics*, while those that cannot because of their rigid, 3-D structures are *thermosets;* highly-flexible polymers of low crystallinity are called *elastomers*.

In terms of structure, a polymer synthesized from a single kind of monomer is called a *homochain polymer* while one prepared from two (or more) monomer types is called a *copolymer*. Homochain polymers synthesized from asymmetric α-olefins (e.g. propylene, vinyl chloride or styrene) or dienes (e.g. butadiene) may be present in one of three different stereochemical arrangements of secondary carbons (D or L) namely, (1) *isotactic* (configuration DDDDD.. or LLLL..) in which the substitutional R groups lie on the same side of the plane formed by the extended chain backbone, (2) syndiotactic (DLDLDLDL..) in which the R groups alternate from one side of the plane to the other, or (3) *atactic* in which there is a random arrangement of the substitutional R groups from one side of the plane to the other (see Figure 1). Generally, isotactic and syndiotactic polymers are partially crystalline while atactic polymers are amorphous. Other polymer properties, e.g. thermal and mechanical, are significantly affected by tacticity; for example, the order of decreasing melting point is generally isotactic, syndiotactic, atactic.

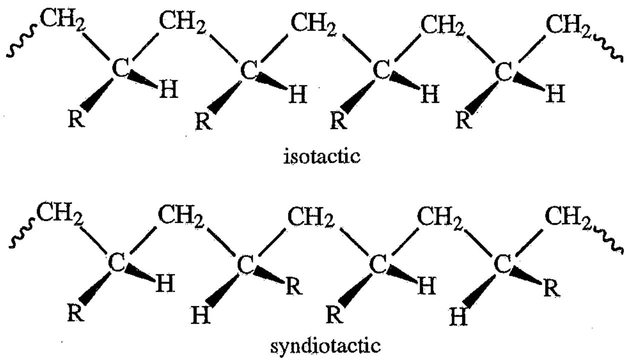

Figure 1. Isotactic and syndiotactic configurations for polymers prepared from asymmetric α–olefins.

Five different copolymer structures are illustrated in Figure 2. Random copolymers have lower crystallinity and greater elasticity. A small amount of comonomer incorporated into a random polymer may act as a plasticizer (e.g. 2-15% vinyl acetate copolymerized with vinyl chloride produces a tough, flexible copolymer) or an agent for producing active sites for cross-linking (e.g. 2% isoprene in polyisobutene). Block polymers may incorporate desirable properties from each of the comonomers, e.g. styrene-butadiene thermoplastic elastomers (natural rubber is a thermoset). Some important elastomers and high-impact polymers (e.g. ABS impact polymers) are graft copolymers.

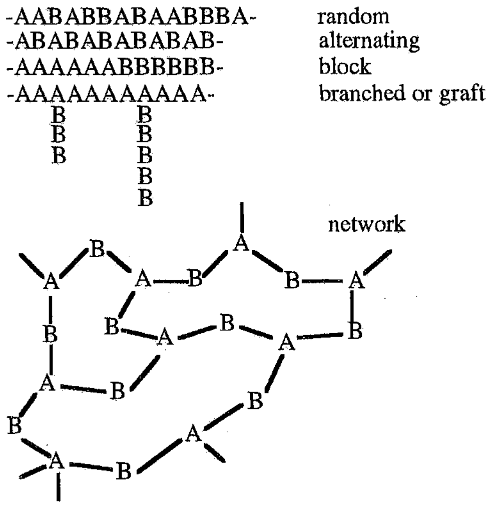

Figure 2. Different structural variations of AB copolymers, where A and B are different monomer residues.

