

Principles and Applications of
EMULSION
POLYMERIZATION

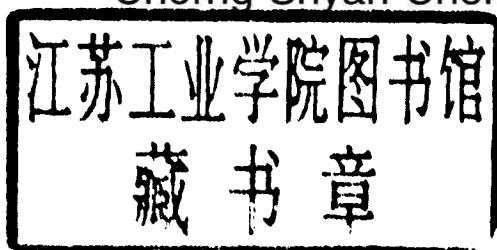


CHORNG-SHYAN CHERN

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PRINCIPLES AND APPLICATIONS OF EMULSION POLYMERIZATION

Chorng-Shyan Chern



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PRINCIPLES AND APPLICATIONS OF EMULSION POLYMERIZATION

PREFACE

Emulsion polymerization is a unique chemical process that has been widely used to manufacture a variety of latex products for numerous applications. Some important examples include synthetic rubbers, adhesives, binders, caulks and sealants, trade paints, industrial coatings, printing inks and overprint varnishes, thermoplastics, emulsion aggregation toners, immunoassay products based on the affinity interaction between the ligand-containing latex particles and the target biomolecules, and monodisperse polymer particles for fine instrument calibration standards. The favorable atmosphere for environmentally friendly emulsion polymers is the major driving force for the rapid advancement of this green technology, though these water-based products have limitations in nature and perhaps they can never achieve the excellent performance properties offered by the solvent-based counterparts. In recent years, the continuously soaring crude oil price (reaching 100 U.S. dollars per barrel in the first quarter of 2008) makes these latex products compete more effectively with solvent-borne polymer systems in a variety of markets. The current trend clearly indicates that emulsion polymerization is an important field that deserves more research and development resources.

This technique, primarily based on (but not strictly limited to) conventional free radical polymerization mechanisms, continues to attract the attention of scientists and industrial professionals since the first introduction of styrene-butadiene copolymers and polyvinyl acetate for latex paints around 1946–1950. Considerable progress in the fundamental understanding of emulsion polymerization mechanisms and kinetics has been made since, not to mention many innovative emulsion polymers successfully developed in industrial laboratories. Extensive theoretical and experimental investigations and industrial product development efforts continue to advance our knowledge about the general features of emulsion polymerization mechanisms and kinetics. However, at present, some key points at issue such as particle nucleation and growth mechanisms and transport of free radicals simultaneous with chemical reactions occurring in the heterogeneous emulsion polymerization systems are still not completely understood. Furthermore, the issue of the colloidal stability of latex particles (i.e., the major reaction loci) may change the concentration of particles during polymerization, and this scenario makes the situation

even more complicated. Besides the evolution of latex particles, determination of the average number of free radicals per particle is another task extremely difficult to undertake. These controversial, yet very important, subjects still remain a great challenge to those who are involved in this multidisciplinary research area.

In addition to the fundamental aspects of polymer chemistry and physics, a researcher dealing with emulsion polymerization must possess some basic knowledge of colloidal and interfacial phenomena, reaction kinetics, transport phenomena, thermodynamics, and polymer reaction engineering in order to effectively design and control latex products with desirable performance properties. Therefore, this book is aimed at providing comprehensive descriptions of conventional and surfactant-free emulsion polymerizations. These two reaction systems have been the most widely studied and employed in the plant production. The book also intends to provide a fundamental insight into some important features of the unique miniemulsion and microemulsion polymerization systems, which are expected to play an important role in emerging markets. Fundamental and quantitative interpretation of the polymerization mechanisms and kinetics involved in the heterogeneous reaction systems are the primary focuses of this volume. These subjects of vital importance, as reflected in a very large number of journal publications in the last half a century, enable the reader to quickly grasp the key reaction parameters that control the rate of polymerization and the particle size and molecular weight of the resultant emulsion polymers. Another goal is to provide introductory information on the colloidal phenomena related to emulsion polymerization and some industrial applications, common industrial emulsion polymerization processes (primarily semibatch and continuous reaction systems), latex particle morphology dealing with various types of multiphase polymer particles, and some important end-use properties of latex products.

