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Synthesis of Sulfur-Containing Polymers Through Multicomponent Polymerizations

Yuzhang Huang[1], *Rongrong Hu*[1], *and Ben Zhong Tang*[1,2]

[1] *South China University of Technology, State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, Center for Aggregation-Induced Emission, No. 381 Wushan Road, Tianhe District, Guangzhou 510640, China*
[2] *The Hong Kong University of Science & Technology, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, Department of Chemistry, Clear Water Bay, Kowloon, Hong Kong, China*

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 sulfur and amine, much effort has been made to develop sulfur and amine-based MCPs for the preparation of sulfur-containing polymers.

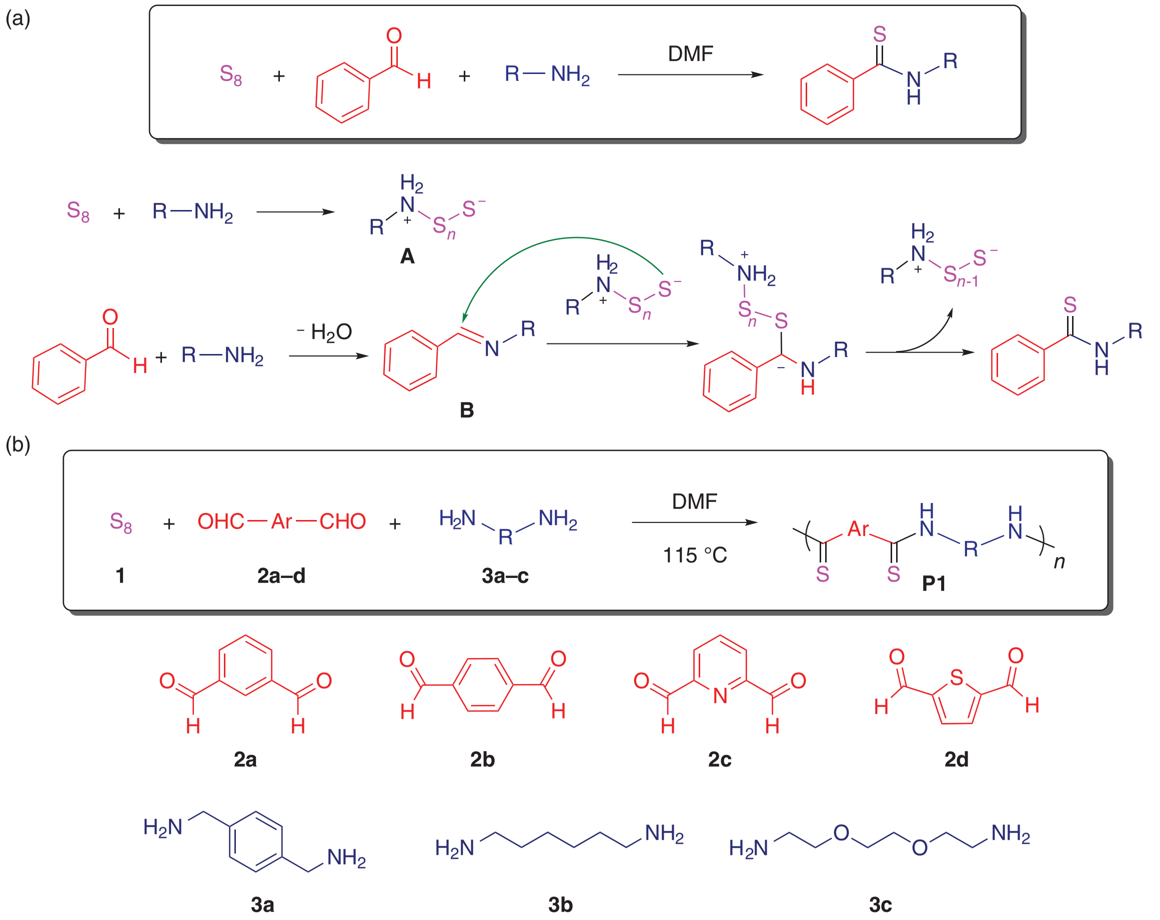
Of all the sulfur-containing polymers, polythioamides are unique types that share similar chemical structures with the widely used traditional polyamide materials. Thioamides, as analogues of amides, also play important roles in organic chemistry [37]. Introducing thioamide group into the repeating unit of the polymer backbone to afford polythioamides is desired considering the fascinating properties such as selective coordination with transition metal ions and the potential hydrogen bonds those could be brought by the NH—C=S moieties [38, 39]. However, the synthesis of polythioamides remained to be a great challenge. To the best of our knowledge, polythioamides were only reported to be prepared from bis(thioester)s or bis(dithioester)s and diamines with harmful byproduct released [40, 41], until recent elemental sulfur-based MCP approaches emerged as to be discussed below.

1.2.1 Multicomponent Polymerization of Sulfur, Dialdehydes, and Diamines

Willgerodt–Kindler reaction of elemental sulfur, aldehyde, and amine reported in 1923 is a classical MCR for the synthesis of thioamides [42]. This reaction can perform smoothly upon heating without any metal catalyst, and the readily available commercial sulfur, aldehyde, and amine reactants could easily generate a large number of diverse thioamide structures from this MCR. Willgerodt–Kindler reaction was hence firstly introduced into polymer synthesis for the construction of polythioamides in 1999 (Scheme 1.1a) [43, 44]. In this reaction, polysulfide anion **A** was firstly formed from the nucleophilic attack of amine to the sulfur ring, which was then reacted with the Schiff base **B** formed from aldehyde and amine, to furnish thioamide.

The MCP of elemental sulfur **1**, isophthalaldehyde **2a**, and 4,4′-trimethylenedipiperidine **3a** was firstly carried out in *N,N*-dimethylformamide (DMF) at 115 °C for one hour to afford polythioamide with a molecular weight (M_w) of 15 300 g mol^{-1} in 85% yield (Scheme 1.1b). The polymerization temperature above the melting point of sulfur (112 °C) is crucial for the MCP, but no obvious change was observed when the temperature was further raised. Among the tested solvents, DMF and dimethylacetamide (DMAc) showed better performance compared with nonpolar solvents such as *o*-xylene, in which insoluble precipitate was formed. Slight excess of sulfur was beneficial to the MCP, and further prolonging the polymerization time increased the yield but decreased the M_w.

Under the optimal polymerization conditions, various aromatic dialdehydes and aliphatic/benzyl diamines were tested for the MCP. However, it was found that simultaneous addition of sulfur, terephthalaldehyde, and *p*-xylylenediamine into the polymerization solution could not afford desired well-defined polythioamide product. It is likely that Schiff base moiety was formed from aldehyde and amine as insoluble precipitate, which inhibited the formation of thioamide. To solve that problem, sulfur and diamine were firstly mixed to form polysulfide anion, and the freshly added dialdehyde was then reacted with amine, followed by the reaction



Scheme 1.1 (a) Willgerodt–Kindler reaction of sulfur, aldehyde, and amine. Source: Refs. [43, 44], and (b) the MCPs of elemental sulfur **1**, dialdehydes **2a–d**, and diamines **3a–c**.

with polysulfide anion to furnish well-defined polythioamide with a high M_w of 69 300 g mol^{-1}.

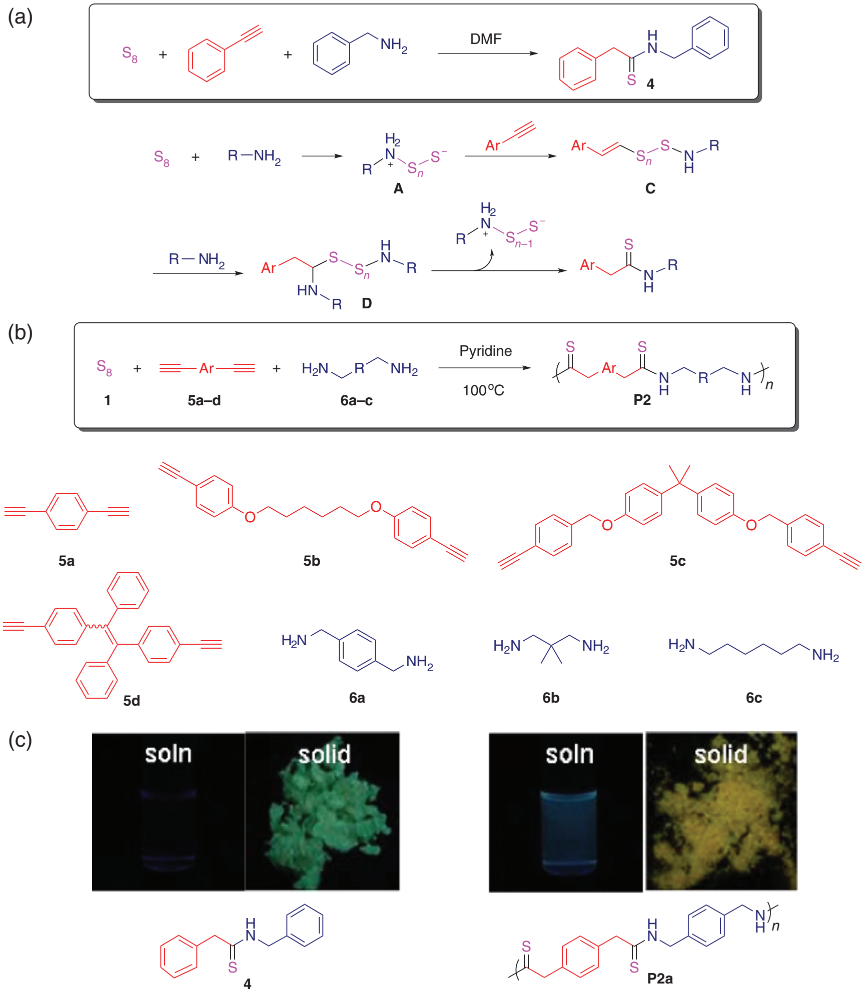
A series of aromatic dialdehydes and diamines were investigated for the MCP, suggesting that only aliphatic/benzyl amines were applicable for this MCP. Due to the low nucleophilicity of the aromatic amines, the key intermediate polysulfide anion could not be generated, and insoluble Schiff base precipitate was formed instead of thioamides.

1.2.2 Multicomponent Polymerization of Sulfur, Diynes, and Aliphatic Amines

The high reactivity and rich chemical property of polysulfide anion may bring many opportunities in MCRs with various reactants. For example, alkynes with carbon–carbon triple bonds are highly reactive species and their MCRs are extensively reported [45]. In fact, an efficient catalyst-free three-component reaction of sulfur, alkynes, and aliphatic amines was reported by Nguyen's group to afford thioamides [46]. Similarly with Willgerodt–Kindler reaction, the polysulfide anions **A** was first generated, which was then reacted with the terminal C≡C bonds of alkyne to yield vinyl polysulfide **C**. Another molecule of amine then attacked the vinyl group to form thioaminal intermediate **D**, and the thioamide product was produced following the cleavage of the S—S bond and the release of the polysulfide anion (Scheme 1.2a).

This promising MCR was developed to an efficient MCP for the synthesis of diverse polythioamides with well-defined structures [47]. A group of aromatic diynes and benzyl/aliphatic diamines were designed as monomers to polymerize with elemental sulfur through the MCP in pyridine, which generally proceed smoothly under the optimal condition to afford polythioamides with high M_ws of up to 127 900 g mol^{-1} in high yields of up to 98% (Scheme 1.2b). High temperature at 100 °C and high diamine monomer concentration of 1.0 M are important for this MCP to obtain satisfying result. Besides the improved reactivity at such high temperature, considering the strong intermolecular hydrogen bonds among thioamide moieties in the product, high temperature could help breaking down these intermolecular interactions and reducing the viscosity of the reaction solution to facilitate the polymerization. Temperature control is hence crucial to this polymerization because the solubility of the monomers/polymers as well as the viscosity of the solution is highly dependent on the temperature. Further increasing the monomer concentration to 1.5 M resulted in gelation and early termination of the polymerization. Despite that, neat polymerization could also proceed to afford polythioamide product. The stoichiometric ratio of alkyne and amine only showed slight effect on the M_w, while excess amount of alkyne could obviously increase the yield.

The obtained polythioamide P**2a** exhibited satisfying thermal stability with its decomposition temperature at 5 wt% weight loss at 284 °C and good solubility in polarized solvents such as DMF and dimethyl sulfoxide (DMSO). Most importantly, unexpected fluorescence was observed for these polythioamides and their small molecular model compounds, even though they did not contain any conventional



Scheme 1.2 (a) The MCR of sulfur, alkyne, and benzyl/aliphatic amine. (b) MCP of sulfur **1**, diynes **5a–d**, and benzyl/aliphatic diamines **6a–c**. (c) The photographs of model compound **4** and P**2a** under UV illumination. Source: Reproduced from Ref. [47]. Copyright 2015 American Chemical Society.

chromophore or large conjugation system. Both DMF solutions and solid powders of the polythioamides emitted blue light upon UV irradiation (Scheme 1.2c). Solvent and temperature influences were investigated to reveal the underlying effect of the intermolecular interactions among thioamide groups. When methanol was added into the DMF solution of P**2a** to break down the hydrogen bonding between thioamide groups, the PL intensity at 470 nm was decreased with hypsochromically shifted emission maximum. Upon decreasing temperature from 60 to −60 °C, the PL intensity at 470 nm was gradually increased because of the enhanced hydrogen bonding at low temperature. This unusual emission behavior of polythioamides was interpreted as the formation of “heterodox clusters” composed of a large number of lone-pair electron-containing electron-rich heteroatoms, owing to the interchain and intramolecular interactions such as hydrogen bonding and $n \rightarrow \pi^*$ interaction between thioamide moieties, which may serve as the chromophore similar to the reported fluorescent hyperbranched poly(amido amine)s (PAMAMs) [48].

