

ADVANCED POLYMER NANOPARTICLES

*Synthesis and Surface
Modifications*

Edited by
Vikas Mittal



CRC Press
Taylor & Francis Group

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Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

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CRC Press is an imprint of Taylor & Francis Group, an Informa business

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Printed in the United States of America on acid-free paper
10 9 8 7 6 5 4 3 2 1

International Standard Book Number: 978-1-4398-1443-7 (Hardback)

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Library of Congress Cataloging-in-Publication Data

Advanced polymer nanoparticles : synthesis and surface modifications / [edited by]

Vikas Mittal.

p. cm.

"A CRC title."

Includes bibliographical references and index.

ISBN 978-1-4398-1443-7 (hardcover : alk. paper)

1. Polymerization. 2. Nanoparticles. 3. Polymers--Surfaces. I. Mittal, Vikas. II. Title.

TP156.P6A38 2011

620.1'92--dc22

2010020564

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Preface

Polymer latex particles are a very important class of polymeric materials, which are used for a large number of commercial applications. These particles are synthesized in the aqueous dispersion phase by numerous synthesis methodologies such as emulsion, miniemulsion, microemulsion, dispersion, suspension, inverse emulsion (in organic phase), polymerization, etc. Over the years, significant enhancement in the techniques dealing with the synthesis and surface tailoring of polymer particles has been achieved, which has also resulted in the widening of the application spectrum of these particles. These advances include use of advanced controlled polymerization means such as nitroxide-mediated polymerization, atom transfer radical polymerization, radical addition fragmentation transfer polymerization, etc., as well as use of advanced stabilizers, surface modifiers, etc. These advances have made it possible to achieve polymer particles with specific sizes consisting of polymer chains of specific molecular weights and tailorable chemical compositions or properties according to the requirement.

Because the advanced synthesis techniques are the key to achieve new functional properties in the polymer nanoparticles, and the surface modifications of these particles are required to ensure their use for specific applications, it is of immense importance to bring readers up-to-date on recent advances in these fields. This information will enable readers to design the required particle systems. This book thus serves the purpose of summarizing the developments in the synthesis and surface modification techniques to generate advanced polymer particles, and the contents have been accordingly organized. Chapter 1 introduces polymer latex technology with an overview of the various conventional and recent synthesis methodologies. Synthesis and characterization of particles with core-shell morphologies have been focused on in Chapter 2. Chapter 3 reports the generation of nonspherical polymer particles by following different synthetic routes. The generation of specific architectures such as block, star, graft, and gradient copolymer particles has been detailed in Chapter 4. Microemulsion polymerization using reversible addition-fragmentation chain transfer controlled radical polymerization is the subject of Chapter 5. In Chapter 6, pH-responsive nanoparticles have been described, whereas the synthesis of smart thermally responsive particles has been reported in Chapter 7. Surface tailoring of various organic and inorganic nanoparticles by polymers is the subject of Chapter 8. Theoretical studies on the kinetics of controlled radical polymerization techniques have been explained in Chapter 9. Chapter 10 reports the synthesis of functional nanoparticles by using the surfactant-free emulsion polymerization

approach. Chapter 11 describes various surface-active initiators as well as polymeric stabilizers developed for polymer nanoparticles in recent years.

At this juncture, I would like to express my heartfelt thanks to Taylor & Francis Group for their kind support during the project. I am equally thankful to Professor Massimo Morbidelli at the Swiss Federal Institute of Technology, Zurich, Switzerland, who has been my guide in polymer latex technology. I am indebted to my family, especially my mother, whose continuous support and motivation have made this work feasible. I dedicate this book to my dear wife Preeti, for her valuable help in coediting the book as well as for her efforts in improving the quality of the book.

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Editor

Dr. Vikas Mittal studied chemical engineering at Punjab Technical University in Punjab, India. He later obtained his master of technology in polymer science and engineering from the Indian Institute of Technology, Delhi, India. Subsequently, he joined Professor U. W. Suter's polymer chemistry group at the Department of Materials at the Swiss Federal Institute of Technology, Zurich, Switzerland, where he worked for his doctoral degree with a focus on the subjects of surface chemistry and polymer nanocomposites. He also jointly worked with Professor M. Morbidelli at the Department of Chemistry and Applied Biosciences on the synthesis of functional polymer latex particles with thermally reversible behaviors.

After completion of his doctoral research, Dr. Mittal joined the Active and Intelligent Coatings section of Sun Chemical Group Europe in London. He worked for the development of water- and solvent-based coatings for food-packaging applications. He later joined BASF Polymer Research in Ludwigshafen, Germany, as a polymer engineer, where he is currently working as a laboratory manager responsible for the physical analysis of organic and inorganic colloids.