While polymers can be prepared over wide ranges of molecular weight, “useful” polymers typically have molecular weights in the range of about 10^4 to 10^6 g/mol (for example, some polypropylenes have molecular weights in the range of 300,000 - 600,00). Moreover, the most desirable features of thermoplastics such as toughness, strength, and elasticity are observed for this range of molecular weight (see Fig. 3). Average molecular weight affects the softening temperature, strength, and liquid viscosity of polymers. Indeed, low-molecular-weight chains form relatively few intermolecular bonds and slide apart too easily; they therefore have low tensile strength and soften or form liquids at low temperature. High molecular weight polymers, on the other hand have high strength and elasticity; however, the high viscosity of the melt makes forming or molding more difficult. At molecular weights above 10^6, melt viscosity is sufficiently high that extrusion or forming is impractical. Chain flexibility, interchain interactions, branching and stereochemical regularity also influence the glass transition temperature T_g, crystallinity and resistance to cold flow. Basic building blocks and properties of some common polymers are summarized in Table 1. A number of excellent textbooks provide additional details on the properties and applications of polymers, e.g. [Billmeyer, 1984; Young and Lovell, 1991; Painter and Coleman, 1994; Fried, 1995; Rodriguez, 1996].

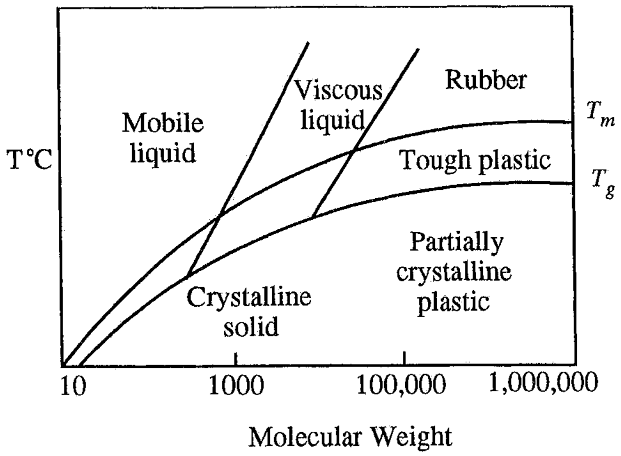

Figure 3. The dependence on molecular weight of melting and glass temperatures and physiochemical properties of polymers [Billmeyer, 1984].

2 Fundamentals of Polymerization Synthesis/Catalysis

Almost all useful polymers are produced by catalytic processes [Candlin, 1981]. Catalysts are essential for initiation and/or control of the polymerization process. Although polymerization catalysts do not strictly conform to the conventional definition of catalysts, i.e., they are rarely recovered unchanged at the end of the reaction but instead are generally incorporated into the product due to unrealistic separation costs, they nevertheless typically catalyze production of more than one ton (10^6 g) of polymer per gram of catalyst [Rempp and Merrill, 1991]. Hence, their designation as catalysts is clearly justified. Polymerization catalysts may be homogeneous or heterogeneous, although most industrial catalysts are heterogeneous.

Table 1. Properties of Common Thermoplastics and Thermosets [data from Callister, 1994; Fried, 1995; Shackelford, 1996; Smith, 1996].

polymer	mer structure	structural state	tens.streng. (MPa)	impact strg (J/m)[a]	density (g/cm^3)	T_g[b] (°C)	T_{max}[c] (°C)	bulk price \$/kg	Applications
thermoplastics									
ABS	copolymer of acrylonitrile, butadiene and styrene	glassy coply with rubbery domains	40	200-600	1.03	–	71-93	2.82-3.04	refrigerator linings, lawn & garden equipment
polyamides (nylon 6,6)	$-NH-[CH_2]_6-NH-C-[CH_2]_4-C-$	highly crystalline, spherulitic struct., H-bonding	75	100	1.15	57	82-150	2.97-7.60	bearings, gears, cams, bushings, tool handles, wire coatings
polycarbonate	$-O-\phi-C-\phi-O-C-$	stiff molecular structure	63-72	650-850	1.20	150	120	4.80-6.35	machine parts, car parts, propellers, instrument panels, CDs
polyethylene, LD[d]	$[-CH_2-CH_2-]$	branched (60% C)[f]	8-16	50-700	0.92	-110	82-100	1.21-1.32	flex.sheet, bottle, toys
polyethylene, HD[e]		linear (95% C)	26-33	25-100	0.95	-90	80-120	1.32-1.39	batteries, tanks, ice trays
polypropylene	$[-CH_2-C(CH_3)H-]$	isotactic (amorp.)	31-41	25-100	0.91	-10	107-150	1.21-1.32	bottles, packing, TV cabinets
polystyrene	$[-CH_2-C(\phi)H-]$	isotactic (crystal.)	36-52	12-20	1.05	100	104	1.32-1.45	Styrofoam, tile, battery cases, toys, lighting
polyvinyl chloride (PVC)	$[-CH_2-C(Cl)H-]$	largely amorphous	41-52	50-125	1.4-1.5	105	110	0.81-3.30	pipe, garden hose, electrical insulation
polyethylene terephthalate (PET)	$-O-CH_2-CH_2-O-C-\phi-C-$	crystalline	49-72	12-35	1.15	70-80	80-120	3.61-3.85	fiber, film, magnetic tape carpet, clothing, tires
thermosets									
phenolic		amorphous, wood and glass reinforced	52	12-900	1.3-1.9		150-288	1.36-2.20	electrical equip. , motor housings, insulators, brake and transmission parts
polyester	$CH-O-C-(CH_2)_x-C-OH$	amorphous, glass reinforced (fiber-glass)	40-90	400-800	1.7-2.3		150-177	1.43-1.67	car panels and body parts, boat hulls, indoor constr. panels, pipes tanks, ducts