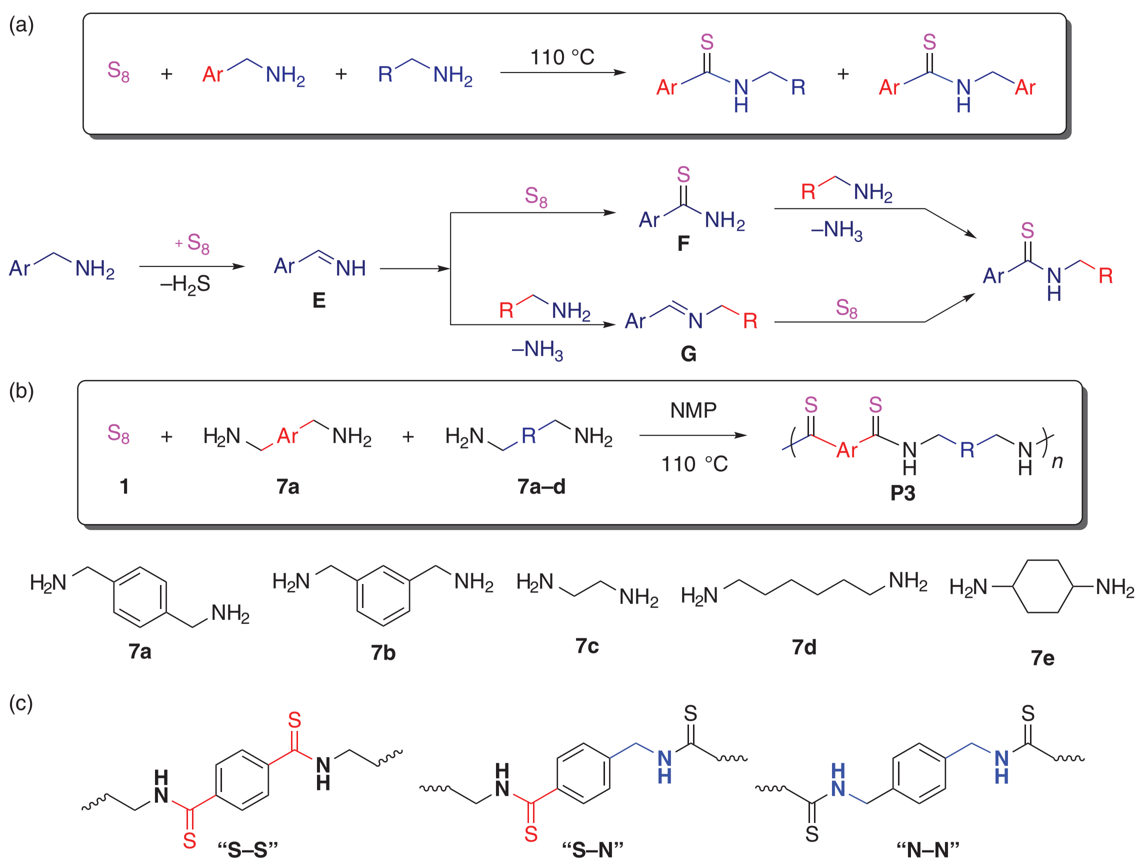
1.2.3 Multicomponent Polymerization of Sulfur, Benzyl Diamines, and Aliphatic Diamines

In addition to nucleophilic attack, benzylamine and sulfur can also undergo oxidation reaction upon heating to form benzaldimine **E**, one of the azomethine derivative [49], which can undergo further reactions to form thioamide. Indeed, a catalyst-free multicomponent selective oxidative reaction of sulfur, benzylamines, and aliphatic amines was reported by Nguyen's group to prepare thioamides at high temperature [50]. According to the proposed mechanism of this reaction (Scheme 1.3a), the benzylamine group was first oxidized by sulfur to afford benzaldimine **E**, which may undergo two different pathways: (i) further oxidation by sulfur to form thiobenzamide **F**, followed by a transthioamidation with amine to afford thioamide, releasing ammonia; or (ii) transimination of benzaldimine and amine to form another azomethine **G**, followed by oxidation with sulfur to afford thioamide product.

Later, Chen's group reported a polymerization of sulfur and diamines based on this MCR (Scheme 1.3b) [51]. The polymerization of sulfur and *p*-xylylenediamine **7a** was performed in *N*-methyl-2-pyrrolidinone (NMP) at 110 °C for 48 hours to afford polymer with a M_w of 55 100 g mol^{-1}. Compared with the optimal temperature at 110 °C, lower temperature at 90 °C gave product with a relatively low M_w of 12 500 g mol^{-1} in 48% yield, while higher temperature at 130 °C provided insoluble products, probably due to the cross-linking formation (C-S-S-C) by the side reaction between thioamides at such temperature [40]. Moreover, similar to the aforementioned MCPs of sulfur, slight excess amount of sulfur was generally beneficial to the polymerization.

It should be noticed that the product structure of the MCP of **1** and **7a** is a mixture of three different repeating units in the polymer chain noted as "S-S", "N-N", and "S-N" structures shown in Scheme 1.3c, which referred to the repeating units whose benzene ring was substituted with two C=S groups, two CH_2NH groups, one C=S group and one CH_2NH group, respectively. According to the aforementioned mechanism, each CH_2NH_2 group of *p*-xylylenediamine could randomly undergo either oxidation reaction with sulfur, or transthioamidation/transimination reaction, to afford NH—C=S group or CH_2NH group, respectively, proved by the characteristic ^1H NMR peaks of the aromatic protons located at δ 7.79 ("S-S"), δ 7.36 ("N-N"), and δ 7.89/7.41 ("S-N").

When another diamine was copolymerized with *p*-xylylenediamine and sulfur through the MCP, the expected product structure was even more complicated. For example, the MCP of *p*-xylylenediamine **7a**, *m*-xylylenediamine **7b**, and sulfur produced a hybrid structure with six possible disubstituted benzene ring structures and even more kinds of repeating structures generated from homo- or cross-coupling of the diamines coexisted in the polymer chain, indicated by the ^1H NMR spectrum,



Scheme 1.3 (a) Proposed mechanism of MCR of sulfur, benzyl amine, and aliphatic primary amine. (b) MCP of sulfur **1**, benzyl diamines **7a**, and aliphatic primary diamines **7a–e**. (c) The structures of three possible units "S–S", "S–N", and "N–N."

suggesting that the oxidation reaction with sulfur, transthioamidation, and transimination reactions randomly occurred regardless of homo- or cross-coupling. This problem has brought great difficulty in obtaining well-defined regular polymer structures.

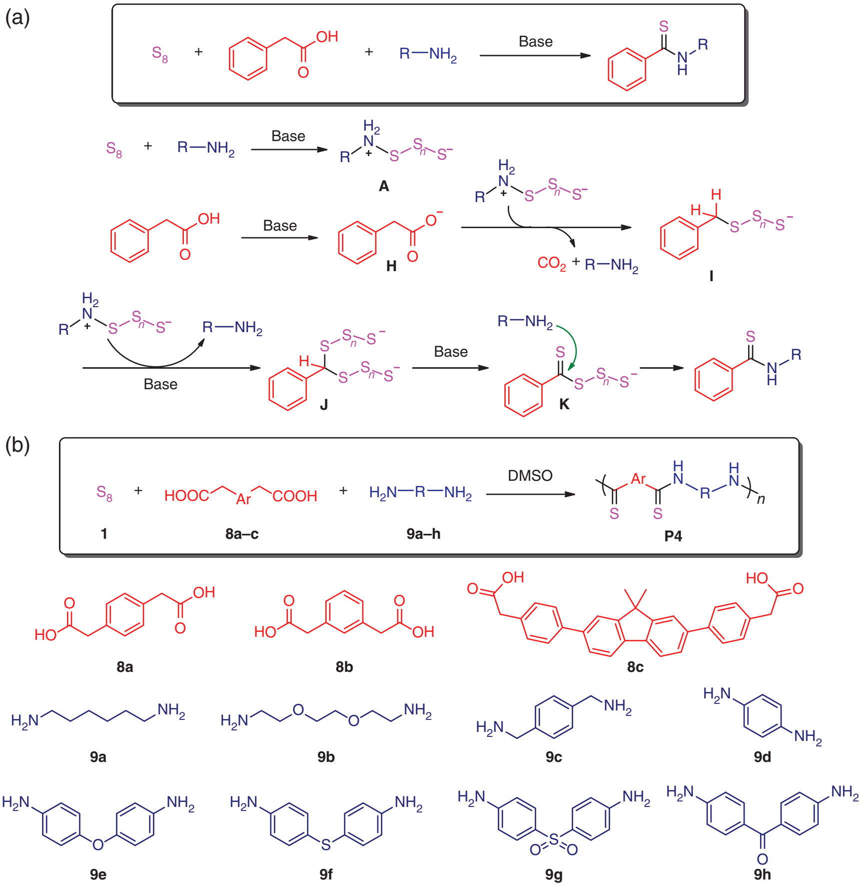
Nonetheless, effort has been made to control the polymer structures and other alkyl diamines such as ethylenediamine **7c**, 1,6-hexamethylenediamine **7d**, and 1,4-cyclohexanediamine **7e**, which can hardly be oxidized by sulfur, but can undergo transthioamidation/transimination reactions, were selected as the third component monomers of the MCP. As a result, in the product of the MCP of sulfur, *p*-xylylenediamine **7a**, and one of these alkyl diamines, besides the homocoupling structure of the *p*-xylylenediamine, there are mainly alternating structures with both two kinds of diamines existed, and the homocoupling structure of the alkyl diamines should not exist. In fact, the MCPs of sulfur, *p*-xylylenediamine **7a**, and 1,6-hexamethylenediamine **7d** or ethylenediamine **7c** afforded high ratios of alternating structures of 80% or 78% in the product, respectively, proving that alternating structure is preferred with alkyl amine monomers. Raising the loading ratio of alkyl diamines is found to be an effective approach to increase the proportion of alternating structure in the polymer product.

1.2.4 Multicomponent Polymerization of Sulfur, Diarylacetic Acids, and Aliphatic/Aromatic Diamines

The aforementioned sulfur-based MCPs generally utilized benzyl diamines or alkyl diamines with strong nucleophilicity as monomers, and less nucleophilic aromatic diamines were not reported in these polymerizations because they could not undergo the crucial ring-opening reaction with sulfur to afford the key intermediate, reactive polysulfide anions. Polythioamides with rigid backbone and conjugated structures from aromatic diamines were hence not accessed yet. The MCR of elemental sulfur, carboxylic acids, and amines was reported by Singh's group to yield thioamide derivatives with the assistance of K_2CO_3 [52], and it's worth mentioning that various amines including aromatic amines were applicable for this MCR with gratifying yields.

To transform this reaction into an efficient polymerization, a series of experimental evidences were obtained to investigate its reaction mechanism and the following steps were proposed. Under basic condition of aliphatic amine or additional inorganic base, cyclic S_8 ring was first reacted with aliphatic or aromatic amine to afford polysulfide anion **A**. The proton of benzyl acid was removed under such basic condition to form **H**, which was then reacted with **A** to release CO_2 and generate intermediate **I**, followed by further reaction with **A** again to afford intermediate **J**. **J** was then transformed to the thiocarbonyl group-containing intermediate **K**, followed by the attack with amine on the thiocarbonyl group to afford thioamide product (Scheme 1.4a).

Encouraged by the rich chemical structures of the polythioamide structures that could be accessed from this reaction, the MCPs of elemental sulfur, diarylacetic acids, and aliphatic/aromatic diamines were developed (Scheme 1.4b) [53]. The



Scheme 1.4 (a) Proposed mechanism of the MCR of sulfur, diarylacetic acids, and amine. (b) MCPs of sulfur **1**, diarylacetic acids **8a–c**, and diamines **9a–h**.

