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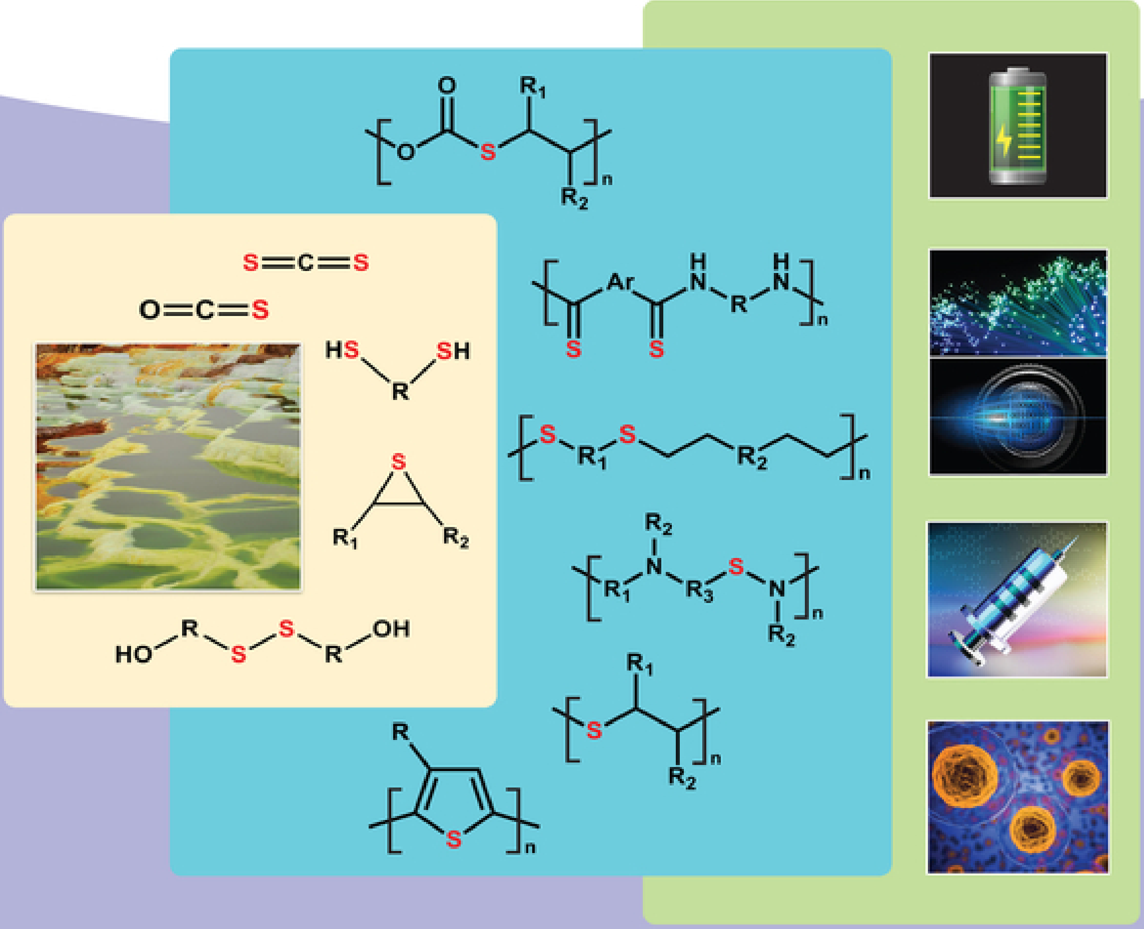
Sulfur-Containing Polymers

From Synthesis to Functional Materials



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Contents

8 Thiophene-Based Polymers: Synthesis and Applications *265*

Haifeng Ji and Xiaojie Zhang

9 High Refractive Index Sulfur-Containing Polymers (HRISPs) *305*

Johannes M. Scheiger and Patrick Theato

Introduction

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1 Scope of This Book

Various elements in nature are continuously cycled through a variety of chemical, biochemical, and physical processes. As the sixth abundant nonmetal element in the earth, sulfur and its natural cycle are closely related to the ecological balance and human life (Figure 1). The ocean is a major part of natural sulfur sources. Sulfur exists in the form of sulfates in the ocean and can also be converted to hydrogen sulfide (H_2S) or carbonyl sulfide (COS), which are released to the atmosphere. In addition to marine sources, natural releases from land including volcanic eruptions, and human activities also emit a variety of sulfur-containing gases into the atmosphere, including methyl sulfide ($(CH_3)_2S$), H_2S, COS, carbon disulfide (CS_2), methyl mercaptan (CH_3SH), and dimethyl disulfide (CH_3SSCH_3) [1, 2]. Sulfur-containing compounds in the atmosphere undergo a series of photochemical reactions and return to the ocean and land through rain. Herein we want to address another conversion route for sulfur-containing compounds: the synthesis of sulfur-containing polymers [3, 4] (Figure 1).