This reference book or textbook is devoted to updating the current development of knowledge of emulsion polymerization. The author also endeavors to incorporate balanced fundamental and applied aspects of various emulsion polymerization processes into this work. This volume is particularly designed for research workers (such as chemists, chemical engineers, materials scientists, and physicists), technical service personnel, professors, and upper-level undergraduate and graduate students. It serves as an introduction to this important field and as a bridge to the more specialist-oriented books, which are available in the marketplace.

This book is dedicated to my Ph.D. thesis advisor, Professor Gary W. Poehlein, who introduced me to this challenging, fascinating research field in 1980s; to my parents, who inspired me to study in early years; and to my family (my beloved wife, Yue-Huan, and two lovely children, Andy and Angela). The author also expresses deep gratitude to Professor Poehlein for critically reviewing the manuscript and for the invaluable comments and thorough discussion to help improve the quality of this book. The assistance of the staff at John Wiley & Sons—especially the Consulting Editor, Dr. E. H. Immergut—through-

out this work is gratefully acknowledged. This challenging project would not have been possible without all your encouragement and full support.

The author would like to conclude this Preface with a verse in the Bible (Psalm 19:1):

The heavens declare the glory of God; and the firmament sheweth his handywork.

Without exception, an emulsion polymerization system, a world situated between the atomic/molecular level and the macro level, is subject to God's words, and it also responds to the ancient poet's praise with one accord. What a wonderful creation of God Almighty that is!

CHORNG-SHYAN CHERN

Taipei, Taiwan
April 2008

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INTRODUCTION

Emulsion polymerization involves the reaction of free radicals with relatively hydrophobic monomer molecules within submicron polymer particles dispersed in a continuous aqueous phase. Nevertheless, this unique polymerization process that is heterogeneous in nature exhibits very different reaction mechanisms and kinetics compared to bulk or solution free radical polymerization. Surfactant is generally required to stabilize the colloidal system; otherwise, latex particles nucleated during the early stage of polymerization may experience significant coagulation in order to reduce the interfacial free energy. This feature may also come into play in determining the number of reaction loci (i.e., polymer particles) available for the consumption of monomer therein. The objective of this chapter is therefore to provide readers with an overview of those subjects such as the free radical polymerization mechanisms and kinetics, the general features of emulsion polymerization, the role of surfactants in emulsion polymerization, and the importance of colloidal stability that is sometimes ignored in this research area.

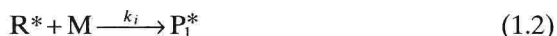
1.1 FREE RADICAL POLYMERIZATION

1.1.1 Free Radical Polymerization Mechanisms

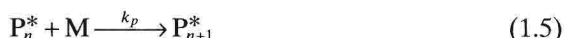
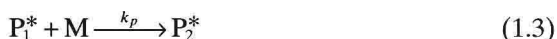
Free radical polymerization of vinyl monomers containing carbon-carbon double bonds has been widely used in industry to manufacture a variety of polymeric materials such as low-density polyethylene, polystyrene, polyvinyl

chloride, polyvinyl acetate, acrylic polymers, and synthetic rubbers, which can be accomplished in bulk, solution, suspension, or emulsion processes. The generally accepted free radical polymerization mechanism involves three kinetic steps in sequence, namely, initiation, propagation, and termination [1, 2].

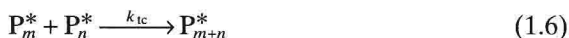
Initiation



Propagation



Termination



where I , R^* , M , P_n^* ($n = 1, 2, 3, \dots$), and P_n represent the initiator, initiator radical, monomer, free radicals with n monomeric units, and dead polymer chains with n monomeric units, respectively. The kinetic parameters k_d , k_i , k_p , k_{tc} , and k_{td} are the thermal decomposition rate constant for the initiator, the initiation rate constant for the primary radical, the propagation rate constant for the reaction between one free radical with n monomeric units and one monomer molecule, the combination termination rate constant, and the disproportionation termination rate constant for the reaction between two free radicals, respectively.

