



Making the Best of Polymers with Sulfur–Nitrogen Bonds: From Sources to Innovative Materials

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Polymers with sulfur–nitrogen bonds have been underestimated for a long time, although the intrinsic characteristics of these polymers offer a myriad of superior properties (e.g., degradation, flame retardancy, film-forming ability, good solubility in polar solvents, and high refractivity with small chromatic dispersions, among other things) compared to their carbon analogues. The remarkable characteristics of these polymers result from the unique chemical properties of the sulfur–nitrogen bond (e.g., its polar character and the multiple valence states of sulfur), and thus open excellent perspectives for the development of innovative (bio)materials. Accordingly, this review describes the most common chemical approaches toward the efficient synthesis of these ubiquitous polymers possessing diverse sulfur–nitrogen bonds, and furthermore highlights their applications in multiple fields, ranging from biomedicine to energy storage, with the aim of providing an informative perspective on challenges facing the synthesis of sulfur–nitrogen polymers with desirable properties.

1. Introduction


Organo-heteroatom (in particular, nitrogen, sulfur, oxygen) containing functional polymers have received extensive attention for broad applications ranging from areas such as gas storage and separations, to catalysis and energy storage.^[1] On one hand, numerous advances have been made in the last few decades concerning the synthesis of polymers with functional groups containing carbon–nitrogen double bonds (e.g., imines,^[2] hydrazones,^[3] and oximes^[4]). On the other hand, little is known about their sulfur-containing analogues,^[5] regardless the fact that sulfur appears in many different functional groups

due to its versatile reactivity, which in turn also allows to address a widespread array of chemical and physical properties. In fact, literature survey reveals that a large diversity of sulfur–nitrogen bond-containing small organic compounds^[6,7] has reputable status due to the unique chemical properties of the sulfur–nitrogen bond (e.g., its polar character and the multiple valence states of sulfur). While, in the last decades, the rapid advent of diverse polymerization methods has offered polymer scientists a powerful synthetic toolbox for accessing manifold examples of polymers decorated with versatile sulfur functional groups (such as thioethers, disulfides, oligosulfides, thioesters, thiocarbonates, thiourethanes, thioamides, and thioureas amongst others),^[8] macro-

molecules featuring sulfur–nitrogen bond and its derivatives within the backbone are scarcely reported. Exception is the first example of a polymeric metal (i.e., inorganic polymer) that does not include any carbon atoms neither in the backbone nor as pendant units, e.g., polythiazyl (polymeric sulfur nitride (SN)_x), which is composed solely of non-metallic elements (sulfur and nitrogen, respectively).^[9] Regardless of the subjective information, or biases presented, it was deemed that organic polymers consisting primarily of carbon, hydrogen atoms and sulfur–nitrogen functional groups have not been reported, until a decade ago, when Bowden and colleagues postulated the very first synthesis of diverse sulfur–nitrogen containing polymers (e.g., poly(sulfenamides), poly(diaminosulfide), and poly(diaminodisulfide)).^[10,11] As the latter is partly correct, an in-depth literature research surveyed that, indeed, some of these polymers are known since early 1990s, when Visco and coworkers reported the synthesis of miscellaneous poly(diaminosulfide)s that were tested as novel solid redox electrodes.^[12] However, due to the lack of a comprehensive manifest on sulfur–nitrogen polymers, it has been difficult to assess the first pioneering studies, thus leading to biases. To address this problem, it may be instructive to review unbiased, hence, systematically the sporadically developed synthetic methods that pave the way for an efficient synthesis of polymers decorated with diverse sulfur–nitrogen bonds. It is also fundamentally important to understand the distinctive chemical characteristics of these polymers, since these characteristics ultimately dictate the performance of the specified polymers in different fields of application ranging from energy storage to biomedicine. Therefore, the selection of examples within the review are in order to stimulate the reader about what is synthetically possible.^[13] Critically,

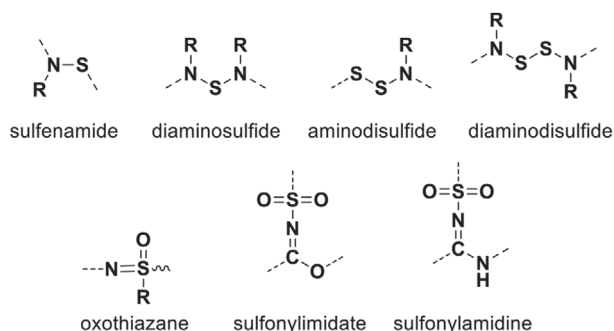
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Scheme 1. Overview of the principal functional groups possessing diverse sulfur–nitrogen bonds.

