SOLID STATE POLYMERIZATION

Edited by

CONSTANTINE D. PAPASPYRIDES
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National Technical University of Athens

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To my wife Dida
—CDP

To my mother Anastasia
—SNV

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PREFACE

Solid state polymerization (SSP) constitutes a valuable technique used industrially mainly for condensation polymers such as polyamides and polyesters. It involves heating the starting material in an oxygen-free atmosphere (i.e., under flowing gas or high pressure or in vacuo), at a temperature below the melting point, increasing the molecular weight of the product while the material retains its solid shape. Its advantages over conventional melt-phase operations are the low polymerization temperatures, eliminating decomposition and undesirable by-product formation, the simplicity and low cost of process equipment, and the less expensive catalyst systems required.

SSP technology dates from 1940 and the first relevant patents of Flory (1939) and Monroe (1962) issued in an increase in prepolymer molecular weight via reactions in the solid state. Since then, the industrial scale for polyamides has been expanded to include PA 66, PA 6, and polyesters such as PET, and their use in overall polymerization layouts is often stated as drying or finishing. In parallel to its application, extensive research is on going in universities and in industry to understand the reaction mechanism and to optimize the process, especially with regard to the low reaction rates and sintering problems. The amount of open literature, especially patents, has increased steadily since 1995, and its investigation has spread to the majority of issues of most immediate concern, since it is an indispensable part of polymer production lines.

The answer to the question “Why study SSP in 2009?” is that the value of SSP lies beyond its obvious role as an extension of conventional polymerization techniques. It can also be used as a recycling method, through which the molecular weight of the postconsumer material is increased, thus permitting processing without severe recycled material deterioration. It offers a feasible tool with which to investigate polymer behavior during polymerization or subsequent processing, due to its simplicity regarding technical requirements. For example, the catalytic performance of organic substances can be tested primarily in SSP and extrapolated further with regard to activity in the melt-phase reaction. Even more, the mechanisms prevailing in a solid-phase reaction can be used and interpreted to overcome a series of problems during conventional polymerization and processing.

In our experience, SSP comprises an “exciting” technique for a student or researcher because it combines fundamentals of polymer science, chemistry, physical chemistry, and engineering. In Chapter 1, the complexity of the process is highlighted and how it involves both chemical and physical steps combined with process mechanisms and apparatus is discussed. These SSP steps are found to control the reaction rate separately and/or jointly, depending on the starting material type and process conditions (i.e., temperature, initial stoichiometry and crystallinity, reacting particle size distribution, condensate content in the surroundings, catalysts presence, etc.). The physical chemical aspects of the process are described further in Chapter 2, where the concept of end-group diffusion is indicated as being the primary difference from melt-phase technique. The reacting system morphology shows how it can influence SSP kinetics, and a model is constructed to predict molecular weight achieved. In the following chapters, SSP kinetics are investigated further, also considering other possible rate-controlling steps, such as chemical reactions and by-product removal. Polyesters and polyamides are examined as prevailing SSP polymers. Especially for polyamides, examples are given where SSP serves as a tool to investigate the effect of additives on polymerization rates.

As depicted in SSP kinetics, the slow process rate handled using catalysts and relevant systems is discussed in Chapter 5, covering metallic, nonmetalic, reactive, and inert additives. In Chapter 6 we describe a specialized application of SSP conducted under high pressure on a laboratory scale. It is shown how SSP can serve as a tool to examine the differences in a series of polyamide monomers and polymers in terms of monomer polymerizability, polyamide structure, and degree of orientation. Finally, Chapters 7 and 8 cover engineering aspects regarding process modeling and industrial application. The relevant knowledge can serve as a guide to develop SSP reactors and design pertinent plants.

Based on the book’s structure, we have gathered and filtered the literature available on the SSP technique. It is hoped that the reader will find information not only to comprehend the pertinent polymerization technique, but also to initiate future investigations, since it is our belief that SSP processes consist of a continuously developing field.

Finally, we wish to cordially thank the indispensable contribution of each chapter author, with whom we enjoyed an excellent collaboration. Also, our warm thanks to the members of the staff at Wiley for all their help and guidance.