MCP of 1,4-phenylenediacetic acid **8a**, aliphatic 1,6-hexanediamine **9a**, and sulfur was first carried out in DMSO at 100 °C for 10 hours under nitrogen with a high diamine concentration of 0.5 M to afford polythioamide with a M_w of 52 300 g mol^{-1} in 81% yield. Prolonging polymerization time to 15 hours could significantly improve the yield to 96% but show little influence on the M_w. The polymerization temperature at 100 °C is again proved to be critical to obtain satisfying results. Compared with the result obtained at 100 °C, both yield and M_w of the product obtained below 100 °C is decreased to 1/3 of the former one, and the M_w of the product obtained above 100 °C is decreased to the half of the former one, probably due to the poor solubility of insoluble salts formed from acid and amine at lower temperature, and the possible side reactions at higher temperature. While the excess amount of sulfur was generally beneficial to the sulfur-based MCPs, it was unexpected that the best polymerization results was obtained with excess amount of diacid and the monomer loading ratio of sulfur, diacid, and diamines of 3.0 : 1.5 : 1.0, unlike other conventional polycondensations that generally require strict stoichiometric balance among the monomers. This is because (i) the diacid and aliphatic diamine can form insoluble salt rapidly, which may inhibit further reactions, and (ii) the reaction between the deprotonated acid and the polysulfide anion is a crucial step for the whole polymerization. Under such optimal polymerization condition without any catalyst or additive, this MCP could proceed smoothly with a series of aliphatic diamines to afford polymers with the M_ws ranging from 13 600 to 54 600 g mol^{-1} in up to 96% yields.

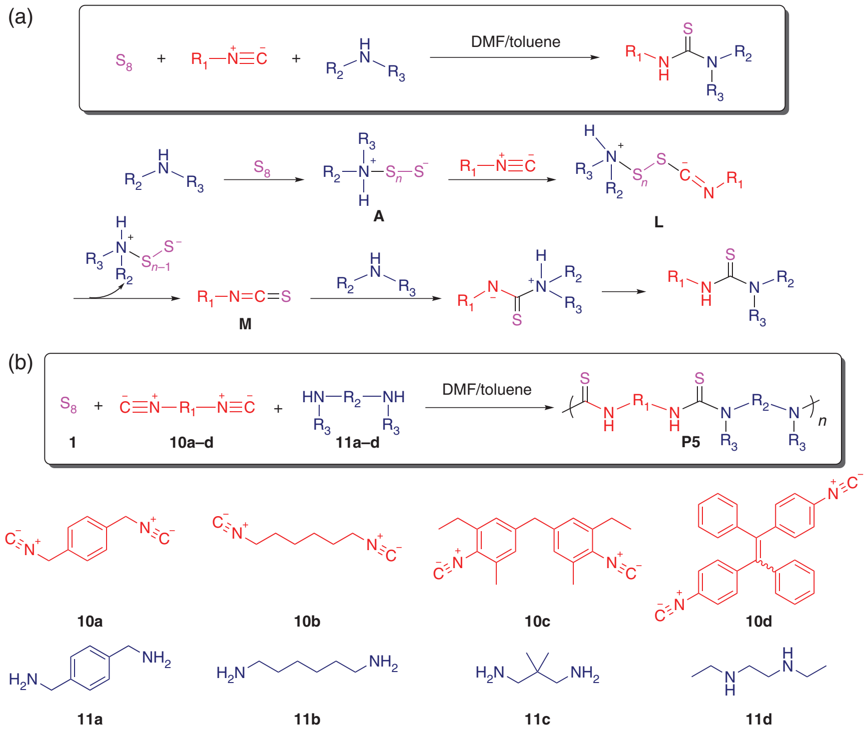
Although aromatic diamines could not react with sulfur even upon heating, with the assistance of additional inorganic or organic base such as K_2CO_3, they could efficiently react with diacids and sulfur at 100 °C under nitrogen in DMSO to produce polythioamides. The best polymerization result was obtained with the monomer loading ratio of sulfur, diacid, and aromatic diamines of 3 : 1 : 1, considering that aromatic diamines with poor alkalinity could not form salt with diamine and hence no excess amount of acid is needed. Five different aromatic diamines were explored for the MCP, which generally afforded polythioamides with high M_ws ranging from 14 900 to 86 200 g mol^{-1} in 69–95% yields. Compared with the electron-poor aromatic diamine monomers, the electron-rich aromatic diamines generally produced polymers with higher M_ws and yields. Secondary diamines were not applicable for this MCP, probably due to their large steric hindrance.

Furthermore, it’s noteworthy that the MCP of sulfur, diacids, and diamines could be conducted with a 200-fold scale under the same condition to afford similar high yields and slightly improved M_ws of the products, regardless of aliphatic or aromatic diamines. Considering the commercial availability of the inexpensive monomers and catalyst-free mild condition of the MCPs, this scalable polymerization might potentially be developed into a convenient and economic approach for the large-scale production of polythioamides.

1.2.5 Multicomponent Polymerization of Sulfur, Diisocyanides, and Aliphatic Diamines

Unlike polythioamides with limited reports, polythioureas with the carbonyl groups in the classical polyurea materials replaced by thiocarbonyl groups are a group of popular sulfur-containing polymers, which have been extensively studied, owing to their applications as dielectric materials [54], self-healing materials [55], and noble metal ion absorbents [56]. The current synthetic approaches for polythioureas generally use sulfur-containing reagents such as carbon disulfide, thiourea, thiophosgene, diisothiocyanate, or 1,1′-thiocarbonyldiimidazole, and the availability of reactants, poor atom economy, and harsh reaction condition have limited the exploration of diverse polythiourea structures.

Recently, a MCR of sulfur, isocyanides, and aliphatic amines was reported to synthesize asymmetric thiourea derivatives (Scheme 1.5a) [57]. In this reaction, the carbenoid carbon atom of isocyanide was first reacted with polysulfide anion **A** to form intermediate **L**, which then underwent S—S bond cleavage to furnish isothiocyanate **M**. The amine then rapidly attacked on the carbon atom of **M** to afford thiourea product. This MCR is more efficient than the abovementioned sulfur-based MCRs, considering that isocyanides are more reactive species compared with alkynes, aldehydes, or acids, which might realize efficient conversion at mild temperature in sterically demanding condition. Moreover, high functional group tolerance of this reaction enables the transformation of hydroxyl group, C=C bonds, C≡C bonds, or ester groups-bearing reactants. It is hence developed into an MCP of sulfur, diisocyanides, and diamines for the facile construction of diverse polythioureas (Scheme 1.5b) [58].



Scheme 1.5 (a) Possible mechanism of MCR of sulfur, isocyanide, and amine [57]. (b) The catalyst-free MCP of sulfur **1**, diisocyanides **10a–d**, and diamines **11a–d**. [58]

Compared with the synthesis of small molecular thioureas, one major challenge of the preparation of polythioureas is their poor solubility in common organic solvents resulted from the strong intramolecular or interchain hydrogen bonding among thiourea moieties embedded in the polymer main chain. DMF/toluene mixed solvent was hence found to be the optimal solvent with balanced reactivity and product solubility for the MCP of sulfur, diisocyanides, and diamines. As expected, with the high reactivity of diisocyanide, the MCP could proceed smoothly at room temperature to afford polythioureas with excellent yields and M_ws. The MCP was also robust, which could be conducted under both nitrogen atmosphere or in air, and there was only slight influence on the yields and M_ws of the polythioureas. The optimal monomer loading ratio of sulfur, diisocyanide, and diamine was found to be 4 : 1 : 1, and higher monomer concentration generally resulted in higher M_ws of the product, but did not show obvious effect on the yields. Neat polymerization of sulfur, diisocyanide **10a**, and diamine **11a** was also succeeded at 100 °C to afford polythiourea with an M_w of 22 100 g mol^{-1} after one hour.

Furthermore, *in situ* IR technique was applied to monitor the formation of polythiourea structures at different temperatures from the characteristic stretching vibration peaks of the newly formed C=S and C—N bonds at ~1540 and 1340 cm^{-1}, respectively, suggesting the rapid completion of the MCPs. The real-time kinetics of the MCP of sulfur, diisocyanide **10a**, and diamine **11a** suggested that polymerization could proceed rapidly and the reaction equilibrium could be reached in two hours at room temperature in air to afford polythiourea with a M_w of 24 400 g mol^{-1} in 82% yield. At elevated temperature of 100 °C, the MCP could even be finished in 10 minutes in air, affording polythiourea with a M_w of 47 600 g mol^{-1} in 81% yield.

Besides the high efficiency and rapid completion of the MCP, the general monomer applicability of the MCP was also an appealing feature. Four aliphatic and aromatic diisocyanides **10a–d** and four primary and secondary aliphatic diamines **11a–d** were selected as monomers to represent different structures, and the MCPs of all the 16 monomer combinations could afford satisfactory results with a great structural diversity of polythioureas obtained with high M_w of up to 242 500 g mol^{-1} in 64–95% yields, demonstrating the wide monomer scope of this MCP.

The success MCP of sulfur, diisocyanides, and diamines was also extended from sulfur to selenium [59], and we have recently reported the efficient MCP of selenium, diisocyanides, and diamines under similar catalyst-free mild condition [60]. Compared with the sulfur-based MCP, the selenium-based MCP is even more efficient, which can be completed in 1 minute at 100 °C or 45 minutes at 40 °C. Moreover, the monomer scope of the selenium-based MCP includes not only primary and secondary aliphatic diamines, but also aromatic diamines, enabling the construction of a large variety of polyselenoureas with unreported structures, good stability, and high M_ws.

The MCPs of elemental sulfur represent a series of economic, convenient, and efficient approaches to directly convert industrial waste sulfur into profitable functional sulfur-containing polymers.

1.3 Cu(I)-Catalyzed Multicomponent Polymerizations of Sulfonyl Azides/Hydrazides

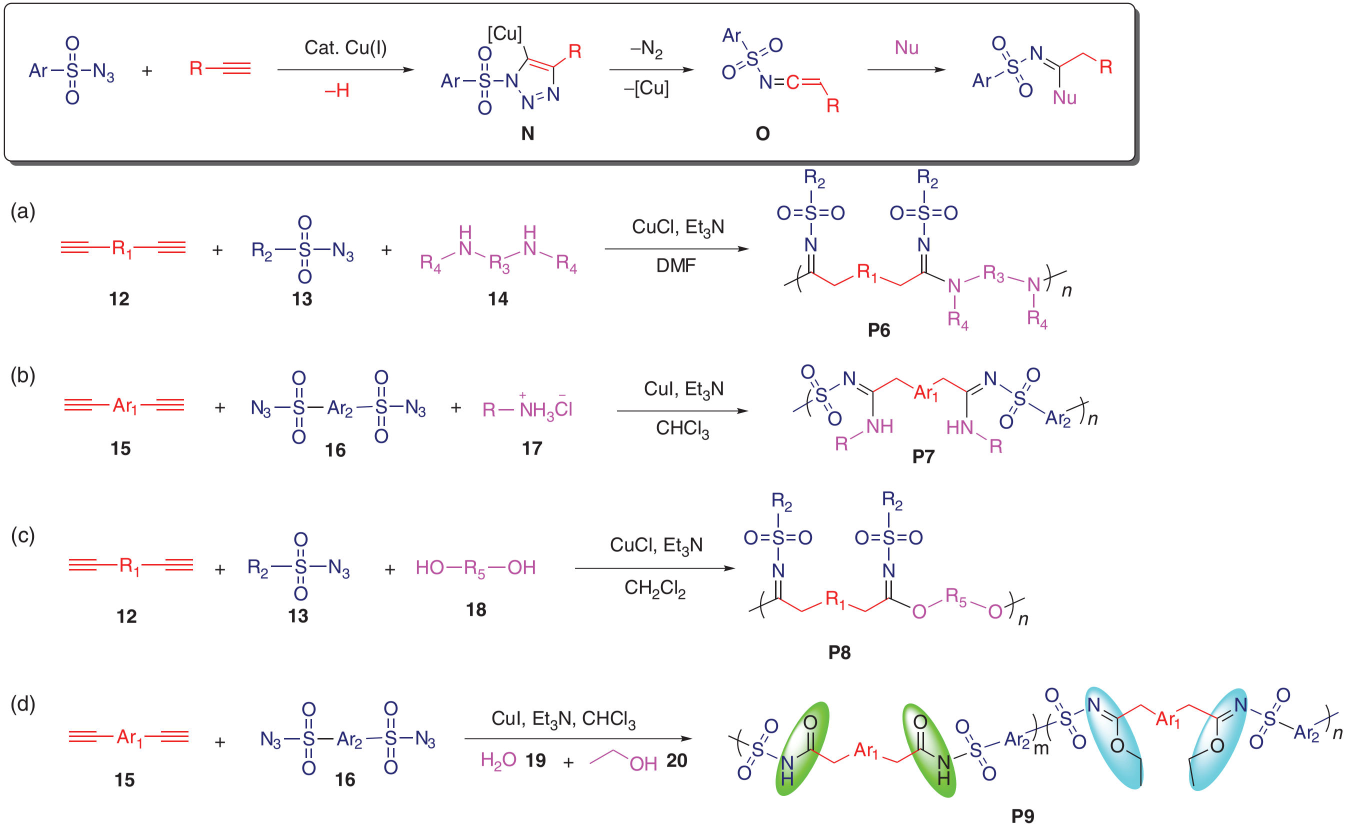
Sulfonyl group-containing polymers, enjoying a series of advantages such as high dielectric ability [61, 62], and excellent mechanical properties [63], are another group of sulfur-containing polymers, which were less explored, due to the lack of efficient synthetic approach. The Cu(I)-catalyzed azide-alkyne cycloaddition as the well-known click reaction can afford stable 1,2,3-triazole product [64]. If a strong electron withdrawing sulfonyl group is installed on the triazole ring, it may undergo ring-opening reaction to release nitrogen gas and form a highly reactive ketenimine species, which can undergo a wide range of different reactions and afford a great diversity of sulfonyl-group containing heteroatom-rich compounds. Based on that, the recently emerged alkyne and sulfonyl azide-based MCPs have brought great opportunity to access sulfonyl group-containing polymers with unique and complex structures as well as functionalities.

