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Radical Polymerization in Industry

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1 INTRODUCTION

The goal of this article is to provide a brief overview of radical polymerization (RP) in industry. It will highlight the role of this technique in the context of polymer industry and review its mechanistic and process aspects from the point of view of industrial polymerization. Then, recent progress in industrial applications of controlled RP will be shown. Of course, treatment of such a multifaceted discipline as industrial RP (IRP) is possible only in very limited depth. Therefore, only the most salient features of IRP will be discussed and references for further reading will be given. In accord with the IUPAC recommendation,[1] the term *radical polymerization* will be used instead of *free radical polymerization*.

Life as we know would not be possible without synthetic polymers, which are commonly called *plastics*. The term *plastics* should not be confused with the technical adjective *plastic*, describing permanent deformation of materials that were strained beyond a certain point. Thus, plastics in this article incorporate all synthetic polymers and macromolecular materials, not only those undergoing plastic (thermoplasts) or elastic (elastomers) deformation but also highly cross-linked and hard thermosetting polymers. Diverse semisynthetic macromolecular materials such as vulcanized rubber, celluloid, or galalith were discovered and already used in the nineteenth century. However, the spread of polymers to every aspect of modern life was possible only after the fundamentals of polymer science were laid down during 1920–1930.[2,3] An account of the history of polymers has been given by Morawetz.[4]

The industrial production of several plastics such as bakelite, polystyrene (PS), low density polyethylene (LDPE), or poly(vinyl chloride) (PVC) already started before World War II. However, only the progress in science and technology and the economic growth of the postwar period allowed the worldwide production of polymers to grow at around 9% per year, from 1.5 million tons (mt) in 1950 to about 230 mt in 2009. Of these 230 mt, 55 mt was produced is Europe[5] (Figure 1). In terms of volume (m^3), the production of polymers exceeds that of iron and steel.

Globally, the long-term growth of plastics is expected to be at around 4% and hence higher than the gross domestic product (GDP) growth. The average worldwide consumption[5] of plastics is significantly below that of the industrialized regions (Figure 2), thus leaving room for future growth.

Up to 2015 and beyond, the fastest growth is expected in Asia. One of the important stimulators of the future demand for polymers is the growing concern about climate change. In fact, more than 14% of all greenhouse gases worldwide are generated by the transportation sector. Reducing the weight of cars through the replacement of metals by plastic can cut a vehicle's weight by up to 30%, resulting in a significant reduction in fuel consumption. The proportion of plastics in a typical Western European car is about 15% today (160 kg), compared with 6% in 1970. By 2020,

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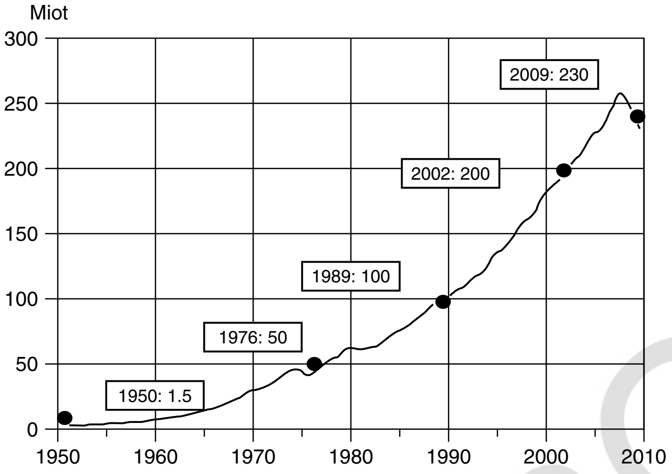


Figure 1 Worldwide production of polymers 1950–2009.

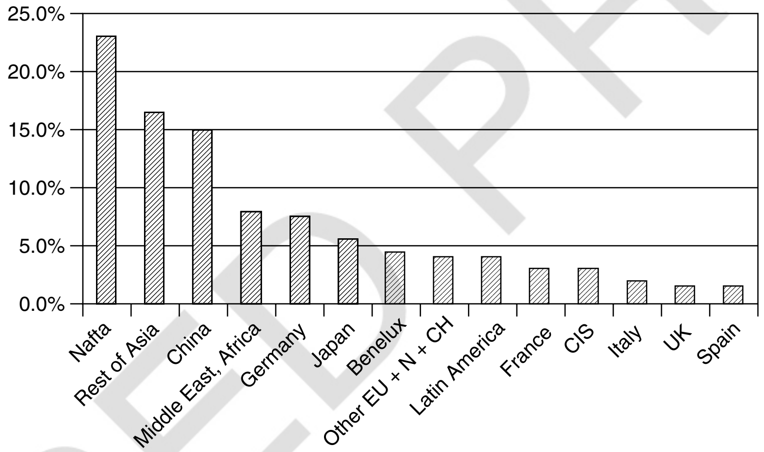


Figure 2 World production of polymers 2009, regional split.

plastics could account for more than 25% of a car's weight.[6]

Countless polymers are known in the literature, but the number industrially manufactured polymers is relatively small. For example in 2009, nine types of polymers accounted for 77% (176 mt)[6] of the 230 mt[5] of polymers produced worldwide (Figure 3). The five most important plastics are thermoplastic polymers, namely polypropylene (PP), high density polyethylene (HDPE), linear low density polyethylene (LLDPE), LDPE, and PVC, of which 143 mt were produced.

The rest are smaller volume polymers such as polyesters, with poly(ethylene terephthalate) (PET) as the most important example, PS as well as engineering plastics, and high-performance polymers. The latter exhibit superior mechanical and thermal properties under a wide range of conditions. As their name suggests, these are used in the manufacture of parts or in applications requiring extraordinary performance rather than for construction, containers, or packaging, which is the domain of commodity polymers. Some examples of engineering plastics and high-performance polymers are acrylonitrile–butadiene–styrene (ABS) copolymers, polycarbonates (PCs), polyamides (PAs), polyurethanes (PURs), polysulfones (PSUs), polyetherketones (PEKs), polyetheretherketone (PEEKs), polyoxymethylene (POM), polyimides (PIs), polyphenylenesulfide (PPS), polyphenylene

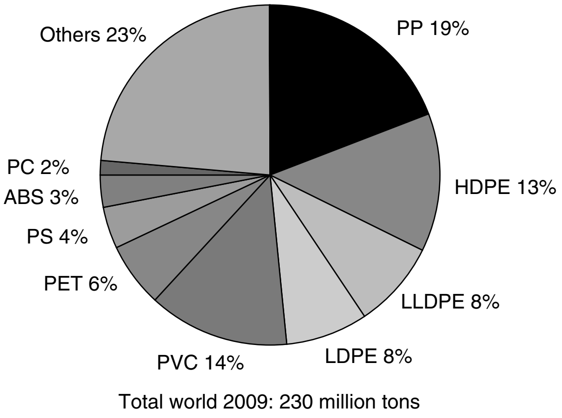


Figure 3 World's largest volume polymers.

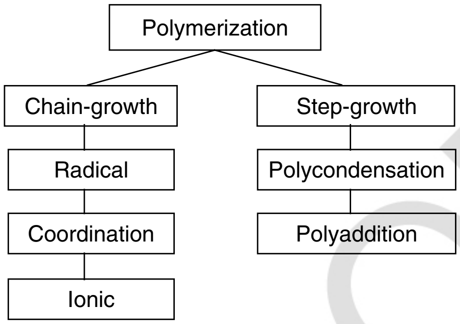


Figure 4 Mechanistic classification of polymerization processes.

oxide (PPO), or fluoropolymers (e.g., Teflon, polytetrafluoroethylene (PTFE), to name just the most relevant. Additionally, there is the important group of thermosetting polymers[7–9] including epoxides, phenol-formaldehyde, urea, and melamine polymers, as well alkyds and unsaturated polyester resins. Last but not least, must be mentioned the silicone-based[10] polymers. A special case is the family of dispersion[11,12] polymers that have in common the same state of aggregation but are diverse from the point of view of their chemical composition. Latest data on production volumes of individual polymers and their regional split have been published.[13]

The classes of polymers differ significantly not only in their production volume but also in their selling price,[14,15] which is 0.5–2.5€ kg^{-1} for commodity polymers, 10–12€ kg^{-1} for PTFE or PSU, and about 60€ kg^{-1} for PEEK. Prices of high-tech polymeric specialties, for example, those for the electronic industry, are even much higher. As the same polymer is often commercialized by different companies under different names, a plurality of trade names[16] exists.

A number of good monographs[17–21] and reference works[22–24] provide detailed information on industrial polymers and their applications. Domininghaus *et al.*[14] provides a compilation of physical and technical data that are important for a professional selection of an optimal polymeric material for a given application.

Synthetic polymers are prepared from low molecular weight building blocks called *monomers* by a process known as *polymerization*. Existing macromolecules can be further modified by polymer analogous reactions. Polymerizations can be divided from a mechanistic point of view[2] into several classes. RP belongs to the class of chain-growth polymerizations (Figure 4).

Polymers produced by RP represent roughly 40–45% of all industrial polymers, which ranks this method among the most important industrial polymerization techniques. Polymers prepared by nonradical processes are not discussed in this article. Abundant literature is available on ionic,[25–29] step-growth,[9, 29–31] coordination,[29, 32–36] and group-transfer polymerization[37] methods.

Nevertheless, it should be noted that there are other industrially important polymer technologies and applications that are based on radical processes. Thus, millions of tons of unsaturated polyester resins[9,31,38] are cured (cross-linked) with radical initiators, predominantly peroxides. The drying of alkyd resins[39,40] also proceeds via the radical mechanism. Photopolymerization of coatings, printing inks, adhesives, and microelectronic components is a multibillion dollar business and still rapidly growing. Radically induced cross-linking[41,42] of polymers, controlled degradation[43–45] of the molecular weight of polypropylene, and modification of polyolefins by grafting[41, 46–48] of polar monomers are other examples. Finally, radicals are very often involved in the thermally and photochemically induced degradation[49,50] of polymers (e.g., in autoxidation) as well as in the mode of action of the necessary stabilizers[51,52] used to prevent or retard this deterioration.

2 GENERAL AND MECHANISTIC ASPECTS OF INDUSTRIAL RADICAL POLYMERIZATION

The dominant position of RP in industry originates from several unique characteristics that differentiate it from other polymerization methods. Thus, in contrast to ionic or coordination polymerization, RP is tolerant of protic solvents and trace impurities such as oxygen or monomer stabilizers. Consequently, it can be conducted in polar solvents such as alcohols or, more importantly, water with monomers that are not rigorously dried or purified. Furthermore, a large number of low-priced monomers are available. Thus, from an economical point of view, RP is the technique of choice. For example, the cost to polymerize styrene by anionic polymerization is about 50% higher[53] than for RP.

2.1 Monomers

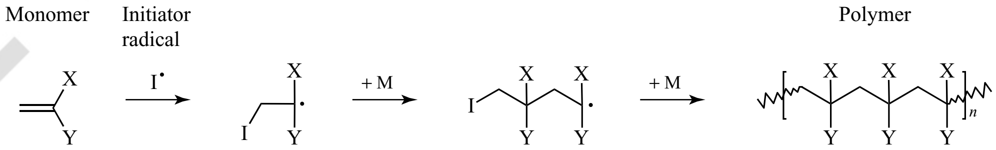
Many molecules containing unsaturated homo or heteronuclear double bonds, dienes, trienes, strained cycloaliphatics, *exo*-methylene-substituted cyclic compounds, or vinylcyclopropanes are amenable[2,54] to RP. However, the major industrial monomers are compounds **1** (Scheme 1) containing C=C double bond(s) where X is primarily X=H, (CH_3) and Y=H, Cl, COOH, COOR, $CONH_2$, CN, $OCOCH_3$, C_6H_5, $–CH=CH_2$), which serve as precursors of the corresponding polymers **2**. Besides the basic monomers that are produced on a very large scale, there exists a variety of specialty monomers that are used to make homopolymers or copolymers with specific properties. Examples are the styrene derivatives 1,4-divinylbenzene, *p*-vinylbenzyl chloride, and *p*-acetoxystyrene, 4-vinyl pyridine, *N*-vinyl pyrrolidone, various esters and amides of acrylic and methacrylic acid (e.g., *n*-butyl acrylate, 2-hydroxyethyl (meth)acrylate, 2-dimethylaminoethyl (meth)acrylate, glycidyl methacrylate, *N*-isopropyl acrylamide), and a variety of (meth)acrylates of polyhydric alcohols (e.g., ethylene glycol, trimethylolpropane, or pentaerythrite). The latter, by virtue of their high functionality, are used as cross-linkers. The synthesis, properties, and applications of specialty monomers are summarized in the book[55] by Havelka and McCormick. A compilation of commercially available specialty monomers for formulations cured by photopolymerization is provided by Webster *et al*.[56]

The most important monomers along with the applicable polymerization processes and typical uses of the polymers are shown in Table 1.

Technological and economic information on the industrial synthesis of monomers can be found in the monograph of Arpe.[57] The current raw material base for monomers consists almost exclusively of crude oil and natural gas and will remain so also in the near future. It should be mentioned[58] that only ∼4–8% of crude oil is used for polymer production, the rest serving predominantly as a source of energy. However, in view of the limited availability and increasing price of oil and gas, a shift[59] to monomers and polymers from renewable[60] resources, a renaissance of coal, as well as increasing importance of chemical recycling[58] of polymeric materials is foreseeable.

2.2 Mechanism of Radical Polymerization

The mechanism of RP is now well understood even though some problems such as control of the stereochemistry of the propagation step or sequence control[61] are still not solved. On the other hand, powerful techniques of controlled RP have been developed in the last 20 years and the first commercial applications are appearing. A comprehensive treatment of the chemical and



1

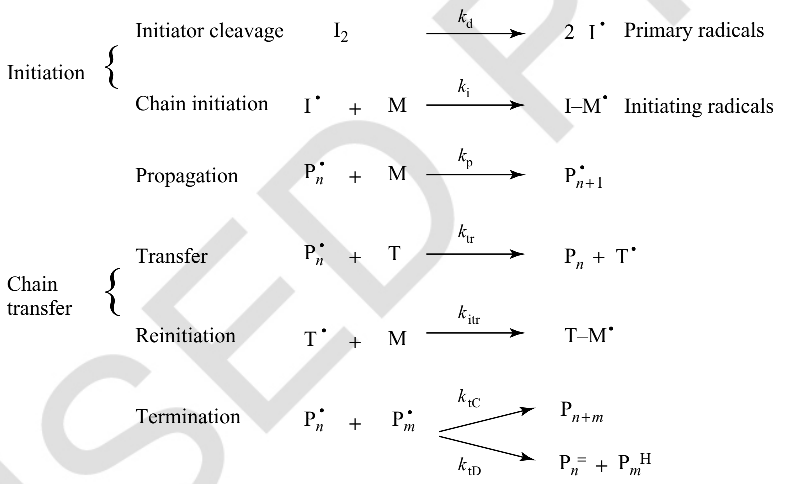
2

Scheme 1 Radical polymerization of a C=C monomer.

Table 1 Major monomers for industrial RP.

Monomer	Polymerization technique						
	G	B	S	E	L	P	Use
Acrylic acid, acrylamide					+		V
Acrylic esters				+	(+)		A,V
Acrylonitrile						+	F
Methyl methacrylate		+	+	+	+		T
Ethene		+	+	(+)	(+)	(+)	F,T
Styrene		+	+	(+)	(+)		T
p-Methyl styrene			+	+			T
N-Vinyl pyrrolidone		+			+		V
Vinyl acetate		(+)	(+)	+	(+)		A,C
Vinyl chloride	+	(+)	(+)	+	(+)		T
Vinyl fluoride		+					C,T
Vinylidene fluoride			+	+			C,T
Trifluorochloro-, tetrafluoroethene			+				T
Butadiene, chloroprene			(+)	+	+		A,C,E,T

Source: Table adapted from Ref. 2. Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 2005.
Polymerization in the gas-phase (G), in bulk (B), in suspension (S), in emulsion (E), in solution (L), by precipitation (P). Main use as adhesive (A), coating (C), elastomer (E), fiber (F), thermoplastic (T), or various (V). + Mainly, (+) less often.



I_2 is initiator, M is monomer, $P_n^\bullet$ is a radical of chain length *n*,
T is a chain transfer species, P_n is a polymer

Scheme 2 Key mechanistic steps of radical polymerization.

mechanistic aspects of RP is provided by the outstanding monographs[54] of Moad and Solomon, Matyjaszewski and Davis[62], and others[63,64] (see also **Kinetics of Polymerizations**, Volume 4). The mechanism of RP consists of several steps as depicted in Scheme 2.

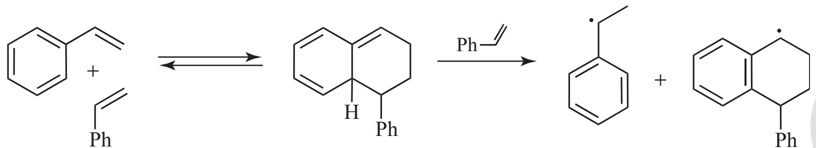
The numerical values for important parameters of RP are given in Table 2.

As the detailed discussion of this generally accepted mechanism is available elsewhere, only those points of industrial importance will be briefly highlighted.

Table 2 General range of values for key parameters of radical polymerization.

$k_d = 10^{-4}–10^{-6}\ s^{-1}$	$k_i \approx k_p = 10^2–10^4\ M^{-1}\ s^{-1}$	$k_{tC} \approx k_{tD} = 10^6–10^8\ M^{-1}\ s^{-1}$
$[I] = 10^{-2}–10^{-4}\ M$	$[M] = 10^{-1}–10\ M$	$[R^{\bullet}_n] = 10^{-7}–10^{-9}\ M$

Source: Data from Ref. 65, p. 274.



3

Initiation

Scheme 3 Mayo mechanism of styrene thermal autopolymerization.

2.3 Initiators and Initiation

Initiation of RP begins with the generation of primary radicals (Scheme 2) from the initiator or initiating system. Addition of the primary radicals to the monomer then affords the initiating radicals. The dissociation of the initiator is generally much slower ($k_d \sim 10^{-5}\ s^{-1}$) than the addition of primary radicals to monomer molecules ($k_i \approx 10^4\ M^{-1}\ s^{-1}$). A comprehensive discussion of all aspects of the different classes of initiators or initiating systems and the various kind of primary radicals (C, O, S, Si, or P-centered) is provided in the monograph[54] of Moad and Solomon. A survey of radical initiators including decomposition kinetics and half-life times can be found in the handbook[66] of Denisov and coworkers and to a smaller extent in the *Polymer Handbook*.[67] Similar information on commercially available initiators is accessible on the websites of the major producers such as AkzoNobel, Arkema, and Wako Chemicals. Braun recounts the origins and development of RP from a historical point of view.[68] The most important initiators and initiating techniques for industry are discussed briefly below (see also rad003 **Overview of Radical Initiation**, Volume 1).

2.3.1 Thermal Autoinitiation

Styrene and its derivatives are the most prominent examples of monomers that generate initiating radicals by a purely thermal reaction without participation of other reagents. For example, at 180 °C, 80% conversion of pure styrene monomer to polymer occurs in 40 minutes. The most accepted mechanism[69] of styrene autoinitiation involving formation of a Diels–Alder adduct **3** (Scheme 3) was proposed by Mayo. Thermal self-initiation of styrene is used industrially to prepare extremely pure PS devoid of any initiator and derived functional groups. Thermal autoinitiation of other monomers (acrylates or methacrylates[70]) is much slower and without any practical importance.