we make no claim that the list of examples to be completed. Accordingly, to provide context and aid readers who are unfamiliar with polymers with sulfur–nitrogen bonds the first section of the review will cover the state-of-the-art sulfur–nitrogen groups (Scheme 1), structurally classified, and the respective monomers and polymers thereof, as a result of the enormous versatility of the synthetic processes. In the second part of the review, selected examples of high added-value applications, which have hitherto been investigated, and particularly rely on the efficient use of these polymers, will be highlighted. Finally, in order to pursue the interest of scientists for polymers with sulfur–nitrogen bonds, the almost endless choices of feasible synthetic combinations that can be employed to obtain these exquisite materials will be presented.

Importantly, approaches focusing on the equally significant synthesis of the inorganic sulfur–nitrogen (i.e., polythiazyl) and sulfur–nitrogen-phosphorous polymers [i.e., poly(thiophosphazene)s, and poly(thionylphosphazene)s] are omitted. Therefore, the reader is encouraged to refer to the literature,^[14] focusing on the synthesis and applications of these respective polymers.

2. Synthesis of Sulfur–Nitrogen Containing Polymers

In the following section, we revisit the chemical methods utilized for the synthesis of manifold polymers with sulfur–nitrogen bond and its derivatives. From a chemical structural perspective, first, the synthesis of polymers composed of a single S–N moiety per repeating unit is discussed, followed by polymers containing multiple S–N moieties. Further, we disclose the synthesis of sulfur–nitrogen units that may be mono or di-oxidized within the polymer backbone. Correspondingly, some key bottlenecks and challenges will also be discussed.

2.1. Poly(sulfenamide)s

Sulfenamides (i.e., thiohydroxylamines, Scheme 1), from a chemical structural perspective, are compounds containing a single bond of divalent sulfur and trivalent nitrogen (i.e., –S–N–), which homolytically are cleaved to aminyl and thiyl radicals.^[15] Numerous investigations on the chemistry of organic



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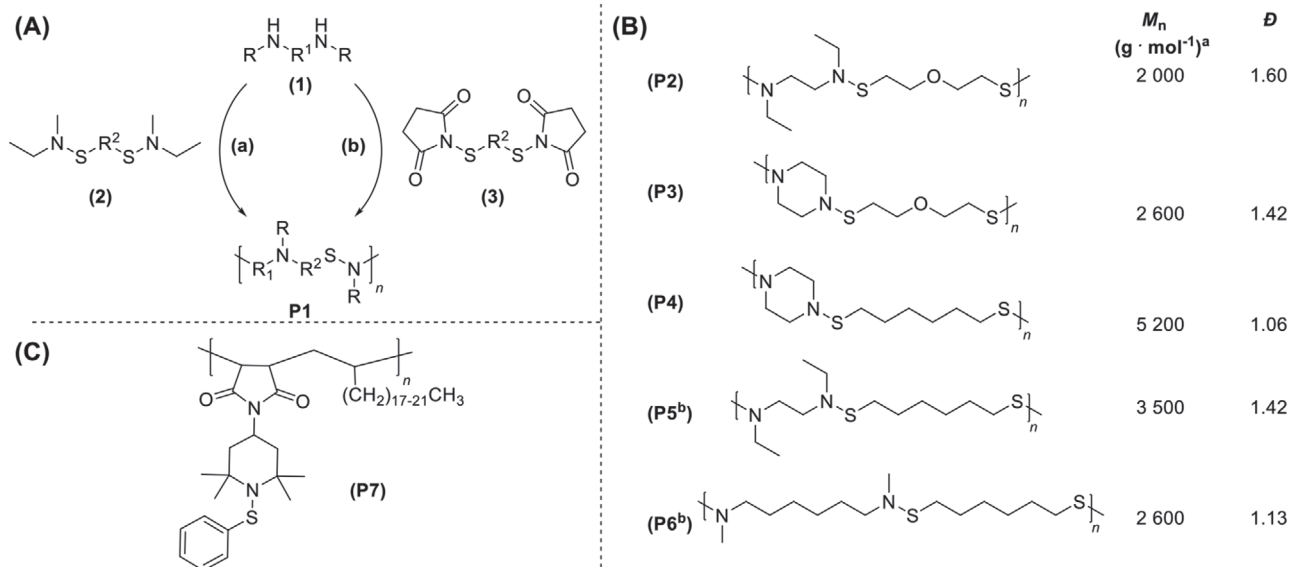