[a] Based on notched Izod test. [b] Glass to liquid transition temperature. [c] Maximum use temperature (no load). [d] Low density. [e] High density. [f] C is crystallinity.

Polymerization Reaction Chemistry. Polymerizations are classified mechanistically as either (1) *step growth* (condensation) or (2) *chain growth* (addition or insertion) reactions. The characteristics of these two different reactions are summarized in Table 2.

Table 2. Characteristics of Step-Growth and Chain-Growth Polymerizations

Step growth	Chain growth
Polycondensation process; any two species (monomer or growing chain) can react as long as functional groups are present.	Chain reaction: initiation, propagation/transfer, termination. Addition occurs during propagation to the ends of growing chains; upon transfer the polymer product is unreactive.
Branched and network polymers can be formed.	Straight-chain and branched-chain polymers are formed.
Catalyst is very desirable but not strictly necessary.	Catalyst, co-catalyst, and/or initiator are required.
Monomer disappears early in reaction.	Monomer concentration decreases steadily with time.
Product oligomers are steadily converted to higher MW product; intermediates can be isolated at any time. MW increases steadily with time.	High MW polymer formed immediately; since product molecules do not undergo further reaction, MW changes very little with time.
MW independent of temperature.	MW decreases with increasing temp.
Monomer concentration decrease is 2nd or higher order.	Monomer concentration decrease is first order.
Long reaction times are essential to obtain high MW.	Long reaction time improves yield but doesn't affect MW.
Medium viscosity increases rapidly near reaction end.	Medium viscosity increases monotonically.
Typical catalysts are organic acids, amines, or metal salts; active sites are cations, acid and alcohol groups.	Active sites are unpaired electrons, anions, cations, and coordination bonds with transition metal complexes.

Step-growth reactions involve a condensation reaction of two different functions **a** and **b** initially present on two different monomers to form a linkage **c** with elimination of water, alcohols, HCl, CO_2 and other molecules; however, as oligomers are formed, any two molecular species having the **a** and **b** functions can react. For example, the formation of a polyester oligomer occurs by a condensation reaction of an acid function with an alcohol

$$\mathrm{HO(CH_2)_xCO}\vdots\mathrm{O\text{-}H} + \mathrm{H}\vdots\mathrm{O\text{-}(CH_2)_xCOOH} \rightarrow \mathrm{HO[\text{-}(CH_2)_xCOO\text{-}]_2H} + \mathrm{H_2O} \qquad (1)$$

which can react further with either a monomer or an oligomer. While catalysts are not strictly necessary, they are highly desirable to accelerate (by orders of magnitude in rate) these relatively slow reactions to the high conversions required for formation of high-molecular-weight polymers. Condensation reactions are typically catalyzed by acids, bases, and/or metal ions. Polymers formed by step-growth condensation include (1) polyesters from reaction of a diacid with a dialcohol catalyzed by toluene sulfonic acid or metal salts, (2) polyurethanes from a diisocyanate and a dialcohol catalyzed by tertiary amines (e.g., 1,4-diazabicyclo[2,2,2]octane) and metal salts (e.g. dibutyltin dilaurate), (3) polyamides (nylons) from a diamine and a diacid, and (4) polycarbonates from transesterification of phenol and a carbonate [Rempp and Merrill, 1991].