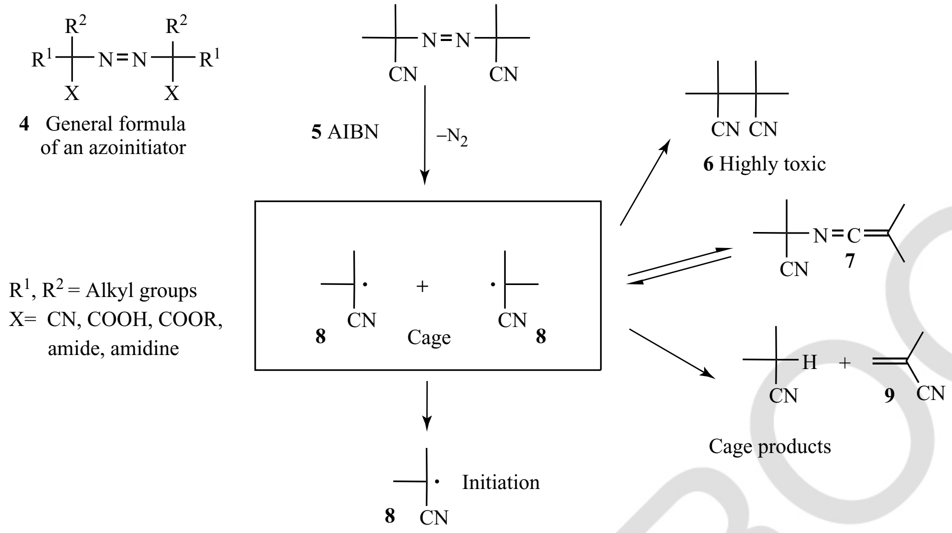
2.3.2 Azoinitiators

Industrially important azoinitiators are symmetrical dialkyldiazenes **4** (Scheme 4) bearing tertiary R groups with substituents (X) which serve to stabilize the incipient radical, thus lowering the decomposition temperature. The most important member of this class is azo-isobutyronitrile **5** (AIBN).

The thermal decomposition of azoinitiators generates two C-centered radicals and nitrogen. The mechanism of the thermal and photochemical decomposition of dialkyldiazenes has been reviewed by Engel.[71] Unfortunately, the yield of initiating radicals is practically never quantitative. In fact, depending on the viscosity of the surrounding media and size of the primary radicals, the latter can undergo an irreversible cage termination reaction leading to inactive products. Hence, only those primary radicals that escape from the solvent/monomer cage participate in chain initiation. This cage effect negatively influences the initiator efficiency (f) which is defined by (1) for an initiator generating n (usually 2) primary radicals and typically[72] lies in the range of 0.5–0.7 (or 50–70%).

$$f = \frac{\text{Rate of initiation}}{n \times \text{Rate of initiator decay}} \qquad (1)$$

The cage termination products may be problematic. For example, the dinitrile **6** formed from AIBN



Scheme 4 Azoinitiators and their decomposition mechanism.

is a highly toxic compound,[73,74] which prevents the use of AIBN for making polymers that would come into contact with foodstuff. The C–N dimer **7** can redissociate[75] into the radicals **8**, thus complicating the polymerization kinetics. Furthermore, the methacrylonitrile **9** is readily copolymerized with the monomer and can influence[76] the polymer properties.

The thermal decomposition of azoinitiators follows first-order kinetics (2), and the temperature dependence of k_d obeys Arrhenius law (3). A very important characteristic of a polymerization initiator is its half-life ($t_{1/2}$) (4), which is the time required to reduce the original initiator concentration by 50%. It can be easily calculated using (2–4) and the tabulated Arrhenius parameters A and E_a.

$$-\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}[t]} = k_\mathrm{d}[\mathrm{I}] \tag{2}$$

$$k_\mathrm{d} = A\mathrm{e}^{-\frac{E_\mathrm{a}}{RT}} \tag{3}$$

$$t_{1/2} = \ln\frac{2}{k_\mathrm{d}} \tag{4}$$

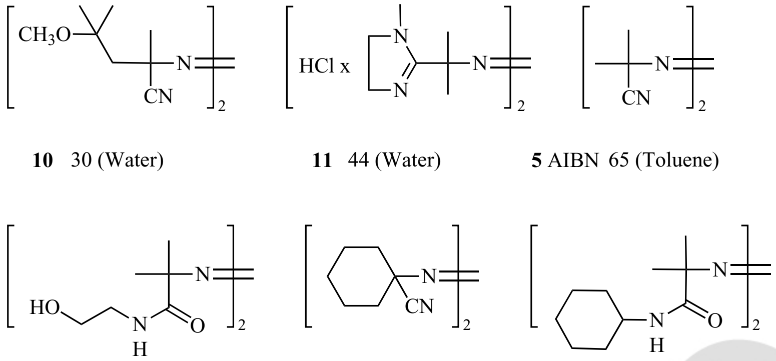
where k_d is the rate constant of initiator decomposition (s^{-1}); [I] is the initiator concentration (M); A is the Arrhenius frequency factor (s^{-1}); E_a is the activation energy for the initiator decomposition (J mol^{-1}); R is 8.3142 J mol^{-1} K^{-1}; T is the temperature in K; and $t_{1/2}$ is the half-life time (s^{-1}).

Activation energies of thermal homolysis of azoinitiators lie in the range of 100–170 kJ mol^{-1} and thus decomposition rates are very sensitive to temperature. For example, $t_{1/2}$ of AIBN decreases from 10 hours at 65 °C to 20 minutes at 90 °C and to ~45 seconds at 110 °C. In terms of volume, AIBN is the most important azoinitiator. There are several other initiators on the market with different cleavage temperatures, solubility in water or organic solvents, or functional groups (X) other than CN. The latter allow introduction of the functionality into the polymeric chain. Examples[77] are compounds **10–14** shown in Scheme 5.

In general, advantage of azoinitiators over the widely used peroxides is their lower tendency to undergo chain transfer reactions. This leads to better defined polymers containing fewer oxygenated impurities, which enhances their thermal or photochemical stability.

2.3.3 Peroxides

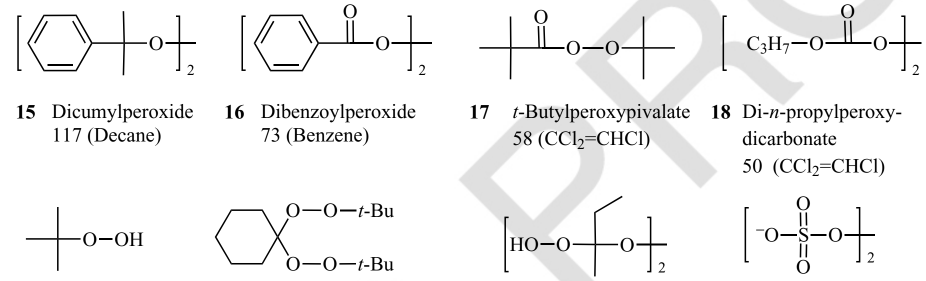
Peroxides $\mathrm{R^1}$–O–O–$\mathrm{R^2}$ are the most important industrial radical initiators, exceeding the production volume of azoinitiators by orders of magnitude. About 45% of the 207 000 tons of peroxides that were utilized[78] in 2007 by the worldwide plastics industry was used to initiate RPs. The rest found application in radically induced cross-linking



10 30 (Water) **11** 44 (Water) **5** AIBN 65 (Toluene)

12 86 (Water) **13** 88 (Toluene) **14** 111 (Ethylbenzene)

Scheme 5 Examples of commercial azoinitiators with indicated temperatures (°C) for a half-life of 10 hours.



15 Dicumylperoxide 117 (Decane)

16 Dibenzoylperoxide 73 (Benzene)

17 *t*-Butylperoxypivalate 58 (CCl_2=CHCl)

18 Di-*n*-propylperoxydicarbonate 50 (CCl_2=CHCl)

19 *t*-Butylhydroperoxide 168 (Benzene)

20 1,1-Di-*t*-butylperoxycyclohexane 97 (Dodecane)

21 Ethyl-methylketone peroxide 105 (–)

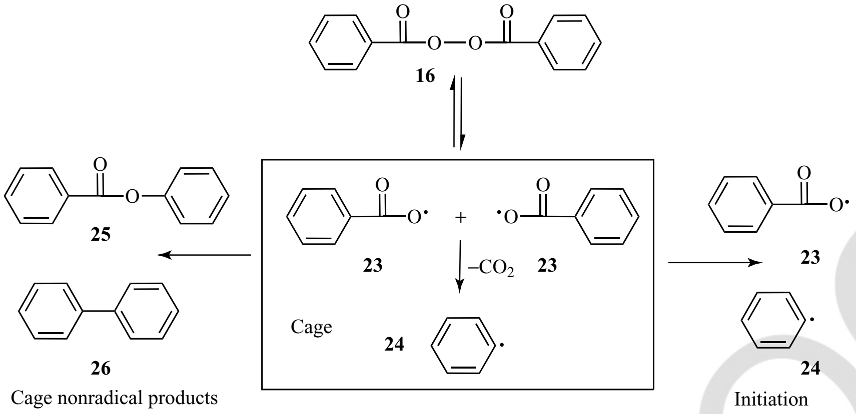
22 Persulfate anion 69 (0.1 M NaOH)

Scheme 6 Examples of commercial peroxide initiators with indicated temperatures (°C) for a half-life of 10 hours.

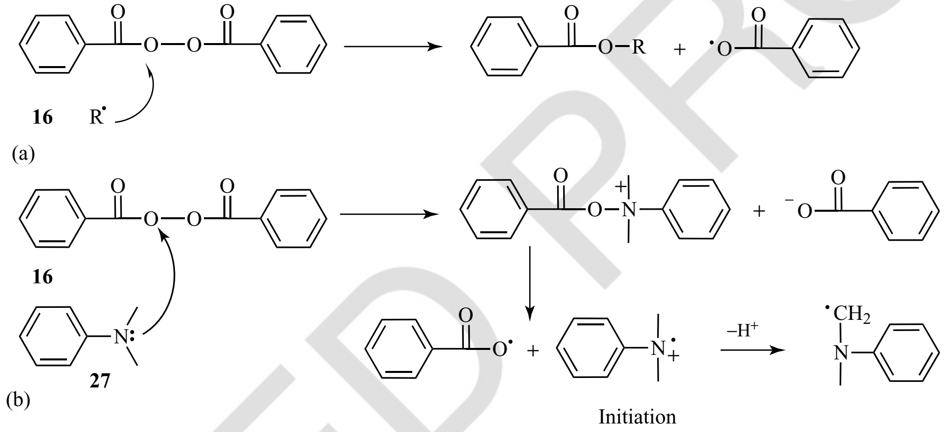
of unsaturated polyester resins and polyethylene, in controlled reduction of molecular weight of polypropylene, and as synergists for flame retardants. A detailed analysis of the markets, applications, and future trends for organic peroxides can be found in the market study[78] of Townsend Polymer Services. The most important commercial peroxide initiators are dialkylperoxides, diacylperoxides, hydroperoxides, peroxyesters, peroxydicarbonates, peroxyketals, ketone peroxides, and inorganic peroxides. Several dozens of derivatives with varying half-life, solubility, and volatility are available on the market. Typical examples are the compounds **15**–**22** shown in Scheme 6.

The chemistry of peroxides was recently reviewed.[79] Generation of radicals from peroxides occurs via homolysis of the weak –O–O–bond. The bond dissociation energies[66,80] of most peroxides lie between 127 (dibenzoyl peroxide) and 211 kJ mol^{-1} (H_2O_2). The nature of the primary radicals depends[54] on the structure of the starting peroxide and the type of cage reactions. For example, thermolysis of dibenzoylperoxide **16** gives rise to the relatively long-lived benzoyloxy radicals **23**. As **23** can also decarboxylate to give phenyl radicals **24**, both these radicals are involved in chain initiation. The competitive irreversible coupling of **23** and **24** yields the cage products **25** and **26** (Scheme 7).

Analogously, hydroperoxides generate alkoxy and hydroxyl radicals, and dialkylperoxides are sources of alkoxy radicals. Aliphatic diacylperoxides yield predominantly alkyl radicals because of the very fast in-cage decarboxylation of primary aliphatic acyloxy radicals. However, the simple homolysis of the –O–O–bond of peroxides is not the sole decomposition mechanism. In fact, the radical chemistry of peroxides is more complex than that of azoinitiators. Diacyl peroxides are susceptible

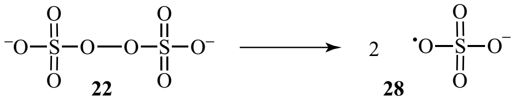


Scheme 7 Thermal decomposition of dibenzoyl peroxide.



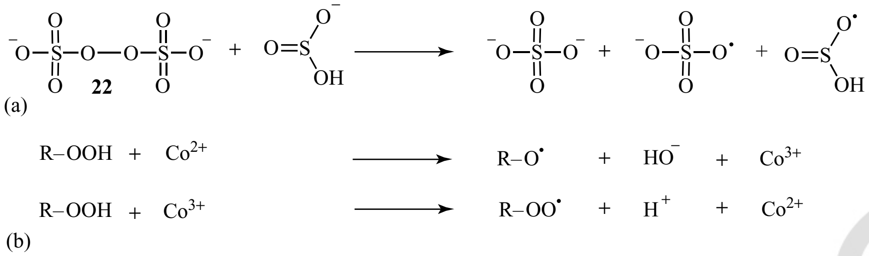
Scheme 8 Induced decomposition of dibenzoyl peroxide with (a) radicals and (b) aromatic amines.

to radical-induced decomposition resulting from homolytic attack of a radical on one of the oxygens of the –O–O–bond (Scheme 8). The consequence is chain transfer from the growing chain to the initiator with the concomitant incorporation of a benzoyloxy group into the polymer in a form of a *secondary* ester. Such end groups may negatively influence the thermal (PS[76]) or hydrolytic (PVC[81]) stability of the polymer. Of practical importance is the decomposition of dibenzoyl peroxide **16** induced[82] by aromatic amines (Scheme 8). As this reaction takes place already at room temperature or even below, addition of an amine synergist (often called *accelerator*) to a polymerizable composition containing **16** allows the polymerization to occur at room temperature or even around 0 °C. Two-component initiating systems consisting of **16** and *N*,*N*-dimethylaniline **27** (or similar derivatives) are widely used for the room-temperature curing[9,31,83] of unsaturated polyesters.



Scheme 9 Radical generation from a persulfate.

The water soluble sodium, potassium or ammonium salts of peroxydisulfuric acid (persulfates) are important initiators for aqueous and emulsion (EP) polymerizations. The mechanism of radical generation from the persulfate dianion **22** depends on pH. Homolytic cleavage affording the sulfate radical anion **28** dominates in neutral media (Scheme 9) whereas heterolytic cleavage occurs in acidic solution.



Scheme 10 Redox reaction between (a) persulfate and hydrogen sulfite, (b) hydroperoxide and Co ions.

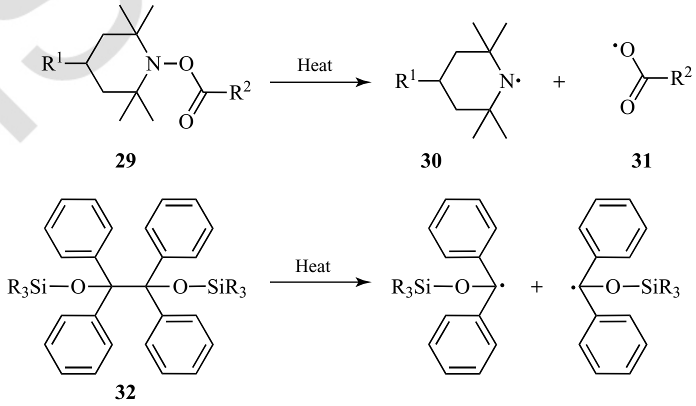
Furthermore, redox reactions occur between persulfates **22** and reducing agents such as 2-mercaptoethanol, thiourea, sulfites,[84] amines, dithionites, or thiosulfates. Such initiating systems are frequently employed in aqueous EPs. In addition to the amine–dibenzoylperoxide system, the redox reaction of hydroperoxides with ions of various transition metals (mostly Co or Mn) is commonly used for the room-temperature curing of unsaturated polyesters. Typically, two-component initiating systems consisting of a hydroperoxide (e.g., cumyl hydroperoxide or ethylmethylketone peroxide **21**) and a Co- or Mn-based accelerator (e.g., cobalt octoate or manganese naphthenate) are used for this purpose (Scheme 10).

Redox-initiated polymerizations were reviewed[85] by Misra and Bajpai. A comprehensive discussion of the initiating mechanism of the different peroxide families is available in the monograph[54] of Moad and Solomon.

Organic peroxides, such as azoinitiators, are unstable compounds and decompose exothermally at relatively low temperatures. They must be handled and stored properly and most require some form of temperature control. Guidelines for the safe handling of these initiators were recently reviewed[86] and are available on the web pages[87] of their manufacturers.

2.3.4 Miscellaneous Radical Initiators

Peroxides are the most important industrial initiators for RP followed by azoinitiators. Much smaller volumes of specialty initiators are also used. One example is 2,3-dimethyl-2,3-diphenyl butane, known as Perkadox® 30 (AkzoNobel), used in styrene polymerization. This C–C dimer thermally dissociates into cumyl radicals ($t_{1/2} = 1$ hour at 259 °C in PhCl). Novel initiators[88] with improved handling and storage stability as compared to peroxides or azo-compounds are highly desirable and are slowly appearing on the market. Examples are sterically hindered *N*-acyloxyamines[89] **29** and silylated benzopinacol[90] derivatives **32** (Scheme 11). The proposed mechanism of action of the *N*-acyloxyamine radical initiators **29** involves[91]



Scheme 11 *N*-Acyloxyamine and silylated benzopinacol initiators.

homolysis of the N–OC bond to generate *N*-aminyl radicals **30** and acyloxy radicals **31**. This contrasts with the NO–C bond homolysis of alkoxyamine initiators for controlled RP.

Initiators for controlled RP are discussed in respective sections.

2.3.5 Photoinitiators

Photoinitiators[92–95] are compounds that generate primary radicals upon irradiation with light of a suitable wavelength (generally UV).

They are niche products used to initiate polymerization (curing) of radically polymerizable/cross-linkable coatings (e.g., on furniture, flooring, metal, plastics, automotive parts, paper, optical fibers), printing inks, and adhesives, or in the production of microelectronic devices. They are not used, however, in the production of bulk, large-volume polymers. Radiation curing in a broader sense[96] also encompasses curing initiated by electron beam[97] (EB) or cationic[92] photoinitiators, but these topics are not treated here.

A UV-curable formulation[97] for a coating, ink, or adhesive consists of a mixture of (i) 30–50% specialty monomers or oligomers,[56] which impart most of the basic properties to the final cured or cross-linked material; (ii) 10–40% reactive diluents or monomers, which permit the adjustment of formulation viscosity and crosslink the oligomer; (iii) 1–20% additives and pigments; and (iv) 0.5–5% photoinitiators which provide the initiating radicals. Functionally terminated low to medium molecular weight polymerizable oligomers are the backbone of UV-curable coatings and determine properties of the cured coating: for example, hardness, chemical resistance, and flexibility. Commonly used oligomers include acrylates of polyhydric alcohols, oligomeric diols, and polyols having epoxy-, urethane-, polyester-, or siloxane backbones. Of less importance are the unsaturated polyesters or thiol–ene systems. Oligomers based on methacrylates are sometimes used in combination with acrylates in order to improve thermal resistance and mechanical hardness of the finished coating.