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July 2008

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FUNDAMENTALS OF SOLID STATE POLYMERIZATION

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Solid State Polymerization, Edited by Constantine D. Papaspyrides and Stamatina N. Vouyiouka

1.1. INTRODUCTION

1.1.1. Polymers and Plastics

Plastics are indispensable contemporary materials used in nearly all areas of daily life, and their production and fabrication are major worldwide industries. The key word related to plastics is *polymers*, organic substances that are built up by small molecules (monomers) joined together with covalent bonds and forming long carbon or heteroatom chains (macromolecules). There may be hundreds, thousands, ten thousands, or more monomers linked together in a polymer molecule, as noted by the Greek root of the word *polymer*, meaning "many parts." Plastics are highly modified polymeric materials that have been or can readily be formed or molded into useful shapes, and a typical commercial plastic resin may contain one or more polymers in addition to various additives and fillers.

Although humankind has used natural polymers, such as animal skins, silk, cellulose, and natural rubber since prehistoric times, the birth of plastics may be traced back to the mid-nineteenth century. More specifically, the true nature of polymer molecules was elucidated in 1920 by the pioneering work of Herman Staudinger, who proposed and defended the macromolecular structure of polymers, differing from the then- prevailing theory that polymers are colloids. Distinct milestones in plastics history (Fig. 1.1) include development of the vulcanization process by Charles Goodyear, transforming the latex of natural rubber to a useful elastomer for tire use; the invention of celluloid, the first

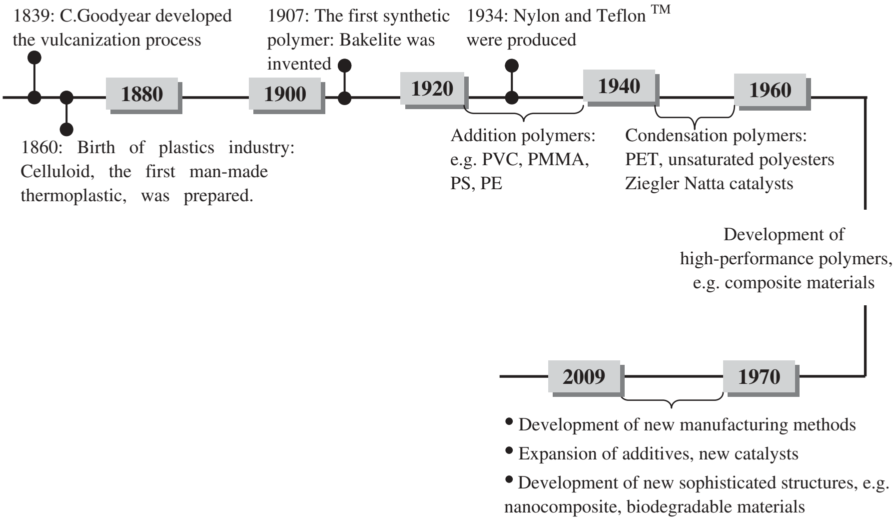


Fig. 1.1. Major milestones in plastics history.

humanmade thermoplastic, created from nitrocellulose and camphor by John Wesley Hyatt; the invention by Leo Baekeland of Bakelite (phenol–formaldehyde resin), which is used due to its excellent thermal and electric insulating properties; the preparation of nylon, an exotic polymer at that time, by Wallace Carothers, who was working at Du Pont during the 1920s and 1930s; and the development of low-pressure catalysts by Ziegler and Natta, which led to the commercialization of polypropylene as a major commodity plastic [1,2]. The last 30 years of plastics development involve progress in polymer chemistry as well as in modification, processing, and fabrication, allowing plastic materials to be shaped at low cost while achieving the desired functionality and characteristics.

The plastics industry is about the same size as that of metals, accounting globally for $120 billion in 2002 for the five major thermoplastics [polyethylenes, polypropylene (PP), polystyrene (PS), poly(vinyl chloride) (PVC), and poly(ethylene terephthalate) (PET)] [3]. Plastics are widely used in commodity products (e.g., textiles, tires, packaging) as well as for engineering materials in the transportation, electrical and electronic, medical, chemical, and biotech industries (Fig. 1.2). Therefore, it is not a false reflection to say that we live in a plastic world, where the characteristics and advantages of plastics render them preferred materials for consumer durables and constructive applications, based on careful end-product design and assessment of the pertinent manufacturing capabilities and costs.