1.3.1 Multicomponent Polymerization of Sulfonyl Azides, Alkynes, and Amines/Alcohols

For example, a Cu(I)-catalyzed MCR of terminal alkynes, sulfonyl azides, and amines was reported to synthesize sulfonyl amidine derivatives by Chang and coworkers [65]. The MCR underwent three steps including the cycloaddition of terminal alkyne and sulfonyl azide, the ring-opening reaction of the unstable triazole ring to generate the highly reactive ketenimine intermediate **O**, and its subsequent nucleophilic attack by amine (Scheme 1.6). Based on this mechanism, similar MCRs with the amine replaced by other nucleophiles such as alcohol and water were successively reported [69].

Choi and coworkers first developed the MCRs of alkynes, sulfonyl azides, and amines into efficient MCPs for the preparation of poly(*N*-sulfonylamidine)s P**6** (Scheme 1.6a) [66]. After a series of polymerization condition optimization on solvents and Cu(I) catalysts, the MCP could be conducted at room temperature in DMF with the catalysis of CuCl to afford improved results. Unlike the sulfur-based MCPs, strict stoichiometric balance between diynes and diamines was required to obtain satisfying polymerization results, while an excess amount of *p*-toluenesulfonyl azide is beneficial to the monomer conversion. On the other hand, organic amine additives such as diisopropylethylamine, 2,6-lutidine, tris(benzyltriazolylmethyl) amine, or triethylamine were found to increase the catalytic activity because they can inhibit the protonation of the diamine monomers and facilitate the formation of the key intermediate Cu-acetylide complex. A great diversity of alkyl groups, diene, aromatic groups, and ethylene glycol-containing diyne monomers, alkylsulfonyl azide and phenylsulfonyl azide monomers with electron-withdrawing groups, electron-donating groups, or sterically hindered groups substituted at different positions of the benzene ring, as well as primary and secondary dialkylamines, and aniline derivatives were selected as monomers for this Cu(I)-catalyzed MCP, affording 26 well-defined poly(*N*-sulfonylamidine)s with M_n values of up to $75\,100\ \mathrm{g\ mol^{-1}}$.

Later, this MCP was extended to a group of optically active amino ester monomers by Tang and coworkers [70]. The Cu(I)-catalyzed MCP of alkynes, sulfonyl azides, and chiral amino esters could be conducted in chloroform at room temperature, affording chiral poly(*N*-sulfonylamidine)s P**7** with high M_ws of up to $35\,900\ \mathrm{g\ mol^{-1}}$ in up to 87% yields (Scheme 1.6b). With the chiral centers introduced from the amino



Scheme 1.6 Cu(I)-catalyzed MCPs of (a) diynes **12**, sulfonyl azides **13**, and diamines **14** [66]. (b) diynes **15**, disulfonyl azides **16**, and chiral amino esters **17**, (c) diynes **12**, sulfonyl azides **13**, and diols **18** [67]. and (d) diynes **15**, disulfonyl azides **16**, water **19**, and alcohol **20** [68].

ester monomers, the resultant polymer backbone could be induced to helically rotate and possess chiroptical properties.

Similarly, alcohols can be used as the third component monomer to replace amines as nucleophiles and react with the ketenimine intermediate to proceed the Cu(I)-catalyzed MCP and afford poly(*N*-sulfonylimidate)s P**8** (Scheme 1.6c) [67]. There are two differences of the alcohol-based MCPs compared with the amine-based MCPs. Firstly, the nucleophilicity of alcohols is not as strong as amines, hence the molecular weights of the poly(*N*-sulfonylimidate)s product are relatively low compared with the poly(*N*-sulfonylamidine)s. Secondly, this MCP is sensitive to water because even trace amount of water can compete with the diol monomers to form *N*-sulfonyl amide structures and terminate the polymerization. Moisture should hence be strictly avoided and dry solvents such as $CHCl_3$ and CH_2Cl_2 should be used instead of DMF. The MCPs of various diynes, sulfonyl azides, and a great variety of primary, secondary, aromatic, cyclic, and bicyclic diols generally occurred smoothly to produce 24 different poly(*N*-sulfonylimidate)s with high M_ws of up to 33 500 g mol^{-1}.

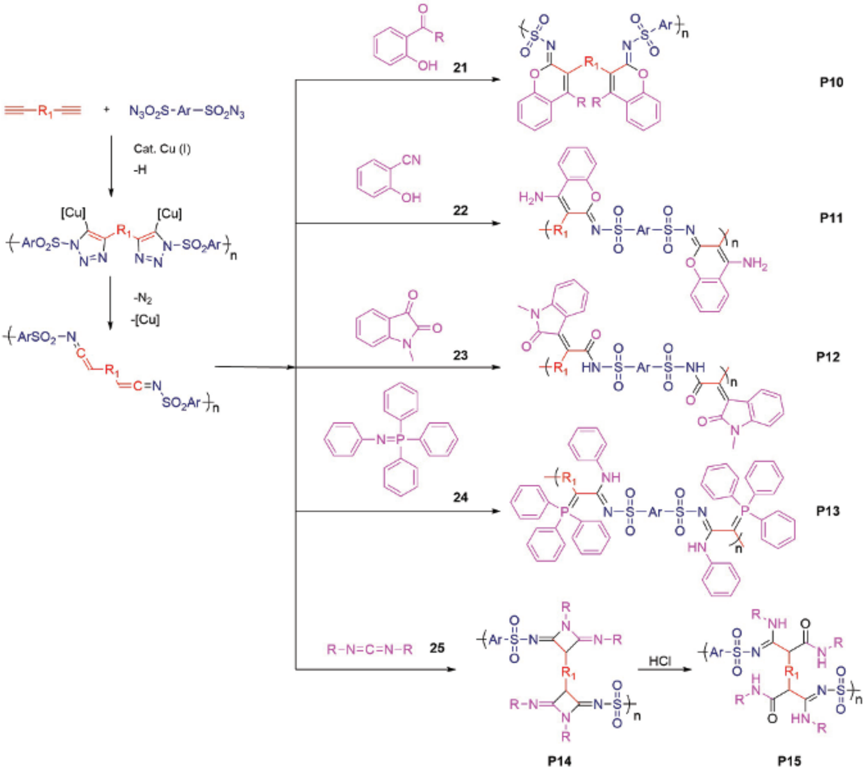
The side reaction with water could also be utilized in the MCPs if disulfonyl azide monomers were used. For instance, a four-component polymerization of diyne, disulfonyl azide, water, and alcohol was reported in $CHCl_3$ in the presence of CuI and triethylamine under nitrogen at room temperature (Scheme 1.6d) [68]. In the resultant polymer product P**9**, both amide and imidate structures co-existed, and their ratio in the polymer chain could be controlled by adjusting the loading ratio of water and ethanol. With the concentrations of water and ethanol were 0.1 and 0.3 M, respectively, a polymer with an amide/imidate ratio of 39/61 and a M_w of 83 900 g mol^{-1} was obtained. In the absence of water, a soluble poly(*N*-sulfonylimidate) product with a high M_w of 257 100 g mol^{-1} could be obtained in four hours. It should be noted that the MCP without ethanol may form poly(*N*-sulfonylamide) as a gel, due to the formation of intermolecular hydrogen bonding among the polyamide chains.

Besides the high efficiency of these MCPs, their functional group tolerance and broad monomer scope are quite unique. Satisfying polymerization results could be obtained regardless of the electronic nature, substitution position, or steric hindrance of the sulfonyl azides. The rigid diamines, diols, or diynes could generally produce polymers with higher M_w compared with flexible monomers, owing to the suppression of the intramolecular cyclizations.

1.3.2 Multicomponent Polymerization of Sulfonyl Azides, Alkynes, and Other Monomers

Besides simple nucleophiles such as amines and alcohols, the ketenimine intermediate formed from alkynes and sulfonyl azides could react with many other reactants in a more complex manner [71–75]. The successful introduction of these MCRs into polymer synthesis could provide access to various heteroatom, heterocycle, or fused heterocycle-containing polymers with unique structures, which could not be synthesized from other reported methods.

For example, Cu(I)-catalyzed MCPs of diynes, disulfonyl azides, salicylaldehyde, or *o*-hydroxyacetophenone were reported at room temperature under nitrogen in the presence of triethylamine in DMAc to produce poly(iminocoumarin)s P**10** with M_ws of up to 64 600 g mol^{-1} in satisfactory yields of up to 99% (Scheme 1.7) [76]. In this MCP, the ketenimine intermediate formed from alkyne and sulfonyl azide was quickly attacked by the OH group of *o*-hydroxyacetophenone to form an anionic intermediate, which then underwent an intramolecular nucleophilic addition on the carbonyl group. After protonation and dehydration, the poly(iminocoumarin) was formed.



Scheme 1.7 The synthetic routes of Cu(I)-catalyzed MCPs of diynes, disulfonyl azides, and various monomers **21–25**.

Similar mechanism also applies to the MCR of diynes, disulfonyl azides, and 2-hydroxybenzonitrile or 2-aminobenzonitrile, and the OH or NH_2 groups from substituted benzonitriles first attack the ketenimine to produce an intermediate, which then undergoes subsequent intramolecular cyclization, protonation, and isomerization to afford amino-substituted iminocoumarin or quinoline structures [72]. These two MCPs were developed under the catalysis of CuCl and triethylamine in CH_2Cl_2 under nitrogen, generating iminocoumarin or quinoline-containing poly(*N*-sulfonylimine)s P**11** with M_ws of up to 37 700 g mol^{-1} in high yields up to 96% (Scheme 1.7) [77]. Moreover, the fused heterocycles iminocoumarin and aminoquinoline structures built *in situ* from the MCP have brought the polymers interesting fluorescence properties.

N-protected isatins with their unique chemical reactivity could also be developed as the third monomer of the alkyne and sulfonyl azide-based MCPs. In fact, the carbonyl group linked on the benzene ring of the *N*-protected isatin could undergo a [2+2] cycloaddition with metal alkynamide intermediate generated from alkyne and sulfonyl azide to form a four-membered ring oxetene structure. In the presence of LiOH, the oxetene underwent ring-opening reaction and acidification to afford 3-alkenyloxindole; in the presence of H_2O and Na_2CO_3, the oxetene underwent isomerization, nucleophilic attack with OH^- to open the four-member ring, and subsequent acidification to afford 3-hydroxyindole [73]. Following these routes, the MCPs of diynes, disulfonyl azides, and *N*-protected isatins were developed at room temperature in CH_2Cl_2/*t*-BuOH under the catalysis of CuI in the presence of LiOH, generating oxindole-containing poly(*N*-acylsulfonamide)s P**12** with M_ws of up to 30 600 g mol^{-1} in 92–98% yield (Scheme 1.7) [78]. Furthermore, a four-component polymerization of diynes, disulfonyl azides, *N*-protected isatins, and water was developed under similar condition in DMF with Na_2CO_3 as the base, affording random copolymers consisting 3-alkenyloxindole moieties and two chiral center-containing 3-hydroxyindole moieties. Interestingly, these poly(*N*-acylsulfonamide)s possess reversibly tunable solubility and hydrophilicity, which can be well-dissolved in alcohol or alcohol/water mixtures, but not in THF or CH_2Cl_2. Opposite solubility of these polymers is realized upon acidification of the polymers.

Iminophosphorane can also undergo [2+2] cycloaddition reaction with ketenimine intermediate, followed by ring-opening reaction to afford a phosphorus amidine product [74], which could be considered as the third monomer of the alkyne and sulfonyl azide-based MCPs to construct heteroatom-rich polymers. We have reported a facile MCP of diynes, disulfonyl azides, and iminophosphorane, which proceeds at room temperature in THF in the presence of CuI and triethylamine with the alkyne monomer concentration of 0.1 M and the monomer loading ratio of alkyne, sulfonyl azide, and iminophosphorane to be 1.0 : 1.0 : 2.5, furnishing N, O, S, and P-containing heteroatom-rich poly(phosphorus amidine)s P**13** with high M_ws of 85 600 g mol^{-1} in 91% yield (Scheme 1.7) [79]. The MCPs of a great diversity of diynes and disulfonyl azides could proceed smoothly and efficiently, including aliphatic and aromatic diynes.