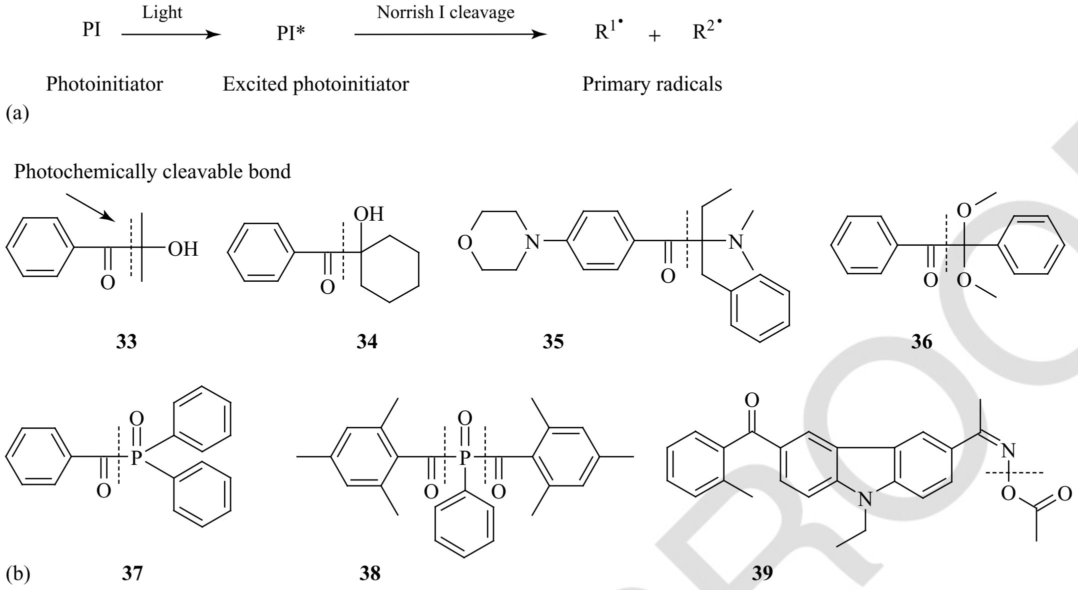
UV-light-triggered radiation curing provides several advantages over thermal curing, which include (i) very rapid cure occurring within seconds, (ii) ambient temperature curing which permits the coating of heat-sensitive substrates such as wood and plastics, (iii) more efficient, compact operations, (iv) zero or low solvent levels, and (v) good film properties and performance. Among the drawbacks of UV curing is the high sensitivity toward oxygen inhibition, the impossibility to cure thick pigmented layers, and the difficulty to cure three-dimensional objects (shadow zones). Details on equipment for UV and EB curing (lamps, electron guns, machinery) can be found in the monograph[98] of Mehmert and coworkers. A comprehensive overview of photopolymerization in polymer science and technology is provided in the four-volume compendium[99–102] of Fouassier and Rabek, and Marrion reviews[103] the chemistry and physics of coatings.

The market study by SRI Consulting[104] provides a detailed analysis of the global market for radiation-curable products. In 2007, the market volume was estimated at 390 000 metric tons with an average growth of 4–5% per year.

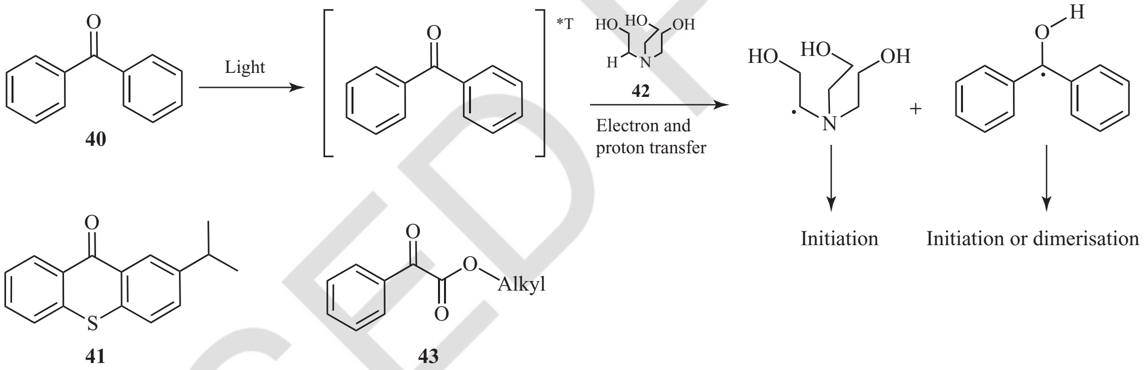
Photoinitiators[92–95] are generally divided into two classes. Compounds undergoing homolytic bond cleavage (Norrish I cleavage) upon irradiation are termed *type I photoinitiators*. Typical examples are α-hydroxyketones **33–34**, α-aminoketones **35**, benzyl dialkylketals **36**, acylphosphine oxides **37**, and bisacylphosphine oxides **38** (see Scheme 12). The oxime esters (e.g., **39**) photoinitiators[95,105,106] were developed for highly specialized applications in electronics such as photocuring of color filter resists and the black matrix resin of liquid crystal displays.

Type II photoinitiators, on the other hand, interact in their excited state with a second molecule (coinitiator) to generate radicals in a bimolecular reaction (Scheme 13). Derivatives of benzophenone **40** and thioxanthone, for example **41**, are the most important type II photoinitiators. Amines such as *N*-methyldiethanolamine, triethanolamine **42**, and esters of 4-dimethylamino benzoic acid are typical examples of coinitiators. The resin matrix itself can also act as a coinitiator if it possesses easily extractable hydrogen atoms. Alkyl phenylglyoxylates **43** are also considered[107] as type II photoinitiators. A compilation of commercially available photoinitiators and a discussion of their chemistry and applications is provided the book by Dietliker.[93]

One of the biggest challenges[95] for the future growth of the UV market is the development of



Scheme 12 (a) Type I photoinitiators and (b) some of their representative examples.

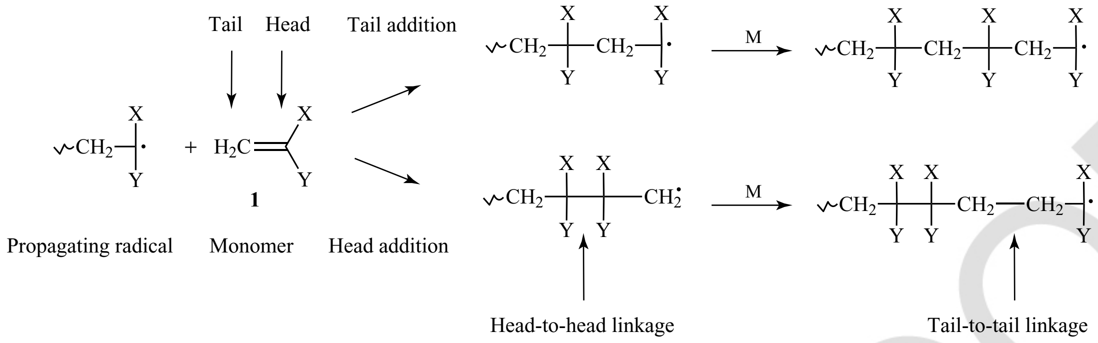


Scheme 13 Type II photoinitiators.

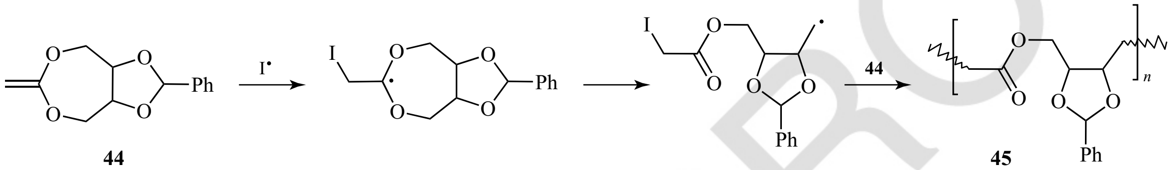
nonextractable, odorless, and low-migration photoinitiators. Such products will be applicable in coatings destined for direct food contact. So far, UV-curable systems are not present in this market because the photoinitiator or its fragments can migrate into foodstuffs.

2.4 Propagation

Propagation is the repeated addition of the growing macroradical to monomer. The rate constants of propagation are typically in the range of $k_\mathrm{p} \sim 10^2$–$10^4\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. The magnitude of k_p depends slightly on the degree of polymerization X_n of the macroradical, at least for the first (∼10) propagations steps. The mechanistics aspects of the propagation step of RP are well understood[54,62,63] and need not to be discussed here. However, one should note that the simplified picture of a 100% regiospecific head-to-tail addition (Scheme 1) which is shown in many introductory texts on polymerization is not completely correct. In fact, head-to-head addition is observed in polymerizations of most monomers. For example, it occurs to the extent of 11% in the polymerization of allyl esters[108] (Scheme 14).



Scheme 14 Regiosequence isomerism—head versus tail addition.



Scheme 15 Ring-opening polymerization of a cyclic monomer.

Of course, even more variations are observed with diene (1,3-butadiene, isoprene, chloroprene) monomers. It should be noted in this context that even the addition of primary radicals (Scheme 2) to monomers **1** is not always regioselective. For example, in the reaction of benzoyloxy radicals **23** with styrene[109,110] tail addition (80%), head addition (6%), and addition (in end effect substitution) to the styrene benzene ring (14%) can be observed. Deliberate synthesis of head-to-head polymers and their properties were reviewed[111] by Vogl and coworkers.

Propagating organic radicals are more or less planar (sp^2 hybridized) and, consequently, the polymers formed by RP are generally atactic. Detailed treatments of the stereochemical aspects of the propagation step in RP are available.[54,62]

In general, polymers produced by RP have higher densities than the starting vinylic monomers. As a consequence, polymerization is accompanied by volume contraction (up to 20% depending on monomer), which can be a significant problem in adhesive, coating, mold-filling (dental fillings), and other applications where volume change (shrinkage) is undesirable. However, only very low shrinkage or even a net increase in volume is observed with special cyclic monomers[2,54,112] undergoing radical ring-opening polymerization (ROP). Each propagation step of ROP results in ring-opening. For example, the ROP of the bicyclic 2-methylene-l,3-dioxepane **44** (Scheme 15) occurs with a small (0.5%) volume expansion. This expansion is probably due to the conversion of the more dense structure of the crystalline monomer **44** into the less dense structure of the amorphous polymer **45**.[113]

At low conversion, the overall rate of polymerization R_p is kinetically first order in monomer and half order with respect to initiator (5), for definition of f see (1).

$$R_p = -\frac{d[M]}{dt} = k_p\left(\frac{k_d}{k_t}\right)^{1/2}[M][I]^{1/2} \tag{5}$$

The kinetic chain length ν (6) is defined as the average number of monomer molecules polymerized by each initiating radical. It can be expressed as the rate of chain propagation divided by the sum of the rates of all of the chain termination processes. In the case of termination by disproportionation, it equals the number average degree of polymerization $\overline{X}_n$.

$$\nu = \frac{k_p[M]}{2(fk_d k_t[I])^{1/2}} \tag{6}$$

Equations (5) and (6) show that increasing the concentration of the initiator will indeed increase the rate of polymerization, although not linearly, but will inevitably result in a polymer of shorter chain length.

The propagation step is potentially a reversible process. Polymerization can occur spontaneously only when the associated free-energy change ΔG_p is negative. ΔG_p is expressed in (7) where ΔH_p represents the enthalpy and ΔS_p represents the entropy change upon propagation.

$$\Delta G_p = \Delta H_p - T\Delta S_p \tag{7}$$

Each monomer can be characterized by a ceiling temperature T_c at which, for a given monomer concentration, the polymerization rate becomes zero.

Common monomers such as ethene, vinyl acetate, and acrylates have very high T_c's (>400 °C) and depropagation does not occur under viable polymerization conditions. Styrene has a significantly lower ceiling temperature and depropagation must be taken into account above 250 °C. The addition of a substituent to the α position of a vinylic monomer greatly reduces T_c. α-Methylstyrene can, for example, be polymerized only at room temperature or below.

2.5 Copolymerizations

Copolymerization of two or more monomers by RP is commonly used in industry to tune the properties of commercial polymers. For example, addition of the polar monomer acrylonitrile to styrene affords a copolymer with much improved oil and grease resistance. Many industrial polymers are prepared from two, three, or even more monomers. In addition to varying chain length and stereochemistry, copolymers differ in their composition (the relative amounts of each monomer incorporated into the copolymer), sequence distribution (the way in which these monomer are arranged within the chain), and architecture (linear or graft or branched) (Figure 5).

Different monomers lead to different radicals, and the relative rates of propagation depend on the steric and electronic properties of both monomer and radical. Therefore, at any given time the ratio at which the monomers are incorporated into the polymer is not equal to their ratio in the monomer mixture. Hence, both the composition of the monomer feed and copolymer will change with conversion and, consequently, batch copolymers will in most cases not have homogeneous composition at the molecular level.

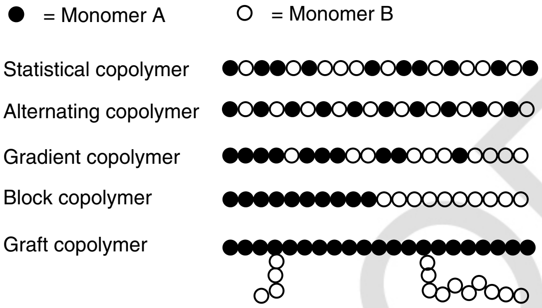
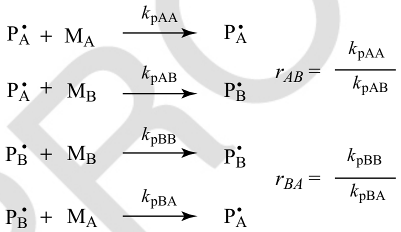


Figure 5 Different types of copolymers.



Scheme 16 Copolymerization of two monomers M_A and M_B.

Several kinetic models of radical copolymerization have been developed (e.g., terminal, penultimate, complex dissociation, and so on) and details can be found in the monographs of Matyjaszewski and Davis[62] or Moad and Solomon.[54] Here, only the simplest, the so-called terminal model[114] of radical copolymerization, will be briefly discussed. This model describes the copolymer composition for the majority of systems reasonably well but is less suitable for copolymerization kinetics, for which the penultimate model is more appropriate.

The terminal model assumes that the reactivity of the polymer radical depends only on the nature of its terminal monomer unit: that is, the penultimate unit on the macroradical does not affect its reactivity. Accordingly, the kinetics of copolymerization of two monomers M_A and M_B is determined by the relative rates of four propagation reactions characterized by four propagation rate constants $k_{pAA}, k_{pAB}, k_{pBB}$, and k_{pBA} (Scheme 16).

The composition of a copolymer formed at a given instant from a specific monomer mixture is

Table 3 Selected terminal model reactivity ratios.

Monomer M_A	Monomer M_B	r_{AB}	r_{BA}
Methyl methacrylate	Ethyl methacrylate	1.0	1.0
Styrene	Acrylonitrile	0.4	0.05
Styrene	Maleic anhydride	0.02	0.01
Vinyl chloride	Vinyl acetate	2.0	0.3
Vinyl acetate	Styrene	0.05	50.0

Source: Data from Ref. 67.

described by the Mayo–Lewis equation[114] (8):

$$\frac{F_A}{F_B} = \frac{f_A}{f_B}\left(\frac{r_{AB}f_A + f_B}{f_A + r_{AB}f_B}\right) \quad (8)$$

where $F_A = (1 - F_B)$ and $f_A = (1 - f_B)$ are the instantaneous mole fractions of monomer M_A in the polymer and in the monomer mixture, respectively, and $r_{AB} = k_{pAA}/k_{pAB}$ and $r_{BA} = k_{pBB}/k_{pBA}$ are the monomer reactivity ratios.

Using this equation, it is possible to predict the copolymer composition for a given monomer mixture from just two parameters, namely, the reactivity ratios (sometimes also called *copolymerization parameters*) r_{AB} and r_{BA}, which are available for many monomers.[67] However, the published data often spans a considerable range. Additionally, several empirical methods[54] for the prediction of reactivity ratios are available, the most widely used being the *Q–e* scheme[115,116] of Alfrey and Price. A few values of the reactivity ratios are given in Table 3 for illustration.

As seen from Table 3, the values of r_{AB} and r_{BA} are generally different. The special case where $r_{AB} = r_{BA} = 1$ occurs with monomers that are very similar, such as the homologous esters of acrylic or methacrylic acids. For this case, the product is a random copolymer and the monomers are incorporated into the copolymer according to their proportions in the monomer mixture. In cases where $r_{AB} < 1$ and $r_{BA} < 1$, a tendency toward alternation is observed because cross-propagation is favored over homopropagation. When r_{AB} and r_{BA} approach zero, an alternating copolymer is obtained. A well-known example is the styrene–maleic anhydride copolymer. The situation where r_{AB} and r_{BA} are both greater than 1 is rare, and copolymers with larger blocks consisting of M_A and M_B are the result. In cases where $r_{AB} < 1$ and $r_{BA} < 1$ (or $r_{AB} > 1$ and $r_{BA} > 1$), there always exists exactly one so-called *azeotropic composition* of the monomer mixture at which the composition of the formed copolymer is the same as that of the monomer mixture. The azeotropic composition is given by (9).

$$\frac{[M_A]_{\text{Azeotrop}}}{[M_B]_{\text{Azeotrop}}} = \frac{1 - r_{AB}}{1 - r_{BA}} \quad (9)$$

Its existence is of significant industrial importance. In fact, a copolymer without compositional heterogeneity can be prepared by conducting simple batch copolymerization if the ratio of both monomers fulfills (9). Analogous composition equations[117,118] for (rare) azeotropic composition of three or four monomers have also been developed.

Finally, when $r_{AB} > 1$ and $r_{BA} < 1$ (or $r_{AB} < 1$ and $r_{BA} > 1$), one monomer will always be preferentially incorporated into the copolymer. These copolymerizations have no azeotropic composition. Of course, kinetic treatment of ternary[54] (three monomers) or even quaternary (four monomers) copolymerization is significantly more complicated. For example, nine distinct propagation reactions and six reactivity ratios must be considered in the terminal model for three monomers.

2.6 Chain Transfer and Chain Transfer Agents

A chain transfer reaction is the interaction of the propagation radical with a nonradical species (T) to produce a dead polymer chain and a new radical (T*) capable of initiating a new propagating chain (refer Scheme 2). Details on the theory can be found in the article[119] by Chieftain and Gizzard or that by Corner.[120] In principle, chain transfer can occur with any species present in the polymerizing system (initiator, solvent, monomer, polymer, adventitious impurity, or deliberately added chain transfer agent) and it always causes a reduction in $\overline{X}_n$, the number-average degree of polymerization.

Table 4 Transfer constants (k_{tr}/k_p) at 50 °C.

	Styrene	Methyl acrylate	Methyl methacrylate	Vinyl acetate
Benzene	2×10^{-6}	2×10^{-5}	4×10^{-6}	1×10^{-4}
Toluene	1×10^{-5}	1×10^{-4}	2×10^{-5}	2×10^{-3}
Ethyl acetate	5×10^{-4}	6×10^{-5}	1×10^{-5}	2×10^{-4}
CCl_4	1×10^{-2}	2×10^{-4}	2×10^{-4}	0.8
1-Butanthiol	20	1.5	0.6	50

Source: Data from Ref. 67.

Furthermore, chain transfer to the polymer results in branching or potentially cross-linking. For example, intramolecular chain transfer (backbiting) leading to branching is observed during the RP of ethylene.[121] Quantitatively, the efficiency of chain transfer to a given species is characterized by its transfer constant $C_{tr} = k_{tr}/k_p$. For efficient chain transfer to occur, the rate constant of reinitiation (k_{itr}) by T* must be equal to or greater than that for propagation (k_p) (refer Scheme 2). The magnitude of the transfer constant depends on the structure of both the transfer agent and the radical. Since the propagation and transfer reactions show similar temperature dependence, chain transfer constants change only slightly with temperature. The transfer constants for variety of monomers and transfer agents can be found in the literature.[67] Most organic compounds have low transfer rates, and transfer is important only when they are present in high concentration, that is, as solvent. Table 4 illustrates the C_{tr} values for a few typical solvents and chain transfer agents at 50 °C.