The corollary of all the aforementioned applications is that global plastic consumption was 230,000 kilotons in 2005. In Europe it was estimated at 106 kg/capita, based on 2001 data, with a prediction of a 50% increase by 2010, and in the United States it was 121 kg/capita in 2001 with a 47% increase projected for 2010 [4]. Plastics segmentation in Western Europe for 2004 revealed that packaging is the biggest single sector, at 37% of total plastics demand, followed by building and construction applications at 20%. In addition to automotive uses (7.5%) and E&E applications (7.5%), there is also a large range of other applications (29%), including agriculture, household, medical devices, toys, leisure, and sports goods [5].

1.1.2. Polymerization Processes

Polymers, the core of plastics, are prepared by a process known as *polymerization*, which involves the chemical combination of monomers. The polymerization mechanism is widely used as a criterion for polymer classification. Accordingly, during the development of polymer science, polymers were classified as either condensation or addition, based on structural and compositional differences, a scheme attributed to W. Carothers, the inventor of nylon. Condensation polymers are formed from polyfunctional monomers through various organic chemistry reactions, resulting in joining the repeating units by bonds of one type, such as ester, amide, urethane, sulfide, and ether linkages. In most cases, the condensation reaction is followed by the liberation of small molecules (by-product,

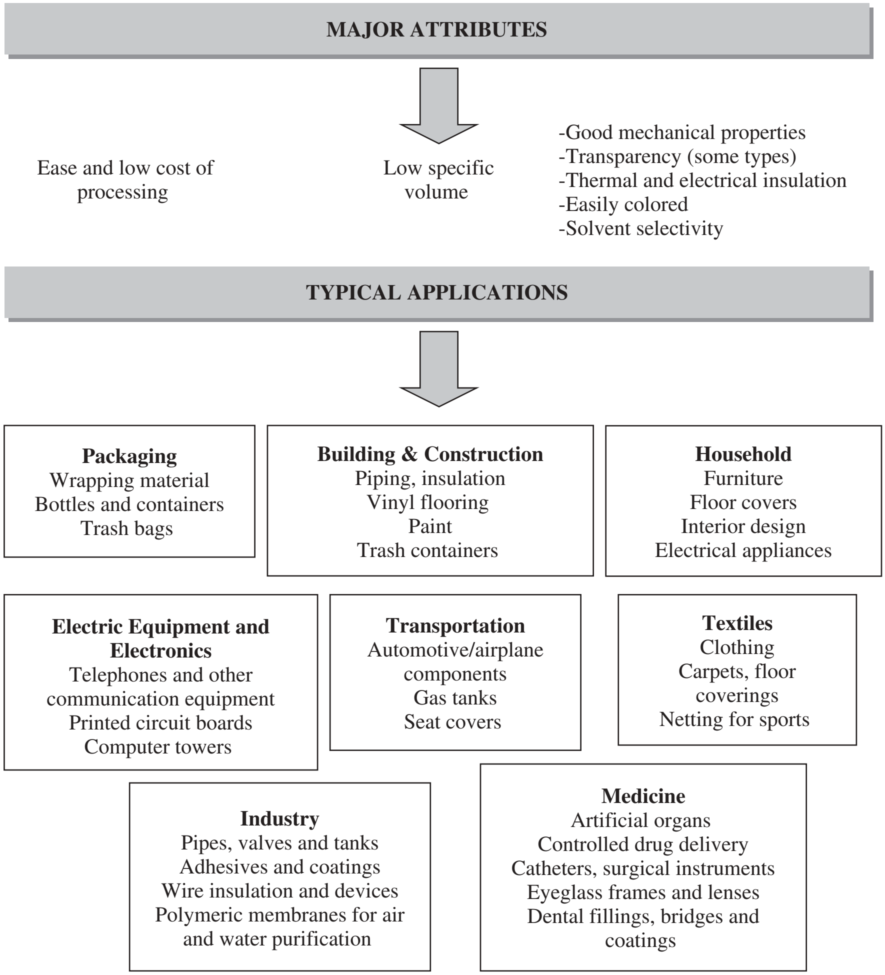


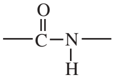
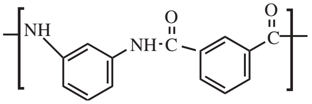
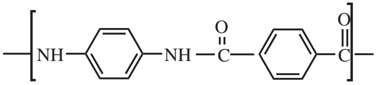
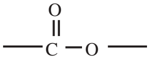
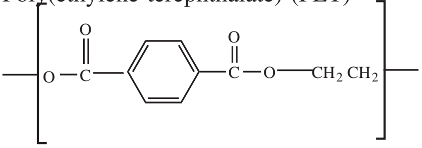
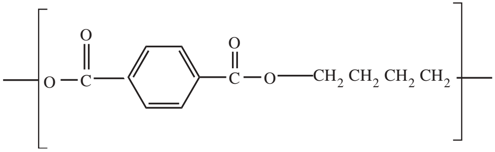
Fig. 1.2. Main attributes and examples of plastics applications.