Chain-growth polymerization involves the reaction of unsaturated monomer compounds (vinylic, acrylic, dienic) or strained heterocyclic monomers (via ring opening) with an active site which links it to a growing chain. Four kinds of sequential elementary steps are involved in chain growth: (1) relatively slow initiation, i.e. formation of an active site on a monomer, (2) rapid propagation by addition of monomers to an active site by opening of the double bond or ring and incorporation of the monomer residue into the chain (for example, growth to a molecular weight of 10^6-10^7 in 0.1 s is typical), (3) transfer of the active site from the macromolecular polymer to end its growth and begin the further growth of another, and (4) relatively slow termination or destruction of active sites. In chain-growth polymerization high-molecular-weight polymers are rapidly formed at low monomer conversions. Polymers produced via chain polymerization include PE, PP, polystyrene, PVC, polyvinyl esters and ethers, and acrylonitrile.

Active sites for chain-growth polymerization include (1) unpaired electrons (in free-radical polymerization), (2) anions having carbon-metal or alkoxide bonds, (3) cations such as carbenium or oxonium ions (with counterions), and (4) coordination bonds with transition metals in Ziegler Natta or metallocene catalysts. The type of active site most effective for a given polymerization is mainly a function of the polarity of the monomer and the acid-base strength of the ion formed [Billmeyer, 1984]. For example, monomers with electron-donating groups attached to the double-bonded carbons form stable carbenium ions and polymerize best with cationic catalysts, while monomers with electron-withdrawing substituent form stable anions and are catalyzed best by anionic catalysts. Coordination polymerization can be considered to be a special class of anionic polymerization, since the charge on the intermediates involves electron withdrawal from the monomer to the polymer [Candlin, 1981]. Free-radical polymerization is an intermediate case with moderate electron withdrawal from the double bond [Billmeyer, 1984].

Quite a number of monomers can be polymerized by more than one of these mechanisms [Billmeyer, 1984]. With the exception of propylene and higher α-olefins, isobutylene, and vinyl ethers most monomers undergoing chain reactions can be polymerized by free radicals; on the other hand, most monomers other than isobutylene, vinylidene chloride , vinyl fluoride, and vinyl esters can be polymerized by coordination catalysts. In fact, coordination catalysis is the only practical route to polypropylene and polymers of higher α-olefins. Isobutylene, on the other hand is only polymerized by a cationic mechanism. During the past two decades coordination catalysis has found increasingly greater application relative to anionic, cationic and free-radical routes because coordination catalysts facilitate polymerizations under relative mild conditions with excellent stereochemical control.

Coordination (or insertion) polymerizations are stereoregulated polyinsertion reactions catalyzed by transition metal complexes, i.e., Ziegler-Natta and metallocene catalysts. These catalysts have the ability to orient the monomer before addition to the chain, thereby controlling the steric conformation of asymmetric carbon atoms of polyvinylic chains.

Ziegler-Natta catalysts polymerize a wide variety of monomers to linear and stereoregular polymers [Billmeyer, 1984]. For example, production of highly-linear polyethylene is catalyzed by this route, in contrast to branched polyethylene formed by radical polymerization. Isotactic polypropylene can be produced at high selectivities approaching 96%. Butadiene and isoprene can be polymerized with high selectivities to cis-1,4, trans-1,4, isotactic,-12,2 or syndiotactic-1,2 depending upon the choice of catalyst and conditions.

Metallocenes are a new generation of highly-stereospecific polymer catalysts (fifth-generation polyolefin catalysts) that are just coming into commercial application which have unprecedented productivity, stereoselectivity, structure-programmability, and product distribution tunability. For example, they enable polymer molecular weight (MW), molecular weight distribution (MWD), comonomer distribution and content, and tacticity to be independently controlled. Products of metallocene polymerization are characterized by narrow MW distributions and uniform chain length. Moreover, these single-site catalysts are the first having the capability to produce either isotactic or syndiotactic polypropylene. Furthermore, this technology can be applied to production of new polyolefin and polystyrene products having properties that compete well with those of more expensive engineering plastics.