Deliberately added chain transfer agents (T) with large C_{tr} are often used in industrial polymerizations to control (limit or reduce) the molecular weight and molecular weight distribution of polymers. The influence of chain transfer on $\overline{X}_n$ can be described by the Mayo equation[122] (10):

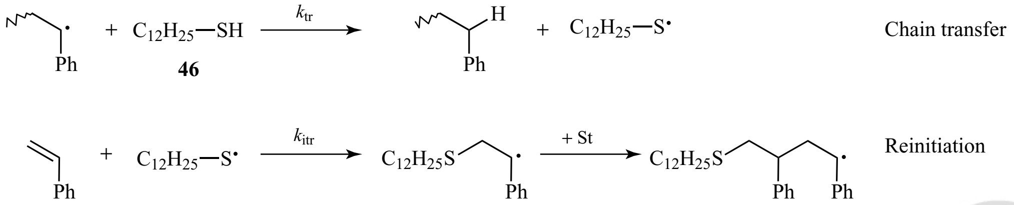
$$\frac{1}{\overline{X}_n} = \frac{1}{\overline{X}_{n0}} + C_{trT}\frac{[T]}{[M]} \qquad (10)$$

where $\overline{X}_n$, $\overline{X}_{n0}$ are the number-average degree of polymerization in the presence or absence of chain transfer, respectively, and C_{trT} is the chain transfer constant of T.

The added transfer agent is said to behave ideally if its chain transfer constant is equal to unity. In this case, the ratio of the rates at which the monomer and transfer agent are consumed by the growing radicals is constant and equal to the ratio of the molar concentrations of the monomer to transfer agent. This means that $\overline{X}_n$ remains constant throughout the polymerization. On the other hand, a transfer agent with $C_{trT} \gg 1$ will be rapidly consumed in early stages of the polymerization. In the case of $C_{trT} \ll 1$, the ratio [T]/[M] increases with conversion, leading to a decrease in $\overline{X}_n$ as the polymerization progresses. Polymers with a broad molecular weight distribution result in both cases. Continuous addition of the monomer or transfer agent during polymerization to maintain a constant the [T]/[M] ratio may help to overcome these problems. The control of the molecular weight of the polymer with the transfer agent translates into control of the viscosity of the reaction mixture and, through mitigation of the gel or the Norrish–Trommsdorff effect,[123,124] into control of the polymerization rate and exothermicity.

Typical chain transfer agents used in industrial synthesis of variety of polymers (PS, poly (methyl methacrylate) PMMA, ABS, acrylic-, styrene-butadiene-, or acrylonitrile-butadiene copolymers) include mercaptans such as *n*-octyl mercaptan, *n*-dodecyl mercaptan, or 2,2-dimethyldecyl mercaptan (*tert*-dodecyl mercaptan). Technical information[125] on mercaptans, as well as examples[126] of their use as chain transfer agents, can be found on the web site of their producers. Chain transfer with *n*-dodecyl mercaptan **46** in the styrene polymerization is exemplified in Scheme 17.

Primary mercaptans are more active chain transfer agents than secondary or tertiary ones. Apolar mercaptans are lipophilic and odiferous compounds of moderate toxicity. Examples of water-soluble and practically odor-free chain transfer agent are mercaptoacetic acid (thioglycolic acid) and 2-mercaptoethanol. Moreover, these agents introduce functionalities (COOH or OH) into the chains providing access to monofunctional[120,127] polymers. A special case of chain transfer is the reversible addition fragmentation chain transfer (RAFT), which is an important method of controlled RP



Scheme 17 Polymerization of styrene with chain transfer with *n*-dodecylmercaptan.

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(see **Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization: Mechanism, Process and Applications**, Volume 4).

2.7 Chain Termination

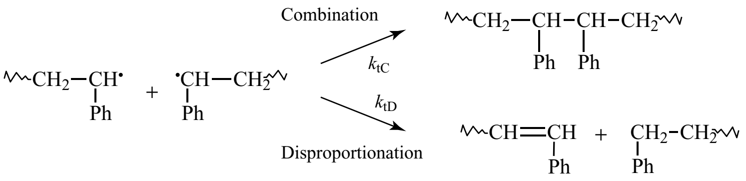
The propagating radicals in RP add a monomer unit every ~1 ms on average and typically terminate after about ~1 s. Polymeric chains with high $\overline{X}_n$ are formed during this short time. Termination of growing radicals occurs via coupling (k_{tC}) or disproportionation (k_{tD}) (Scheme 18). The corresponding rate constants are very high, $k_t \sim 10^7 - 10^9\ M^{-1}\ s^{-1}$, approaching the diffusion-controlled limit.

Sterically undemanding radicals terminate preferentially through coupling (styrene), whereas radicals derived from 1,1-disubstituted monomers generally undergo disproportionations (methyl methacrylate). The self-termination of growing macroradicals is a diffusion-controlled process. Therefore, the termination rate constants depend strongly on the chain lengths, and k_t decreases with increasing viscosity of the polymerizing mixture. The increase of viscosity in bulk polymerizations at medium to high conversions slows down the movement of large chains to such a level that their self-termination becomes very slow. On the other hand, monomer molecules may still diffuse rapidly. As a consequence, an autoacceleration phenomenon known as the Norrish–Trommsdorff or gel effect[123,124] may occur.

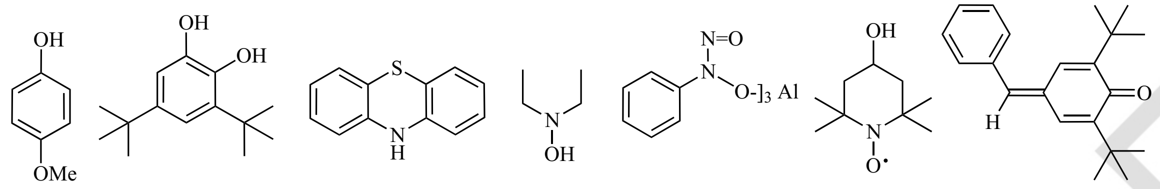
Macroradicals can also terminate by reaction with radicals derived from the initiator. Finally, another very important source of termination reactions is the deliberately added molecules called *inhibitors* or oxygen (oxygen inhibition).

2.7.1 Inhibitors

Pure monomers must be protected during storage from polymerization by mixing them with small amounts of polymerization inhibitors, species able to rapidly and efficiently scavenge propagating and/or primary radicals. Moreover, the presence of inhibitors is also necessary during the synthesis and purification (e.g., distillation) of monomers. In fact, a distinction between storage and in-process stabilizers is sometimes made. An ideal inhibitor will prevent polymerization during what is termed an *induction period*. Once consumed, polymerization proceeds at a normal rate. Species that do not show a distinct induction period but rather slow down polymerization are called *retarders*. This topic was reviewed by Bovey and Kolthoff[128] and Tüdos and Földes-Berezsnich.[129] Common inhibitors include stable radicals such as galvinoxyl, nitroxide radicals, diphenylpicrylhydrazyl, phenols, quinones, nitrones, nitro and nitroso compounds, phenothiazine, and salts of transition metals which can trap C-centered radicals by electron transfer. Examples of industrially important inhibitors (Scheme 19) are *p*-methoxyphenol **47**, 2,4-di-*t*-butyl catechol **48**,

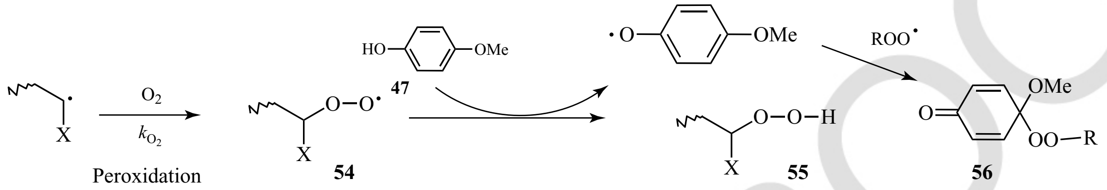


Scheme 18 Termination of polystyrene macroradicals by combination and disproportionation.



47 **48** **49** **50** **51** **52** **53**

Scheme 19 Examples of polymerization inhibitors.



Scheme 20 Inhibition of polymerization with *p*-methoxyphenol.

phenothiazine **49**, *N*,*N*-diethylhydroxylamine **50**, salts of *N*-nitroso phenylhydroxylamine **51**, and 4-hydroxy-TEMPO **52**. An example of a retarder is 2,6-di-*t*-butyl-7-phenyl quinone methide **53**, which is used in combination with nitroxide radicals as a storage stabilizer[130] for radiation-curable coating or ink compositions.

The phenolic inhibitors **47–48**, which are used mostly as storage stabilizers, require[131,132] traces of oxygen in order to be fully effective. The phenols themselves are rather poor scavengers of C-centered radicals. The latter, however, react very rapidly with oxygen, affording peroxy radicals **54** which are efficiently transformed into nonradical products, namely, hydroperoxides **55** and cyclohexadienones **56**, by reaction with phenols (Scheme 20).

For this reason, the oxygen content in large storage tanks containing acrylic or methacrylic acid and *p*-methoxyphenol (100–200 ppm) as polymerization inhibitor is continuously monitored and maintained at a specific level. An illustrative case of a runaway acrylic acid polymerization caused by insufficient inhibition was reported[133] by Levy and Penrod.

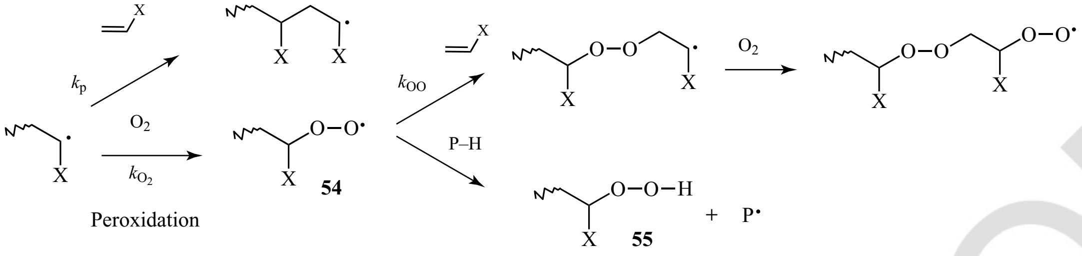
On the other hand, phenothiazine **49** is a good hydrogen donor to both C-centered and peroxy radicals and, therefore, an excellent inhibitor[132,134] even in the absence of oxygen.

The liquid and rather volatile (bp 125 °C) *N*,*N*-diethylhydroxylamine **50** is used as in-process inhibitor in distillations of monomers such as styrene, divinylbenzene, isoprene, and butadiene.

In precise laboratory work with monomers, the inhibitors are often removed by distillation, by filtration over a pad of aluminum oxide, or by a suitable extraction procedure. In industrial polymerizations, such purifications would be too expensive. Therefore, in most cases, the inhibitor is not removed but consumed by the additional initiator.

2.7.2 Oxygen Inhibition

RPs are tolerant to protic solvents but suffer from oxygen inhibition when conducted in air-saturated media or under an air atmosphere. The dioxygen molecule, due to its biradical ground state character, reacts with carbon-centered radicals to give peroxy radicals **54**. The rate of this peroxidation reaction is much greater[135] ($k_{O_2} \sim 10^8-10^9$ M^{-1} s^{-1}) than the typical rates[54] of propagation ($k_p \sim 10^2-10^4$ M^{-1} s^{-1}). Hence, at equal monomer and oxygen concentrations, the peroxidation would be 10^4-10^7 faster than propagation (Scheme 21). The concentration of dissolved oxygen in monomers is on order[136] of 10^{-3} M, whereas the concentration of monomers is generally in the range of 0.1–10 M. Even so, the vast majority of carbon-centered radicals in air-saturated monomers are converted into the peroxy radicals **54**. The latter add only very sluggishly[137] ($k_{OO} \sim 0.1-3$ M^{-1} s^{-1}), in what is now a rate-determining step, to monomers affording new C-centered radicals. As these C-radicals react again preferentially with oxygen, the result is an alternating copolymer with oxygen. The normal polymerization will be possible only when the majority of dissolved oxygen is consumed. This can



Scheme 21 Oxygen inhibition.

occur if the rate at which it is replenished from the air-exposed surface is sufficiently low. The oxygen copolymers are polymeric peroxides that are thermally and photochemically unstable and thus impair the properties of the final polymer. Moreover, peroxy radicals[138] abstract H atoms from the surrounding substrates (PH) to yield new radicals and the hydroperoxides **55**. The latter are potential sources of new radicals, which may further complicate the polymerization.

The influence of oxygen on radical and other polymerizations has been reviewed by Bahanu and Kishore.[139] To prevent these detrimental effects, measures must be taken to exclude oxygen by conducting the polymerization under vacuum or nitrogen, or in a refluxing solvent. Oxygen inhibition is a serious problem and is much more difficult to avoid in the photopolymerization of thin films and coatings due to the very large surface. Here, it leads to incompletely cured, tacky surfaces with poor mechanical properties. Different methods to overcome oxygen inhibition in these applications were reviewed[140] by Scranton and coworkers. Latest strategies involve an admixture of oxygen-scavenging additives,[141,142] use of monomers with high functionality,[143] or singlet oxygen[144] sensitizers. It should be noted that oxygen inhibition is not a problem for every RP process. The radical thiol–ene click reaction, which is becoming an important tool for polymer synthesis,[145–147] is much less sensitive to oxygen.

3 POLYMERIZATION PROCESSES

3.1 General Comments

Rather than listing the complete literature dealing with industrial polymerization processes and the related reactor technology, we refer the reader to good introductory texts.[148–150]

Industrial polymerizations differ from the processes used for synthesis of low molecular compounds in several respects. For one, it is usually not possible to purify the final polymer by standard distillation or crystallization techniques. Polymers obtained by classical RP are always mixtures of macromolecules with varying degrees of polymerization and deviation from the idealized structure. Separation of these mixtures is not possible on an industrial scale. Elimination of residual monomers, initiators, or solvents can also be a difficult and costly task requiring special methods and equipment.

The properties of the polymer, for example, its molecular weight distribution which influences its mechanical properties and processability, often strongly depend on the method (e.g., suspension polymerization or EP) by which it is prepared.

An important feature of polymerization in solution or in a melt is the dramatic increase, often by several orders of magnitude, of the viscosity during the reaction. This viscosity increase is the cause of the autoacceleration effect called the Norrish–Trommsdorff effect.[123,124] It complicates mixing and pumping of the reaction mass and significantly reduces the rate of heat transfer and, therewith, the efficiency of the reactor cooling. Temperature control of industrial polymerizations is a very critical task because of the highly exothermic nature of RPs. In many cases, a rapid and, therefore, almost adiabatic runaway polymerization would cause temperature increase of many hundreds of degrees,[151] leading to serious consequences such as fire, reactor rupture, or environmental contamination. For example,[152] the adiabatic temperature increase at 100% conversion of monomer into polymer is

1810 °C for ethylene, 721 °C for acrylonitrile, 542 °C for vinylchloride, and 336 °C for styrene.

In fact, the average heat of polymerization ΔH_p of a vinylic monomer is about $-82\,\text{kJ mol}^{-1}$, which is the difference between the sum of the energies of the two C–C single bonds ($\sim 2 \times 346\,\text{kJ mol}^{-1}$) formed in the polymer and the bond energy of a C=C bond ($\sim 610\,\text{kJ mol}^{-1}$) of the monomer. The actual heats of polymerization vary as a result of secondary effects such as steric strain in the polymer or differences in the resonance stabilization or hydrogen bonding, and solvation between the monomer and polymer. For example, ΔH_p varies[153] from $-35\,\text{kJ mol}^{-1}$ for α-methyl styrene to $-163\,\text{kJ mol}^{-1}$ for tetrafluoroethene (25 °C, liquid monomer $\geq$ solid polymer). Detailed discussion of the thermodynamics of polymerization is provided in the monograph[153] of Sawada. Data on the heats, entropies, free-energy changes, and ceiling temperatures of polymerization of many monomers can be found there or in the *Polymer Handbook*.[67]

3.2 Polymerization Techniques

The different polymerizations according to the classification on Figure 4 can be carried out in several ways: bulk polymerization, precipitation polymerization, solution polymerization, slurry polymerization, gas-phase polymerization, suspension polymerization, or EP. The polymerization techniques that are important for industrial RP are briefly highlighted.

3.2.1 Bulk Polymerization

The only components of a bulk polymerization mixture are monomers, the initiator, and, optionally, a chain transfer agent. The initiator may be omitted in the case of thermal autoinitiation of styrene. The main advantage of bulk polymerization is that a very pure polymer is produced. Furthermore, as the polymer is not diluted, the volume yield of the polymer is high. However, the high increase of viscosity during the polymerization makes the stirring and removal of the heat of polymerization difficult. A special type of bulk polymerization is precipitation polymerization. Here, the polymer is not soluble in its own monomer (e.g., PVC in vinylchloride) and precipitates during the polymerization. Examples of polymers prepared by bulk polymerization are PMMA, general-purpose (or crystalline) PS, and LDPE.

3.2.2 Solution Polymerization

Solution polymerization is related to bulk polymerization but the components are dissolved in a suitable solvent. Both the heat generation and viscosity of the polymerization mixture are lower because of dilution. The thermal control of the reactor is also facilitated because the lower viscosity allows more efficient cooling. Optionally, cooling can be achieved by refluxing the solvent. The drawback of solution polymerization is that the polymer must be freed from the solvent if it is needed in pure form.

3.2.3 Suspension Polymerization

Suspension polymerization enjoys the advantages of bulk polymerization but is not plagued with problems of high viscosity and difficult thermal control. In this technique, pure monomers containing the dissolved initiator and, optionally, chain transfer agent are dispersed (suspended) in a continuous water phase (1–1.5 times by mass) in form of small droplets in the size range of 50–1000 µm. Both monomer and coreactants must be insoluble in water. The dispersion of the organic (or oil) phase in water is effected by stirring in the presence of added surfactants. Frequently used surfactants are amphiphilic polymers such as poly(vinyl alcohol), partially hydrolyzed poly(vinyl acetate), or hydroxypropyl methyl cellulose. Micronized inorganic powders such as $CaCO_3$, $MgCO_3$, or $Ca_3(PO_4)_2$ are also used. The advantage of these inorganic “pickering dispersants” is that they can be easily removed from the polymer by treatment with diluted acid. The droplet size and size distribution are complex functions of the type and concentration of the dispersant, stirring parameters, reactor, and stirrer geometry, as well as the physical properties of the dispersed and continuous phases. From a kinetic point of view, each droplet behaves as a small bulk polymerization reactor. The droplets are transformed during the polymerization into rigid spherical polymer particles which are easily isolated by filtration. The main advantage of suspension polymerization is the easy thermal control of the reactor and virtually constant viscosity of the reaction mass as a whole. The purity of polymers prepared by this technique is higher than that obtained in EP and is comparable to that of bulk or solution polymerization. Examples of polymers made by suspension polymerization are PS and PMMA. The most important production process[154] for PVC is suspension polymerization of vinylchloride in pressurized (8–12 bar, because of the low boiling point of vinylchloride) reactors. PVC is not soluble in vinylchloride and precipitates in the monomer droplets which are finally transformed into porous polymer particles ("powder" suspension polymerization).