These alkyne and sulfonyl azide-based MCPs were not only convenient for the preparation of polymers with five- or six-membered heterocycles embedded in the backbone as discussed above, but also proved to be effective for the construction of polymers with readily openable small ring heterocycles, which remained to be a great challenge due to their synthetic difficulties and poor stability. This was realized by a recently reported room temperature MCP of terminal diynes, disulfonyl azides, and carbodiimides under nitrogen with the catalysis of CuI, producing heteroatom-rich multisubstituted azetidine ring-bearing polymers P**14** with good stability in air and common organic solvents, and M_ws of up to 74 500 g mol^{-1}

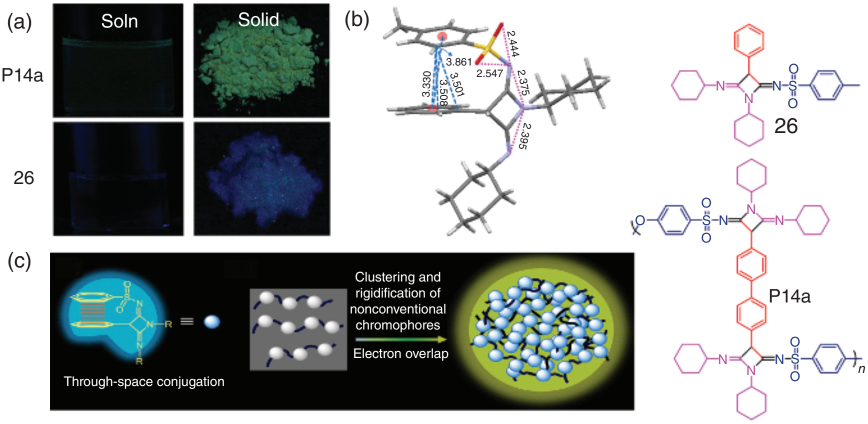


Figure 1.1 (a) The fluorescence photos of solutions and powders of P**14a** and **26** taken under 365 nm UV irradiation. (b) Single crystal structure of **26** with indicated distances (Å) between π–π stacked aromatic rings and distances between atoms with lone-pair electrons. (c) Schematic illustration of the unconventional luminescence of model compound **26** and polymers. Source: Reproduced from Ref. [80]. Copyright 2018 American Chemical Society.

in yields up to 89% (Scheme 1.7) [80]. With the large ring strain of the azetidine rings, these four-membered rings in polymer skeleton could facilely transformed into amide and amidine moieties through acid-mediated ring-opening reactions to afford polymers with new structures and tunable properties.

Interestingly, unexpected fluorescence at 502–536 nm was observed in the solid powders of the azetidine ring-containing polymers and model compounds, considering that there was no conventional chromophore existed in these structures (Figure 1.1). Single crystal analysis of model compound **26** suggested the existence of through-space π–π interaction, lone-pair electronic interactions among N and O atoms, and intermolecular C—H· · ·O and C—H· · ·π interactions, which rigidified the conformation of the molecules, maintained the stability of spatial configuration, and strengthened the through-space π–π conjugation. The unconventional luminescence of these polymers is hence attributed to the clusteroluminogens formed by through-space electronic interactions of heteroatoms and phenyl rings, evidenced by X-ray photoelectron spectroscopy (XPS) analysis. In the solid state, the chain entanglement and intra-/interchain interactions led to the rigidification of nonconventional chromophores and high density of clustering, resulting in bright emission; in the solution state, these through-space interactions and intra-/interchain interactions were broken and thus no emission could be observed.

These alkyne and sulfonyl azide-based Cu(I)-catalyzed MCPs generally enjoy high efficiency, mild condition, excellent functional group tolerance, and high atom economy, which can proceed smoothly at room temperature, release nitrogen gas as the only byproduct, and generate polymers with defect-free well-defined structures and high M_ws in high yields, demonstrating fascinating synthetic approaches for the construction of polymers with unique and complex heteroatom-rich structures.

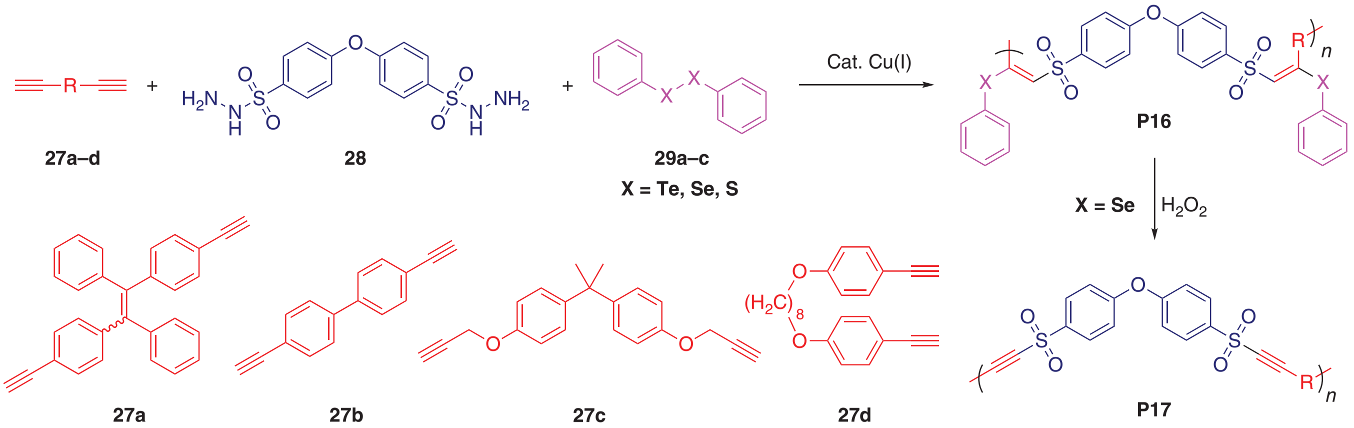
1.3.3 Multicomponent Polymerization of Sulfonyl Hydrazide, Alkynes, and Diphenyl Dichalcogen

Sulfonyl hydrazides, which are usually odorless, stable, and easy to be synthesized, are another type of popular sulfonyl source in organic synthesis [81]. For example, an efficient Cu(I)-catalyzed regio- and stereospecific selenosulfonation of alkynes, arylsulfonohydrazides, and diphenyl diselenide was reported to generate selenovinyl sulfones by Liu et al. [82] A radical mechanism was proposed for this MCR: firstly, sulfonylhydrazide was reacted in the presence of copper salt and $K_2S_2O_8$ to release N_2 and generate a sulfonyl radical, which was then regiospecifically added on alkynes to form a relatively stable β-sulfonyl vinyl radical. The phenyl selenol radical generated from diphenyl diselenide was then coupled with the vinyl radical to afford thermodynamically stable (E)-β-selenovinyl sulfone product. This MCR was then developed into the MCPs of alkynes, arylsulfonohydrazides, and diphenyl dichalcogen for the construction of chalcogen-rich poly(vinyl sulfone)s (Scheme 1.8) [83]. The MCP of diyne **27a**, arylsulfonohydrazides **28**, and diphenyl diselenide **29a** was found to proceed smoothly in the presence of $Cu(MeCN)_4PF_6$ and $K_2S_2O_8$ in DMF/CH_3CN (v/v, 1/1) at room temperature for 24 hours. This MCP applies to various aromatic and aliphatic diynes **27a–d** and diphenyl dichalcogens **29a–c**, producing regio- and stereoselective poly(vinyl sulfone)s P**16** with M_ws of up to 20 800 g mol^{-1} in yields of up to 92%.

One unique feature of the selenium-containing poly(vinyl sulfone) is that it can be completely transformed to poly(ethynyl sulfone) P**17** with the phenyl selenol species cleaved from the polymer upon the post-modification by oxidation with H_2O_2, enabling facile modulation of the polymer properties. For example, the fluorescence quantum yield of a tetraphenylethene-containing poly(vinyl sulfone) is 2.7%, which increased about five-fold to 13.4% after it was oxidized to remove the phenyl selenol species, because the heavy atom effect caused from selenium atoms disappeared.

1.3.4 Topological Polymers Prepared from Sulfonyl Azides and Alkyne-Based MCPs

Topological polymers with different connection of repetitive units of the polymers have attracted much attention recently in fields regarding biomaterials, coatings, and photoelectric materials [84–86]. Encouraged by the high efficiency and mild condition of the aforementioned Cu(I)-catalyzed MCPs, sulfonyl group-containing polymers with unique topological structures could be designed and synthesized. For example, a series of mono-functional alkyne-containing polymer or dendronized macromonomers were designed for the Cu(I)-catalyzed MCPs of mono-functionalized alkynes, bis-sulfonyl azides, and diamines/diols [87]. Through diversity-oriented synthesis and “graft through” strategy, 54 samples of graft and dendronized polymers P**18** and P**19** with large bulky side chains and high M_n of up to 1 041 000 g mol^{-1} were prepared, despite of the severe steric hindrance from the macromonomers (Scheme 1.9a). The construction of topological polymers from



Scheme 1.8 Cu(I)-catalyzed MCPs of diynes **27a–d**, aryl sulfonyl hydrazide **28**, and diphenyl dichalcogen **29a–c** towards regio- and stereoselective chalcogen-rich poly(vinyl sulfone)s and the post-modification of the selenium-containing poly(vinyl sulfone) by oxidation. [83]

MCP approaches enables simultaneous manipulation of both main chain and side chain structures.

MCP is also a powerful tool for the construction of hyperbranched polymers from simple tuning of monomer combinations. For example, we have reported the preparation of N, O, S, P-containing heteroatom-rich functional hyperbranched polymers from the MCPs of alkyne monomers with three or four functional groups, disulfonyl azide, and iminophosphorane (Scheme 1.9b) [88]. Hyperbranched poly(phosphorus amidine)s P**20** with different topological structures and high M_ws of up to 441 700 g mol^{-1} were obtained in high yield at room temperature in the presence of CuI and triethylamine from the monomer combination strategies such as $A_3 + B_2 + C$ or $A_4 + B_2 + C$.

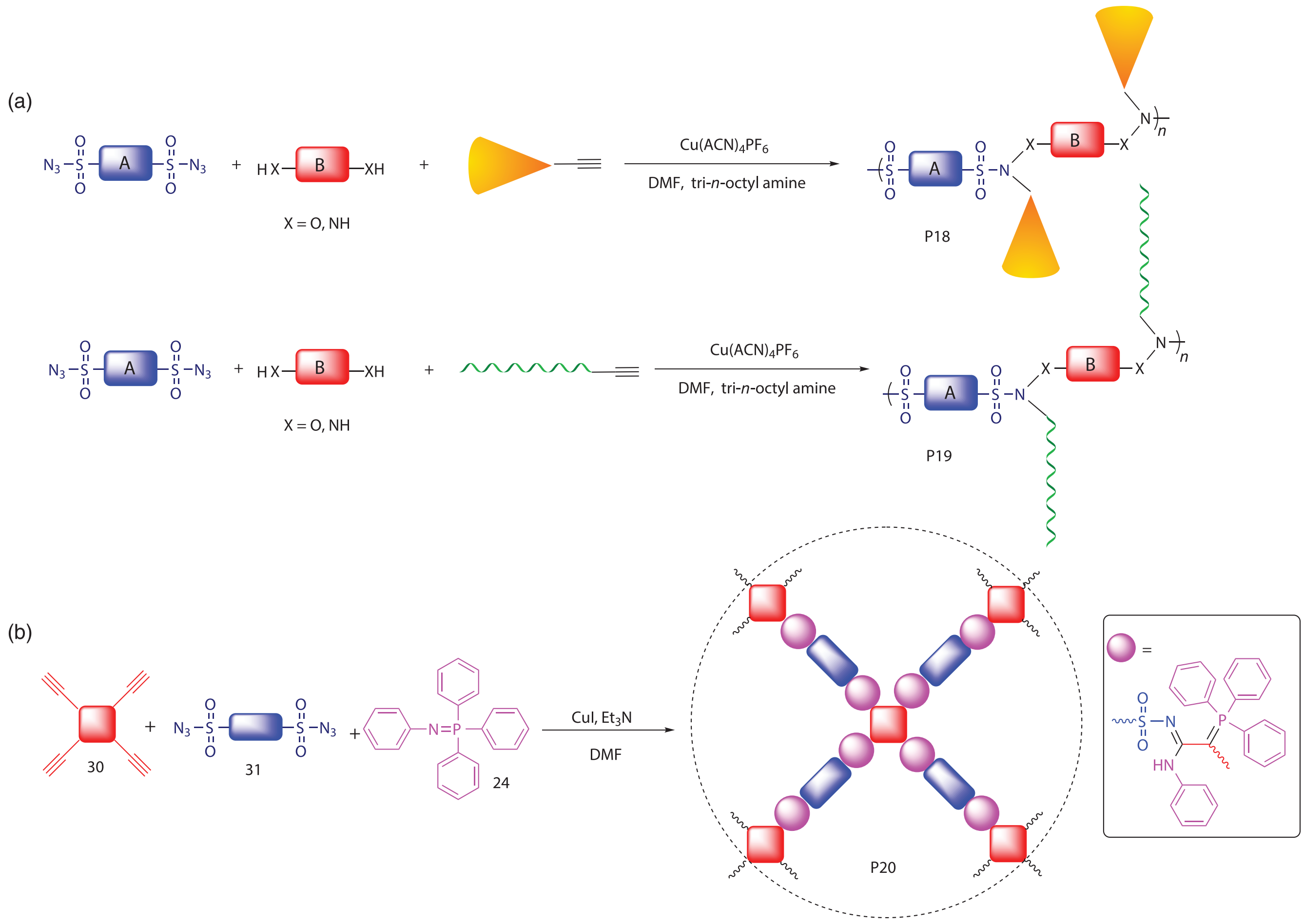
The high efficiency, mild condition, high atom economy, wide monomer scope, and versatile monomer combinations of these sulfonyl azide and alkyne-based MCPs have enabled the facile construction of functional polymers with various topological structures.