His research interests include organic–inorganic nanocomposites, novel filler surface modifications, thermal stability enhancements, polymer latexes with functionalized surfaces, etc. He has authored more than 40 scientific publications, book chapters, and patents on these subjects.

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*Polymer Latex Technology: An Overview**

V. Mittal

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1.1 Introduction

Polymer nanoparticles find use in a number of applications like coatings, adhesives, paints, etc. The applications of these nanoparticles are significantly affected by their physical properties as well as surface morphology, which can be controlled by the synthesis process used to generate such particles. Emulsion polymerization and its modified methodologies are the most commonly used techniques to achieve polymer nanoparticles. These techniques also allow the generation or surface functionalization of the particles either *in situ* or by following separate specific steps. Polymerization of monomer by emulsion polymerization offers significant advantages in the whole polymerization process as compared to bulk and solution polymerization methods. It allows better control of the heat and viscosity of the system, and emulsion polymerization allows the achievement of an increase in molecular weight of the polymer chains without negatively impacting the rate of polymerization [1]. In emulsion polymerization, most of the monomer is present as monomer droplets in the aqueous phase, which diffuses to the polymerizing particles during the course of polymerization. The diffusion of the monomer is

* The work was carried out at Institute of Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland.

possible when the monomer is partially water soluble. Thus, emulsion polymerization is not very effective with extremely hydrophobic and extremely hydrophilic monomers. The extremely hydrophobic monomers would always stay in the monomer droplets, leading to no polymerization, whereas the hydrophilic monomers would polymerize mainly by homogenous polymerization and not micellar polymerization. To circumvent these difficulties, miniemulsion polymerization is used [2,3]. In this technique, the diffusion of the monomer molecules through the aqueous phase is not required, as the monomer droplets are directly polymerized. Therefore, such a technique has no problem in achieving the polymerization of even extremely hydrophobic monomers. To polymerize very hydrophilic monomers, inverse miniemulsion can be used. Combination of controlled polymerization methods like nitroxide-mediated polymerization, atom transfer radical polymerization, and reversible addition fragmentation chain transfer polymerization with the emulsion and miniemulsion polymerization methods has further enhanced the possibilities of achieving functional polymer particles [4]. By using these techniques, synthesis of functional block copolymer or graft copolymer particles can be achieved, which is not possible by using conventional emulsion polymerization techniques owing to the very short lifetime of the radicals. The surface morphologies of the particles can also be efficiently controlled or tuned by using such controlled polymerization methods, which expands the spectrum of application of these particles. This chapter aims to provide an overview of the conventional emulsion polymerization methods and the more advanced methods of synthesizing polymer particles.

1.2 Emulsion Polymerization

Emulsion polymerization is a heterogeneous polymerization technique that uses water as dispersion medium for the polymerization of water-insoluble monomers in the form of suspended particles. Styrene, methyl methacrylate, butyl acrylate, etc. are examples of the most commonly used monomers for the generation of polymers by emulsion polymerization. The surfactants are generally used to provide colloidal stability to the system. The surfactant can be cationic, anionic, or nonionic, and its amount exceeds the critical micelle concentration significantly. The surfactants form micelles in the system in which the polymerization takes place. Thus, this process can be visualized as a bulk polymerization in each of the suspended particles. Polymerization by this mode helps to circumvent the problems of heat and viscosity control generally associated with bulk polymerization. By changing the amount of surfactant, the molecular weight of the polymer chains can be increased without decreasing the polymerization rate, which is not possible in other modes of polymerization. The presence of a significant amount of surfactant

in the system can lead to certain disadvantages; however, many applications of particles are not affected by the presence of surfactants. Surfactant-free polymerization can also be used to generate polymer particles in order to circumvent the problems associated with the use of emulsifier, but in this case, the mode of polymer nucleation is completely different.

As mentioned previously, the amount of the surfactant exceeds the critical micelle concentration in the emulsified emulsion polymerization process. The micelles formed as a result of this excess amount have a size in the range of 10 nm, and one micelle generally consists of 100–200 surfactant molecules [1]. Surface tension of the solution decreases with the addition of surfactant at critical micelle concentration. A host of other solution properties are also affected at critical micelle concentration of the surfactant, which include conductivity, turbidity, osmotic pressure, etc. [5]. However, in the emulsion polymerization process, it is the reduction in the surface tension of the aqueous phase that is of prime importance. Because surfactants are amphiphilic molecules containing one hydrophobic part and one hydrophilic part, in the micelle they orient themselves in a way so that the hydrophobic part forms the inner part of the micelle and the hydrophilic part radiates away from this inner part of the micelle into the aqueous phase. The resulting hydrophobic space inside the micelle owing to the self-assembly of the surfactant molecules is an ideal place for the hydrophobic monomer to reside and also provides an ideal environment for the radicals to enter the micelle. Figure 1.1 shows the representation of the association of the surfactant molecules after the critical micelle concentration of the surfactant is reached [6]. When the inverse emulsion polymerization is used, then the hydrophilic part of the surfactant forms the inner part of the micelles and the hydrophilic chains intermix with the organic dispersion phase.