3.2.4 Emulsion Polymerization

EP, like suspension, mini emulsion, and microemulsion polymerization, is a type of heterogeneous polymerization. It should be noted that heterogeneous polymerizations are not only radical in nature. Heterogeneous polymerizations in aqueous dispersed media have been reviewed[155] by Charleux and Ganachaud.

EP provides polymer particles of 50–1000 nm dispersed in a continuous medium, most often water. Such polymeric dispersions are called *latexes*. Synthetic latexes were known already in 1930s but it was the work during the United States Synthetic Rubber Program[156] (1939–1945) which established EP as a unique and industrially viable technique. In the second half of the twentieth century, the method was further developed and attained a high level of technical and theoretical understanding. Today, about 10% of all synthetic polymers or some 20% of those prepared by RP ($>20 \times 10^6$ tons per year) are made by EP.[157] The process is named *emulsion polymerization* for historical reasons because it was originally targeted with the polymerization of emulsified monomer droplets, and only later it was realized that polymerization occurs not in the monomer droplets but mainly within the monomer-swollen latex particles. Among the abundant literature, the excellent monograph of Herk[158] which covers the history, mechanism, as well as industrial applications of EP; the books of Asua[150,159]; or the recent book of Chern[160] which additionally treats the related mini emulsion and microemulsion polymerizations can be highlighted. Therefore, only the key aspects of classical EP will be discussed here. The simplest EP system consists of a continuous aqueous phase, a practically water-insoluble monomer, a water-soluble initiator, and a colloidal stabilizer (emulsifier or surfactant). The monomer is dispersed to form small (0.01–0.1 mm) droplets which are stabilized against coalescence by a layer of surfactant molecules. It is important to note at this point that "water-insoluble" monomers used in EP in reality have a very small but measurable solubility in water: for example, the solubility of styrene at $50\,^{\circ}\mathrm{C}$ is 4.3×10^{-3} M (see p. 78 of Ref. 158 for the water solubility of industrial monomers). If the concentration of the surfactant is above the critical micelle concentration (CMC), the formation of micelles occurs. These generally spherical micelles with a diameter of a few nanometers contain $\sim 10^2$ surfactant molecules and are swollen by the monomer which migrates from the "reservoir" droplets through the water phase. The number of micelles ($\sim 10^{17}-10^{19}\ \mathrm{l}^{-1}$) is many orders of magnitude higher than the number of monomer droplets ($\sim 10^{10}\ \mathrm{l}^{-1}$). Consequently, the surface area of the micelles is 3–5 orders of magnitude larger than that of the droplets. The hydrophilic primary radicals formed in the water phase from the water-soluble initiator (e.g., ammonium persulfate) do not enter the lipophilic micelles. They preferentially add to and propagate with the monomer dissolved in water until the resulting oligomeric radicals are lipophilic enough to enter (nucleate) the micelles. Nucleation of the monomer droplets is insignificant because of the much larger surface of the micelles compared to the droplets.

Rapid propagation then follows in the monomer-swollen micelles leading to latex particles in a process called *heterogeneous nucleation*. A different process called *homogeneous nucleation* occurs if the amount of surfactant is below the CMC. In this case, the oligomeric waterborne radicals continue to propagate until they became insoluble enough that they undergo coil-to-globule transition. The resulting hydrophobic globules are swollen with monomer and became latex particles, too. Both heterogeneous and homogeneous nucleation may be operative in a given system. Monomer droplets, monomer-swollen micelles, and monomer-swollen latex particles coexist during the

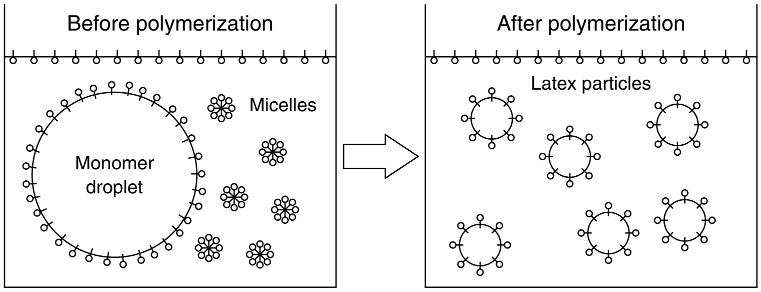


Figure 6 Emulsion polymerization.

nucleation phase. As the polymerization proceeds, the number of micelles decreases as they are either transformed into latex particles or dissociate to provide surfactant to stabilize the increasing surface area of the latex particles or globules formed by homogeneous nucleation. At the end of nucleation (monomer conversion of 5–10%), all micelles have disappeared and 10^{17}–10^{18} latex particles per liter are present. They are now the main sites of polymerization. New monomer diffuses from the droplets into the latex particles to replace the monomer consumed there through polymerization. Consequently, the size of latex particles increases and that of droplets decreases until they disappear completely. The polymerization then continues in the monomer-swollen latex particles until the monomer is depleted. The result is a polymeric dispersion in water or a latex (Figure 6).

As the change of viscosity during the course of EP is very small (similar to suspension process), the control of the polymerization reactor is simplified. EP never proceeds to 100% conversion, but leaves some residual monomer in the waterborne polymer that must be removed. This can be performed either via stripping with steam or nitrogen, or through postpolymerization by addition of fresh initiator.

It is important to note that the basic mechanism of RP is the same in bulk, suspension, and EP. However, the distinctive feature of EP is the radical compartmentalization. In fact, the radicals that are situated in different particles cannot terminate by bimolecular termination. Because of the small size of the latex particles, only one propagating radical is inside at a given time. Hence, the polymer chain in the particle grows until a new radical enters and terminates with the growing one. Therefore, on average, 50% of particles contain one radical and the rest none. Nevertheless, due to the enormous number of particles, the overall radical concentration in the latex is about one order of magnitude higher than in a typical bulk polymerization (10^{-8} M). Consequently, the polymerization rates are higher in EPs as compared to bulk or suspension process. Radical compartmentalization also allows longer radical life times, resulting in polymer chains of a higher degree of polymerization. The lifetime of the propagating radicals in the particles is inversely proportional to the frequency at which new radicals enter the particles and terminate with the growing ones. The entering frequency for a given concentration of the initiator decreases with the number of particles. Hence, it is possible to increase the rate of polymerization and the molecular weight of the polymer by simply increasing the number of particles, for example, by changing the monomer to surfactant ratio.

The continuous phase in conventional EP is water. Water-soluble monomers (e.g., acrylamide) can be polymerized via *inverse EP*. In this process, an aqueous solution of the water-soluble monomer and surfactant is dispersed in an organic phase (e.g., hexane) and the polymerization is initiated by lipophilic initiators. The process proceeds via a mechanism similar to aqueous EP and results in a dispersion of an aqueous solution of water-soluble polymer in an organic phase.

About 50% of emulsion polymers are commercialized as waterborne dispersions. It is important to note that emulsion polymers have in common the same state of aggregation but are diverse in chemical composition. A comprehensive overview of waterborne polymeric dispersions together with their applications and markets is available in the monograph[11] of Urban and Takamura and of Daniel and Pichot.[12] The main waterborne dispersions and their respective markets are shown in Table 5.

Table 5 Waterborne polymer dispersions by product class.

- Styrene–butadiene copolymers (paper coatings, paperboard, carpet backing, adhesives and sealants, additives for mortar and bitumen), 37%.
- Polyacrylates, polymethacrylates, styrene–acrylate copolymers (paints, coatings, adhesives, inks, paper, and leather coatings), 30%.
- Vinyl acetate homo- and copolymers (paints, adhesives for paper and wood), 28%.

A substantial part of emulsion polymers is commercialized as dry products. Examples are styrene–butadiene rubber (SBR), acrylonitrile–butadiene rubber (nitrile rubber), about 75% of ABS copolymer, a small part of PVC, water-redispersible powders[11] for the construction industry, and polymeric modifiers[11] for plastics (e.g., impact modifiers, processing aids, rheology modifiers, and so on). Diverse techniques for the isolation of the polymer from the dispersion are available: for example, direct spray-drying of the emulsion or its coagulation followed by drying of the filter cake.

Standard laboratory formulations for EP contain water, the monomer, the initiator, and the surfactant. Commercial recipes are often much more complicated, containing up to 20 components. A large number of monomers are used in EP either alone to give homopolymers or, more frequently, as mixtures to provide copolymers. In general, random copolymers are obtained with an inhomogeneous monomer distribution throughout the chains. Individual monomers impart specific properties to the final polymer. Acrylonitrile, for example, improves solvent resistance, while vinyl chloride improves fire retardancy and acrylates provide good stability against light and heat. An important polymer property that must be controlled is the glass transition temperature T_g, which strongly influences the film formation from a latex and the mechanical properties of the film. The T_g of a copolymer can be estimated with the simple Fox equation (11) or with recently developed[161] more sophisticated models.

$$\frac{1}{T_g} = \frac{W_{M1}}{T_{g1}} + \frac{W_{M2}}{T_{g2}} + \cdots + \frac{W_{Mn}}{T_{gn}} \qquad (11)$$

where T_g refers to the copolymer, T_{g1}, $T_{g2}, \ldots$ refer to the individual homopolymers, and W_{M1}, $W_{M2}, \ldots$ are the weight fractions of monomers M1, M2, … in the copolymer.

In addition to the principal monomers that make up largest part of the latex (e.g., butadiene, styrene, and so on), small amounts (typically 2–5% based on the dry polymer) of the so-called functional monomers are often used. These important comonomers contain functional groups (COOH, NH_2, OH) that impart special properties to both the colloidal system and the polymer. As EP usually provides polymers of impractically high molecular weight, chain transfer agents, usually mercaptans, are often used. Other common additives include electrolytes (buffers) and metal ion sequestering agents. A typical list of the components of an industrial EP formulation is shown in Table 6.

Table 6 Components of an industrial emulsion polymerization recipe.

- **Monomers (50–55 wt%)**

Principal monomers leading to high T_g: methyl methacrylate, styrene, acrylonitrile, vinyl chloride, vinyl acetate
Principal monomers leading to low T_g: methyl acrylate, 2-ethylhexyl acrylate, *n*-butyl acrylate, 1,3-butadiene
Functional monomers: acrylic and methacrylic acid, itaconic acid, fumaric acid, 2-hydroxyethyl acrylate, acrylamide

- **Initiators (0.3–0.5 wt%)**

Thermal initiators: sodium, potassium or ammonium persulfate, water-soluble azo-compounds
Redox initiators: *t*-BuOOH or persulfate + $Na_2S_2O_5$

- **Surfactants (0.5–3 wt%)**

Ionic surfactants: sodium lauryl sulfate, sodium or potassium salts of fatty acids (soaps), salts of alkylbenzene sulfonates
Nonionic surfactants: *O*-polyoxyethyleneated long-chain alcohols or alkyphenols

- **Chain transfer agents**: mercaptans
- **Sequestering agents**: ethylenediamine tetraacetic acid (EDTA) (for complexing of adventitious metal ions, to prevent among other things their uncontrolled reaction with the redox initiator)
- **Electrolytes**: alkali metal phosphates (to control the pH)
- **Water, sometimes deionized (45%)**

3.2.5 Mini- and Microemulsion Polymerization

The majority of dispersion polymers are prepared by conventional EP. However, two variants of classical EP, *mini*- and *microemulsion polymerizations*, are of industrial interest and will, therefore, be briefly mentioned. A comprehensive discussion of the physicochemical and technological aspects of mini emulsion polymerization can be found in the monograph[162] of Mittal. The size of the monomer droplets in a mini emulsion polymerization[160, 162–166] is significantly reduced (30–500 nm) relative to that in EP ($>10^4$ nm). These small droplets are obtained by intensive homogenization in the presence of a surfactant and a small amount of extremely hydrophobic costabilizer, sometimes called *hydrophobe* (e.g., hexadecane or cetyl alcohol). The hydrophobe cannot migrate through the aqueous phase and thus prevents the diffusion of monomer molecules from smaller droplets to larger ones (Ostwald ripening) through establishment of counteractive osmotic pressure in the smaller droplets. As a result, kinetically stable mini emulsions are obtained which can be polymerized by both water- and oil-soluble initiators. In contrast to the classical EP, the locus of polymerization in a mini emulsion is within the emulsion droplets. The resulting latex can be viewed as a polymerized copy of the original mini emulsion. An important consequence for industry is that water-insoluble compounds (monomers, polymers, inorganic solids, pigments, carbon black, additives, etc.) can be directly incorporated/encapsulated[165,166] into the polymer particles by dissolving/dispersing them in the monomer prior to polymerization. A practical industrial example is the encapsulation of light stabilizers[167] to render them easily dispersible in coating formulations. This is not possible via classical EP since the monomer and the species dissolved/dispersed in it need to diffuse through the aqueous phase to the growing polymer particles. Mini emulsion polymerization bears some similarity to suspension polymerization. In both cases, the polymerizing droplet behaves as an individual batch reactor. The main difference is in the size and stability of the particles. Ostwald ripening is much less important in suspension polymerization because of the very large size of the particles; hence, addition of hydrophobes is not necessary.

The monomer droplets are even smaller (1–30 nm) in microemulsion polymerization.[160, 168–171] Microemulsions are thermodynamically stable, isotropic, transparent, or translucent systems which are obtained upon intensive homogenization using a combination of an anionic surfactant (e.g., sodium dodecyl sulfate) and a nonionic cosurfactant (e.g., 1-pentanol). This special surfactant system creates an interfacial tension at the oil/water interface close to zero. The high amount of surfactant in microemulsion formulation leads to a complete surfactant coverage of the droplets. As in mini emulsion polymerization, the locus of polymerization is within the emulsion droplets. The result is very small (∼5–50 nm) polymer particles in coexistence with empty micelles. A particle contains only a small number of polymeric chains having a very high molecular weight not achievable via conventional emulsion or mini emulsion polymerization. Potential applications[160,171] of microemulsion polymerization include the synthesis of ultrafine latex particles, water-soluble polymers with very high molecular weights for use as flocculants, nanostructured porous materials, functionalized colloidal particles, and transparent colloidal systems for photochemical applications.

3.3 Types of Industrial Polymerization Reactors

Polymer reaction engineering along with the design of polymerization reactors is a huge discipline on its own. The excellent book[150] of Assua, the handbook[148] of Meyer and Keyrentjes, or the chapter of Cunningham and Hutchinson in Ref. 62 is recommended as introductory reading. Polymerization reactors can be grouped according to the method by which the reactants are added to the reaction vessel (Figure 7).

- In a *batch reactor*, all the reactants are charged to the reaction vessel at the beginning and no material is added to or removed from the reactor during polymerization. After its completion, the contents are discharged and the reactor is prepared for the next batch. Batch reactors are the simplest to operate, but offer the least control over the polymerization. Thus, copolymerization of monomers with different reactivity ratios or

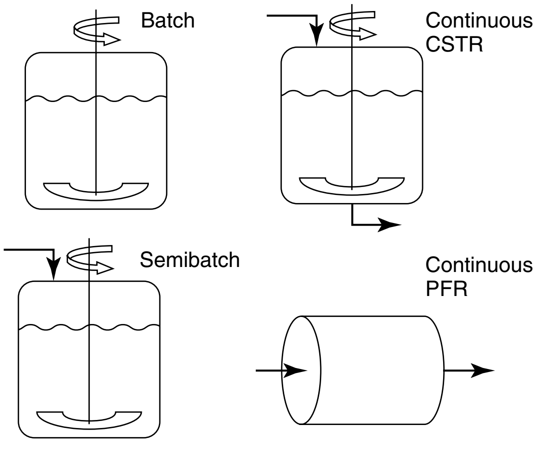


Figure 7 Types of reactors commonly used in radical polymerization.

outside the azeotropic monomer feed composition will result in a broad distribution of copolymer composition. On the other hand, batch reactors are readily adaptable to new set of reaction conditions and to new products.

- In a *semibatch* (or semicontinuous) reactor, the starting materials can be added, and/or the products removed, during the polymerization. Often, only a portion of the total amount of reactants is initially charged into the reactor. The polymerization is then started, and more reactants are added during reaction in order to control various parameters such as reaction rate, molecular weight, or copolymer composition distribution. Any reactant can be fed at a selected, individual rate.

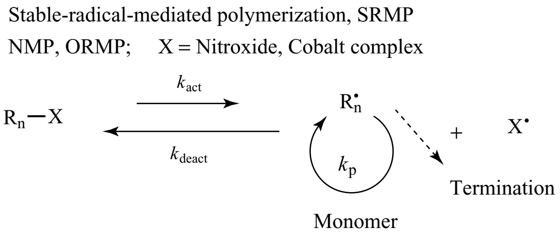
  Semibatch operation is commonly used to control the copolymer composition distribution. The compositional drift can be substantially reduced by maintaining a constant ratio of monomers in the reactor. Continuous feeding of initiator and monomers in the desired ratio helps to control the molecular weight and to minimize the risk of a thermal runaway reaction because the monomer concentration remains low throughout the polymerization (monomer-starved conditions). Semibatch reactors are widely used in EP: for example, stainless steel vessels ranging in size from 20 to 200 m^3 and equipped with a stirrer.
- In a *continuous reactor*, the reactants are introduced and the products as well as unconsumed reactants are withdrawn continuously. Continuous reactor systems include continuous stirred tank reactors (CSTR), plug flow reactors (PFR), or combinations of both. The polymerization may take place in a single reactor or in a cascade of reactors in which the monomer conversion gradually increases. Continuous reactors are preferred for large-volume polymers with a limited number of variations in polymerization conditions. They offer simplicity of operation, high throughput rates, uniform product quality, and, hence, relatively low operating costs.

4 CONTROLLED REVERSIBLE-DEACTIVATION RADICAL POLYMERIZATION

A 2010 IUPAC recommendation[172] proposes the term *controlled reversible-deactivation radical polymerization* (CRDRP) for polymerizations previously called *controlled radical polymerization* (CRP) or *living radical polymerization* (LRP).

It was the pioneering discovery[173,174] of living anionic polymerization by Michael Szwarz in 1956 that initiated the rapid development of this field, which has many important applications in industry. Over the years, other controlled and living polymerizations such as group-transfer polymerization, living carbocationic polymerization, living ring-opening metathesis polymerization, or living transition-metal-catalyzed alkene polymerization were developed. A review of the state of the art of controlled and living polymerizations in year 2010 was compiled[175] by Müller and Matyjaszewski. Its preface also gives clear definitions of the sometimes controversial terms “controlled” and “living”.

RP is one of the most important industrial polymerization techniques. However, prior to the mid-1990s, classical RP did not allow the synthesis of polymers with precisely designed molecular architectures such as block, comb, or star copolymers or polymers with defined terminal functional groups or with predetermined and narrow molecular weight distributions. This was, however, possible with the aforementioned nonradical processes. This situation started to change dramatically with the seminal work[176,177] of Otsu, who in 1982 proposed a reversible deactivation of the growing chains in RP using the so-called iniferters.



Scheme 22 Stable-radical-mediated polymerization.

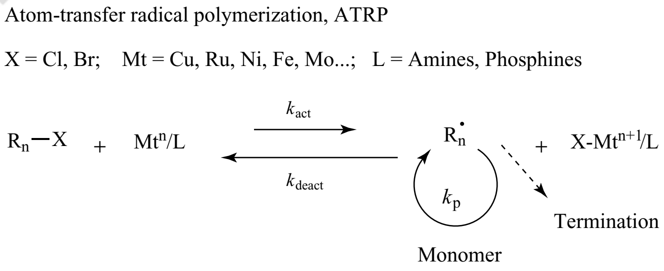
Today, a plethora of CRP techniques are available. All are based on reversible deactivation of growing chains. Most of these chains are in a dormant form and the period of chain growth of an individual propagating chain may be extended from ~1 s in conventional RP to a few hours in CRDRP. At any given instant, only a small fraction of chains are growing. However, as long as the interconversion of active and dormant forms is rapid compared to propagation, all chains are able to grow at the same rate. Therefore, the polymerization takes on much of the character of a living polymerization. Nonetheless, it is important to note that, even though chain termination and irreversible chain transfer are suppressed to a very low level in such RPs, they are not completely absent.