The above three-reaction mechanism reflects its characteristic chain addition polymerization; the rate of consumption of monomer is relatively slow, but the molecular weight of polymer builds up rapidly, as shown schematically in Figure 1.1.

Chain transfer reactions are also a part of the free radical reaction system. These reactions, as the name implies, transfer the radical activity from a growing chain to another species such as monomer, polymer, initiator, solvent, or a deliberately added chain transfer agent. For example, chain transfer of a propagating radical to monomer or polymer can be represented as follows:



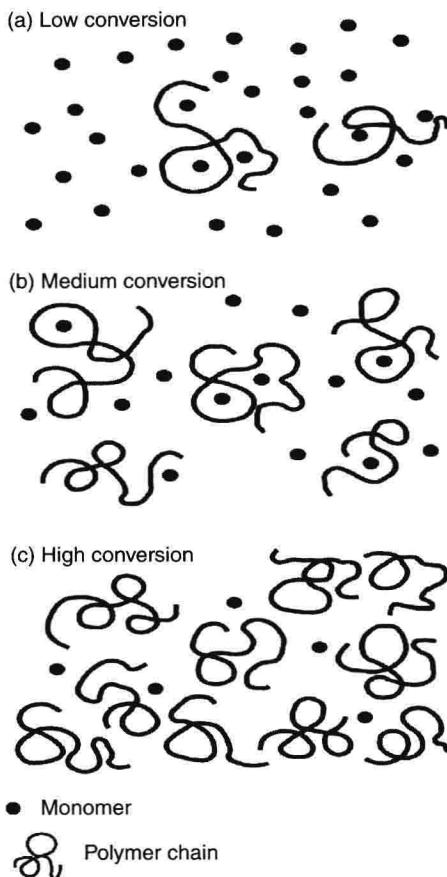


Figure 1.1. A schematic model for free radical polymerization at different levels of monomer conversion.

where $k_{tr,m}$ and $k_{tr,p}$ are the rate constants for the chain transfer reaction of a propagating radical with monomer and polymer, respectively. Both P_1^* and P_m^* may reinitiate the free radical chain polymerization to form linear and branched polymer chains, respectively, or participate in the termination reactions.

1.1.2 Free Radical Polymerization Kinetics

Assuming that the concentration of free radicals remains relatively constant during polymerization (the pseudo-steady-state assumption), the rate of polymerization (R_p) for bulk or solution polymerization can be expressed as

$$R_p = k_p[M](fk_d[I]/k_t)^{1/2} \quad (1.10)$$

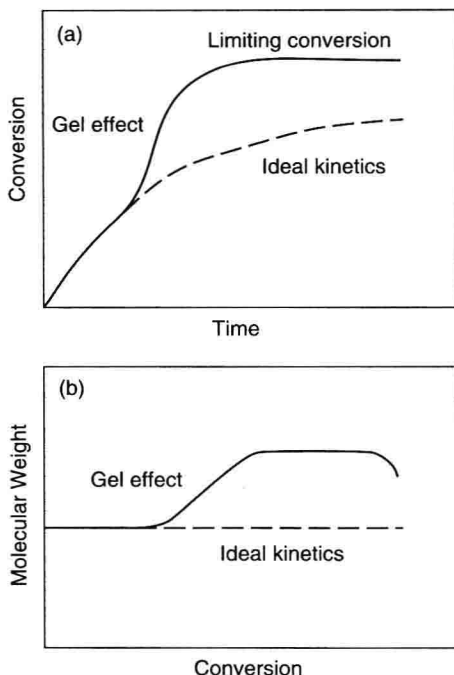


Figure 1.2. (a) Monomer conversion as a function of time. (b) Weight-average molecular weight as a function of conversion for free radical polymerization.

