Preface

Can you imagine water being thickened as a highly viscoelastic gel upon dissolving just one small drop of detergent inside? Yes, it is possible, although not expected from aqueous solutions containing small solute molecules, such as the everyday detergents we use. Such a fascinating phenomenon results from the three-dimensional network built-up in solutions by so-called “wormlike micelles”: giant, flexible micelles which entangle like a dish of spaghettis, imparting fascinating elasticity to their solutions. Now imagine this elastic gel being illuminated by UV light, or heated up, or adding a drop of lemon and suddenly it reverts back to water? And this can be repeated, over many, many cycles? This is the world of “smart” wormlike micelles, which we describe in this book.

Wormlike micelles (also called rod-like micelles, thread-like micelles, cylindrical micelles, elongated micelles, giant micelles) are one type of morphologies that are spontaneously adopted by surfactant molecules in aqueous solution, conditional on a number of factors such as surfactant shape, concentration, and physicochemical parameters. These types of micelles exhibit strong viscosifying capacities and a rheological behavior similar to polymer solutions; however, unlike polymers, wormlike micelles are constantly breaking and reforming, in a dynamic equilibrium. Because of their unique microstructures and rheological response, wormlike micelles have found applications in personal care products, drag reduction, and most importantly in the oil upstream industry for oilwell stimulation. In the academic community, wormlike micelles are regarded as ideal models of “living” or “equilibrium” polymers, and research on these giant micelles has been burgeoning over the last three decades. Wormlike micelles represent a very active area of soft matter and have imparted new life to the traditional field of surfactants. Recently, the emergence of “smart” wormlike micelles represents a new avenue in the design of intelligent materials and holds great promise in terms of specialized applications.

A major scientific challenge of the past decade pertaining to the field of soft matter has been to craft “adaptable” materials, inspired by nature, which can dynamically alter their structure and functionality on demand, in response to triggers produced by environmental changes. Among these, “smart” surfactant wormlike micelles are indeed a recent area of development, yet offer a myriad of possibilities, given the simplicity of the design, which relies on the spontaneous organization of small amphiphilic molecules. The “switching” on and off of micellar assemblies has now been reported using electrical, optical, thermal, or pH triggers and is now envisaged for multiple stimuli. The structural changes happening at the nanoscopic level, in turn, induce major changes in the macroscopic characteristics, affecting properties such as viscosity and elasticity, leading in some cases to an effective “sol/gel” transition. These new materials offer tremendous potential in a broad spectrum of applications.

Over the years, we have designed “Smart Wormlike Micelles” responsive to different stimuli, seeking applications in drug delivery, oil, and gas production, in which formulations are inherently subject to the impact of environmental factors such as pH, temperature, salinity, or the presence of hydrocarbons. The rise in interest in the field and its rapid development make this a propitious moment to bring together all the information that has been accumulating in this area over the last few years. We thought it would be timely to share our experience and summarize the latest developments with those involved in this area or simply interested in this topic. One of us contributed a comprehensive review on the general properties of wormlike micelles [1], and we three joined together last year to co-author a critical review on the state of the art of smart wormlike micelles [2]. Shortly after, Springer Editor June Tang became aware of our work and the newly-published review, and invited us to extend this review into a Springer Brief-style monograph. Thus we reorganized our review, rewrote, and updated some of its chapters into this Brief. In particular, the Chap. 5 has been completely rewritten based on our very recent work in this area.

One of our goals is to showcase cutting-edge formulation technologies and the attractive properties of smart wormlike micelles to a large audience, both scientists already active in the field and those interested to learn about it. In this monograph, we start in Chap. 1 by briefly introducing the basic properties of wormlike micelles, which have been well described in several comprehensive reviews. The following chapters are then organized according to the type of trigger: heat, light, pH, CO_2 in Chaps. 2–5. Chapter 6 gathers research on triggers that have received limited attention to date, such as redox potential, hydrocarbons, and also smart reverse micelles and the emerging field of multi-stimuli responsiveness. In all chapters describing individual triggers, the structure follows a logical sequence: the molecular structure of the surfactants and/or hydrotropes, the microstructures formed in aqueous solution, and the corresponding macroscopic behavior (mainly the rheological response). Finally, applications of these smart wormlike micelles (prospective and current) are discussed in Chap. 7, with a particular highlight on applications in the oil upstream industry.

While we have attempted to integrate a wide range of studies so as to present an up-to-date and comprehensive picture of smart wormlike micelles, some areas, in particular polymeric wormlike micelles have not been dealt with to a great extent, as our objective was to focus mainly on surfactant systems. The rapid development of polymeric wormlike micelles however leads us to ponder over the two following open questions unsolved so far: Can the critical packing parameter theory be extended to predict the morphologies of polymeric micelles? If yes, how can we determine packing parameters, that is, the length and volume of the hydrophobic parts, the surface area of the hydrophilic portion, from the polymer architecture?

This monograph summarizes a large number of papers scattered across many scientific journals. We sincerely thank the authors whose results have been cited in this book, and thank Dr. Yongmin Zhang, whose Ph.D. thesis on CO_2-switchable wormlike micelles enabled us to considerably expand Chap. 5. We also would like to thank the editors, Heather Feng and June Tang from Springer for the invitation to write this book, for their patience in waiting for our manuscript, as well as their constant and kind reminders to push this monograph ahead. Finally, YF would like to thank the funding from National Natural Science Foundation of China (Grant No. 21173207, 21273223), Science and Technology Department of Sichuan Province (Grant No: 2010JQ0029, 2012NZ0006), and the start-up fund from Sichuan University.

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