CRDRP makes possible the synthesis of block copolymers by sequential addition of different monomers. Moreover, if the initiating species are fully consumed prior to any appreciable chain growth, all chains grow at the same rate and the molecular weight distribution of the polymer is much narrower than in a conventional RP.

Presently, the most important CRDRP techniques are the following:

- *Stable-radical-mediated polymerization* (SRMP), which embraces the nitroxide-mediated RP (NMP) (see **Nitroxide-Mediated Polymerization and its Applications**, Volume 4, rad059 note, however, that IUPAC recommends[172] the term *aminoxyl* instead of *nitroxide*) and organometallic-mediated RP (ORMP). The deactivation involves reversible coupling with persistent (stable) radicals (Scheme 22).
- *Atom-transfer radical polymerization* (ATRP) (see **Atom Transfer Radical Polymerization (ATRP) and Addition (ATRA) and Applications**, Volume 4). rad060 The deactivation of the radicals involves reversible atom transfer or reversible group transfer catalyzed usually, though not exclusively, by transition-metal complexes (Scheme 23).
- *Degenerate-transfer RP* (DTRP) in which the deactivation of the radicals involves degenerative transfer of a group (or atom). Most prominent is the RAFT polymerization (see **Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization: Mechanism, Process and Applications**, Volume 4) (Scheme 24). rad058

A detailed treatment of CRDRP is beyond the scope of this article and the reader is referred to recent review articles,[178–186] monographs,[175] and other articles in this encyclopedia (see **Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization: Mechanism, Process and Applications**, rad058 **Nitroxide-Mediated Polymerization and its Applications**, rad059 **Atom Transfer Radical Polymerization (ATRP) and Addition (ATRA) and Applications**, rad060 **Sb, Bi, Te, and I-Transfer Polymerization and Applications**, rad061 and **Fundamentals of Controlled/Living Radical Polymerization**, Volume 4). rad078

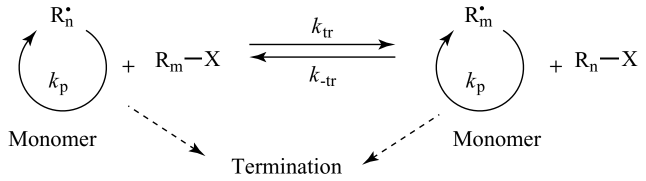


Scheme 23 Atom-transfer radical polymerization.

Degenerate-transfer radical polymerization, DTRP

X = S-(C=S)Z; RAFT: Z = SR; MADIX: Z = OR

Atom or group transfer: X = I, TeR, SbR_2



Scheme 24 Degenerate-transfer radical polymerization.

4.1 Industrial Applications of Controlled Reversible-Deactivation Radical Polymerization

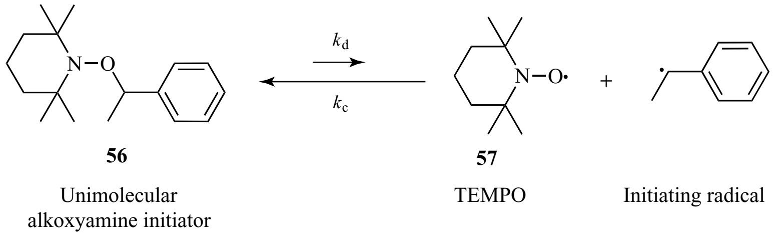
CRDRP opens completely new possibilities for the design and synthesis of novel materials via RP. As is often the case when revolutionary technologies emerge, very optimistic forecasts of their commercial potential appear. Thus, in 2000 the potential market for CRDRP products was anticipated to exceed 20 billion US$ per year.[187] Today, 10 years later, the known industrial applications of CRDRP are very few. It is now clear that CRDRP will not replace classical RP for the production of large-volume commodity polymers. However, its potential for the development and production of high-value polymeric specialties remains intact. Possible target products include adhesives, binders, compatibilizers, cross-linkers, dispersants, emulsifiers, leveling agents, lubricants, sealants, and thermoplastic elastomers. These products are expected to find applications in various industries such as aerospace, aircraft and automobile, biomedical and cosmetic, coatings, electronics, home and personal care, and nanotechnology. The industrial obstacles and achievements of CRDRP were reviewed[187] recently in a very detailed manner by Destarac. Not all CRDRP techniques known today are equally well suited for upscaling from small laboratory experiments into large-scale industrial processes. For example, the controlling agent must be cost effective and ecologically sound. Furthermore, residual metals in ATRP or the chemical nature of the end groups (RAFT) may be an issue.

4.1.1 Nitroxide-Mediated Radical Polymerization

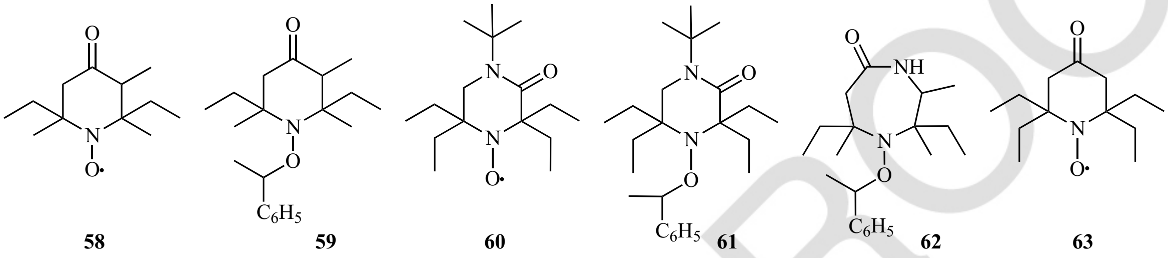
NMP can be performed using the combination of a nitroxide radical controller with a conventional radical initiator such as AIBN or dibenzoylperoxide. However, the initiator-to-controller ratio is slightly different for each polymerization system. In fact, due to the cage reactions of the primary radicals, excess of the initiator is required to ensure 1 : 1 stoichiometry between the nitroxides and *available* primary radicals. For this reason, unimolecular alkoxyamine initiators such as **56** are preferred because their homolysis along the relatively weak[188] ($\approx$110–140 kJ mol^{-1}) NO–R bond affords the nitroxide and initiating radical in exactly 1:1 ratio (Scheme 25).

Yet another possibility is the so-called *in situ* NMP.[189] The required nitroxide radicals are synthesized directly in the polymerizing mixture by addition of radicals generated from conventional initiators to nitric oxide, nitroso compounds, or nitrones, or by the oxidation of suitable secondary amines or hydroxylamines. This method is of potential interest for industrial applications because the nitroxide precursors are cheap. However, a prerequisite for the process optimization is a thorough understanding of the underlying mechanisms.

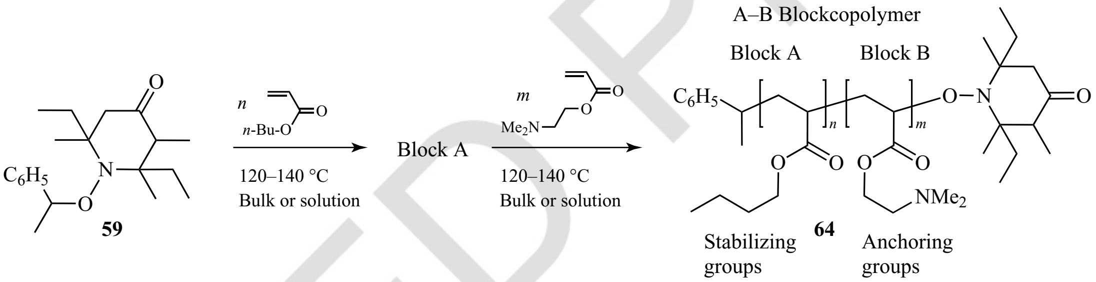
It should be noted at this point that 2,2,6,6-tetramethyl-piperidine-*N*-oxyl (TEMPO) **57** and the related alkoxyamines, for example, **56**, can only be used for controlled polymerization of styrene and not other monomers such as acrylates. To overcome this limitation, Ciba (now part of BASF) has developed a range of proprietary cyclic nitroxides and unimolecular alkoxyamine initiators



Scheme 25 Unimolecular alkoxyamine initiator.



Scheme 26 Sterically hindered cyclic nitroxides and alkoxyamine initiators.

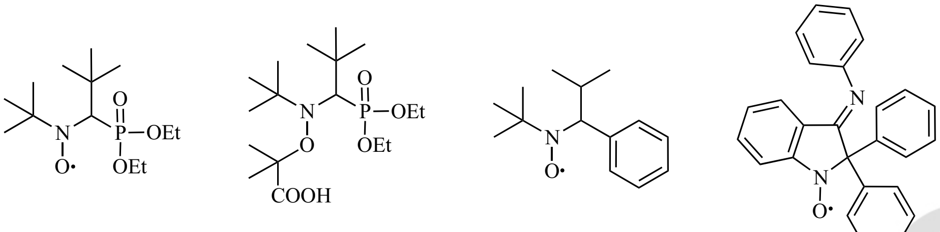


Scheme 27 Amphiphilic block copolymer as pigment dispersant.

that are suitable for controlled polymerization of both styrene and acrylates. Examples of these sterically highly hindered piperidine,[190] piperazinone,[191–193] or diazepanone[194] nitroxides and alkoxyamines **58–62** are shown in Scheme 26.

The piperazinone nitroxide **60** belongs to the most effective[193] cyclic six-membered nitroxides for NMP known today and its synthesis[191,193] is simpler than that[195,196] of the equally effective[195] tetraethyl-piperidone-*N*-oxyl **63**. The industrial NMP process was reported[197] by Ciba in 2003. Using NMP, Ciba developed and commercialized a range of block copolymer pigment dispersants[197–203] which offer advantages in rheology of pigment concentrates, their stability, and coloring properties. The optimal block copolymer pigment dispersant consists of (i) a B-block bearing suitable anchoring groups (e.g., dialkylamino), which adsorb to the surface of a pigment particle; and (ii) an A-block with stabilizing groups which compatibilize the dispersant within the medium and prevent pigment agglomeration and coagulation. The design and synthesis of the amphiphilic blockcopolymer **64** by NMP using the alkoxyamine initiator **59** is exemplified in Scheme 27. The chemistry and physics of polymeric pigment dispersants have been reviewed[202] by Auschra and Pirrung.

In 2005, Elf Atochem (now Arkema) commercialized SG-1 (**65**), an acyclic phosphonylated α-hydrido nitroxide[204,205] and BlocBuilder® MA[206] (**66**), its related alkoxyamine[206–208] which allows controlled polymerization of styrenic, acrylic, and some acrylamido monomers (Scheme 28).



65 SG-1 **66** Blocbuilder® **67** TIPNO **68**

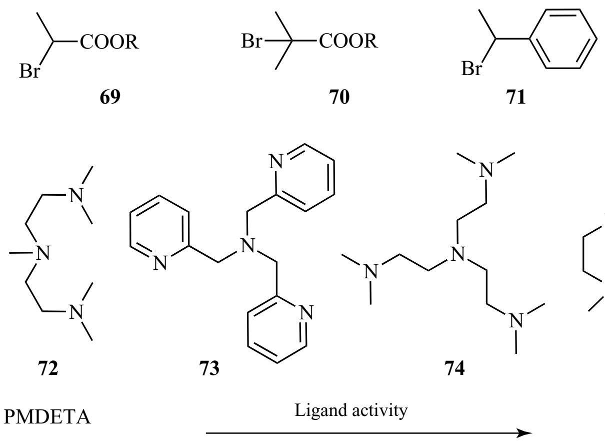
Scheme 28 Acyclic and indolyl nitroxides and alkoxyamines.

Recently, Arkema reported the development[209] of NMP-based block copolymers (Nanostrength®) consisting of PMMA surrounding a center block of poly(butyl acrylate). However, only the central poly(butyl acrylate) block is controlled. These copolymers can be used as tough thermoplastics, thermoplastic elastomers, or toughening additives for epoxy thermosets. NMP is not suitable for polymerization of nonconjugated monomers such as vinyl acetate, vinyl chloride, or *N*-vinyl pyrrolidone. Also unsolved is the controlled homopolymerization of methacrylates although promising results were reported[210] with the indolyl nitroxide **68**. However, well-controlled and living copolymerization of methyl methacrylate with only 5–10% of styrene[211] or acrylonitrile[212] or as little 1% of 9-(4-vinylbenzyl)-9-*H*-carbazole[213] is possible. From the industrial point of view, it is important that NMP, ATRP, and RAFT are amenable[155, 214–220] to aqueous emulsion or mini emulsion polymerization even though some issues[221] remain to be solved. One issue is that NMP requires relatively high temperatures, typically in the range of 100–140 °C. Interesting attempts have been made to use nitroxide mediators in radical photopolymerization.[222]

A low-cost and upscalable synthesis of nitroxides or the related alkoxyamines is necessary to allow their use in industrial NMP. For example, the relatively expensive TEMPO **57** can be replaced by the much cheaper and industrially available 4-hydroxy-2,2,6,6-tetramethyl-piperidine-*N*-oxyl or its readily available derivative 4-alkoxy- or 4-acyloxy for polymerization of styrene. The nitroxides **58**,[190,194] **60**,[191,193] and **65**[223,224] can be prepared by simple reactions without expensive organometallic reagents, as is the case for the TIPNO[225] (*N*-tert-butyl-*N*-2-methyl-1-phenylpropyl nitroxide) nitroxide **67** which is very popular in academic laboratories. Similarly, transformation of the nitroxide into the corresponding alkoxyamine initiator (e.g., **58** to **59** or **65** to **66**) must be industrially feasible. A variety of methods for the preparation of alkoxyamimes exist,[226–229] but only a few are suitable for large-scale, multiton synthesis. The reported industrially relevant methods rely on coupling of nitroxides with C-centered radicals, which, in turn, are generated from either activated alkyl halides with Cu or Cu(I) salts[230] or from hydrocarbons and *t*-butylhydroperoxide.[231] In most cases, the nitroxide group remains covalently attached to the NMP polymer. This is usually not a problem, but, nevertheless, possibilities[232] for its removal exist.

4.1.2 *Atom-Transfer Radical Polymerization*

ATRP is arguably among the most versatile CRDRP method for building complex polymer architectures with a high degree of precision. It can be run over a large range of temperatures, starting at 0 °C or below, with a broad range of monomers (with the exception of acids) using relatively easily accessible (optionally functionalized) initiators. Despite this, the method was not readily accepted by industry because of the large amounts of metallic catalysts (0.1–1 mol% vs monomer) and ligands required. Even though several methods for catalyst removal[233] exist, they are too expensive on an industrial scale. Significant progress was made possible with the invention of activators regenerated by electron transfer (ARGET)[181, 234–236] and initiators for continuous activator regeneration (ICAR)[181,237] modifications of ATRP by Matyjaszewski and coworkers. In ARGET–ATRP, an excess of reducing agent (e.g., ascorbic acid, copper(0), or tin octoate) relative to catalyst is used to continuously regenerate the Cu(I) activator species



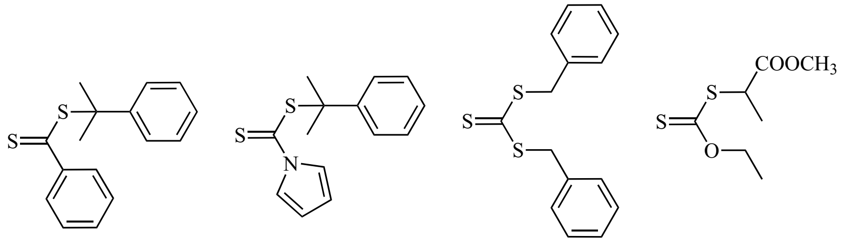
Scheme 29 Alkyl halides and ligands for ATRP.

by reduction of Cu(II) products which are formed by unavoidable radical termination. In ICAR–ATRP polymerization, radicals are continuously generated by conventional initiators (e.g., AIBN) to reduce the Cu(II) species and thus regenerate the active Cu(I) activators. Using these techniques, the amount of Cu catalyst can be reduced[238] by several orders of magnitude down to 10–50 ppm. This low amount of residual Cu catalyst may be acceptable for some applications. Use of ARGET to reduce the concentration of the Cu catalyst in solution–ATRP in batch, semibatch, and continuous reactors has been reviewed.[239]

A new dimension in the reduction of Cu catalyst in ATRP is represented by the single-electron-transfer-controlled radical polymerization (SET-CRP) developed by Percec *et al.*[240–243] In this method, Cu(0) activates the polymerization and is converted by transfer of an electron to the alkyl halide (initiator or dormant chain) into a Cu(I) species. The latter rapidly disproportionates in polar solvents (H_2O, alcohols, dipolar aprotic solvents) in the presence of amine ligands into Cu(0) and the Cu(II) deactivator. The atomic Cu(0) catalyst is much more reactive than the Cu(I) species used in ATRP, so that only small amounts have to be used. SET-CRP allows rapid polymerization of both activated (acrylates, methacrylates) and nonactivated (vinyl chloride) monomers in environmentally friendly solvents at room temperature with even less catalysts than ARGET or ICAR. It is expected that these new advances will facilitate implementation of ATRP in industry, which up to now, similarly to other CRDRP techniques, has not proceeded as fast as originally expected. Matyjaszewski at Carnegie Mellon University founded the ATRP Consortium (1996–2001) and the CRP Consortium (2001–present)[244] with the goal to assist major industrial companies in this transfer. One success was registered by Kaneka, which commercialized[180,187] moisture and photocurable telechelic polyacrylates prepared by ATRP for use as sealants and adhesives, or in coatings. In addition, at least two start-up companies, "ATRP Solutions,"[245] and "Warwick Effect Polymers,"[187,246] are fostering industrial ATRP. Finally, the availability of the ATRP reagents deserves a brief comment. Copper and Cu(I) salts as well as the typically used alkyl halides, for example, **69–71** (Scheme 29), are readily available. The situation is more complicated with the amine ligands. Only N,N,N',N'',N''–pentamethyl-diethylenetriamine (PMDETA) **72** is commercially available (e.g., BASF) in large quantities but not the most effective[235] ligands, for example, **73–75**.

4.1.3 Degenerate-Transfer Radical Polymerization

By far the most important method of DTRP is RAFT, which is an extremely versatile tool for the synthesis of complex polymeric architectures in bulk, organic, or water solution or in dispersed media. It is compatible with the widest range of



76
Dithioester

77
Dithiocarbamate

78
Trithiocarbonate

79
Xanthate (MADIX agent)

Scheme 30 Examples of RAFT/MADIX agents.

polymerizable monomers of all CRDRP techniques. From the process point of view, a RAFT agent can simply replace the conventional chain transfer agent, requiring little or no change in established industrial setups. This broad applicability puts[247] RAFT in the position to become a key industrial CRP method. All aspects of RAFT are covered in the "*Handbook of RAFT Polymerization*"[248] and in recent reviews.[209,247,249–251]

Similar to alkoxyamines in NMP, RAFT agents must be readily available. A recent overview[252] covers various RAFT agents and their synthesis. Scheme 30 shows examples **76–79** of typical RAFT agents. Note that RAFT using xanthates as controlling agents is called *macromolecular design by interchange of xanthates* (MADIX).[253]

The trithiocarbonate **78** (BlocBuilder® DB)[206] was developed by Arkema to commercial stage, and the xanthate **79** (Rhodixan® A1) can be obtained under licence from Rhodia. However, RAFT polymers are always yellow to red in color, which is clearly not acceptable in many applications. Fortunately, a variety of methods[251,254] are available to remove the thiocarbonylthio end group from the polymer or use it for further transformations, for example, for synthesis of block copolymers. Advances in synthesis of degradable "green" polymer materials via RAFT have been reviewed[255] by Perrier and Semsarilar. Rhodia recently reported[256,257] the use of MADIX for the development and commercialization of Rhodibloc® RS block copolymers for the stabilization of emulsions.