Polymer materials play an incredibly important role in modern life. The richness of polymer materials derives from the diversity of their constituent elements, such as carbon, nitrogen, oxygen, silicon, and sulfur. Unlike other chemical commodities, sulfur is mostly “involuntary” produced. It mainly arises from petroleum refineries and natural gas processing, thus creating a global surplus of sulfur. Production of sulfur reached more than 60 million tons in 2013 with a rising trend [5]. Global sulfur capacity tends to be in excess thus the use of sulfur needs to find a new direction. Actually, sulfur has been recognized as a valuable chemical agent since antiquity: employed as far back as 1600 B.C.E. by the Egyptians to bleach cotton fabric. Since the “chemical” invention of sulfur in explosives by the Chinese, the use of sulfur

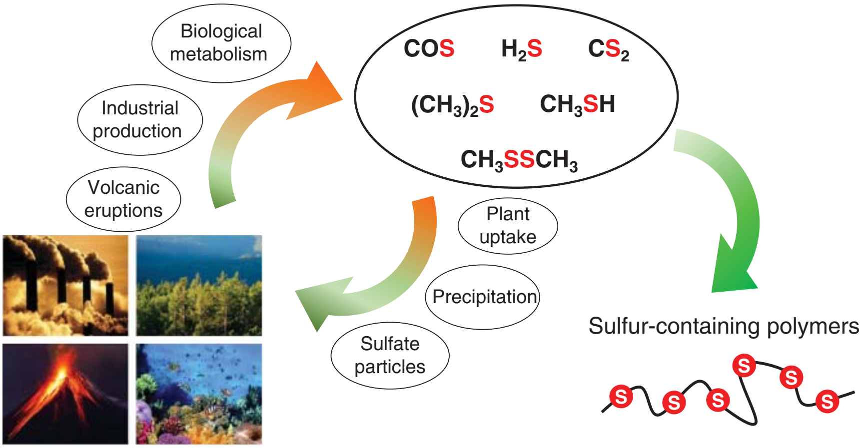

Figure 1 Sulfur cycle in nature and the formation of sulfur-containing polymers.

is closely linked with the development of chemical science. From the raw material of sulfuric acid to rubber industry auxiliaries, the mid-19th century witnessed the first applications of sulfur in polymer chemistry such as the vulcanizing agent of rubber. After the development of polymer chemistry in the last century, sulfur and sulfur-containing moieties have been increasingly involved in the construction of various polymers.

The purpose of this book is to summarize the latest development of sulfur-containing polymers, focusing on the utilization of sulfur-containing compounds and corresponding polymerization methods, analyzing the intrinsic relationship between polymer structure and its properties and applications. This book covers the state-of-the-art syntheses of a spectrum of sulfur-containing polymers from various sulfur resources including elemental sulfur, CS_2, COS, and mercaptan. In-depth mechanistic understanding relating to the chain polymerization is particularly presented for the readers. Of course, various types of sulfur-containing polymers, including poly(thioester)s, poly(thioether)s, poly(thioamide)s, poly(thiocarbonate)s, poly(thiourethane)s, and poly(thiourea)s with linear or hyperbranched (dendrimer) architectures, are discussed. High-tech applications of these sulfur-containing polymers in energy, optical and biomaterials are discussed in detail. This book will provide the latest knowledge in this area in a comprehensive way to the readers including students in the colleges, engineers in research organizations in the polymer community.

2 Sulfur-Containing Polymers

2.1 Building Feedstocks

The presence of sulfur atoms in polymer structure, depending on the kind of functional group, can bring some important properties, such as mechanical, electrical, optical, and then adhesion to metals, resistance to heat, chemicals, radiation, bacteria, biocompatibility, and so on. These are some of the functional groups: sulfide (–S–), polysulfide ($-S_n-$), sulfonyl ($-SO_2-$), sulfinyl (–SO–), sulfo ($-SO_3H$), as well as some organic groups containing sulfur atoms, such as thioester [–(C=O)–S–], monothio- or dithiocarbonate [–O–C(=S)–O–], [–O–(C=O)–S–], or [–S–(C=O)–S–], as well as thiourethane [–NH–(C=O)–S–] or [–NH–(C=S)–O–] and other sulfur-nitrogen groups. Sulfur-containing polymers can be used as high-performance engineering plastics, chemically stable ion-exchange membranes in electromembrane processes, proton-conducting electrolytes, as well as optical, optoelectronic and photochemical materials. Some polymers are employed in biomedical applications, for example, sulfopolymers as biomembranes and blood-compatible materials, polysulfates and polysulfonates as antithrombotic or antiviral agents. The presence of sulfur, particularly in the form of disulfide bridges, has played an important role in biopolymers and self-healing materials.