condensate), such as water in the case of polyamides. On the other hand, addition polymers are formed from monomers without the loss of a small molecule; consequently, the repeating unit has the same composition as the monomer and does not contain functional groups as part of the backbone chain. Typical examples of condensation and addition polymers are depicted in Table 1.1.

Some years later than Carothers, Flory [6] highlighted the variations in the mechanism through which polymer molecules are built up, distinguishing between step- and chain-growth polymers. *Step-growth polymers* are formed by the stepwise reaction between functional groups of the reactants, and the size of polymer molecules increases at a relatively low rate, proceeding slowly from monomer to dimer, trimer, tetramer, pentamer, and so on. As a result,

TABLE 1.1. Typical Condensation and Addition Polymers

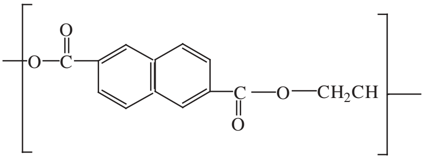
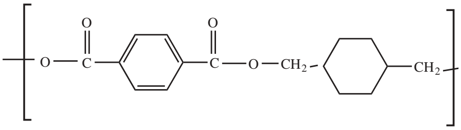
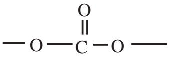
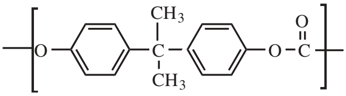
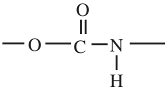
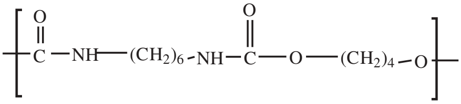
Condensation Polymers

Polymer	Characteristic Linkage	Indicative Repeating Units	
Polyamides (PAs)	 $-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{\vert}}{N}-$	Poly(tetramethylene oxamide) (PA 42) $-[HN(CH_2)_4NHCOCO]-$	Linear PAs (nylons)
		Poly(tetramethylene adipamide) (PA 46) $-[HN(CH_2)_4NHCO(CH_2)_4CO]-$	
		Poly(hexamethylene adipamide) (PA 66) $-[HN(CH_2)_6NHCO(CH_2)_4CO]-$	
		Poly(hexamethylene sebacamide) (PA 610) $-[HN(CH_2)_6NHCO(CH_2)_8CO]-$	
		Poly(dodecamethylene adipamide) (PA 126) $-[HN(CH_2)_{12}NHCO(CH_2)_4CO]-$	
		Poly(dodecamethylene sebacamide) (PA 1210) $-[HN(CH_2)_{12}NHCO(CH_2)_8CO]-$	
		Polycaproamide (PA 6) $-[HN(CH_2)_5CO]-$	
		Polyundecanamide (PA 11) $-[HN(CH_2)_{10}CO]-$	
		Polydodecanamide (PA 12) $-[HN(CH_2)_{11}CO]-$	
		Poly(*m*-phenylene isophthalamide) (Nomex) 	
		Poly(*p*-phenylene terephthalamide) (Kevlar) 	
Polyesters (PEs)	 $-\overset{\overset{O}{\|}}{C}-O-$	Poly(ethylene terephthalate) (PET) 	
		Poly(butylene terephthalate) (PBT) 	

(*Continued overleaf*)

TABLE 1.1. (*Continued*)

Condensation Polymers

Polymer	Characteristic Linkage	Indicative Repeating Units
		Poly(ethylene naphthalate) (PEN) 
		Poly(dimethylene cyclohexane terephthalate) (PCT) 
Polycarbonate (PCs)	 $-O-\overset{\overset{O}{\parallel}}{C}-O-$	Poly(bisphenol A carbonate) (BPA-PC) 
Polyurethane (isocyanate polymers)	 $-O-\overset{\overset{O}{\parallel}}{C}-\underset{\underset{H}{\mid}}{N}-$	Polyurethane (Perlon U or Igamid U)  $-\!\!\left[\overset{\overset{O}{\parallel}}{C}-NH-(CH_2)_6-NH-\overset{\overset{O}{\parallel}}{C}-O-(CH_2)_4-O\right]\!\!-$