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sulfenamides have been reported up to now. For instance, it was shown that sulfenamide derivatives can undergo nucleophilic substitution reaction on sulfur or nitrogen atom, due to the polarization of the S–N bond. Aside, oxidation can take place either at the sulfur or at the nitrogen atom. In addition, the S–N bond is stable at neutral pH, but can be hydrolyzed in water under acidic conditions.^[16]

A critical drawback for this class of compounds is that their nomenclature is not descriptive, and has not yet been thoroughly systematized. Historically, the term “sulfenamide” referred to a variety of different functional groups such as RSSNR², RSN(R)SR, and R²NSNR. To address this issue, we recommend that a consistent rubric be used to distinguish these functional units, thus, the structure unit depicted in Scheme 1 will be referred as the sulfenamide functional group. According to this nomenclature, the first synthesis of



Scheme 2. A) The synthesis of main-chain poly(sulfenamides) (**P1**) attempted on two different methods (a,b), both of them relying on transamination reaction of diamines with activated dithiol derivatives (**2**) and (**3**), respectively. B) Synthesis of poly(sulfenamides) (**P2**)–(**P6**) from the bench-stable dithiosuccinimides (**3**) by employing method (b); ^aThe absolute M_n and \mathcal{D} were measured with multi-angle laser light scattering and refractive index detectors unless otherwise noted. ^bThe M_n and \mathcal{D} were measured versus polystyrene standards using a calibration curve and the reflective index peaks of the polymer. C) Tentative structures for a side-chain poly(sulfenamide) derivative, i.e., sulfenamide-modified Uvinul 5050H.

this class of small molecules dates back to 1911.^[17] Since then, sulfenamides have been extensively studied as intermediates in organic and peptide synthesis.^[18] Because of their attractive chemical properties, sulfenamides were explored intensively in various industries (such as flame retardants, pharmaceuticals, fungicides and in rubber vulcanization).^[19–21] In fact, some of these properties made sulfenamides very attractive functional groups to pursue the synthesis of macromolecules. According an in-depth literature search, the synthesis of main-chain poly(sulfenamides) was first reported by Bowden and colleagues in 2011.^[10,11] Accordingly, the first two attempts were in terms of two different methods, both of them relying on transamination reaction of diamines with activated dithiol derivatives ((**2**) and (**3**) in **Scheme 2A**, respectively).^[22] To aid the reader, the conventional method of transamination (i.e., amine exchange) for activated thiol compounds is based on the displacement of an amine of relatively weak basicity by another of stronger basicity. The reaction is thermodynamically favorable, and the equilibrium is displaced by removing the amine of weaker basicity from the reaction mixture. Importantly, the volatility of the replaced amine regulates the efficiency of the reaction; in other words, the amine being displaced should be more volatile than the displacing amine. Alternatively, by using an excess of the displacing amine, amines of similar basicity could be also exchanged.

In the first attempt shown in **Scheme 2A** (i.e., (a)), disulfenamide derivatives (**2**) were the choice of activated dithiol derivatives for the transamination reaction of diamine (**1**), while in the second attempt (e.g., (b)), dithiosuccinimides (**3**) were the employed reaction counterparts. The sulfenamides (**2**), used in the former attempt, were synthesized from the reaction of *N*-ethylmethylamine and disulfenylchloride derivatives. The latter compound (**3**), in turn, was generated in situ from the

reaction of the respective dithiol with sulfuryl chloride, SO_2Cl_2 . The disulfenylchloride derivatives were considerably unstable and hard to be isolated, thus making this approach challenging. Once left overnight exposed to air, these molecules generate disulfides. In order to drive the polymerization to completion, the polymerization with method (a) was performed at temperatures above the boiling point of the side product, i.e., *N*-ethylmethylamine (e.g., 37 °C), or even higher reflux temperatures (depending on the solvent used for the polymerization reaction). While, in the second attempt, dithiols were activated with a milder agent, *N*-chlorosuccinimide, to yield the more reactive dithiosuccinimide derivatives (**3**).