With a series of synthetic breakthroughs in recent years, new chemistries suitable for the synthesis of various polymers containing sulfur atoms have been developed, and thus many novel materials with promising properties have been reported. As a way to provide sustainable polymers, some sulfur-containing polymers are synthesized from *waste* of petrochemical resources, which is an advance in waste utilization. Over the past 20 years, researchers have synthesized and prepared a wide variety of sulfur-containing polymers, but there are few books on comprehensive introduction of the synthesis and applications of sulfur-containing polymers. The rapid development of this field can be visualized by the increase of research reports published in recent years (Figure 2). However, there are relatively few monographs on sulfur-containing polymers.

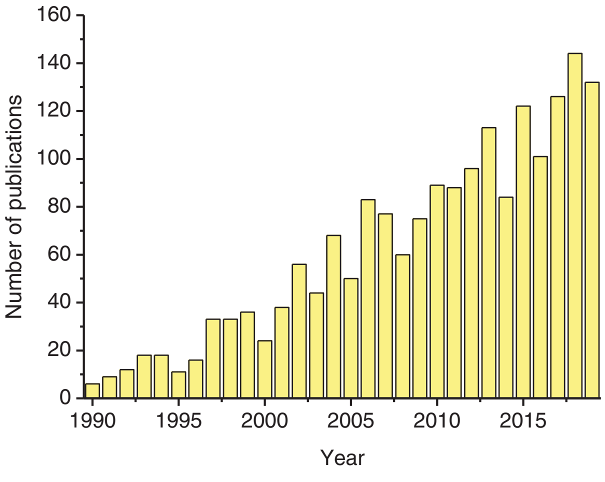

Figure 2 Scientific publications with the key word "sulfur-containing polymers" published from 1990 to 2019 (Web of Science).

Furthermore, books that focus specifically on the synthetic methods and the correlation between polymer microstructure and macroscopic properties are still lacking. This book is intended to meet the development needs in this field, introduce the synthesis methods of various sulfur-containing polymers in detail, and provide directions for the design of new methods and new polymerization systems.

Via the in-depth study of sulfur chemistry, diversified chemical transformation strategies have been developed to synthesize various sulfur-containing compounds, including thiourea, episulfide, and a large category of sulfur-containing medicinal compounds. To date, sulfur can also be used directly in the synthesis of sulfur-containing polymers by multicomponent polymerizations (MCPs). Except for sulfur, many sulfur-containing moieties and their comonomers have been developed for the synthesis of sulfur-containing polymers, which are summarized in Figure 3. Noteworthy, sulfur-containing one-carbon (C1) monomers (e.g. CS_2, COS) are a kind of important resource as two bulk and cheap compounds from which polythiocarbonates, polythioethers, polythioureas, and poly(thioester)s can be obtained by many polymerization methods. Meanwhile, sulfur-containing moieties with disulfide bond, thioester function groups, or basing on thiophene can also provide sulfur-containing polymers with particular properties. For each type of monomer, researchers have developed and advanced various polymerization methods to achieve an accurate and efficient synthesis of the target products.

2.2 Synthetic Methods

Roughly, Chapters 1, 4, 6, and 8 introduce step polymerization processes for sulfur-containing polymers. MCP is an emerging polymer synthetic method that combines three or more monomers in a one-pot reaction, resulting in a highly efficient, huge structural diversity, high atomic economy, and a well-defined structure polymer. By way of elemental sulfur based MCPs (Figure 4, (1)), polythioamides and polythioureas can be synthesized directly, as summarized by Prof. Rong Rong Hu in Chapter 1. While based on other sulfur containing moieties, many polymers with different microstructures can also be produced by MCPs. Sulfonyl group-containing polymers can be derived from the sulfonyl azide or sulfonyl hydrazide-based MCPs, and the sequence-controlled sulfur-containing polymers can be prepared from the multicomponent tandem polymerizations of thiol or sulfur-containing heterocycle monomers.