Addition Polymers

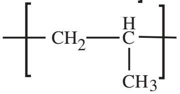
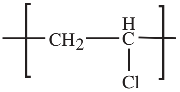
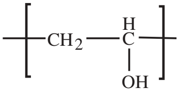
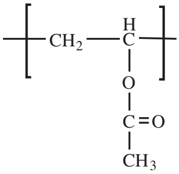
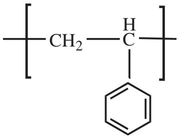
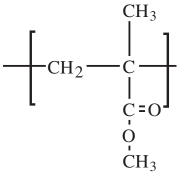
Polymer	Structure
Polyethylene (PE)	$-\!\!\left[CH_2CH_2\right]\!\!-$
Polypropylene (PP)	 $-\!\!\left[CH_2-\underset{\underset{CH_3}{\mid}}{\overset{H}{C}}\right]\!\!-$
Poly(vinyl chloride) (PVC)	 $-\!\!\left[CH_2-\underset{\underset{Cl}{\mid}}{\overset{H}{C}}\right]\!\!-$
Poly(vinyl alcohol) (PVOH)	 $-\!\!\left[CH_2-\underset{\underset{OH}{\mid}}{\overset{H}{C}}\right]\!\!-$

TABLE 1.1. **(*Continued*)**

Addition Polymers	
Polymer	Structure
Poly(vinyl acetate) (PVA)	 $\left[-CH_2-CH(OC(=O)CH_3)-\right]$
Polystyrene (PS)	
Poly(methyl methacrylate) (PMMA)	 $\left[-CH_2-C(CH_3)(C(=O)OCH_3)-\right]$

high-molecular-weight polymer is formed only near the end of polymerization (i.e., at high monomer conversion, typically greater than 98%). *Chain-growth polymers* are prepared in the presence of an initiator, so as to provide reacting species (e.g., free radicals, cations, or anions), which act as reaction centers, and polymerization occurs by successive additions of a large number of monomer molecules in the chain, usually over a short period.

According to Flory's theory [6], step-growth polymerization kinetics can be described as either second or third order, assuming equal reactivity of the functional end groups (i.e., the intrinsic reactivity of all reactive moieties is constant and independent of molecular size). The overall reaction rate is expressed as a rate of decrease in the monomer concentration, and the reaction order depends on whether a catalyst is involved. For a bimolecular stepwise equilibrium reaction a–A–a/b–B–b type (functional groups a and b) [equation (1.1)], the reaction rate is given by (1.2) and (1.3) for catalyzed (second order) and uncatalyzed (third order) polymerization, respectively. It should be noted that certain step-growth polymerizations are self-catalyzed, so third-order kinetics indicate that one of the functional groups exhibits catalytic behavior [e.g., group b in (1.3)], and thus its effect on polymerization must be included in the rate equation. In addition, the reverse (depolymerization) reaction term can be ignored when the condensation by-product is removed continuously as it is formed.

$$n\text{a} - \text{A} - \text{a} + n\text{b} - \text{B} - \text{b} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{a} - [\text{AB}]_n - \text{b} + (2n-1)\text{ab} \tag{1.1}$$

$$r = -\frac{d[\text{a}]}{dt} = -\frac{d[\text{b}]}{dt} = k_f[\text{a}][\text{b}][\text{catalyst}] - k_r[\text{AB}][\text{ab}] \xrightarrow{[\text{ab}]=0} -\frac{d[\text{b}]}{dt} = k_2[\text{a}][\text{b}] \tag{1.2}$$

$$r = -\frac{d[\text{a}]}{dt} = -\frac{d[\text{b}]}{dt} = k_f[\text{a}][\text{b}][\text{b}] - k_r[\text{AB}][\text{ab}] \xrightarrow{[\text{ab}]=0} -\frac{d[\text{b}]}{dt} = k_3[\text{a}][\text{b}]^2 \tag{1.3}$$

where k_f is the rate constant for polymerization, $k_r(k_f/K_{\text{eq}})$ the rate constant for depolymerization, K_{eq} the equilibrium constant, $k_2 = k_f$ [catalyst] the rate constant for catalyzed polymerization (second order), k_3 the rate constant for uncatalyzed polymerization (third order), and [a] and [b] the functional group concentrations (i.e., [a] = 2[a − A − a] and [b] = 2[b − B − b], where [a − A − a] and [b − B − b] are the concentrations of the bifunctional monomers). Integration of (1.2) and (1.3) differs according to whether the functional groups are in equimolar stoichiometry, resulting in relevant kinetic expressions for catalyzed and uncatalyzed step-growth polymerization (Table 1.2).