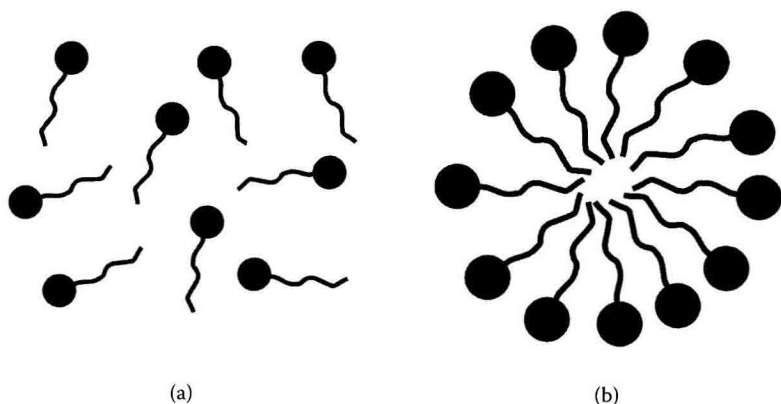


FIGURE 1.1

Organization of the surfactant molecules (a) below and (b) above the critical micelle concentration of the surfactant in the aqueous solution.

The monomers used for emulsion polymerization are water insoluble (water soluble for inverse emulsion polymerization). However, the monomer should have some extent of water solubility in order to diffuse through the aqueous phase as required during the course of polymerization. When the monomer is added to the system, a part of the monomer enters the micelles and a part is dissolved in the aqueous phase owing to partial water solubility. However, the majority of the monomer is present in the form of monomer droplets. The size of the monomer droplets is much larger than that of micelles; however, their number is much lower as compared to the micelles. Water-soluble initiators are generally used to initiate the polymerization reaction. The initiator generates the radicals in the aqueous phase owing to thermal dissociation. The generated radicals have the possibility of entering either the micelles or the monomer droplets. However, experimental evidence proves the absence of droplet polymerization. The radicals do not enter the monomer droplets, as the radical entities are hydrophilic in nature whereas the monomer droplets are hydrophobic. Also, because the number of monomer droplets is much smaller than the number of micelles, it is micelles that capture the majority of the radicals. Also, the unique architecture of the micelles provides attractive conditions for the radicals to enter. Figure 1.2a shows the mechanism of the micellar nucleation for the generation of polymer particles. This mode of nucleation is also termed heterogeneous nucleation. The homogenous mode of particle nucleation is also possible when (a) the amount of surfactant is below its critical micelle concentration, (b) no surfactant is used during the polymerization, or (c) the monomer is significantly water soluble.

In this mode of nucleation, the generated radicals in the aqueous phase start reacting with the dissolved monomer molecules. However, after adding a few monomer units in the chains, these chains no longer remain water soluble and come out of the solution. These chains are not stable on their own and keep collapsing with each other in order to attain stability. They also adsorb a certain amount of surfactant from either the micelles or the aqueous phase itself. Partial stability is also provided by the negative charges from the initiator moieties. In the case of the surfactant-free polymerization, the initiator charges are the only source of colloidal stability of the particles. Figure 1.2b shows the process of homogenous nucleation.

The emulsion polymerization process is generally divided into three intervals. The first is the particle formation interval. The radicals are generated in the aqueous phase after the thermal dissociation of the initiator. These radicals start entering the micelles and initiate polymerization. These active micelles where the polymerization starts to take place are then referred to as polymer particles. The number of particles in this interval keeps increasing owing to the continuous entry of the generated radicals in the micelles. This also leads to continuous increase in the rate of the polymerization. As the polymerization of the monomer in the particles proceeds, the size of the particles keeps increasing and the amount of monomer in the particles keeps depleting. However, this depletion of the monomer is replenished by the absorption of