Except for MCPs, thiol-based click polymerization features remarkable advantages and has also been nurtured into a powerful technique for the preparation of sulfur-containing polymers (Figure 4, (2)), as introduced in Chapter 4 by Prof. An Jun Qin and Prof. Ben Zhong Tang. Owing to the high efficiency of click chemistry, a variety of click reactions can be utilized including thiol-ene, thiol-yne, thiol-epoxy, thiol-isocyanate, and thiol-halogen clicks. Polymerization based on these click reactions have yielded various sulfur-containing polymers. Thiol-ene click polymerization can produce poly(thioether)s via a radical process or thiol-Michael

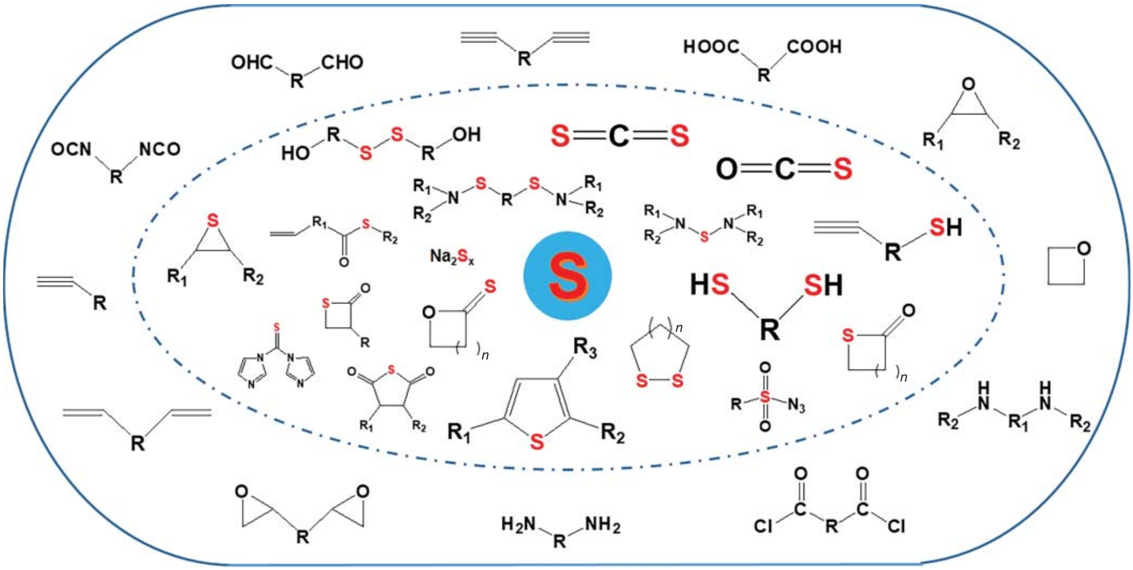

Figure 3 Sulfur-containing compounds and the comonomers.

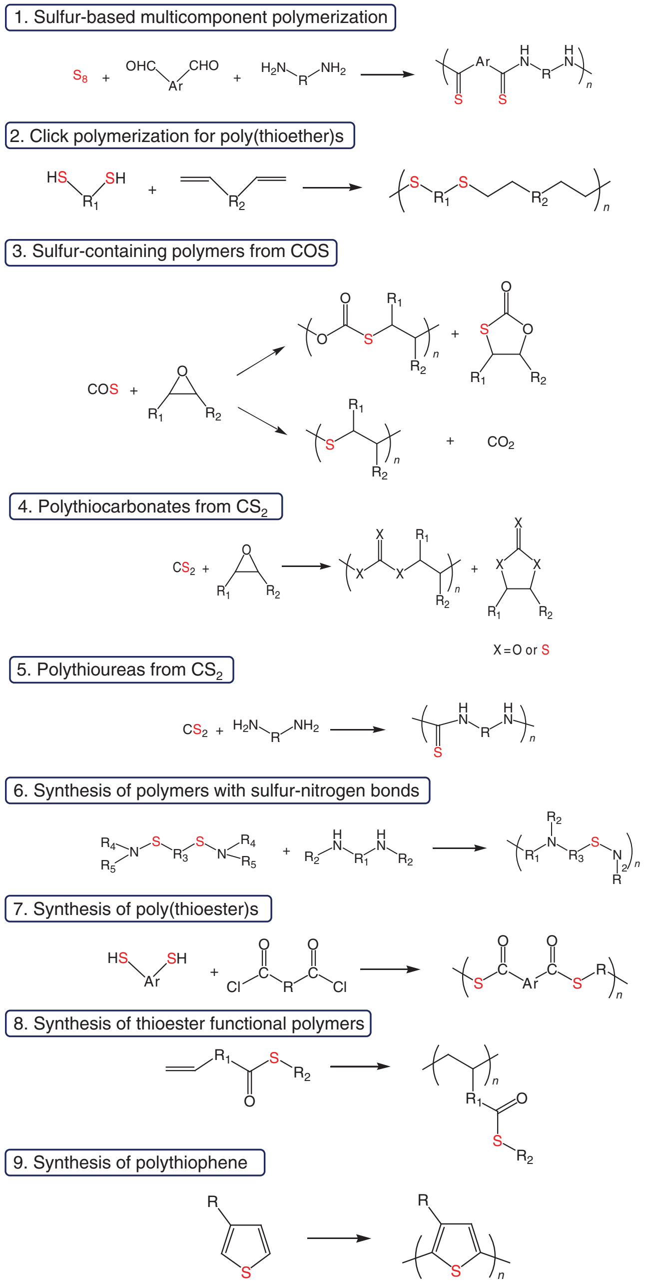

Figure 4* Selected synthetic methods for sulfur-containing polymers.