TABLE 1.2. Kinetic Expressions for Step-Growth Polymerization

	Integrated Kinetic Expressions	Polymerization Conversion and Degree
	$[\text{a}] = [\text{b}] = \text{c}$	
Catalyzed reaction	$\frac{1}{c_t} - \frac{1}{c_0} = k_2 t, \quad \frac{1}{(1-p_t)} - 1 = \overline{X_n} - 1 = c_0 k_2 t$	$p_t = \frac{c_0 - c_t}{c_0}$
Uncatalyzed reaction	$\frac{1}{c_t^2} - \frac{1}{c_0^2} = 2k_3 t, \quad \frac{1}{(1-p_t)^2} - 1 = \overline{X_n}^2 - 1 = 2c_0^2 k_3 t$	$\overline{X_n} = \frac{1}{1-p_t}$
	where k_2 and k_3 are the reaction rate constants for second- and third-order kinetics, c_0 the initial concentration of a or b groups, c_t the concentration of a or b groups at any given time t, $\overline{X_n}$ the number-average degree of polymerization, and p_t the polymerization conversion.	
	$[\text{a}] \neq [\text{b}], [\text{a}] < [\text{b}], r = \frac{[\text{a}]_0}{[\text{b}]_0}$	
Catalyzed reaction	$\frac{1}{[\text{b}]_0 - [\text{a}]_0} \ln \frac{[\text{b}]_t[\text{a}]_0}{[\text{b}]_0[\text{a}]_t} = k_2 t$	$p_t = \frac{[\text{a}]_0 - [\text{a}]_t}{[\text{a}]_0}$
Uncatalyzed reaction	$\frac{1}{([\text{b}]_0 - [\text{a}]_0)^2} \ln \frac{[\text{b}]_t[\text{a}]_0}{[\text{a}]_t[\text{b}]_0} - \frac{1}{[\text{b}]_0 - [\text{a}]_0}\left(\frac{1}{[\text{b}]_t} - \frac{1}{[\text{b}]_0}\right) = k_3 t$	$\overline{X_n} = \frac{1+r}{1+r-2rp_t}$
	where $[\text{a}]_0$ and $[\text{b}]_0$ are the initial concentrations of groups a and b, and $[\text{a}]_t$ and $[\text{b}]_t$ are the concentrations of groups a and b at any given time t.	

Chain-growth polymerization requires the presence of initiating species that can be used to attach monomer molecules in the beginning of polymerization. Free-radical, anionic, and cationic chain-growth polymerizations share three common steps: initiation, propagation, and termination, which are described by kinetics [7]. For instance, in the case of free-radical polymerization, initiation may be represented by two steps: the formation of radicals ($R^\bullet$) and the reaction of $R^\bullet$ with monomer (M). Due to the fact that the formation of free radicals is the slowest step and therefore rate controlling, the rate of initiation (r_i) is described through

$$\mathrm{I} \xrightarrow{\text{slow}} n\mathrm{R}^\bullet$$

$$\mathrm{R}^\bullet + \mathrm{M} \xrightarrow{\text{fast}} \mathrm{RM}^\bullet$$

$$r_i = \frac{d[\mathrm{R}^\bullet]}{dt} \quad \Rightarrow \quad -\frac{d[\mathrm{I}]}{dt} = k_d[\mathrm{I}] \tag{1.4}$$

where k_d is the dissociation rate constant and n is the number of free radicals $R^\bullet$ ($n = 1$ or 2) formed during the breakdown of one molecule of the initiator I.

The propagation step can be represented by a single general reaction, and the relevant rate expression is

$$\mathrm{M}_i^\bullet + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_{i+1}^\bullet$$

$$r_p = -\frac{d[\mathrm{M}]}{dt} = k_p[\mathrm{M}][\mathrm{M}^\bullet] \tag{1.5}$$

where k_p is the propagation rate constant and $[\mathrm{M}^\bullet]$ is the total concentration of all radical species ($[\mathrm{M}^\bullet] = \sum_{i=1}^{\infty} [\mathrm{M}_i^\bullet]$).