1.4 Multicomponent Polymerizations with Thiol-Related Monomers

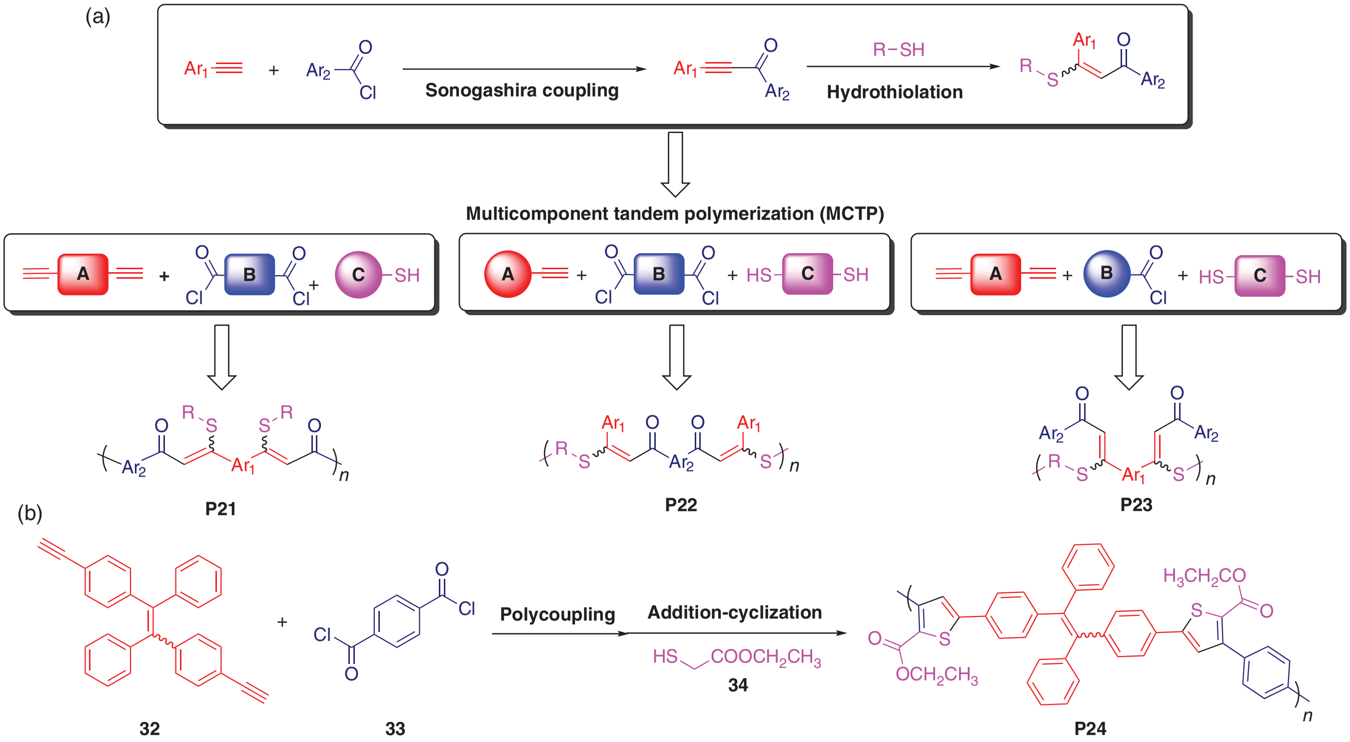
Thiols are a group of simple, readily available, and reactive compounds for the synthesis of sulfur-containing materials from a series of versatile reactions, especially nucleophilic additions considering that thiols are generally strong nucleophiles. In MCPs where the simple nucleophilic addition of thiol was combined with other reactions in a one-pot procedure, sulfur-containing polymers with complex structures and advanced functionalities could be accessed.

1.4.1 One-Pot Multicomponent Tandem Polymerization of Alkyne, Carbonyl Chloride, and Thiol

For example, a one-pot, two-step, three-component tandem polymerization of alkyne, carbonyl chloride, and thiol was designed, combining the Sonogashira coupling reaction of alkyne and carbonyl chloride, as well as the subsequent thiol addition on the alkynone intermediate in a single polymerization. Both two reactions share high efficiency, common solvent THF, and compatible reaction condition, enabling the multicomponent tandem polymerization (MCTP) to proceed efficiently at room temperature in the presence of $Pd(PPh_3)_2Cl_2$, CuI, triethylamine, and n-Bu_3P to afford sulfur-rich alkylthiol-substituted polymers with high regioselectivity, good stereoselectivity, high M_ws (up to 59 100 g mol^{-1}), and high yields (up to 98%) [89]. The MCTP is applicable to both aliphatic and aromatic thiols, and polymers P**21–23** with tunable polymer backbones and optical/photophysical properties could be accessed from the same MCTP with different monomer combination strategies such as “$A_2 + B_2 + C_1$,” “$A_2 + B_1 + C_2$,” or “$A_1 + B_2 + C_2$” (Scheme 1.10a).



Scheme 1.9 One-pot synthesis of a library of (a) graft, dendronized, and (b) hyperbranched polymers by Cu(I)-catalyzed sulfonyl azide and alkyne-based MCPs. Source: Reproduced from Ref. [88]. Copyright 2020 Georg Thieme Verlag KG.



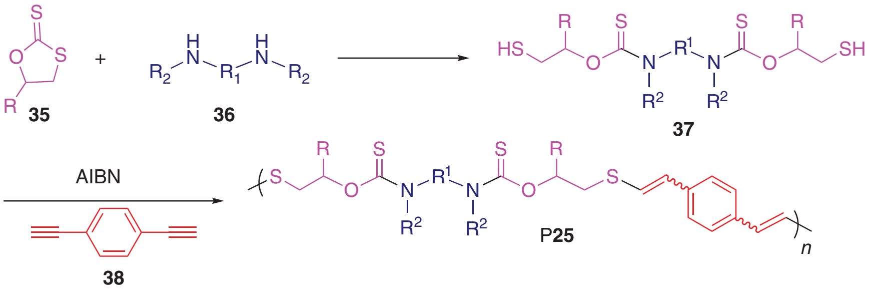
Scheme 1.10 Multicomponent tandem polymerizations of alkynes, carbonyl chlorides, and thiols/ethyl 2-mercaptoacetate for the synthesis of (a) P**21–23** and (b) poly(arylene thiophenylene) P**24**. [90]

More reactions could be integrated into this MCTP when normal thiol in the aforementioned MCTP of alkyne, carbonyl chloride, and thiol was replaced with ethyl 2-mercaptoacetate. After the Sonogashira coupling reaction and hydrothiolation, the intermediate may further undergo the Fiesselmann cyclocondensation to furnish a multisubstituted thiophene ring in a one-pot procedure [91]. The MCTP of tetraphenylethene-containing diyne **32**, the terephthaloyl dichloride **33**, and ethyl 2-mercaptoacetate **34** was hence reported to afford thiophene-containing polymer P**24** with well-defined structures and high M_w of $156\,000\ \mathrm{g\,mol^{-1}}$ in 93% yield (Scheme 1.10b) [90]. In this MCTP, the polymerization not only linked the functional groups from monomers together, but also built new functional unit such as multisubstituted aromatic thiophene ring embedded in the polymer backbone, demonstrating its high synthetic efficiency.

1.4.2 Multicomponent Polymerizations with Cyclic Dithiocarbonate

To solve the problem that thiol compounds are generally smelly, too reactive to prepare and store limited the exploration of thiol monomers. Sulfur-containing heterocycle such as five-membered cyclic dithiocarbonate, which could generate thiol group in situ, would serve as thiol precursor to develop MCPs from the combination with highly efficient thiol-click reactions [92]. Through the ring-opening reaction of sulfur-containing heterocycle with nucleophile to generate thiol group, and the sequential thiol-based click reaction, sulfur-containing polymers with strict moiety sequence could be afforded.

For example, the MCP of cyclic dithiocarbonate **35**, diamine **36**, and diyne **38** was reported by Ochiai et al. in the presence of 2,2′-azobisisobutyronitrile (AIBN) to produce sequence-controlled polymer P**25** (Scheme 1.11) [93]. The nucleophilic ring-opening reaction of cyclic dithiocarbonate was induced by diamine to generate mercaptothiourethane intermediates **37**, and the resulting thiol groups of **37** then underwent thiol-yne radical addition with diyne monomer **38** to provide desirable polymers P**25** with well-defined sequence of the functional units. The polymer product could be fine-tuned by changing the amount of AIBN, which may influence the concentration of thiyl radicals. Excess amount of AIBN led to insoluble polymer due



Scheme 1.11 MCPs of five-membered cyclic dithiocarbonates **35**, diamines **36**, and diyne **38**. [93]

to the crosslinking caused by further addition of thiyl radical to double bonds in the polymer product. The MCP of diyne, various diamines and dithiocarbonates proceeded smoothly to afford sulfur-containing polymers with M_ws ranging from 9 000 to 81 700 g mol^{-1} in excellent yields of up to 99%.

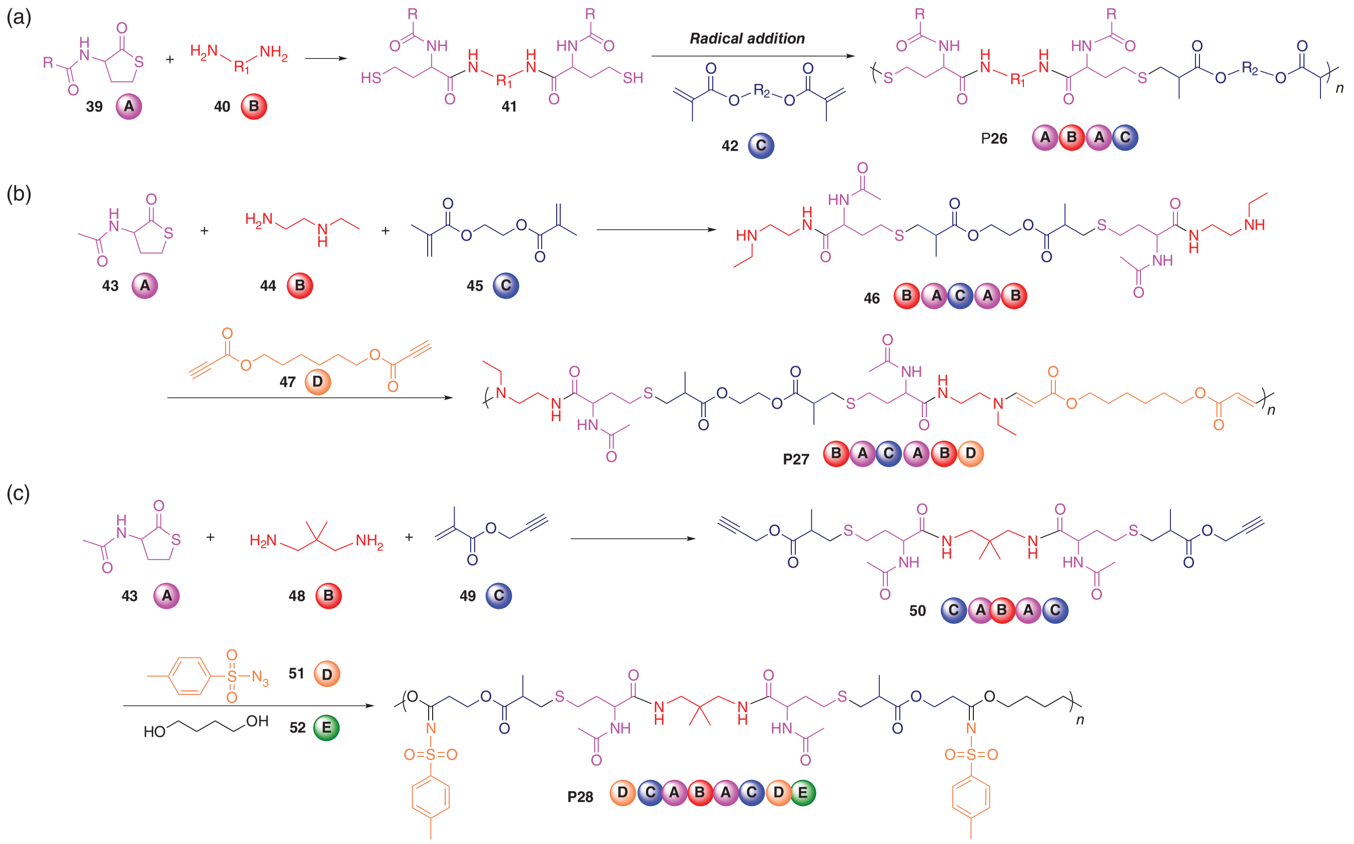
1.4.3 Multicomponent Polymerizations with Cyclic Thiolactone

Similarly, cyclic thiolactones can be converted to sulfhydryl species through ring-opening reaction with various nucleophiles such as amines, which are also popular monomers of MCPs for the preparation of sequence-controlled sulfur-containing polymers [94]. For example, Hong's group reported the catalyst-free MCP of thiolactone **39**, diamines **40**, and bis(methacrylate)s **42** through the sequential ring-opening reaction of thiolactone by amine, and thiol-Michael addition reaction on the CH=CH$_2$ group of methylacrylates (Scheme 1.12a), producing a series of ABAC-type sequence-controlled polymer P**26** with M_ns ranging from 10 700 to 48 000 g mol^{-1}. In this MCP, the primary diamine monomers serve two roles including nucleophile to open the thiolactone ring, and activating the CH=CH$_2$ bonds of dimethylacrylate. On the other hand, secondary amine could also activate the vinyl bonds but could not open the thiolactone ring, which is not applicable to this MCP.