* IUPAC nomenclature suggests square brackets for repeating units, while this book retain round brackets in some places.

addition process. Thiol-yne click polymerization, a complement of the former, can proceed in a bis-addition or mono-addition manner to furnish poly(thioether)s or poly(vinyl sulfide)s with different regio-/stereoregularity. Other thiol-based click polymerizations, including thiol-epoxy, thiol-isocyanate, and thiol-halogen click polymerizations, can be applied to prepare poly(β-hydroxythioether)s, poly(thiourethane)s, and poly(thioether)s.

Next, polymers containing sulfur-nitrogen functional groups are unique functionalized polymers featuring the advantages of sulfur and nitrogen solely. In Chapter 6, Prof. Patrick Theato discussed the synthetic methods comprehensively for this kind of sulfur-containing polymers, reactions involving disulfenamide derivatives and diamines and other delicate designed are discussed thoroughly. On the other hand, poly(disulfide)s have their utility in biological applications owing to the dynamic nature of the disulfide bond, which offers attractive options for intra-cellular delivery of drugs or other materials specifically in cancer cells. A variety of synthetic methodologies for poly(disulfide)s are introduced in Chapter 11, contributed by Prof. Suhrit Ghosh.

Polythiophene and its derivatives have very promising prospects in organic electronic applications. In Chapter 8, Prof. Xiao Jie Zhang introduced the advanced methods for the synthesis of thiophene-based polymers (Figure 4, (9)). In this chapter, several classical or innovative synthetic methods are introduced, along with their results in the structural characteristics. Some recent methods, like Ni-catalyzed catalyst transfer homopolymerization allowing for a precise control of the regioregularity and the molecular weight, transmetalation copolymerization with remarkable control and coupling methods (e.g. solid-state polymerization) for highly crystallizable material are presented.

Chapters 2, 3, 5, and 7 mainly present the chain polymerization reaction for synthesizing sulfur-containing polymers. CS_2 and COS, an important class of sulfur-containing C1 compounds, have been utilized to copolymerize with epoxides via chain polymerization process, as described in chapters 2 and 3, wrote by Prof. Donald J. Darensbourg and his coworkers and Prof. Xing-Hong Zhang and his coworkers, respectively. Both monomers can be derived directly from sulfur. The inexpensive and abundant COS is industrially synthesized from natural gas and elemental sulfur, meanwhile COS can be derived from CS_2 or sulfur and carbon monoxide. Since 2013, many efforts have been made for developing a variety of new COS-based copolymers, including poly(monothiocarbonate)s and poly(thioether)s (Figure 4, (3)) [6–8]. These materials are excellent candidates for applications as structural or functional materials because of their unique thermal, mechanical, optical, and electrical properties. Utilization of CS_2 in forming polymer materials also attracted more and more attention (Figure 4, (4)) [9]. CS_2 can also be employed in the synthesis of versatile poly(thiourea)s at low temperature and pressure in the presence of amines and pyridine (Figure 4, (5)). Of special note, *oxygen-sulfur exchange reaction* (O/S ER) is a common phenomenon in the copolymerization of CS_2 (or COS) with epoxides (Figure 5). O/S ER has been well investigated for its complex intrinsic quality and great potential functionality. It can be simply defined as the exchange reaction of sulfur

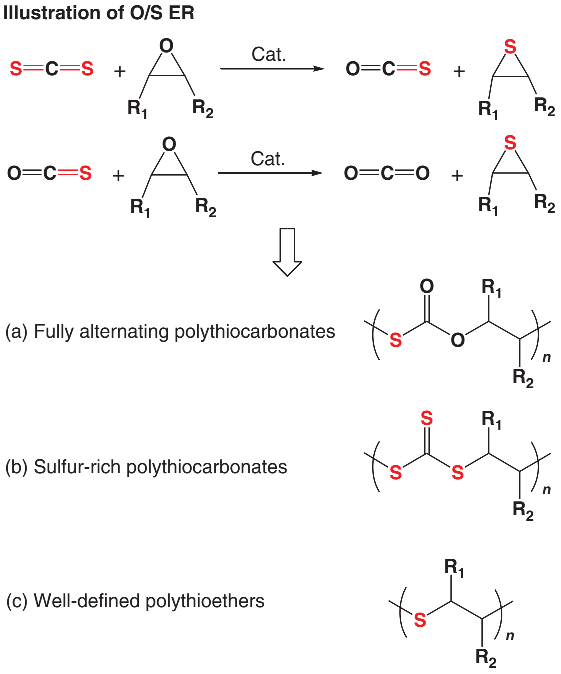

Figure 5 Definition of *oxygen-sulfur exchange reaction* (O/S ER) and application of O/S ER for synthesizing sulfur-containing polymers.