The former method (e.g., method (a)) of polymerization was only effective in a polar protic solvent (i.e., methanol), and the kinetics of the polymerization were hindered by the lack of solubility of the formed polymer. Hence, only oligomers were obtained in a low yield with a modest molecular weight ($M_w = 2\,900\text{ g mol}^{-1}$). Noteworthy, the method adopted in the second attempt, i.e., (b), based on the synthesis of poly(sulfenamides) from the bench-stable dithiosuccinimides (**3**) could also proceed in polar aprotic solvent (e.g., methylene chloride or chloroform, 1.2 M) under catalyst-free and considerably mild conditions, i.e., at ambient temperature. By taking advantage of this approach, diverse aliphatic and cycloaliphatic dithiosuccinimides were reacted with three different secondary diamines for 24 h to deliver well-defined poly(sulfenamides) **P2**–**P6** with number-average molecular weights up to 5 200 g mol^{-1} and yields of polymerization that ranged from 90% to 97%, respectively (**Scheme 2B**), with dispersity (\mathcal{D}) values in the range of 1.06–1.60. Since the synthesis of polymers in the presence of primary diamines resulted in cross-linked and insoluble polymers, secondary diamines were preferentially utilized. The mechanism of the polymerization reaction was attributed to

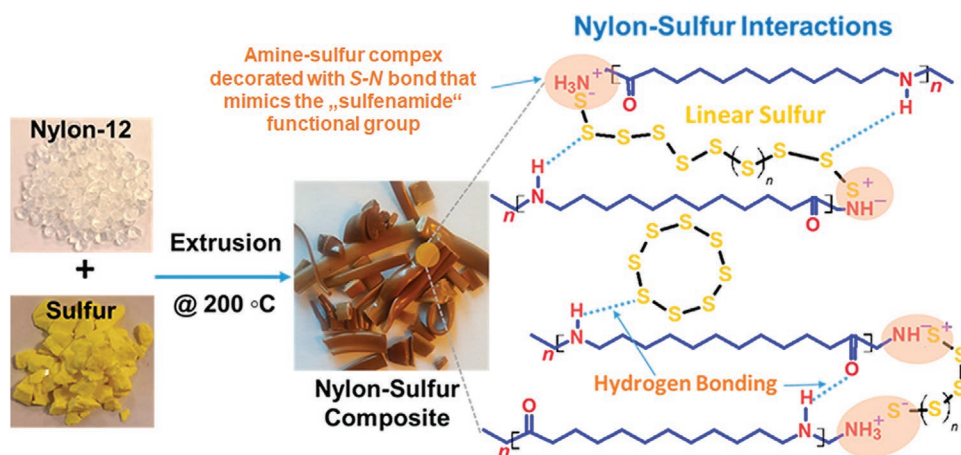


Figure 1. Synthesis of an amine–polysulfur complex decorated with miscellaneous S–N bonds that mimic the sulfenamide functional group via “inverse vulcanization” of linear sulfur chains within a nylon matrix. Reproduced with permission.^[25] Copyright 2020, American Chemical Society.

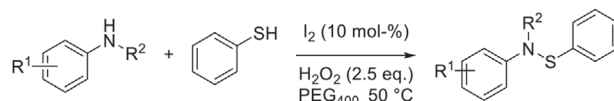
S_N2 reaction pathway. These polymers were stable in most conventional organic solvents, whereas, they readily degraded in water with rate constants that were several orders of magnitude higher than the neutral and acidic degradation of esters.^[23] For instance, slow rates of decomposition were observed under neutral ($k = 4.7 \times 10^{-4} \text{ s}^{-1}$) and basic conditions ($k = 8.0 \times 10^{-5} \text{ s}^{-1}$), while, under acidic conditions it was impossible to measure the decomposition rate, since the degradation was excessively rapid. Aside, NMR studies indicated that $\approx 75\%$ of the degradation product was the thiosulfinate.