where f is the initiator efficiency factor and $[M]$ and $[I]$ are the concentrations of monomer and initiator, respectively. It should be noted that the term $(fk_d[I]/k_t)^{1/2}$ represents the concentration of free radicals. At low monomer conversions, the rate of polymerization can be adequately predicted by Eq. (1.10). The conversion first increases and then gradually levels off with the progress of polymerization (Figure 1.2). However, for many free radical reactions, after a certain conversion, the termination rate constant (k_t) becomes chain length dependent due to the influence of diffusion of free radicals on the bimolecular termination reaction. Under these circumstances, k_t decreases significantly with increasing conversion, thereby leading to the severely retarded bimolecular termination reaction and then autoacceleration of the polymerization rate. This is termed the gel effect or Trommsdorff effect [3–6]. In general, k_p is relatively independent of the chain length of P_n^* because the rather mobile monomer predominates in the propagation reaction. Nevertheless, when the reaction temperature is below the T_g of the polymerizing medium, the propagation reaction may also become diffusion-controlled at very high conversions. Thus, k_p decreases continuously toward the end of polymerization and complete conversion cannot be achieved (termed the limiting conversion) [5, 6]. Mechanistic models based on the concept of free volume adequately describe

the key features of the diffusion-controlled polymer reactions [3–6]. These peculiar kinetic phenomena are shown in Figure 1.2a.

The kinetic chain length (ν) can be calculated according to the following equation:

$$\nu = k_p[M]/[2(fk_dk_t[I])^{1/2}] \quad (1.11)$$

It should be noted that ν is inversely proportional to $[I]^{1/2}$, and thus any attempt to increase the rate of polymerization (i.e., to shorten the batch cycle time) by increasing the concentration of initiator inevitably results in polymer with a shorter chain length. Equation (1.11) predicts that molecular weight will change with the ratio $[M]/[I]^{1/2}$ during the course of the reaction if the rate constants are indeed constant. By contrast, molecular weight is strongly dependent on conversion due to the diffusion-controlled polymer reactions (Figure 1.2b).

1.2 EMULSION POLYMERIZATION

1.2.1 Conventional Emulsion Polymerization

Emulsion polymerization, which is a heterogeneous free radical polymerization process, involves emulsification of the relatively hydrophobic monomer in water by an oil-in-water emulsifier, followed by the initiation reaction with either a water-soluble initiator (e.g., sodium persulfate (NaPS)) or an oil-soluble initiator (e.g., 2,2'-azobisisobutyronitrile (AIBN)) [7–15]. This polymerization process was first commercialized in the early 1930s, and since then it has been widely used to produce environmentally friendly latex products with a variety of colloidal and physicochemical properties. If desired, these water-based polymer dispersions can be readily converted into bulk resins. Some representative monomers used to synthesize emulsion polymers include ethylene, butadiene, styrene, acrylonitrile, acrylate ester and methacrylate ester monomers, vinyl acetate, and vinyl chloride. Because the compatibility between the polymer produced and water is very poor, an exceedingly large oil–water interfacial area is generated as the particle nuclei form and grow in size with the progress of the polymerization. Thus, effective stabilizers such as ionic surfactants, nonionic surfactants, or protective colloids (e.g., hydroxyethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone and dextrin), which can be physically adsorbed or chemically incorporated onto the particle surface, are generally required to prevent the interactive latex particles from coagulation. Satisfactory colloidal stability can be achieved via the electrostatic stabilization mechanism [16], the steric stabilization mechanism [17, 18], or both. Latex products comprise a very large population of polymer particles ($\sim 10^1$ – 10^3 nm in diameter) dispersed in the continuous aqueous phase. Although the performance properties of most of the water-based polymers are often inferior to