atom in CS_2 (COS) with the oxygen atom in epoxides generates COS (CO_2) and episulfides under the specific catalytic conditions. By inhibiting O/S ER, fully alternating poly(monothiocarbonate)s (Figure 5a) can be synthesized from the copolymerization of COS with epoxides. Importantly, O/S ER can also be utilized to synthesize well-defined poly(thioether)s from COS (or CS_2) as the sulfur source (Figure 5b). A deep understanding of O/S ER is conducive to enriching the preparation of sulfur-containing polymers; meanwhile it can also serve as an efficient way to produce high value-added, functional materials from renewable resources.

In synthetic methodology, *supramolecular anion* strategy has been proposed for controlling the polymerization of oxygen-containing monomers via organocatalysis. It has also been developed for polymerization of many types of monomers with heteroatoms (e.g. O, S, N). Supramolecular anions incorporate Lewis acids in the growing species, such as triethyl borane (TEB) or (thio)ureas [(T)Us]. In these systems, the basicity and nucleophilicity of these growing anions capped with TEB or (T)Us can also be mediated by the types, structures of these Lewis acids, as well as the related supramolecular interactions that are typically involved with hydrogen and organic coordination bonds. That is, the performance of the growing oxyanions can be regulated by altering these neutral Lewis acids.

Thioester-containing polymer is an emerging polymer having sulfur-substituted ester group. In Chapter 5, Prof. Wei Min Ren and his coworkers describe the recent research progress on synthesizing polythioesters, including aromatic, semi-aromatic, and aliphatic polymers. They focus on the copolymerization of cyclic thioanhydride with epoxides or episulfides to afford the polythioesters with well-defined structures. On the other hand, the synthesis of polymers having thioester groups in different position in the polymer backbone is well demonstrated by Prof. Remzi Becer, in Chapter 7. They introduced several types of thioester-containing polymers, such as thioester groups in the unit (via ring-opening polymerization of cyclic thioesters, condensation, or thia-Michael polymerization), side chain (using acrylate monomers), and the end of chain (using ATRP or RAFT initiators). The introduction of thioesters will change the flexibility of the backbone or the sidechain in contrast to its ester or amide analogues. The side or end thioesters groups can also be converted to the free thiol via post modification. These variations of thioester-containing polymers bring the opportunities towards fantastic applications.

Selenium is a semimetallic element lying in the group XVI (chalcogen element, with O and S) of the periodic table. Of course people want to incorporate selenium element into polymer backbone for achieving special polymers. In this book, Prof. Hua Ping Xu and his coworkers provide a special chapter demonstrating the synthesis and properties of selenium-containing polymers via step growth polymerization, radical polymerization, and ring-opening polymerization in recent years (see Chapter 10). Impressively, this chapter described a series of selenium-containing dynamic covalent bonds like Se—Se, Se—S, Se—Te, and Se—N and the applications in protein-based, intelligent, and adaptive materials.

2.3 Applications

Sulfur-containing polymers possess various classes and cover a broad property range, such as excellent thermal stability, high refractivity, and selective absorption to some heavy metal ions, self-healing property, enhanced dielectrical property, and unique electrochemical property. Sulfur-containing polymers have attracted increasing scientific attention and industrial interest in the past two decades. Sulfur-containing polymers generally possess large number of heteroatom-containing functional groups such as thioamides, thioureas, thiophene, thiazol, thiocarbonates, thioesters, thioethers, sulfonamide, and sulfonyl groups, which endow the polymer materials with the aforementioned properties. The authors in this book have discussed the applications of those sulfur-containing polymers.

Of special note, sulfur plays a crucial role in the area of high refractive index polymers (HRIPs) owing to the high polarizability and chemical versatility. New materials with improved optical properties, e.g. a high refractive index, low dispersion, and low birefringence, have been reported from sulfur containing HRIPs. Sulfur moieties can be incorporated into all relevant optical polymer classes such as polyimides and polyamides, polycarbonates and polyesters, poly(meth)acrylates, and new polymers introduced in this book to improve their optical properties. Details of HRIP materials are summarized in Chapter 9, which was contributed by Prof. Patrick Theato.