Another avenue was undertaken to synthesize polymers decorated with side-chain sulfenamide functional groups. For instance in 2016, Wilen and colleagues, reported on polymers bearing the sulfenamide functionality.^[24] Accordingly, two commercially available polymers, i.e., Uvinul 5050 H ((P7) in Scheme 2C) and Sabostab UV 94, were post-modified with benzenesulfonyl chloride at ambient temperature to yield sulfenamide substituted derivatives.^[19] The unique flame-resistant properties of these materials, which are based on the increased thermal stability as a result of the increased number of substitutions of the nitrogen atom, are further discussed at Section 3.3.

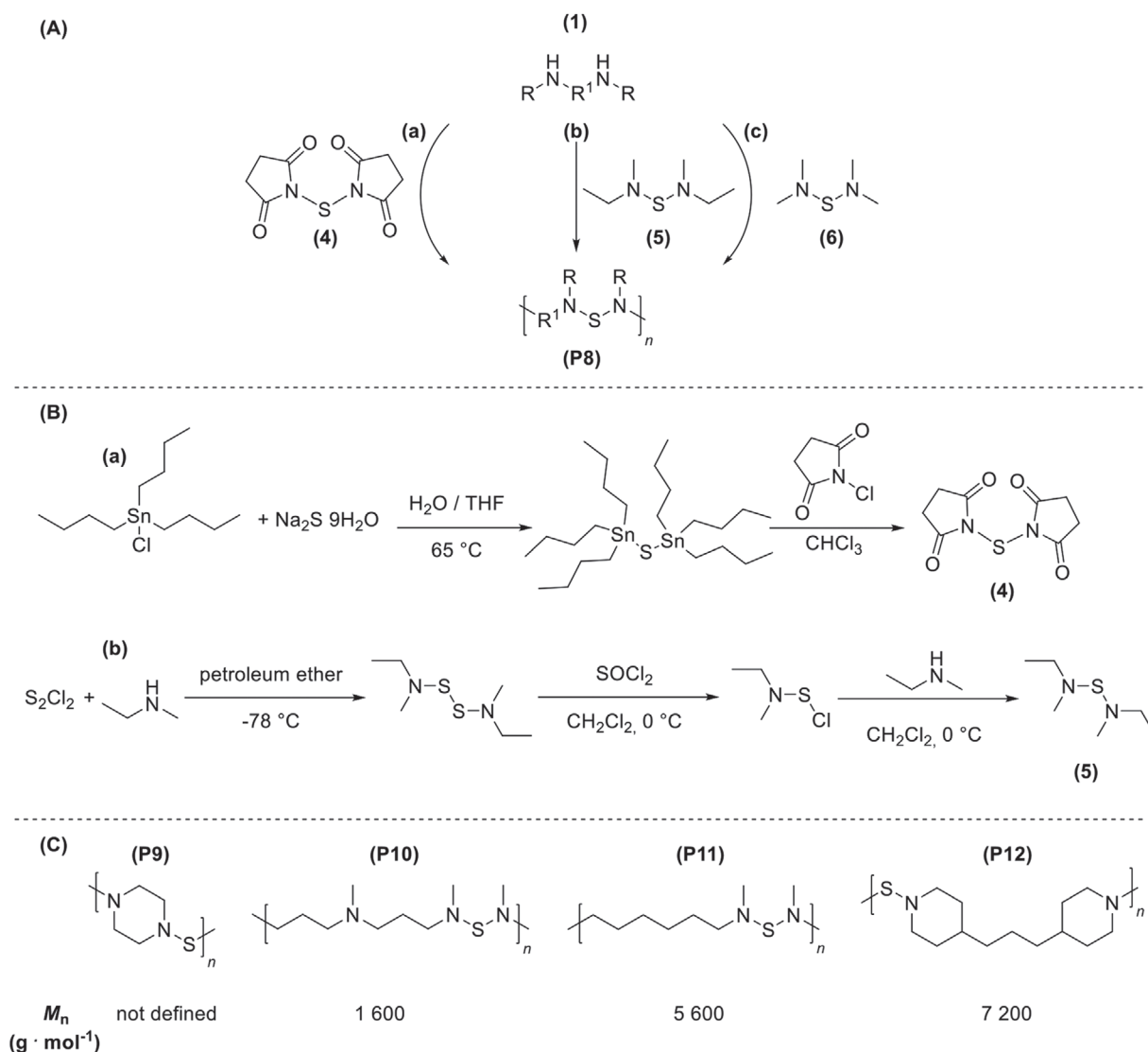
In summary, poly(sulfenamide)s possess a functional group that was previously unknown in polymer chemistry. Nevertheless, this class of polymers presents new opportunities in macromolecular chemistry, as they can add a range of additional properties to the system in question because of the multifunctional attributes arising from the sulfur–nitrogen bond. Hence, there is a clear technological need for exploring new monomers and polymerization methods to improve the synthesis of poly(sulfenamide) derivatives. Very recently, Alhassan and colleagues^[25] employed “inverse vulcanization”^[8,26] to stabilize, linear sulfur chains within an engineered polymer (i.e., nylon) matrix by forming an amine–polysulfur complex, which was decorated with miscellaneous S–N bonds that mimic the sulfenamide functional group (Figure 1). Particularly in order to form the amine–polysulfur complex, polysulfur chains (2.5–30 wt%) produced under extrusion conditions were reacted with the terminal amino groups of Nylon-12 in the molten state (above the melting temperature (T_m) of Nylon-12, i.e., $T_m = 172 \text{ }^\circ\text{C}$). On one hand, the nanocomposites were further processed into films,