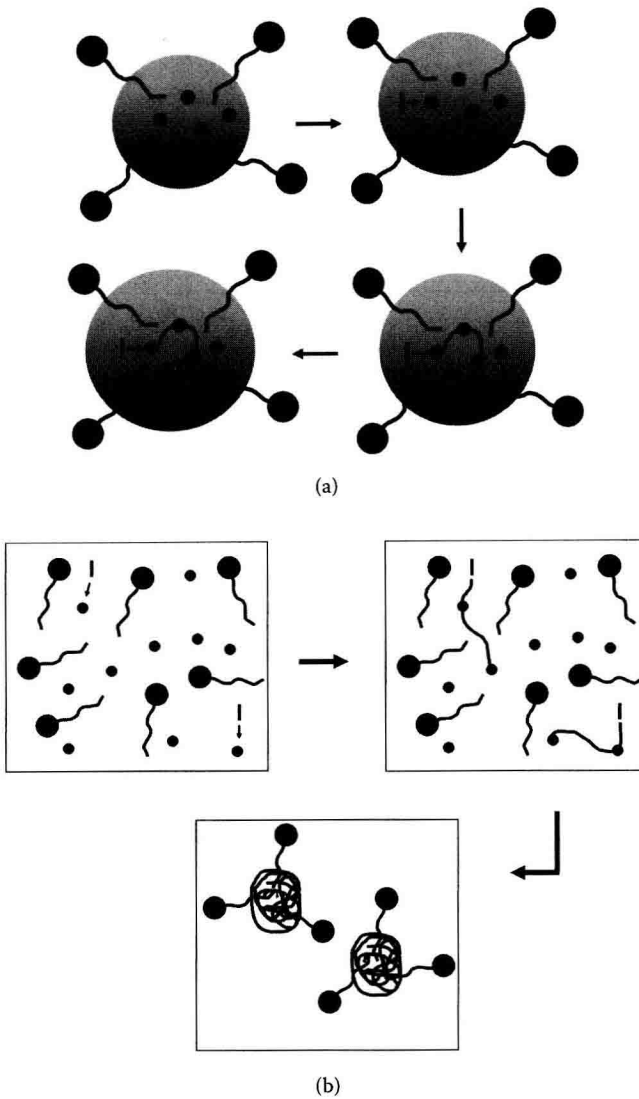
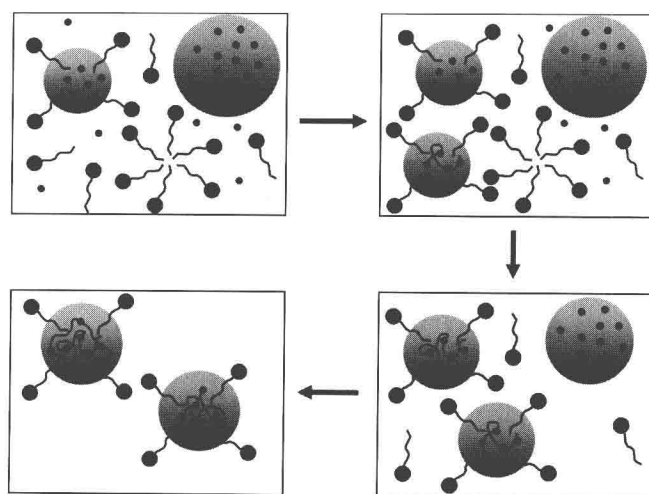


FIGURE 1.2

(a) Representation of micellar nucleation mechanism for the generation of polymer particles.
 (b) Homogenous nucleation mechanism for the synthesis of polymer particles.

the monomer from the aqueous phase. The aqueous phase in turn absorbs more monomer from the monomer droplets. Therefore, a mass transfer from the monomer droplets to the polymer articles keeps taking place during the course of polymerization. For this diffusion process to take place, the monomer is required to be partially soluble in water. As the polymer particles become bigger in size and their surface area increases as a function of time or

**FIGURE 1.3**

Schematic of various intervals of the emulsion polymerization process.

monomer conversion, they require more amount of surfactant to remain stable. The surfactant dissolved in the aqueous phase is continuously adsorbed on the surface of the polymer particles, leading to the reduction of the surfactant amount in the solution to lower than the critical micelle concentration. This in turn destabilizes the remaining micelles and these micelles disappear, providing their surfactant for the stabilization of the polymer particles. Thus at the end of the first interval, no micelle is left and most of the surfactant is used to stabilize the polymer particles. It has to be noted that the final number of polymer particles is much lower than the original number of micelles. Also, roughly 15% of the monomer is polymerized by the end of the first interval [1]. Figure 1.3 represents the various intervals of emulsion polymerization.

Once excess surfactant is no longer present in the system, no new particles nucleate. This marks the beginning of the second interval of emulsion polymerization. Because no new particles nucleate, the amount of the particles remains almost constant; this also leads to an almost constant polymerization rate in this interval. The size of the polymer particles, however, keeps increasing as a function of conversion. The monomer present in the monomer droplets continues to replenish the monomer in the aqueous phase as well as monomer-swollen polymer particles. After a certain extent of conversion, the monomer droplets also disappear. This also signals the start of the final interval of the emulsion polymerization process. The concentration of the monomer in the polymer particles keeps decreasing, and as a result the rate of polymerization also steadily decreases. Because the monomer is almost consumed, the polymerization rate virtually falls to zero. Figure 1.4 shows the evolution of the particle size as a function of conversion.