Owing to the sulfur-metal coordination, the copolymers of thioamides (—NH—(C=S)—NH—) show excellent metal-ion removal ability and can extract Pd and Au salts from their aqueous solution in an easy and efficient way (see Chapter 1). Polymers with disulfide groups have also been used as self-healing materials result from sulfur–sulfur interactions, which is a research hotspot in the field of polymers.

This book also emphasizes the application of sulfur-containing polymers in medical and biomaterials areas. Disulfide-containing polymers also had been exploited extensively for applications of targeted drug and gene carriers, bioimaging, drug conjugates, and self-healing materials, which are intensively discussed in Chapter 12 by Prof. De Cheng Wu. With proper design of these properties and other functionalities integrated in the monomer structures, a group of practical applications such as optical materials, optoelectronic devices, biological materials, self-healing materials, metal ion removal materials, engineering plastics, and rechargeable batteries could be realized (Figure 6). However, not all reports provide full insight into the properties of sulfur-containing polymers, which may reduce the attractiveness of new materials in terms of follow-up investigations and ultimately their real-life applications. In this book, we selected and highlighted

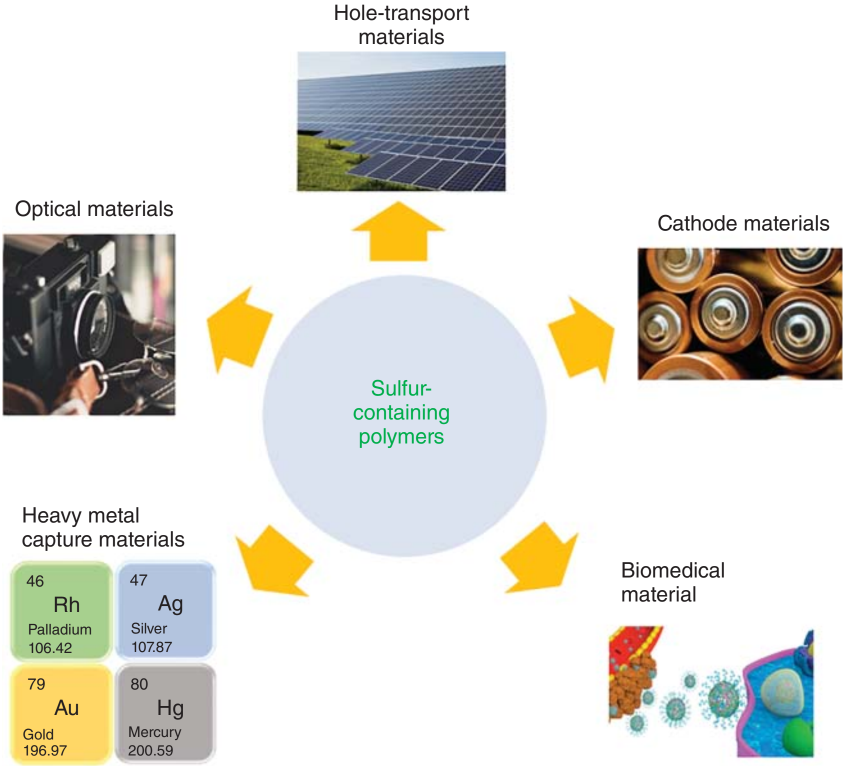

Figure 6 The application of sulfur-containing polymers in diverse areas.

some typical examples to raise the reader's interest in these newly emerged polymer structures.

3 Concluding Remarks

To provide readers with an in-depth and systematic understanding of sulfur-containing polymers, synthetic methods and applications of various sulfur-containing polymers are summarized in this book. Due to the extensive attention received by sustainable polymers in scientific research and industrial production, this book focuses on sulfur-containing monomers from natural sources, including sulfur, CS_2, and COS. In order to promote the rapid development of synthetic methods for sulfur-containing polymers and enrich the types and properties of sulfur-containing polymers, relationship between the synthetic methods and polymer structure as well as polymer structure and its property are emphasized in each chapter. To the best of our knowledge, this book might be the first monograph that comprehensively discusses sulfur-containing polymers, meeting the demands of the rapid development in this field. We are particular grateful to all contributing authors for their hard work to have this book completed as scheduled for the readers.

While it must be pointed out that the sulfur-containing polymers covered in this book are part of them [10, 11], for example, very recent research results in sulfur-containing chitin and chitosan derivatives field have not been included [12]. Also polyphenylene sulfide, which has been industrially produced on a large scale, is not discussed in detail [13]. This book also does not involve the direct application of elemental sulfur in free radical mechanisms [14]. Meanwhile, another well-known application of sulfur-containing polymers is not collected in this book, polymers with high sulfur contents are a class of electroactive cathode materials for Li–S batteries, which exhibit high specific capacity and energy density. Sulfonated polymers generally possess high proton conductivity and mechanical strength, which have been employed as ion-exchange membranes in fuel cell. Details can be found in recent review papers [15–19]. Nevertheless, we hope that this book could be useful to the readers in the entire field in sulfur chemistry.