3 Industrial Polymerization Processes.

Some general principles. The objective in commercial polymerization is to produce economically a polymer of high purity and controlled MW at high rates. Keys to meeting this objective are (1) operation within a narrow temperature range at high conversion and low residence time and (2) removal or minimization of byproducts and impurities. Crucial to the control of reaction temperature is the removal of reaction heat from highly-exothermic addition polymerizations in the range of 70-100 kJ/mol (adiabatic temperatures of 200-400°C) [Rodriguez, 1996]. Temperature control is critical, since (1) MW distributions are broadened by temperature gradients; (2) polymers formed as solids (e.g. in gas-phase PE processes) soften around their maximum-use temperature, may become tacky, and aggregate; and (3) prolonged operation at high temperature causes catalyst deactivation and polymer degradation.

Accordingly, a variety of unique reactor designs which utilize a variety of fluid media are necessary to produce the wide range of commercial polymer products. Because of the high cost of separating and recovering catalyst from the polymer product, there is also a strong incentive to use catalysts that leave harmless residues and are sufficiently active to minimize to ppm levels the concentration of residue in the product.

Polymerization reactor and process types. Most polymerizations are carried out in liquid-phase, batch reactors; however, a relatively few-large scale processes, e.g. those for PE and

PP production, are continuous. Continuous processes are preferred because of their smoother operation, more uniform product and lower operating cost; however, they are not practical for many polymerizations.

Liquid-phase Polymerizations. Four different kinds of liquid-phase, batch (or continuous, stirred-tank reactor) systems are used: (1) *bulk polymerization* of liquid monomer with initiators in the absence of diluent or solvent, (2) *solution polymerization* of monomer dissolved in a solvent using soluble catalysts, (3) *suspension polymerization* of relatively large (10-1,000 micron) droplets of insoluble monomer plus catalysts suspended in water, and (4) *emulsion polymerization* of finely divided (0.5 - 10 micron) droplets of insoluble monomer suspended in water with water-soluble catalysts in micelles. The advantages, disadvantages and applications of these different reactor types are summarized in Table 3.

Table 3. Advantages, Limitations, and Applications of Four Types of Liquid-Phase Polymerizations

Reaction Types	Advantages	Limitations	Applications
Bulk	high yield/reactor vol., easy polymer recovery, casting option	removal of unreacted monomer, heat removal, auto acceleration	condensations, LDPE, polystyrene, nylon, methyl methacrylate
Solution	efficient heat removal and mixing, low-med. viscosity, easy removal of catalyst residues	low yield/reactor vol., solvent recovery is expensive, solvent fire hazards	low-P LLDPE, acrylics, polyvinyl alcohol, PVC, polybutadiene
Suspension	excellent heat removal and mixing, solvent cost & recovery minimal, low viscosity, easy polymer recovery	instability of suspension, low polymer purity due to suspending agents, high reactor cost, auto accel., batch reactor required	styrenic ion-exchange resins, vinyl polymers, e.g. PVC, styrene-acrylonitrile
Emulsion	excellent heat removal, good mixing, low viscosity, low solvent cost, higher rates than suspension, high MW polymers, sticky polymers easily handled	low polymer purity due to dispersing agents and catalyst residues, no catalyst recovery or filtration possible, batch reactor required, high reactor cost	many industrial polymers, synthetic rubbers, polybutadiene, PVC, latex paints, adhesives, and coatings

Gas-Phase Polymerizations. Efficient large-scale production of PE and PP from gaseous monomers using a heterogeneous catalyst has been practiced since about 1968 [Candlin, 1981; Rodriguez, 1996]. Reactors are fluidized beds (Union Carbides, Shell, BP Chemicals, Himont and Mitsui Petrochemical), horizontal reactors with weirs and rotating paddles (Amoco and El Paso), or helically-stirred reactors (BASF). Powdered catalysts are combined with gaseous monomer at the entrance to the reactor. Temperature is controlled by operation at a low conversion per pass through the reactor while removing heat from the monomer in an external heat exchanger before recycle to the reactor. The principle advantage of the gas-phase reaction is that the polymer product is easily separated from the monomer. Given catalysts of high activity and stereoselectivity, separation of the catalyst residue from the polymer is unnecessary.

