



Opinion

Transforming Waste Sulfur into Practical Resources to Realize the Sustainable Future

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Opinion

Broadening Beyond Carbon: Expanding the Elemental Scope for Circular Polymer Systems

Polymer materials, such as synthetic rubbers and plastics, are fundamental to modern society due to their diverse properties and widespread applications. However, increasing reliance on petroleum-derived resources and escalating waste disposal issues have spurred intensive research into the degradation and recycling of conventional hydrocarbon-based polymers. These efforts have been largely focused on carbon-based backbones, but achieving a truly circular economy will require diversifying the scope of elements and chemistries involved in material design.

Among the various elements that could play a role in such a transition, sulfur is of particular interest because it is produced in vast quantities as a byproduct of petroleum and natural-gas refining. Despite its abundance, a significant portion remains underutilized, representing both an environmental challenge and an untapped opportunity for sustainable material innovation that aligns with global initiatives such as the Sustainable Development Goals (SDGs).

In this article, we highlight recent advances and our own efforts toward developing sulfur-containing materials through environmentally harmonized synthetic strategies. We further discuss how integrating such approaches could open new pathways for sustainable and reprocessable polymer systems.

Sulfur as a Surplus Resource

Approximately seven million tons of sulfur are generated annually as a byproduct of petroleum refining, much of which remains unused [1]. This large surplus poses environmental and storage challenges, but it also represents an untapped resource for developing sustainable functional materials. The effective utilization of waste sulfur can foster a circular economy by creating recyclable and reusable materials through reversible disulfide chemistry, directly contributing to SDG 12 (Responsible Consumption and Production). Moreover, the dissociation of disulfide bonds under reductive conditions enables the design of degradable polymers, providing a pathway to address the escalating issue of microplastic pollution (SDG 14 (Life Below Water)).

While sulfur chemistry may not directly address climate change, it is important that the development of sulfur-based materials incorporates low-energy, environmentally harmonized synthetic methods to minimize greenhouse gas emissions, aligning with the goals of SDG 13 (Climate Action).

Building on this perspective, the next step is to examine how sulfur has been incorporated into functional polymer systems. Recent research efforts have explored various approaches to design sulfur-containing materials, ranging from elemental sulfur polymers to complex hybrid systems.

Development of Sulfur-Containing Materials

Efforts to convert surplus sulfur into functional polymers date back several decades [2]. Early attempts to homopolymerize elemental sulfur (S₈) by heating [3] yielded



unstable products that readily depolymerized and exhibited poor solubility, making them unsuitable for practical use. A major breakthrough came with “inverse vulcanization”, which stabilizes sulfur by copolymerizing it with organic comonomers, thereby enabling the preparation of sulfur-rich polymer networks with enhanced durability [4].

This approach has demonstrated the potential of sulfur-based polymers in several areas, including energy storage [5], high-refractive-index optical materials [6], and even environmental remediation [7]. These examples illustrate the versatility of sulfur chemistry and its relevance to both advanced technologies and sustainable innovation.

Despite these advances, challenges remain for practical and sustainable implementation. Inverse vulcanization typically requires high reaction temperatures (often above 160°C), leading to significant energy consumption that conflicts with the principles of environmentally harmonized synthetic methods. Furthermore, the resulting polymers often exhibit poor solubility, limiting their processability and broader application.

To advance sulfur-based materials toward sustainable social implementation, it is essential to establish alternative synthetic strategies that operate under mild conditions and overcome solubility issues. These directions will be further considered in the following section.

Environmentally Harmonized Synthetic Methods

To overcome the high energy consumption associated with chain-growth polymerization, recent research has focused on developing environmentally harmonized step-growth routes for sulfur-based polymers. A simple aqueous method to prepare linear sulfur (LS) has been reported, offering a promising energy-efficient pathway for sulfur activation [8,9]. These developments have opened new opportunities to design sulfur polymers with longer chain lengths under mild and sustainable conditions. In Figure 1, both the LS and conventionally synthesized polysulfides are illustrated schematically to highlight the differences in their synthetic routes. In the LS method, S₈ undergoes base-induced ring opening, forming short sulfur oligomers (typically fewer than eight sulfur atoms) with anionic terminal species. The chain length depends on the type and stoichiometry of the base used, whereas in conventionally synthesized polysulfides, radical pathways at elevated temperatures generally yield longer sulfur chains.