Taking advantages of the different reactivity of primary and secondary amines, an asymmetric amine **44** with both a primary amine and a secondary amine group was designed for a four-component polymerization (Scheme 1.12b) [95]. Firstly, the primary amine group of **44** was reacted with thiolactone **43** to open the ring and generate thiol group, which then underwent thiol-ene addition with dimethylacrylates **45** to generate an BACAB-type compound **46** with two terminal secondary amine groups. Dipropiolate **47** was then added to proceed the amino-yne addition reaction to afford an BACABD-type sequence-controlled polymer P**27** with a M_n of 59 800 g mol^{-1} in 81% yield.

Based on this similar tandem strategy, a five-component polymerization of thiolactone **43**, diamine **48**, propargyl methacrylate **49**, sulfonyl azide **51**, and diol **52** was designed in a one-pot procedure to directly afford a sequence-controlled polymer P**28** with multiple building units (Scheme 1.12c) [96]. In this MCP, the propargyl methacrylate **49** with both an activated CH=CH$_2$ group and a terminal alkyne group is designed as the orthogonal monomer to combine two sequential MCRs. In the first step, monomers **43**, **48**, and **49** were reacted through the abovementioned amine-thiol-ene reaction to afford the intermediate **50** with two remaining terminal alkyne groups. The sulfonyl azide **51** and diol **52** were then added into the reaction solution together with copper catalyst and organic base to undergo the Cu(I)-catalyzed MCR of alkyne, sulfonyl azide, and alcohol. The DCABACDE-type sequence-controlled polymer P**28** was then obtained with a M_n of 72 600 g mol^{-1}.

It is worth mentioning that this tandem MCP strategy could also be applied for the preparation of sequence-controlled topological polymers by using monomers with multiple functional groups such as diethylenetriamine [97], demonstrating the



Scheme 1.12 Sequence-controlled sulfur-containing polymers prepared from (a) three-component polymerization of thiolactones **39**, primary diamines **40**, and bis(methacrylate)s **42**, (b) four-component polymerization of thiolactone **43**, asymmetric diamine **44**, dimethylacrylate **45**, and dipropiolate **47** [95], and (c) five-component polymerization of thioactone **43**, diamine **48**, propargyl methacrylate **49**, sulfonyl azide **51**, and diol **52**. [96]

great potential of these MCPs in the construction of diverse topological functional materials.

1.5 The Applications of Sulfur-Containing Polymers Prepared from MCP

The abovementioned MCP products generally possess large number of heteroatom-containing functional groups such as thioamides, thioureas, sulfonyl groups, and thioethers, which may endow the polymer materials with a series of functionalities such as the coordination with various metal ions and intermolecular interactions, considering that there are many strong and unique sulfur-involved interactions such as sulfur–metal coordination, sulfur–sulfur interaction, and hydrogen bonding between S=C groups and active protons. With proper design of these properties and other functionalities integrated in the monomer structures, there are a group of practical applications such as fluorescence chemosensors, metal ion removal or enrichment, and bioimaging could be realized.

1.5.1 Chemosensors

Detection of transition metal ion is of scientific significance and practical implication in environmental and industrial applications. With the promising selective interaction between the heteroatoms of these sulfur-containing MCP polymer products and particular transition metal ions, together with a fluorescence signal output that is dependent on the coordination of transition metal ion analyte, these polymers could serve as chemosensors for transition metal ions. For example, aggregation-induced emission (AIE) property could be facilely introduced to these MCP product by simply adopting AIEgen-containing monomers to produce AIE-active metal ion-responsive sulfur-containing polymers [98, 99].

The poly(phosphorus amidine)s P**13a** prepared from the Cu(I)-catalyzed MCP of tetraphenylethene-containing diyne, disulfonyl azide, and iminophosphine was found to be a fluorescence chemosensor of Pd^{2+} (Figure 1.2a) [79]. The fluorescence intensity of the nanoaggregates of P**13a** in DMSO/water mixture with 50 vol% water was gradually decreased with the progressive addition of $PdCl_2$ solution while the emission profile remained the same. The relative PL intensity (I_0/I) versus Pd^{2+} concentration fitted a linear relationship with a large quenching constant of 207 600 M^{-1}, suggesting high sensitivity towards Pd^{2+}. Moreover, high selectivity of Pd^{2+} compared with other metal ions was observed under same condition, attributing to the specific strong interaction between Pd^{2+} and the phosphorus atoms on the polymer chain. Similarly, the amino substituted iminocoumarin-containing poly(*N*-sulfonylimine) P**11a** was found to be a fluorescence chemosensor of Ru^{3+} with the quenching constant of 89 200 M^{-1} (Figure 1.2b) [77]. The PL intensity of the nanoaggregates of P**11a** in DMSO/water mixture with 50 vol% water was quenched upon the addition of Ru^{3+} selectively, while the other tested 15 metal ions did not show obvious interference. Several other AIE-active sulfur-containing

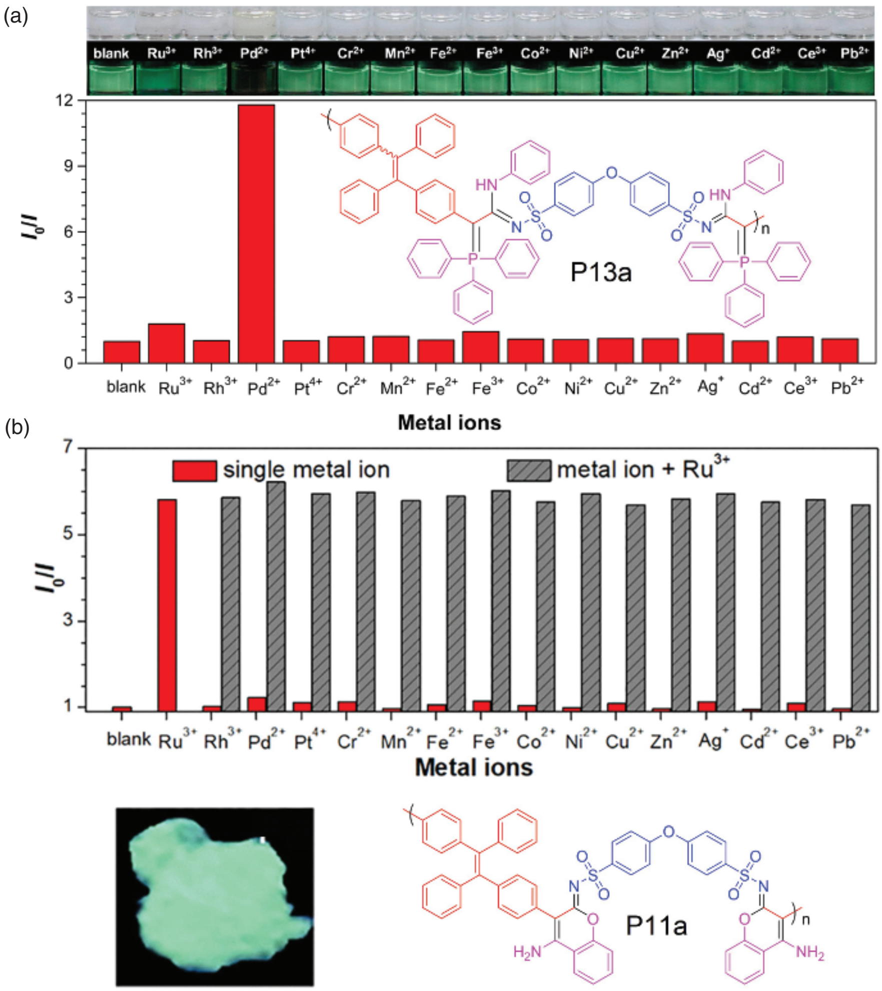


Figure 1.2 (a) Fluorescence Photos of P**13a** in DMSO/water mixtures with 50 vol% water containing different metal ions taken (upper) in daylight and (lower) under UV lamp. Relative intensity (I_0/I) of solution of (a) P**13a** and (b) P**11a** versus different metal ions. I_0 = PL intensity without metal ions. Source: Reproduced from Refs. [77, 79]. Copyright 2017, 2019 American Chemical Society.

MCP polymer products were found to be sensitive and selective fluorescence chemosensors for transition metal ions [88, 90], proving their potential application as efficient chemosensors.

1.5.2 Metal Ion Removal/Enrichment

Besides the detection of existence of metal ions, it is also crucial to remove low concentration toxic metal ions or recover trace amount of precious metal ions from aqueous system. Thanks to the high affinity of sulfur with transition metal ions, the strong coordination between trace amount of metal ions and the sulfur coordination sites in the repeating unit of the sulfur-rich polymers may crosslink the polymer and result in poor solubility of the polymer-metal complexes, which hence precipitated out from the solution to realize removal or enrichment of the trace amount of metal ions.

For example, polythiourea P**5a** prepared from the MCP of sulfur, isocyanide, and amine had shown great potential in mercury detection and removal [58]. Into the Hg^{2+}-containing aqueous solution, when the polythiourea was added, the thiourea groups rapidly coordinated with Hg^{2+} to crosslink the polymers and form insoluble polythiourea-Hg^{2+} complex precipitate, accompanying with the emission quenching of the fluorescent polythiourea (Figure 1.3). The polythioureas could hence be utilized to detect mercury pollution with high sensitivity ($K_{sv} = 224\,900\,M^{-1}$) and high selectivity, clean Hg^{2+} contaminant in the polluted water with high removal efficiency (>99.99%) to achieve drinking water standard from a single treatment, and monitor the real-time mercury removal process by fluorescence change. Both DMF solution and solid powder of P**5a** could efficiently absorb Hg^{2+} from aqueous solution and the latter possessed better performance.

Thioamide was also a well-known ligand for precious metal ions such as Au^{3+}. Similarly, the polythioamide P**4a** prepared from the MCP of sulfur, acid, and amine hence could be used to extract Au^{3+} with superior selectivity among 16 different metal ions, high efficiency (>99.99%), high sensitivity (10 ppb), and high extraction capacity (up to 0.60 g Au^{3+}/g polymer) rapidly (within one minute) (Figure 1.4) [53]. The sulfur atoms on the thioamide groups could coordinate with Au^{3+} in a 2 : 1 ratio to crosslink the polymers and form precipitates in the aqueous solution. Most importantly, the gold enrichment test was carried out directly from the acidic leaching solution of discarded electronic waste with high concentrations of interference metal ions such as Ni^{2+} and Cu^{2+}. The polythioamide could still selectively extract Au^{3+} with a high recovery efficiency of 97%, demonstrating great performance of the polythioamide under practical condition. Moreover, elemental gold with high purity could be facilely recovered by simple pyrolysis of the polythioamide-Au^{3+} complex precipitates from the aqueous solution.

1.5.3 Cell Imaging

The fluorescent sulfonylimine-containing polymer P**15a** could also be applied in cell imaging [80]. The cell staining capability of P**15a** and LysoTracker Red (LTR), a lysosome imaging dye, were investigated in Hela cell, which showed remarkable blue and red fluorescence, respectively, under UV irradiation with the excitation wavelength of 405 nm. By merging two images, the cell staining region were almost completely coincident with Pearson's correlation coefficient of 0.96, indicating good cell staining specificity to lysosomes (Figure 1.5), which may be attributed to the weak alkalinity from amine structure. Besides, P**15a** enjoyed excellent performance in both photobleaching and cell viability tests, suggesting its potential application as lysosome-specific dye in biological imaging.