Last but not least, it should be mentioned that the first industrially applied CRP was most likely the iodine-transfer polymerization[258] used by Daikin Industries for the preparation of fluorinated thermoplastic elastomers.[187]

5 MAIN COMMERCIAL POLYMERS MADE BY RADICAL POLYMERIZATION

It is beyond the scope of this article to discuss the synthesis and properties of the individual polymers that are made by RP. A detailed overview appears, for example, in the "*Industrial Polymers Handbook*"[17] or the book[18] by Campo. The monograph[259] of Scheirs and Priddy provides in-depth information on all aspects of styrenic polymers and copolymers. Excellent monographs[11,12] on dispersion polymers are also available. Abundant information on PVC can be found in the "*Practical Guide to Polyvinyl Chloride*"[260] and in the special issue (2002, vol. 27(10)) of *Progress in Polymer Science*. The technical processes of PVC production have been reviewed[154] by Saeki and Emura. Development of PVC from its discovery to mass production is recounted by Braun.[261] Comprehensive information on polyethylenes, including LDPE which is made by RP, is available in "*Practical Guide to Polyethylene*"[262] or in Ref. 121.

6 CONCLUSION

Conventional RP has reached a very high level of sophistication and is among the most important industrial polymerization techniques; about 45% of all synthetic polymers are made via this method. The most rapidly developing area of synthetic polymer chemistry today is CRP. Even though considerable progress has been made in CRP during the last two decades, only a very small part of its tremendous potential could be put into industrial practice up to now. However, the recent advances in CRP give reason to expect that new, high-valued products, rather than replacements for existing polymers, will be developed in the very near future.

REFERENCES

1. S. Penczek and G. Moad, *Pure Appl. Chem.*, 2008, **80**, 2163–2193.
2. H.-G. Elias, *Macromolecules*, Wiley-VCH Verlag GmbH, Weinheim, 2005, vol. 1.
3. R. Olby, *J. Chem. Educ.*, 1970, **47**, 168–174.
4. H. Morawetz, *Polymers: The Origin and Growth of a Science*, John Wiley & Sons, Inc, New York, 1985.
5. PlacticsEurope, Plastics— the Facts 2010, http://www.plasticseurope.org/plastics-industry/market- data.aspx. (accessed 14 July 2011).
6. L. Bewley, G. D. Morris, and N. Alperowicz, *Plastics. Chem. Week*, 2010. October 18th.
7. J.-P. Pascault, H. Sautereau, J. Verdu, and R. J. J. Williams, *Thermosetting Polymers*, Marcel Dekker, New York, 2002.
8. S. H. Goodman, *Handbook of Thermoset Plastics*, Noyes Publications, New Jersey, 1998.
9. W. F. Gum, W. Riese, and H. Ulrich, eds., *Reaction Polymers: Polyurethanes, Epoxies, Unsaturated Polyesters, Phenolics, Special Monomers, and Additives. Chemistry, Technology, Applications, Markets*, Hanser Publishers, Muenchen, 1992.
10. R. G. Jones, W. Ando, and J. Chojnowski, eds., *Silicon Containing Polymers*, Kluwer Academic Publishers, Dordrecht, 2000.
11. D. Urban and K. Takamura, eds., *Polymer Dispersions and their Industrial Applications*, Wiley-VCH Verlag GmbH, Weinheim, 2002.
12. J.-C. Daniel and C. Pichot, eds., *Les Latex Synthétiques: Élaboration— Propriétés— Applications*, Lavoisier, Paris, 2006.
13. M. McCoy, M. S. Reisch, and *et al*., A. H. Tullo, Facts and Figures of the Chemical Industry, *Chem. Eng. News*, 2010, **88**, 54–62.
14. H. Dominighaus, P. Elsner, P. Eyerer, and T. Hirth, *Kunststoffe: Eigenschaften und Anwendungen*, 7th edn, Auflage, Springer-Verlag, Berlin Heidelberg, 2008.
15. Kunststoff-Information, Polymerpreise, http://www.kiweb.de/. (accessed 14 July 2011).
16. Fachinformationszentrum Chemie, ed., *Index of Polymer Trade Names*, Wiley-VCH Verlag GmbH, Weinheim, 1992.
17. E. S. Wilks, ed., *Industrial Polymers Handbook*, Wiley-VCH Verlag GmbH, Weinheim, 2001.
18. E. A. Campo, *Industrial Polymers*, Carl Hanser Verlag, Munich, 2008.
19. M. Chanda and S. K. Roy, *Industrial Polymers, Specialty Polymers and Their Applications*, CRC Press, Boca Raton, FL, 2009.
20. F. Mohammad, *Specialty Polymers: Materials and Applications*, Anshan, Kent, 2007.
21. J. A. Brydson, *Plastic Materials*, 7th ed, Butterworth-Heinemann, Oxford, 1999.
22. G. Franz, Oxidation, *Ullmann's Encyclopedia of Industrial Chemistry*, 6th edn, Wiley-VCH Verlag GmbH, Weinheim, 2003.
23. H. S. Mark, ed., *Encyclopedia of Polymer Science and Technology*, 3rd edn, John Wiley & Sons, Inc, New York, 2004.
24. *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th edn, John Wiley & Sons, Inc, New York, 2007.
25. H. L. Hsieh and R. P. Quirk, *Anionic Polymerization: Principles and Practical Applications*, Marcel Dekker, New York, 1996.
26. K. Matyjaszewski, ed., *Cationic Polymerizations: Mechanisms, Synthesis & Applications*, Marcel Dekker, New York, 1996.
27. R. Faust and T. D. Shaffer, eds., *Cationic Polymerization: Fundamentals and Applications*, ACS Symposium Series, American Chemical Society, Washington, DC, 1997, vol. 665.
28. H. L. Hsieh, Industrial applications of anionic polymerization: an introduction, *Applications of Anionic Polymerization Research*, ACS Symposium Series, American-break Chemical Society, Washington, DC, 1998, vol. 696, pp. 28–33.
29. K. Matyjaszewski, Y. Gnanou, and L. Leibler, eds., *Macromolecular Engineering*, Wiley-VCH Verlag GmbH, Weinheim, 2007, vol. 1.
30. M. E. Rogers and T. E. Long, eds., *Synthetic Methods in Step-growth Polymers*, John Wiley & Sons, Inc, Hoboken, NJ, 2003.
31. K. G. Johnson and L. S. Yang, Preparation, properties and applications of unsaturated polyesters, in *Modern Polyesters*, eds. J. Scheirs and T. E. Long, John Wiley & Sons, Inc, Hoboken, NJ, 2003, pp. 699–713.
32. K. J. Ivin and J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, CA, 1997.
33. W. Kuran, *Principles of Coordination Polymerisation*, John Wiley & Sons, Ltd, Chichester, 2001.
34. B. Rieger, L. S. Baugh, S. Kacker, and S. Striegler, eds., *Late Transition Metals Polymerization Catalysis*, Wiley-VCH Verlag GmbH, Weinheim, 2003.
35. Y. V. Kissin, *Alkene Polymerization Reactions with Transition Metal Catalysts*, Elsevier, Amsterdam, 2008.
36. R. Hoff and R. T. Mathers, eds., *Handbook of Transition Metals Polymerization Catalysts*, John Wiley & Sons, Inc, Hoboken, NJ, 2010.
37. O. W. Webster, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 2855–2860.
38. H. J. Lanson, *Chemistry and technology of alkyd and saturated reactive polyester resins*, ACS Symposium Series, American Chemical Society, Washington, DC, 1985, vol. 285, pp. 1181–1204.
39. J. W. Gooch, *Emulsification and Polymerization of Alkyd Resins*, Kluwer Academic Publishers, New York, 2002.
40. Z. W. Wicks, Alkyd resins, *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th edn, John Wiley & Sons, Inc, Hoboken, NJ, 2004, vol. 2, p 147–169.
41. J. Jagur-Grodzinski, *Prog. Polym. Sci.*, 1992, **17**, 361–415.
42. B. I. Chaudhary, S. S. Sengupta, J. M. Cogen, and M. Curto, *Polym. Eng. Sci.*, 2011, **51**, 237–246.
43. C. Tzoganakis, J. Vlachopoulos, and A. E. Hamielec, *Polym. Eng. Sci.*, 1988, **28**, 170–180.
44. A. Psarreas, C. Tzoganakis, N. McManus, and A. Penlidis, *Polym. Eng. Sci.*, 2007, **47**, 2118–2123.
45. H. Guangjian and C. Tzoganakis, *Polym. Eng. Sci.*, 2011, **51**, 151–157.
46. G. Moad, *Prog. Polym. Sci.*, 1999, **24**, 81–142.

47. E. P. Collar and J. M. Garcia-Martinez, On chemical modified polyolefins by grafting of polar monomers: a survey based on recent patents literature, *Recent Patents on Materials Science*, Bentham Science Publishers, 2010, vol. 3, pp. 76–91.
48. E. Passaglia, S. Coiai, and S. Augier, *Prog. Polym. Sci.*, 2009, **34**, 911–947.
49. G. Scott, ed., *Mechanism of Polymer Degradation and Stabilisation*, Elsevier, London, 1990.
50. N. S. Allen and M. Edge, *Fundamentals of Polymer Degradation and Stabilisation*, Elsevier, Barking, 1992.
51. H. Zweifel, *Stabilization of Polymeric Materials*, Springer, Berlin, Heidelberg, 1998.
52. H. Zweifel, ed., *Plastic Additives Handbook*, Hanser Publishers, Munich, 2001.
53. J. Scheirs and D. Priddy, eds., *Modern Styrenic Polymers*, John Wiley & Sons, Ltd, Chichester, 2003, p. 557.
54. G. Moad and D. Solomon, *The Chemistry of Radical Polymerization*, 2nd edn, Elsevier, Oxford, 2006.
55. K. O. Havelka and C. L. McCormick, eds., *Specialty Monomers and Polymers: Synthesis, Properties, and Applications*, ACS Symposium Series, American Chemical Society, Washington, DC, 2000, vol. 755.
56. G. Webster, G. Bradley, and C. Lowe, *A Compilation of Oligomers & Monomers Commercially Available for UV Today*, Sita Technology, Edinbourgh, 2001.
57. H.-J. Arpe, *Industrial Organic Chemistry*, 5th edn, Wiley-VCH Verlag GmbH, Weinheim, 2010.
58. F. Sasse and G. Emig, *Chem. Eng. Technol.*, 1998, **21**, 777–789.
59. R. Diercks, J. D. Arndt, S. Freyer, *et al*., *Chem. Eng. Technol.*, 2008, **31**, 631–637.
60. M. N. Belgacem and A. Gandini, eds., *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, Oxford, 2008.
61. J.-F. Lutz, *Polym. Chem.*, 2010, **1**, 55–62.
62. K. Matyjaszewski and T. P. Davis, eds., *Handbook of Radical Polymerization*, John Wiley & Sons, Inc, Hoboken, NJ, 2002.
63. M. Buback and A. M. Herk, eds., *Radical Polymerization: Kinetics and Mechanism*, Wiley-VCH Verlag GmbH, Weinheim, 2007.
64. K. Matyjaszewski and W. A. Braunecker, Radical polymerization, in *Macromolecular Engineering*, eds. K. Matyjaszewski, Y. Gnanou, and L. Leibler, Wiley-VCH Verlag GmbH, Weinheim 2007, vol. 1, pp. 161–215.
65. G. Odian, *Principles of Polymerization*, 3rd edn, John Wiley & Sons, Inc, New York, 1991.
66. E. T. Denisov, T. G. Denisova, and T. S. Pokidova, *Handbook of Free Radical Initiators*, John Wiley & Sons, Inc, Hoboken, NJ, 2003.
67. J. Brandup, E. H. Immergut, and E. A. Grulke, eds., *Polymer Handbook*, 4th edn, John Wiley & Sons, Inc, New York, 1999.
68. D. Braun, *Int. J. Polym. Sci.*, 2009. Article ID 893234 http://www.hindawi.com/journals/ijps/2009/893234.html. (accessed 14 July 2011).
69. H. K. Hall, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 440–455.
70. G. Clouet, P. Chaumont, and P. Corpart, *J. Polym. Sci., Part A: Polym. Chem.*, 1993, **31**, 2815–2824.
71. P. S. Engel, *Chem. Rev.*, 1980, **80**, 99–150.
72. G. Ayrey, *Chem. Rev.*, 1963, **63**, 645–667.
73. H. Ishiwata, T. Inoue, and K. Yoshihira, *J. Chromatogr.*, 1986, **370**, 275–279.
74. P. J. Fordham, J. W. Gramshaw, and L. Castle, *Food Addit. Contam.*, 2001, **18**, 461–471.
75. J. Krstina, G. Moad, R. Ian Willing, *et al*., *Eur. Polym. J.*, 1993, **29**, 379–388.
76. J. Krstina, G. Moad, and D. H. Solomon, *Eur. Polym. J.*, 1989, **25**, 767–777.
77. Wako Pure Chemical Industries, Azoinitiators, http://www.wako-chem.co.jp/specialty/index.htm. (accessed 14 July 2011).
78. Plastics Additives 7. A global study, *Organic Peroxides, Townsend Polymer Services and Information*, Houston, 2007, Chapter 15.
79. Z. Rappoport, ed., *The Chemistry of Peroxides*, John Wiley & Sons, Ltd, Chichester, 2006, vol. 2, Parts 1–2.
80. Y. R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Boca Raton, FL, 2007.
81. W. H. Starnes, *Prog. Polym. Sci.*, 2002, **27**, 2133–2170.
82. S. Srinivas and K. G. Taylor, *J. Org. Chem.*, 1990, **55**, 1779–1786.
83. P. F. Bruins, ed., *Unsaturated Polyester Technology*, Gordon and Breach, New York, 1976.
84. J. R. Ebdon, T. N. Huckerby, and T. C. Hunter, *Polymer*, 1994, **35**, 250–256.
85. G. S. Misra and U. D. N. Bajpai, *Progr. Polym. Sci.*, 1982, **8**, 61–131.
86. J. A. Klein and G. R. Mros, *Process Saf. Prog.*, 2006, **25**, 303–310.
87. Arkema, Organic Peroxides Safety, http://www.arkema-inc.com/index.cfm?pag=320. (accessed 14 July 2011).
88. K. Studer, P. Nesvadba, T. Jung, *et al*., *Prog. Org. Coat.*, 2008, **61**, 119–125.
89. M. Roth, R. Pfaendner, P. Nesvadba, and M.-O. Zink, WO2001/090113 A1, Ciba SC, 2001.
90. E. De Leon-Saenz, G. Morales, R. Guerrero-Santos, and Y. Gnanou, *Macromol. Chem. Phys.*, 2000, **201**, 74–83.
91. P. Nesvadba, L. Bugnon, and T. Wagner, *Chimia*, 2010, **64**, 56–58.
92. J. V. Crivello and K. Dietliker, eds., *Photoinitiators for Free Radical Cationic and Anionic Photopolymerization*, John Wiley & Sons in association with SITA Technology, Chichester, 1998.
93. K. Dietliker, *A Compilation of Photoinitiators Commercially Available for UV Today*, Sita Technology, Edinburgh, 2002.
94. H. F. Gruber, *Prog. Polym. Sci.*, 1992, **17**, 953–1044.
95. K. Dietliker, R. Hüsler, J. L. Birbaum, *et al*., *Prog. Org. Coat.*, 2007, **58**, 146–157.
96. J. P. Fouassier, X. Allonas, and J. Lalevée, Polymerization under light nd other exteernal stimuli, in *Macromolecular Engineering*, eds. K. Matyjaszewski, Y. Gnanou, and L. Leibler, Wiley-VCH Verlag GmbH, Weinheim 2007, vol. 1, pp. 643–672.
97. C. Lowe, G. Webster, S. Kessel, and I. McDonald, *Chemistry and Technology for UV and EB Formulation for Coatings, Inks and Paints*, John Wiley & Sons in association with SITA Technology, Chichester, 1997.