The supramolecular integration of LS into polymeric frameworks has recently been demonstrated through the use of metal-ligand coordination, enabling the construction of well-defined sulfur-containing polymers under mild and environmentally harmonized conditions such as at room temperature and aqueous media [10,11]. These coordination-

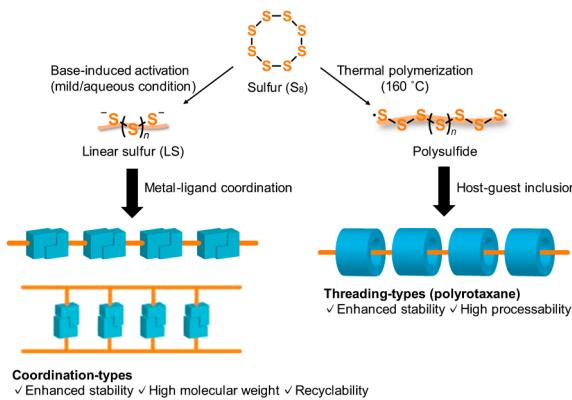


Figure 1 Supramolecular strategies for stabilizing sulfur polymers from elemental sulfur (S₈). Linear sulfur (LS) forms coordination-type architectures under mild aqueous conditions via base-induced ring opening of S₈, whereas threading-type (polyrotaxane) architectures stabilize polysulfide chains synthesized at high temperature through host-guest inclusion. The terminal structures (anionic for LS and radical for polysulfides) indicate their formation mechanisms.

driven assemblies provide an effective route to stabilize LS chains and prevent their thermal degradation, thereby facilitating the formation of high-molecular-weight sulfur polymers. The resulting materials exhibit dynamic yet robust architectures. In contrast to LS-based systems synthesized under mild conditions, previous studies employing polysulfide chains prepared at elevated temperatures (160°C) have demonstrated that threading-type (polyrotaxane) architectures can stabilize sulfur chains through host-guest inclusion [12]. These systems highlight another supramolecular strategy to suppress the decomposition of sulfur-rich polymers (Figure 1), improving their processability and stability. Together with LS-based coordination systems, such supramolecular designs provide a versatile platform for further functionalization and property tuning, offering new opportunities for sustainable sulfur polymer development. This architecture also enables structural control and dynamic adaptability that could be extended toward optically, electronically, or mechanically responsive systems, representing a design route beyond conventional disulfide-based networks.

In an emerging and strategic direction, the introduction of LS units into conventional carbon-based polymers represents a new approach to enhance existing materials with dynamic and reversible properties unique to sulfur. The practical studies on this concept are currently in progress in our laboratory and will be reported in due course. Our ongoing studies have revealed that the incorporation of linear sulfur units can yield unique mechanical characteristics beyond those associated with conventional disulfide linkages, highlighting an emerging aspect of sulfur polymer chemistry and suggesting new opportunities for material design.

Final Opinion

A sustainable and circular society cannot be realized solely through carbon-based materials. The concept of a circular economy should encompass not only hydrocarbons but also other elements and materials that are abundant yet underutilized. Sulfur, as one of the most surplus industrial byproducts, provides a unique opportunity to implement this broader elemental strategy.

Our recent approaches to sulfur-based polymer design demonstrate that surplus sulfur can be transformed into functional materials with recyclability, reusability, and high processability under environmentally harmonized conditions. Beyond these sustainable aspects, sulfur chemistry also offers pathways to create high-value functional polymers, such as optically, electronically, or mechanically responsive systems, thereby bridging sustainability with advanced material performance.

Such materials not only contribute to resource circulation but also align with the SDGs, particularly those targeting responsible production (SDG 12) and climate action (SDG 13). Ultimately, expanding material design beyond carbon-centered systems will diversify the foundations of polymer science and help establish a truly circular materials economy. Sulfur chemistry, bridging surplus resources and sustainable functionality, represents one of the most promising pathways toward this goal.

Keywords

Multi-element resource recycling society; Sulfur-containing polymers; Environmentally harmonized synthesis; Step polymerization; Supramolecular stabilization.

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Conflict of interest

The authors declare no competing financial interest.

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Hiroyasu Yamaguchi

Hiroyasu Yamaguchi received his Ph.D. degrees (1998) from Osaka University under the supervision of Prof. Akira Harada and Prof. Mikiharu Kamachi. He was a postdoctoral research associate at the Venture Business Laboratory of Osaka University (1998), a research associate (1998–2007), an assistant professor (2007–2009), a lecturer (2009–2011), and an associate professor (2012) at the Graduate School of Science, Osaka University. He was promoted to a professor at the same university in 2012. His research field is supramolecular functional chemistry utilizing bio-related polymers and stimuli-responsive polymers. (The university name was changed from "Osaka University" to "The University of Osaka" in April 2025.)



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Yuichiro Kobayashi is an Assistant Professor in the Department of Macromolecular Science, Osaka University. Born in Saitama, Japan (1982), he received his Ph.D. from JAIST in 2011 and began his career in Prof. Akira Harada's group at Osaka University. From 2014 to 2016, he was a specially appointed Assistant Professor under Profs. Susumu Kitagawa and Takashi Uemura. He rejoined Prof. Harada's group in 2016 and has served in Prof. Hiroshi Yamaguchi's group since 2019. His research focuses on synthesizing and characterizing functional supramolecular polymers for advanced materials applications.