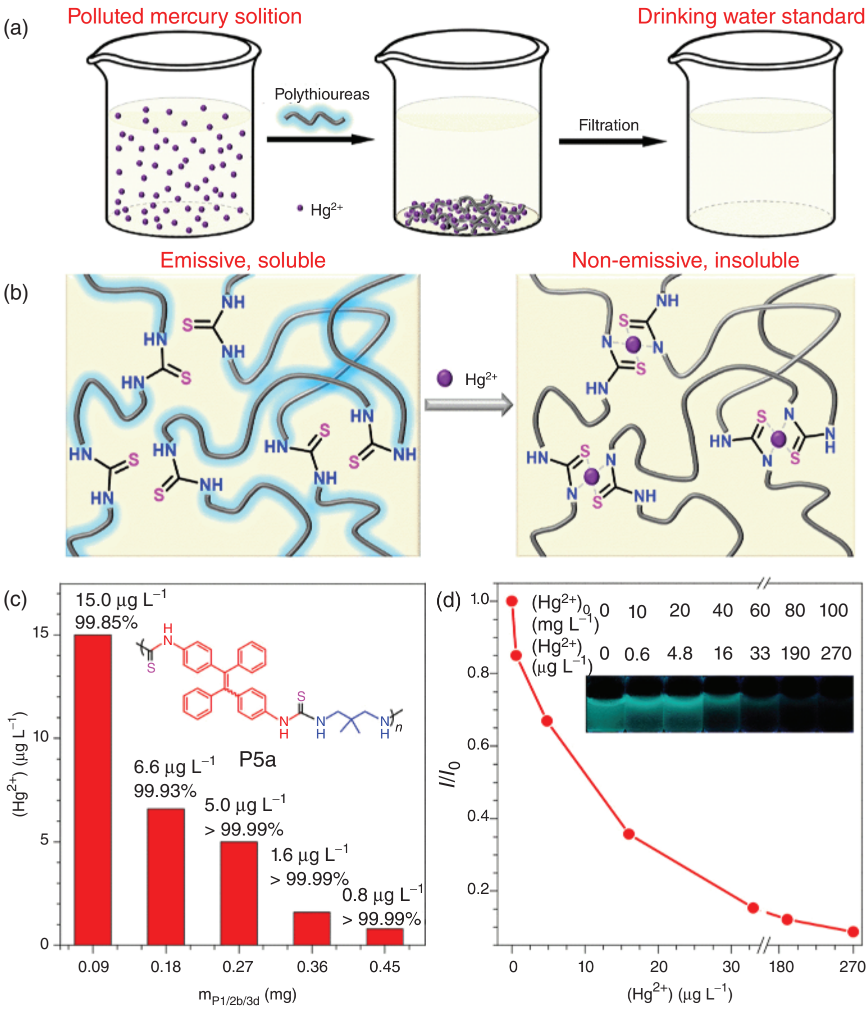


Figure 1.3 (a) Schematic diagram of facile mercury removal process. (b) The proposed mechanism for mercury removal with polythioureas. (c) The mercury removal efficiencies of different amount of P**5a** in DMF solution with 2 mL of Hg^{2+} solution ($[Hg^{2+}]_0 = 10\,mg\,L^{-1}$). (d) The plot of relative emission intensity (I/I_0) versus $[Hg^{2+}]$ when DMF solution of P**5a** ($0.27\,mg\,mL^{-1}$) was mixed with $HgCl_2$ solutions with $[Hg^{2+}]_0$ ranging from 10 to $100\,mg\,L^{-1}$. I_0 = PL intensity in the absence of Hg^{2+}. Inset: fluorescence photographs of the resultant solutions taken upon UV irradiation. Source: Reproduced from Ref. [58]. Copyright 2018 American Chemical Society.

1.6 Conclusion

The various sulfur-containing functional groups such as thioamide, thiourea, sulfonamide, sulfonimine, and thiyl groups have endowed new functionalities to the MCP products, in addition to the classical sulfur-containing polymer materials such

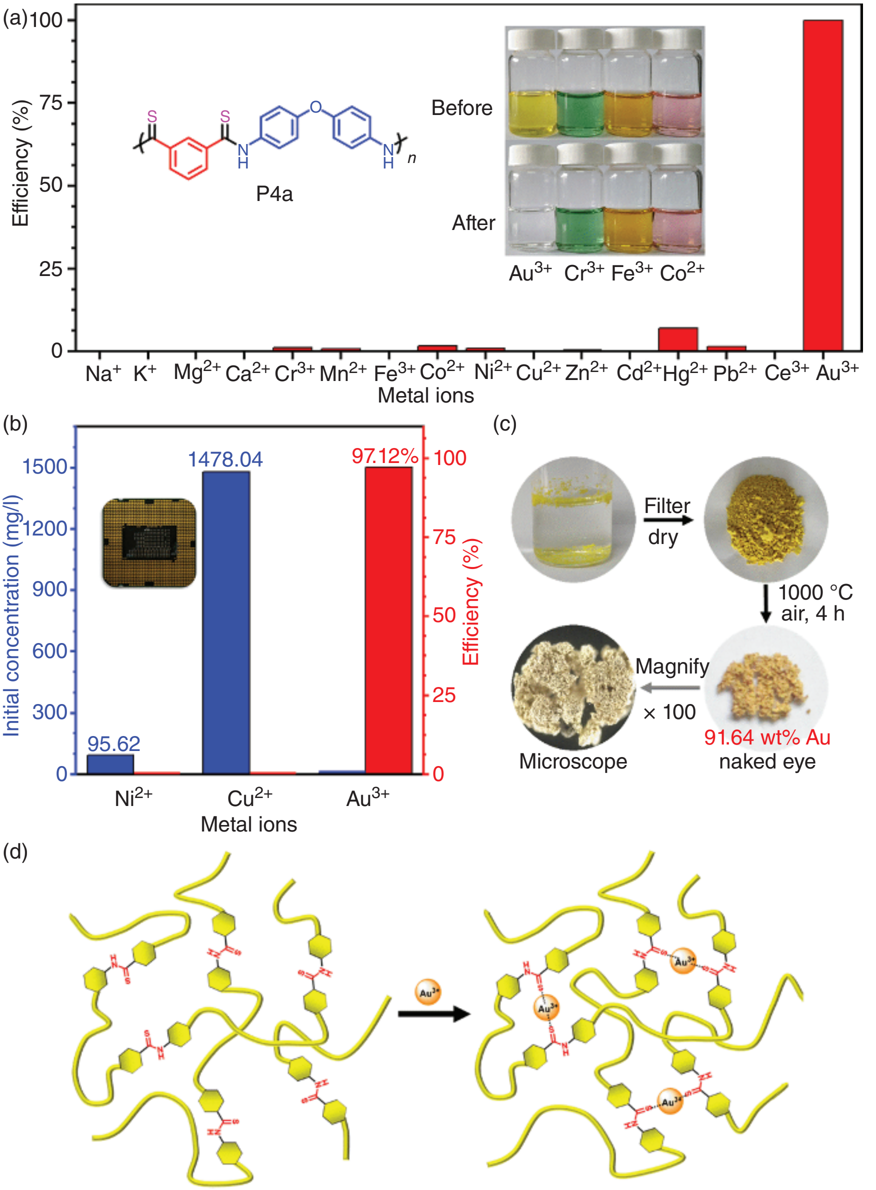


Figure 1.4 (a) Selective enrichment of Au^{3+} by P**4a** in 16 mixed metal ions. (b) The initial concentrations of Au^{3+}, Ni^{2+}, and Cu^{2+} and the selective extraction of Au^{3+} by P**4a** from the leaching solution of a discarded CPU. (c) The gold recovery process with P**4a**. (d) The proposed mechanism for the extraction of Au^{3+} with polythioamides. Source: Reproduced from Ref. [53]. Copyright 2019 American Chemical Society.

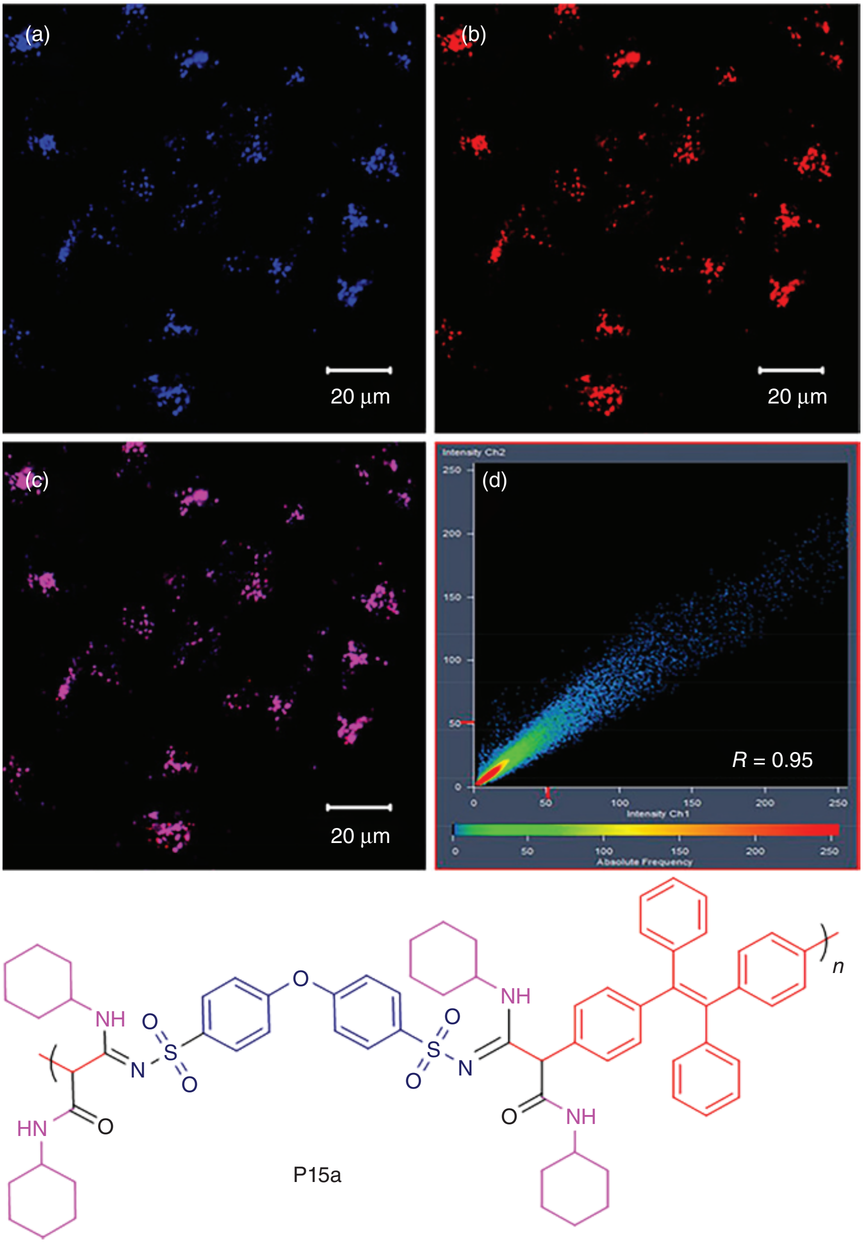


Figure 1.5 Confocal images of HeLa cells stained with (a) P**15a** and (b) LysoTracker Red (LTR). (c) Merged image of panels a and b. (d) Scatter plot indicating an overlap coefficient between the imaging result of P**15a** and LTR (inset: calculated Pearson's correlation coefficient). Source: Reproduced from Ref. [80]. Copyright 2018 American Chemical Society.

as polythiophenes, polythioethers, etc. MCPs prove to be economic, convenient, and efficient powerful synthetic approaches for the preparation of sulfur-containing polymers from economic and readily available monomers, which generally enjoy high efficiency, atom economy, operational simplicity, and wide monomer scope.

Elemental sulfur can be converted to C=S group-containing polythioamides or polythioureas from its catalyst-free MCPs with amines, together with aldehydes, alkynes, benzyl amines, carboxylic acids, or isocyanides; Sulfonyl-containing moieties can be easily introduced into polymer skeleton from the Cu(I)-catalyzed room temperature MCPs of sulfonyl azides, alkynes, and nucleophiles or other monomers, as well as the MCP of sulfonyl hydrazide, alkyne, and diphenyl dichalcogen; MCTP strategy could be used to combine two or more successive highly efficient reactions into a one-pot procedure, and from thiol, or five-membered cyclic dithiocarbonate or thiolactone, regio- and stereoselective or sequence-controlled sulfur-containing polymers could be obtained. It should be mentioned that with the unique feature of MCPs, through different monomer combinations, sulfur-containing polymers with different main chain structures and topological structures can be facilely constructed, and both mainchain and sidechain of the polymer product can be simultaneously tuned, to afford a large library of polymers. Preliminary investigation of their applications in fluorescent chemosensors, heavy metal ion removal or precious metal ion recovery, and bioimaging were conducted, suggesting the great potential of these sulfur-containing polymers. It is anticipated that from the fascinating MCP approaches, a wide range of sulfur-containing polymer materials could be explored to find their practical applications related to environment, health, and materials.

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