Termination occurs through combination or disproportionation and the reaction rate is, respectively,

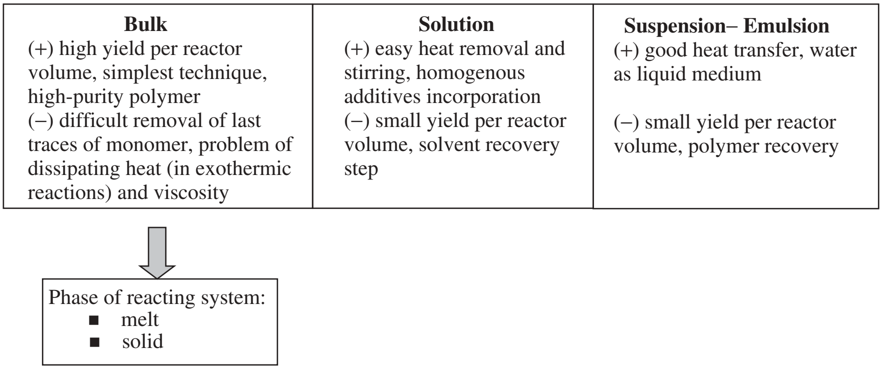
$$r_t = -\frac{d[\mathrm{M}^\bullet]}{dt} = k_t[\mathrm{M}^\bullet]^2 \tag{1.6}$$

where k_t is the overall rate constant for termination.

At steady-state conditions, ($d[\mathrm{R}^\bullet]/dt = -d[\mathrm{M}^\bullet]/dt$), the rate of polymerization is

$$r_p = -\frac{d[\mathrm{M}]}{dt} = k_p[\mathrm{M}]\left(\frac{r_i}{k_t}\right)^{1/2} = k_p[\mathrm{M}]\left(\frac{k_d[\mathrm{I}]}{k_t}\right)^{1/2} \tag{1.7}$$

Apart from polymerization mechanism, the technique applied also plays a fundamental role in polymer industry. There are four commonly used methods for performing polymerization: bulk, solution, suspension, and emulsion (Fig. 1.3). Meanwhile, polymers can be also prepared in the gas or vapor state, in a plasma environment, and in the solid phase.



Bulk	**Solution**	**Suspension– Emulsion**
(+) high yield per reactor volume, simplest technique, high-purity polymer (–) difficult removal of last traces of monomer, problem of dissipating heat (in exothermic reactions) and viscosity	(+) easy heat removal and stirring, homogenous additives incorporation (–) small yield per reactor volume, solvent recovery step	(+) good heat transfer, water as liquid medium (–) small yield per reactor volume, polymer recovery

Phase of reacting system:
- melt
- solid

Fig. 1.3. Polymerization techniques: advantages and drawbacks.

Solid state polymerization (SSP), the book's primary topic, is associated with the bulk (or mass) method and is a widely used technique, especially for condensation polymers. When high degrees of polymerization are required, it is used as an indispensable extension of the melt or solution technique.

1.1.3. Introduction to Solid State Polymerization

Solid state polymerization (SSP) comprises a subcase of bulk polymerization techniques, used for both step- and chain-growth polymers with strong industrial interest in condensation polymers. The fundamental principle of the technique involves heating the starting material in an inert atmosphere or in vacuo, at a temperature below its melting point but permitting the initiation and propagation of typical polymerization reactions.

Dry monomers can be submitted to solid state polymerization as well as solid prepolymers (i.e., low-molecular-weight polymers derived from conventional polymerization techniques). The former process is usually referred as *direct SSP*; meanwhile, in the latter case, post-SSP (SSP finishing) is used to further increase the molecular weight and to improve processability and end-product properties, respectively [8–10]. To the same perspective, SSP is proved to be an efficient recycling technique [11,12], through which the molar mass of the postconsumer material is increased, thus permitting processing without severe recycled material deterioration.

The open literature on SSP dates from 1960 (Fig. 1.4); meanwhile, in-house industrial research and development are also being performed, covering all possible topics of the process: namely, chemistry, chemical physics, and process engineering aspects. Based on the SSP references histogram, it can be seen that the years of high publication activity belong to the period 1960 through 1977. However, since then, SSP still consists of a continuous investigation topic, presenting an increasing number of patents as the years go by, especially after 1995. Additionally, SSP expands to different contemporary peak research issues, such as