Catalytic Processes for PE Production. There are four principal types of commercial PE-production plants: (1) free-radical, high-pressure bulk polymerization to LDPE; (2 and 3) coordination-catalyzed, slurry-suspension, moderately-low pressure Phillips and Ziegler-Natta polymerizations to HDPE and LLDPE; and (4) gas-phase, fluid-bed polymerization to produce HDPE and LLDPE. Operating conditions, typical catalysts, and reactor types used in the four principal processes are summarized in Table 4.

Table 4. Process Characteristics for Production of Polyethylene

Process Type	Reactor Type	Catalyst Types	Operating Conditions	Products
free-radical, bulk, high-pressure	tubular	initiators, dil.O_2	1000-3000 atm, 100-300°C, 10-30% conv.	LDPE
Phillips, coordin., slurry, mod.pressure	large loop	CrO_3, Cr complx/SiO_2, SSCs[a]	80-150°C, 20-35 atm, τ = several hours[b]	HDPE, LLDPE
Ziegler-Natta coordin., slurry	CSTR	$TiCl_4$/Al alkyl/$MgCl_2$ SSCs	50-100°C, 20-35 atm, τ = 3-5 hours	HDPE, LLDPE
gas-phase, coord. powder catalyst	fluidized bed	CrO_3, Cr complx/SiO_2, SSCs	80-120°C, 20-35 atm, 2-3% conv.per pass, τ = 3-5 hours	HDPE, LLDPE

[a] SSC = single site catalysts or metallocenes. [b] τ = reactor residence time

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Mechanism of Free Radical Polymerization

Free radical polymerizations are typically initiated by thermal decomposition of an organic peroxide such as benzoyl peroxide, azo-compounds, or redox systems such as Fe^{2+} / H_2O_2; organic peroxides form peroxo radicals which then react to form a monomer free radical:

$$\text{R-O-O-R} \rightarrow 2\ \text{R-O}^* \text{ (designated as R'}^*\text{)} \quad (1)$$

$$R'^* + CH_2{=}CHX \rightarrow R'CH_2CHX^* \quad (2)$$

Propagation then occurs by successive addition of monomers:

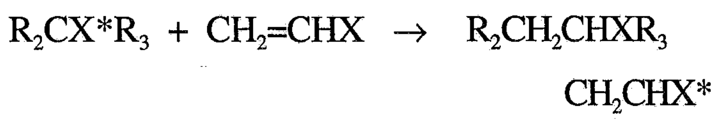
$$R'CH_2CHX^* + CH_2{=}CHX \rightarrow R'(CH_2CHX)CH_2CHX^* \quad (3)$$

$$R'(CH_2CHX)CH_2CHX^* + CH_2{=}CHX \rightarrow R'(CH_2CHX)_2CH_2CHX^* \quad (4)$$

Chain transfer can take place by transfer of an unpaired electron from a growing chain to a saturated monomer or polymer where R_1, R_2, and R_3 refer to chains of arbitrary length:

$$R_1CH_2CHX^* + R_2CHXR_3 \rightarrow R_1CH_2CH_2X + R_2CX^*R_3 \quad (5)$$

This process results in branching if a monomer is now added at the site of the unpaired electron in the $R_2CX^*R_3$ radical:



$$R_2CX^*R_3 + CH_2{=}CHX \rightarrow \underset{\qquad\quad CH_2CHX^*}{R_2CH_2CHXR_3} \quad (6)$$

Termination typically occurs by transfer of a H atom from one polymer radical to another:

$$R_1CH_2CHX^* + R_2CH_2CHX^* \rightarrow R_1CH_2CH_2X + R_2CH{=}CHX \quad (7)$$

Terminative coupling of two polymer radicals sometimes occurs, although this is a low probability event since the resulting head-to-head groups in the -CHX-CHX- structure have high steric hindrance and a less favorable electronic configuration relative to the head-to-tail structure.