molds, and threads without any change in morphology, which was confirmed with *in-depth* morphological characterization via scanning electron microscopy (SEM) and transmission electron microscopy (TEM). On the other hand, the dynamic mechanical and thermal analysis results showed that the glass transition temperature and storage modulus of the nylon–sulfur composites decreased with the increasing sulfur content (T_g , from 58.9 to 50.1 $^\circ\text{C}$, and E' , from 1700 to 1640 MPa). Indeed, the composites possessing 10 wt% of sulfur loading possessed the highest modulus and lowest elongation at break compared to compositions containing higher sulfur concentration. This work, undoubtedly, underpins the potential of using the “inverse vulcanization” to access processable materials in one-step that contain S–N bonds in polymers, as the method can be extended to other thermoplastic polymers and easily scaled up.

Last but not at least, we can evidently emphasize that the present literature survey clearly depicts the numerous organic synthesis methods, which can be adopted as alternative novel methodologies toward this class of polymers. For instance, the metal-free, iodine-catalyzed dehydrocoupling reaction in the presence of hydrogen peroxide has been described as an efficient method for the preparation of sulfenamides from anilines and various thiols in good to excellent yields (Scheme 3).^[27] But what makes the process unique is the fact that the reaction can be performed in a non-toxic reaction medium (i.e., polyethyleneglycol, PEG₄₀₀), and presents high atom economy and wide functional group tolerance at the same time. Hence, this reaction can be considered as a mild, clean, and efficient procedure for the synthesis of a variety of poly(sulfenamide)s. In fact, the employed aniline derivatives are also readily commercially available starting materials.



Scheme 3. The unprecedented iodine-catalyzed N–H/S–H dehydrocoupling reaction of thiophenol and various anilines in the presence of hydrogen peroxide has been described as an efficient method for the preparation of sulfenamides in good-to-excellent yields.



Scheme 4. A) The synthesis of main-chain poly(diaminosulfide)s (**P8**) attempted on two different methods (a) and (b), both of them relying on the reaction of diamines with activated sulfur transfer agents, e.g., (**4**), (**5**) and (**6**), respectively. B) The synthesis of two sets of sulfur transfer reagents: (a) The synthesis of a dithiosuccinimide (**4**); (b) representative synthesis of bisaminosulfide (**5**), which is also applicable for the synthesis of sulfur transfer agent (**6**). C) Synthesis of *N*-*S*-*N* bond polymers, i.e., poly(diaminosulfide)s (**P9**)–(**P12**).