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1

Synthesis of Sulfur-Containing Polymers Through Multicomponent Polymerizations

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1.1 Introduction

Sulfur-containing polymers represent a group of popular advanced materials that have attracted much attention owing to their broad range of fascinating properties such as high refractivity [1], coordination with metal ion [2], self-healing property [3], dielectrical property [4], and unique electrochemical property [5]. The well-known sulfur-containing polymers include polythioethers [6], polythiophenes [7], polyoligosulfides [8], and vulcanized rubbers [9], which are generally prepared from classical thiol-ene/yne addition reactions [10], thiol-epoxy reaction [11], transition-metal catalyzed polycouplings [12], and other ring-opening reactions [13]. High sulfur-content materials with excellent optical properties were also reported to be prepared through inverse vulcanization with elemental sulfur [14, 15]. However, the widely studied sulfur-containing polymers are still quite limited. Sulfur-containing polymers with new and complex structures remain rare, and their design and synthesis still face many challenges such as complicated and unstable monomer structures [16], poor solubility of polymers [17], chaotic product structures [18], etc. One effective approach is to develop new sulfur-containing polymer structures based on the exploration of new synthetic methodologies.

Multicomponent polymerizations (MCPs) as emerging polymer synthetic approaches combine three or more monomers in a one-pot reaction to construct complex polymers with high efficiency, great structural diversity, high atom economy, and well-defined structures [19]. During the past decade, with the inspiration from the progress in organic multicomponent reactions (MCRs), great effort has been made by polymer chemists to solve the problems regarding polymer solubility, structural regularity, narrow monomer scope, low conversion, molecular weight

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control, inhibition of side reactions, sequence control and topological control of the structures, and so on, and a series of efficient MCPs have been developed [20]. For example, the three-component Passerini polymerization of dialdehyde, dicarboxylic acids, and isocyanides was reported to access a class of polyesters [21]. Different combinations of various monomers were also applied to obtain sequence-regulated poly(ester-amine)s and hyperbranched polymers [22, 23]. Many other MCPs such as Ugi four-component polymerizations [24], Biginelli polymerizations [25], Kabachnik–Fields polymerizations [26], alkyne, aldehyde, and amine A^3-polycouplings [27], and a group of alkyne-based MCPs were reported [28–32]. Moreover, through diversity-oriented synthesis from different combinations of multiple types of monomers [33, 34], MCPs can easily afford libraries of polymer materials with structural similarities.

Recently, MCPs prove to be powerful and popular tools for the construction of sulfur-containing polymers with unique structures and functionalities. The sulfur-related MCPs have been developed rapidly nowadays, and their recent progress will be summarized in this chapter. With their rich chemical properties and high reactivity, sulfur-containing reactive reagents including elemental sulfur, sulfonyl azides, sulfonyl hydrazides, thiols, and cyclic thiolactones were utilized as the sulfur sources of the MCPs; newly reported organic MCRs such as sulfur and amine-based MCRs, sulfonyl azide and alkyne-based MCRs, and thiol-related addition or ring-opening reactions were applied in polymer synthesis as new MCPs; sulfur-containing linear or hyperbranched polymers with unique structures such as polythioamides, polythioureas, polysulfonylamides, polysulfonylimines, and polythioethers have been accessed, which were proved to find potential applications in transition metal ion detection, removal, enrichment, cell imaging, and so on. This chapter will only focus on the synthesis, structures, and functionalities of sulfur-containing polymers prepared from MCPs, and other synthetic approaches or polymer structures will be introduced in other chapters.

1.2 Multicomponent Polymerizations of Elemental Sulfur

Elemental sulfur, as the abundantly existed and inexpensive nature source, is an ideal raw material for the preparation of sulfur-containing functional polymer materials. Large amount of sulfur was produced from the worldwide petroleum industry and the major applications of sulfur are limited to the production of few chemical commodities such as sulfuric acid, fertilizers, and vulcanized rubber [35]. Whereas there are several allotropes of elemental sulfur existed in nature, the well-known stable species of sulfur at room temperature is the crown-shaped eight-member ring S_8 with rich chemical properties. For example, sulfur ring could be easily opened with the nucleophilic attack of amine to form polysulfide anion (R-NH-S_x^-) with high reactivity [36], which can act as new nucleophile to attack other active centers to afford various product structures. Attracted by the unique reactivity of elemental