A simplified sequence of elementary steps for the case of heterogeneous coordination polymer-ization can be written as follows [Billmeyer, 1984; Rempp and Merrill, 1991; Rodriguez, 1996] where [TMC] is the transition metal complex, AR a metal alkyl, and M is a monomer:

Initiation: $$[TMC] + AR = [TMC]\text{-}AR \quad (8)$$

$$[TMC] + M = [TMC]\text{-}M \quad (9)$$

$$M\text{-}[TMC]\text{-}AR \rightarrow [TMC]\text{-}A\text{-}M\text{-}R \quad (10)$$

Propagation: $$M\text{-}[TMC]\text{-}A\text{-}M_x\text{-}R \rightarrow [TMC]\text{-}A\text{-}M_{x+1}\text{-}R \quad (11)$$

Chain transfer: $$M\text{-}[TMC]\text{-}A\text{-}M_x\text{-}R \rightarrow [TMC]\text{-}A\text{-}M\text{-}R + M_x \quad (12)$$

Termination: $$M\text{-}[TMC]\text{-}A\text{-}M_x\text{-}R \rightarrow [TMC]\text{-}A\text{-}M + M_xR \quad (13)$$

Both mechanisms predict a rate of propagation which is first order in monomer concentration.

Kinetics of Free Radical Polymerization

The mechanistic scheme with chain transfer omitted can be written in the following simplified form:

Initiation: $I \rightarrow 2R^*$ (1)

Addition: $R^* + M \rightarrow M_1^*$ (2)

Propagation: $M_1^* + M \rightarrow M_2^*$ (3)

$M_2^* + M \rightarrow M_3^*$

$M_x^* + M \rightarrow M_{x+1}^*$

Termination: $M_x^* + M_y^* \rightarrow M_x + M_y$ (4)

From Eqn. 12-41, the rate of initiation is $r_i = k_i\,[I]$, while the rate of addition from Eqn. 12-42 is $r_a = 2\,fr_i$ <u>where f is the fraction of R* formed in Eqn. 12-41 which reacts in Eqn. 12-42</u> and the factor of 2 accounts for the two-times greater production of R* in Eqn. 12-41 relative to 12-42. Thus, $r_a = d[M_1^*]/dt = d[M^*] = 2f\,k_i\,[I]$, since <u>early in the reaction the total concentration of radicals in the reacting system is approximately equal to the concentration of M_1^* radicals formed during addition</u>.

<u>At steady state the rate of initiation of free radicals is equal to the rate of their termination</u>, i.e. $r_a = -2r_t = d[M^*]/dt$ or $2fk_i[I] = 2k_t\,[M^*]^2$; this expression can be solved for the concentration of polymer radicals, i.e.,

$$[M^*] = (f\,k_i\,[I]\,/\,k_t)^{0.5} \tag{5}$$

The overall rate of reaction is essentially the rate of propagation, since the rate of propagation greatly exceeds that of initiation (or termination):

$$r_{overall} = r_p = -d[M]/dt = k_p\,[M][M^*] \tag{6}$$

Substituting for [M*] from Eqn. 12-45 we find

$$r_p = k_p (f\, k_i / k_t)^{0.5} [M][I]^{0.5} \qquad (7)$$

which indicates that early in the reaction the rate of polymerization is first order in monomer concentration and half-order in initiator concentration. Since the initiator concentration may be approximately constant at a point early in the reaction, the rate of polymerization is in this case first order in monomer concentration. If k_i is measured by nonsteady-state methods, the value of k_p can be obtained.

Rate constants for initiation, propagation, and termination are within the ranges of 3 - 20 x 10^{-6} s^{-1}, 250 - 18,000 l/mol s, and 4 - 1,100 x 10^{-6} l/mol s respectively; activation energies for initiation, propagation and termination are 124 - 160, 16 - 30, and 2 - 21 kJ/mol respectively, while values of f are in the range of 0.6 - 1.0.