98. R. Mehnert, A. Pincus, I. Janorski, and R. Stove, *UV & EB Curing Technology and Equipment*, John Wiley & Sons in association with SITA Technology, Chichester, 1998.
99. J.-P. Fouassier and J. F. Rabek, eds., *Radiation Curing in Polymer Science and Technology: Fundamentals and Methods*, Elsevier, London, 1993, vol. 1.
100. J.-P. Fouassier and J. F. Rabek, eds., *Radiation Curing in Polymer Science and Technology: Photoinitiating Systems*, Elsevier, London, 1993, vol. 2.
101. J.-P. Fouassier and J. F. Rabek, eds., *Radiation Curing in Polymer Science and Technology: Polymerization Mechanisms*, Elsevier, London, 1993, vol. 3.
102. J.-P. Fouassier and J. F. Rabek, eds., *Radiation Curing in Polymer Science and Technology: Practical Aspects and Applications*, Elsevier, London, 1993, vol. 4.
103. A. R. Marrion, ed., *The Chemistry and Physics of Coatings*, 2nd edn, The Royal Society of Chemistry, Cambridge, 2004.
104. U. Fink, F. Hajduk, Y. Wei, and Y. Ishikawa, *Radiation Curable Coatings*, SRI Consulting, 2008.
105. H. Kura, J. Tanabe, H. Oka, *et al*., *New Oxime Ester Photoinitiators for Color Filter Resists*, RadTech Report, RadTech International North America, 2004, vol. 18 (3), pp. 30–35.
106. K. Dietliker, T. Jung, J. Benkhoff, *et al*., *Macromol. Symp.*, 2004, **217**, 77–97.
107. A. G. Merzlikine, S. V. Voskresensky, E. O. Danilov, *et al*., *Photochem. Photobiol. Sci.*, 2007, **6**, 608–613.
108. A. Matsumoto, M. Kikuta, and M. Oiwa, *J. Polym. Sci., Polym. Lett. Ed.*, 1986, **24**, 7–11.
109. G. Moad, E. Rizzardo, and D. H. Solomon, *Macromolecules*, 1982, **15**, 909–914.
110. G. Moad, D. H. Solomon, S. R. Johns, and R. I. Willing, *Macromolecules*, 1982, **15**, 1188–1191.
111. O. Vogl, M. F. Qin, and A. Zilkha, *Prog. Polym. Sci.*, 1999, **24**, 1481–1525.
112. N. Moszner and U. Salz, *Prog. Polym. Sci.*, 2001, **26**, 535–576.
113. N. Moszner, T. Volkel, and V. Rheinberger, *Macromol. Chem. Phys.*, 1997, **198**, 749–762.
114. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, 1944, **66**, 1594–1601.
115. T. Alfrey and C. C. Price, *J. Polym. Sci.*, 1947, **2**, 101–106.
116. G. C. Laurier, K. F. O'Driscoll, and P. M. Reilly, *J. Polym. Sci., Polym. Symp.*, 1985, **72**, 17–26.
117. G. Moad, D. H. Solomon, T. H. Spurling, and D. J. Vearing, *Aust. J. Chem.*, 1986, **39**, 1877–1881.
118. F. Quella, *Makromol. Chem.*, 1989, **190**, 1445–1452.
119. J. Chiefari and E. Rizzardo, Control of free radical polymerization by chain transfer methods, in *Handbook of Radical Polymerization*, eds. T. P. Davis and K. Matyjaszewski, John Wiley & Sons, Inc, Hoboken, NJ, 2002, pp. 629–690.
120. T. Corner, *Adv. Polym. Sci.*, 1984, **62**, 95–142.
121. K. S. Whiteley, Polyethylene, in *Industrial Polymers Handbook*, ed. E. S. Wilks, Wiley-VCH Verlag GmbH, Weinheim, 2001, vol. 2, p. 643–691.
122. F. R. Mayo, *J. Am. Chem. Soc.*, 1943, **65**, 2324–2329.
123. R. G. W. Norrish and R. R. Smith, *Nature*, 1942, **150**, 336–337.
124. V. E. Trommsdorff, H. Köhle, and P. Lagally, *Makromol. Chem.*, 1948, **1**, 169–198.
125. Arkema. Mercaptans, http://www.arkema-inc.com/index.cfm?pag=123. (accessed 14 July 2011).
126. Chevron Phillips Chemical, Mercaptans, http://www.cpchem.com/bl/specchem/en-us/Pages/Mercaptans.aspx. (accessed 14 July 2011).
127. B. Boutevin, J.-M. Lusinchi, Y. Pietrasanta, and J.-J. Robin, *Eur. Polym. J.*, 1994, **30**, 615–619.
128. F. A. Bovey and I. M. Kolthoff, *Chem. Rev.*, 1948, **42**, 491–525.
129. F. Tüdos and T. Földes-Berezsnich, *Prog. Polym. Sci.*, 1989, **14**, 717–761.
130. S. Ilg, E. Pighetti, P. Nesvadba, and A. Fuchs, WO 2006/111494 A1, CibaSC, 2006.
131. J. J. Kurland, *J. Polym. Sci., Polym. Chem. Ed.*, 1980, **18**, 1139–1145.
132. L. B. Levy, *J. Polym. Sci., Polym. Chem. Ed.*, 1985, **23**, 1505–1515.
133. L. B. Levy and J. D. Penrod, *Plant/Oper. Prog.*, 1989, **8**, 105–108.
134. S. Schulze and H. Vogel, *Chem. Eng. Technol.*, 1998, **21**, 829–837.
135. B. Maillard, K. U. Ingold, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1983, **105**, 5095–5099.
136. L. Gou, C. N. Coretsopoulos, and A. B. Scranton, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 1285–1292.
137. P. Neta, R. E. Huie, and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1990, **19**, 413–513.
138. K. U. Ingold, *Acc. Chem. Res.*, 1969, **2**, 1–9.
139. V. A. Bhanu and K. Kishore, *Chem. Rev.*, 1991, **91**, 99–117.
140. L. Gou, B. Opheim, and A. B. Scranton, Methods to overcome oxygen inhibition in free radical photopolymerizations, in *Photochem. UV Curing*, ed. J. P. Fouassier, Research Signpost, Trivandrum, 2006, pp. 301–310.
141. C. Belon, X. Allonas, C. Croutxe-barghorn, and J. Lalevee, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 2462–2469.
142. M. Höfer, N. Moszner, and R. Liska, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6916–6927.
143. L. Feng and B. I. Suh, *J. Appl. Polym. Sci.*, 2009, **112**, 1565–1571.
144. R. Shenoy and C. N. Bowman, *Macromolecules*, 2010, **43**, 7964–7970.
145. C. E. Hoyle and C. N. Bowman, *Angew. Chem. Int. Ed.*, 2010, **49**, 1540–1573.
146. M. J. Kade, D. J. Burke, and C. J. Hawker, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 743–750.
147. A. B. Lowe, *Polym. Chem.*, 2010, **1**, 17–36.
148. T. Meyer and J. Keurentjes, eds., *Handbook of Polymer Reaction Engineering*, Wiley-VCH Verlag GmbH, Weinheim, 2005.
149. W. Keim, *Kunststoffe. Synthese, Herstellungsverfahren, Apparaturen*, Wiley-VCH Verlag GmbH, Weinheim, 2006.
150. J. M. Asua, ed., *Polymer Reaction Engineering*, Blackwell Publishing, Oxford, 2007.
151. D. H. Sebastian and J. A. Biesenberger, *Polym. Eng. Sci.*, 1979, **19**, 190–197.
152. U. Onken and A. Behr, *Chemische Prozesskunde, Band 3*, Georg Thieme Verlag, Stuttgart, 1996, p. 81.
153. H. Sawada, *Thermodynamics of Polymerization*, Marcel Dekker, New York, 1976.

154. Y. Saeki and T. Emura, *Prog. Polym. Sci.*, 2002, **27**, 2055–2131.
155. B. Charleux and F. Ganachoud, Polymerizations in aqueous dispersed media, in *Macromolecular Engineering*, eds. K. Matyjaszewski, Y. Gnanou, and L. Leibler, Wiley-VCH Verlag GmbH, Weinheim, 2007, vol. 1, pp. 605–642.
156. V. Herbert and A. Bisio, *Synthetic Rubber: A Project That Had to Succeed*, Greenwood Press, Westport, 1985.
157. J. M. Asua, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 1025–1041.
158. A. Mv. Herk, ed., *Chemistry and Technology of Emulsion Polymerization*, Blackwell Publishing, Oxford, 2005.
159. J. M. Asua, ed., *Polymeric Dispersions: Principles and Applications*, Kluwer Academic Publishers, Dordrecht, 1997.
160. C.-S. Chern, *Principles and Applications of Emulsion Polymerization*, John Wiley & Sons, Inc, Hoboken, 2008.
161. W. Brostow, R. Chiu, I. M. Kalogeras, and A. Vassilikou-Dova, *Mater. Lett.*, 2008, **62**, 3152–3155.
162. V. Mittal, ed., *Miniemulsion Polymerization Technology*, John Wiley & Sons, Inc and Scrivener Publishing, Hoboken,NJ, Salem, 2010.
163. J. Ugelstad, M. S. El-Aasser, and J. W. Wanderhoff, *J. Polym. Sci., Polym. Lett. Ed.*, 1973, **111**, 503–513.
164. I. Capek and C. S. Chern, *Adv. Polym. Sci.*, 2001, **155**, 101–165.
165. M. Antonietti and K. Landfester, *Prog. Polym. Sci.*, 2002, **27**, 689–757.
166. J. M. Asua, *Prog. Polym. Sci.*, 2002, **27**, 1283–1346.
167. C. Schellenberg, C. Auschra, W. Peter, *et al*., WO 2005/023878 A1, Ciba SC, 2005.
168. M. Antonietti, R. Basten, and S. Lohmann, *Macromol. Chem. Phys.*, 1995, **196**, 441–466.
169. I. Capek, *Adv. Colloid. Interface Sci.*, 1999, **82**, 253–273.
170. I. Capek, *Adv. Colloid. Interface Sci.*, 1999, **80**, 85–149.
171. P. Kumar and K. L. Mittal, eds., *Handbook of Microemulsion Science and Technology*, Marcel Dekker, New York, 1999.
172. A. D. Jenkins, R. G. Jones, and G. Moad, *Pure Appl. Chem.*, 2010, **82**, 483–491.
173. M. Szwarc, *Nature*, 1956, **176**, 1168–1169.
174. K. Matyjaszewski and A. H. E. Mueller, *Prog. Polym. Sci.*, 2006, **31**, 1039–1040.
175. A. H. E. Müller and K. Matyjaszewski, eds., *Controlled and Living Polymerizations*, Wiley-VCH Verlag GmbH, Weinheim, 2010.
176. T. Otsu and M. Yoshida, *Makromol. Chem., Rapid Commun.*, 1982, **3**, 127–132.
177. T. Otsu, M. Yoshida, and T. Tazaki, *Makromol. Chem., Rapid Commun.*, 1982, **3**, 133–140.
178. D. A. Shipp, *J. Macromol. Sci., Polym. Rev.*, 2005, **C45**, 171–194.
179. D. H. Solomon, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 5748–5764.
180. K. Matyjaszewski and J. Spanswick, *Mater. Today*, 2005, **8**, 26–33.
181. W. A. Braunecker and K. Matyjaszewski, *Prog. Polym. Sci.*, 2007, **32**, 93–146.
182. G. Moad, E. Rizzardo, and S. H. Thang, *Acc. Chem. Res.*, 2008, **41**, 1133–1142.
183. O. Jung Kwon, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6983–7001.
184. M. F. Cunningham, *Prog. Polym. Sci.*, 2008, **33**, 365–398.
185. S. Yamago, *Chem. Rev.*, 2009, **109**, 5051–5068.
186. F. di Lena and K. Matyjaszewski, *Prog. Polym. Sci.*, 2010, **35**, 959–1021.
187. M. Destarac, *Macromol. React. Eng.*, 2010, **4**, 165–179.
188. J. L. Hodgson, L. B. Roskop, M. S. Gordon, *et al*., *J. Phys. Chem. A*, 2010, **114**, 10458–10466.
189. V. Sciannamea, R. Jerome, and C. Detrembleur, *Chem. Rev.*, 2008, **108**, 1104–1126.
190. A. Kramer and P. Nesvadba, US 6353107 B1, Ciba SC, 2002.
191. P. Nesvadba and A. Kramer, M.-O. Zink, US 6479608 B1, Ciba SC, 2002.
192. H. Fischer, A. Kramer, S. R. A. Marque, and P. Nesvadba, *Macromolecules*, 2005, **38**, 9974–9984.
193. S. Miele, P. Nesvadba, and A. Studer, *Macromolecules*, 2009, **42**, 2419–2427.
194. P. Nesvadba, L. Bugnon, and R. Sift, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 3332–3341.
195. C. Wetter, J. Gierlich, C. A. Knoop, *et al*., *Chem.— Eur. J.*, 2004, **10**, 1156–1166.
196. K. Sakai, K.-I. Yamada, T. Yamasaki, *et al*., *Tetrahedron*, 2010, **66**, 2311–2315.
197. C. Auschra, E. Eckstein, R. Knischka, and P. Nesvadba, *Asia Pac. Coat. J.*, 2003, **16**, 20–23.
198. C. Auschra, E. Eckstein, A. Muehlebach, *et al*., *Prog. Org. Coat.*, 2002, **45**, 83–93.
199. C. Auschra, E. Eckstein, R. Knischka, *et al*., *Eur. Coat. J.*, 2004, **26**, 31–32, 34–35.
200. C. Auschra, E. Eckstein, R. Knischka, *et al*., *Eur. Coat. J.*, 2005, **156**, **158**, **160**, 162–163.
201. F. O. H. Pirrung and C. Auschra, *Polym. Prepr.*, 2005, **46**, 316–317.
202. F. Pirrung and C. Auschra, Polymeric dispersants, in *Macromolecular Engineering*, eds. K. Matyjaszewski, Y. Gnanou, and L. Leibler, Wiley-VCH Verlag GmbH, Weinheim 2007, vol. 4, pp. 2135–2180.
203. A. T. Termaten, M. van der Sluis, F. Pirrung, and C. Auschra, *Polym. Prepr.*, 2008, **49**, 353–354.
204. C. Le Mercier, J. F. Lutz, S. Marque, *et al*., *Use of Phosphonylated Nitroxides and Alkoxyamines in Controlled/”Living” Radical Polymerization*, ACS Symposium Series, American Chemical Society, Washington, DC, 2000, vol. 768, pp. 108–122.
205. J. Marchand, L. Autissier, Y. Guillaneuf, *et al*., *Aust. J. Chem.*, 2010, **63**, 1237–1244.
206. Arkema. BlocBuilder, http://www.arkema-inc.com/index.cfm?pag=1257. (accessed 14 July 2011).
207. J. Nicolas, B. Charleux, O. Guerret, and S. Magnet, *Macromolecules*, 2004, **37**, 4453–4463.
208. D. Gigmes, J. Vinas, N. Chagneux, *et al*., SG1 and BLOCBUILDER technology: a versatile toolbox for the elaboration of complex macromolecular architectures, *Controlled/Living Radical Polymerization: Progress in RAFT, DT, NMP & OMRP*, ACS Symposium Series, American Chemical Society, Washington, DC, 2009, vol. 1024, pp. 245–262.
209. P. Gerard, L. Couvreur, S. Magnet, *et al*., Controlled architecture polymers at Arkema: synthesis, morphology and properties of all-acrylic block copolymers, *Controlled/Living Radical Polymerization: Progress in RAFT,*

DT, NMP & OMRP, ACS Symposium Series, American Chemical Society, Washington, DC, 2009, vol. 1024, pp. 361–373.

210. Y. Guillaneuf, D. Gigmes, S. R. A. Marque, *et al*., *Macromolecules*, 2007, **40**, 3108–3114.
211. B. Charleux, J. Nicolas, and O. Guerret, *Macromolecules*, 2005, **38**, 5485–5492.
212. J. Nicolas, S. Brusseau, and B. Charleux, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 34–47.
213. B. Lessard, E. J. Y. Ling, M. S. T. Morin, and M. Maric, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 1033–1045.
214. J. Nicolas, B. Charleux, and S. Magnet, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 4142–4153.
215. M. Save, Y. Guillaneuf, and R. G. Gilbert, *Aust. J. Chem.*, 2006, **59**, 693–711.
216. B. Charleux and J. Nicolas, *Polymer*, 2007, **48**, 5813–5833.
217. P. B. Zetterlund, Y. Kagawa, and M. Okubo, *Chem. Rev.*, 2008, **108**, 3747–3794.
218. J. K. Oh, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6983–7001.
219. C. Dire, S. Magnet, L. Couvreur, and B. Charleux, *Macromolecules*, 2009, **42**, 95–103.
220. T. E. Enright, M. F. Cunningham, and B. Keoshkerian, *Macromol. React. Eng.*, 2010, **4**, 186–196.
221. P. B. Zetterlund, *Macromol. Theory Simul.*, 2010, **19**, 11–23.
222. D.-L. Versace, J. Lalevee, J.-P. Fouassier, *et al*., *Macromol. Rapid Commun.*, 2010, **31**, 1383–1388.
223. J.-P. Gillet, O. Guerret, and P. Tordo, WO 2000/040526 A2, Elf Atochem, 2000.
224. O. Guerret, J.-L. Couturier, and C. Le Mercier, WO 2002/048159 A1, Atofina, 2002.
225. D. Benoit, V. Chaplinski, R. Braslau, and C. J. Hawker, *J. Am. Chem. Soc.*, 1999, **121**, 3904–3920.
226. D. A. Tirrell, *J. Polym. Sci., Part A: Polym. Chem.*, 1998, **36**, 2667–2668.
227. P. Nesvadba, *Chimia*, 2006, **60**, 832–840.
228. D. Bertin, D. Gigmes, and S. R. A. Marque, *Recent Res. Dev. Org. Chem.*, 2006, **10**, 63–121.
229. A. C. Greene and R. B. Grubbs, Current methods for *N*-alkoxyamine synthesis, *Controlled/Living Radical Polymerization: Progress in RAFT, DT, NMP & OMRP*, ACS Symposium Series, American Chemical Society, Washington, DC, 2009, vol. 1024, pp. 81–93.
230. J.-L. Couturier, WO 2009/010693 A2, Arkema, 2009.
231. H.-J. Kirner, F. Schwarzenbach, P. A. van der Schaaf, *et al*., *Adv. Synth. Catal.*, 2004, **346**, 554–560.
232. Y. Guillaneuf, P.-E. Dufils, L. Autissier, *et al*., *Macromolecules*, 2009, **43**, 91–100.
233. Y. Shen, H. Tang, and S. Ding, *Prog. Polym. Sci.*, 2004, **29**, 1053–1078.
234. W. Jakubowski and K. Matyjaszewski, *Angew. Chem. Int. Ed.*, 2006, **45**, 4482–4486.
235. N. V. Tsarevsky and K. Matyjaszewski, *Chem. Rev.*, 2007, **107**, 2270–2299.
236. R. Nicolay, Y. Kwak, and K. Matyjaszewski, *Angew. Chem. Int. Ed.*, 2010, **49**, 541–544.
237. K. Matyjaszewski, W. Jakubowski, K. Min, *et al*., *Proc. Natl. Acad. Sci. U.S.A.*, 2006, **103**, 15309–15314.
238. L. Mueller and K. Matyjaszewski, *Macromol. React. Eng.*, 2010, **4**, 180–185.
239. N. Chan, M. F. Cunningham, and R. A. Hutchinson, *Macromol. React. Eng.*, 2010, **4**, 369–380.
240. V. Percec, T. Guliashvilli, J. S. Ladislaw, *et al*., *J. Am. Chem. Soc.*, 2006, **128**, 14156–14165.
241. B. M. Rosen and V. Percec, *Chem. Rev.*, 2009, **109**, 5069–5119.
242. X. Jiang, B. M. Rosen, and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 403–409.
243. S. Fleischmann, B. M. Rosen, and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 1190–1196.
244. Controlled radical polymerization consortium at Carnegie Mellon University, http://www.chem.cmu.edu/groups/maty/crp/. (accessed 14 July 2011).
245. ATRP Solutions, http://www.atrpsolutions.com/. (accessed 14 July 2011).
246. Warwick Effect Polymers, http://www.warwickeffectpolymers.co.uk/. (accessed 14 July 2011).
247. S. Perrier and C. Barner-Kowollik, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 5715–5723.
248. C. Barner-Kowollik, ed., *Handbook of RAFT Polymerization*, Wiley-VCH Verlag GmbH, Weinheim, 2008.
249. G. Moad, *Aust. J. Chem.*, 2006, **59**, 661–662.
250. A. B. Lowe and C. L. McCormick, *Prog. Polym. Sci.*, 2007, **32**, 283–351.
251. G. Moad, E. Rizzardo, and S. H. Thang, *Polym. Int.*, 2011, **60**, 9–25.
252. G. Moad, E. Rizzardo, and S. H. Thang, *Aust. J. Chem.*, 2009, **62**, 1402–1472.
253. S. Perrier and P. Takolpuckdee, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 5347–5393.
254. H. Willcock and R. K. O'Reilly, *Polym. Chem.*, 2010, **1**, 149–157.
255. M. Semsarilar and S. Perrier, *Nat. Chem.*, 2010, **2**, 811–820.
256. M. Destarac, *Polym. Prepr.*, 2008, **49**, 179–180.
257. M. Destarac, S. Deroo, H. Lannibois-Drean, *et al*., MADIX technology: from innovative concepts to industrialization of block copolymers for emulsion stabilization, *Controlled/Living Radical Polymerization: Progress in RAFT, DT, NMP & OMRP*, ACS Symposium Series, American Chemical Society, Washington, DC, 2009, vol. 1024, pp. 347–359.
258. G. David, C. Boyer, J. Tonnar, *et al*., *Chem. Rev.*, 2006, **106**, 3936–3962.
259. J. Scheirs and D. Priddy, eds., *Modern Styrenic Polymers*, John Wiley & Sons, Ltd, Chichester, 2003.
260. S. G. Patrick, *Practical Guide to Polyvinyl Chloride*, Rapra Technology, Shawbury, 2005.
261. D. Braun, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 578–586.
262. C. Vasile and M. Pascu, *Practical Guide to Polyethylene*, Rapra Technology, Shawbury, 2005.

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Abstract: The position of radical polymerization (RP) in the context of polymer industry is highlighted. The mechanistic steps of RP are discussed from an industrial point of view. An overview of industrial initiators including photoinitiators, chain transfer agents, and monomer stabilizers is given. The most important polymerization processes with focus on emulsion polymerization (EP) and dispersion polymers as well as types of polymerization reactors are presented. The progress of controlled RP toward commercialization is reviewed.

Keywords: industrial radical polymerization; industrial monomers; initiators; photoinitiators; copolymerization; chain transfer agents; polymerization inhibitors; monomer stabilization; oxygen inhibition; polymerization processes; controlled radical polymerization.