2.2. Poly(diaminosulfide)s

The adoption of unusual functional groups into polymers would not only enhance, but would also impart polymers with new and interesting physicochemical properties. As an on-going challenge in similar manner to sulfenamide, diaminosulfide (i.e., a sulfenamide substituted with a second amine), is still a rather underestimated functional group in the area of macromolecules, although a century has passed since its discovery.^[28] In the early examples, diaminosulfides have been applied in the high-temperature vulcanization of diverse polymers (such as polyethylene)^[29] and as sulfur transfer reagents.^[30] It took more than 90 years until polymer chemists have shown interest in the utilization of diaminosulfides as monomers for the synthesis of diverse polymers. Indeed, Bowden and colleagues were the first to perform pioneering studies on the synthesis of

poly(diaminosulfide), motivated by the chemical properties of this functional group in small molecules. Accordingly, as shown in **Scheme 4A**, poly(diaminosulfide)s (**P8**) were synthesized by reacting secondary diamines with sulfur transfer reagents, e.g., (**4**), (**5**), and (**6**), by using, respectively, methods (a) and (b).^[31] While, most of the employed diamine compounds were commercially available, the challenge in the polymerization was to develop the useful sulfur transfer agents. The first polymerization attempts were considered to be performed in the presence of sulfur dichloride, i.e., SCl_2 , which is quite often used in the synthesis of small molecule diaminosulfides. However, the use of SCl_2 has several drawbacks arising from the fact that this molecule has a low boiling point (59 °C). Further, SCl_2 is challenging to purify, since it should be handled under inert atmospheres, and importantly reacts with several other functional groups such as alcohols and alkenes. Aside, SCl_2 releases the

corrosive gas HCl during its utilization. Therefore, three different sulfur transfer agents were developed in order to pursue an efficient polymerization ((4), (5), and (6) in Scheme 4A).

Since the reactions of *N*-thiosuccinimides with amines are well-recognized in organic synthesis,^[32] in the first attempts, the molecule (4) indicated in approach (a) (Scheme 4A) was explored as a sulfur transfer reagent. The synthesis of molecule (4), (approach (a) in Scheme 4B), was straightforward, however, the purification was challenging since (4) was poorly soluble in most conventional organic solvents (such as, benzene, chloroform, dimethyl sulfoxide and methylene chloride). In similar manner, using *N*-chlorophthalimide instead of *N*-chlorosuccinimide has not resolved the problem with limited solubility of the sulfur transfer agents. Eventually, the sulfur transfer agents (5) and (6), shown in method (b) and (c), Scheme 4A, were applied in the synthesis of the targeted polymer (P8) that structurally resembles polythiazyl derivatives.^[9] The sulfur transfer agent (5), as well (6), can be readily synthesized in two steps, feature significantly good solubility properties ((b) in Scheme 4B) and can be directly utilized in the synthesis of polymers (P9)–(P12), as shown in Scheme 4C. Accordingly, the polymerizations were performed either in benzene or chloroform at the reflux temperatures of the respective solvents for up to 96 h. The isolated polymers were with molecular weight in the range of $1\ 600 < M_n < 7\ 200\ \text{g mol}^{-1}$ ($1.6 < \bar{D} < 3.7$). The polymerization with piperazine yielded an insoluble polymer (P9) in common organic solvents (Scheme 4C), and the polymer synthesized with *N*-methyl-3,3'-bis(methylamino)dipropylamine, i.e., (P10), had limited stability in polar protic solvents (such as, methanol and water) during the isolation process via precipitation. This was mainly attributed to the internal, tertiary amine unit within the polymer backbone that underwent intramolecular reaction with the dithiosulfide repeating unit in the presence of the polar solvents, hence triggering the degradation of the polymer into compounds with an analytically undefined structure. The latter finding was also in agreement with a prior study demonstrating that dithiosulfides reacted in water to form sulfur monoxide, which in turn possessed a half-life of seconds and decomposed into SO₂ and elemental sulfur, respectively.^[33] The experimental results indicated that the dithiosulfide functional group was stable in apolar aprotic solvents, and degraded slowly in polar protic solvents. In contrast, the polymerization reaction performed with 1,6-bis(methylamino)hexane yielded polymer (P11) with moderate molecular weights (M_n of $5\ 600\ \text{g mol}^{-1}$, \bar{D} of 3.4). In similar manner, poly(dithiosulfide) (P12) was synthesized from 1,3-bis(4-piperidyl)propane, as diamine source. (P12) was isolated with a M_n of $7\ 200\ \text{g mol}^{-1}$ ($\bar{D} = 3.3$) in excellent yield (<96%), and the composition was characterized by elemental analysis to confirm the chemical structure shown in Scheme 4C. Accordingly, the calculated weight composition of the repeating unit was C (64.95%), H (10.06%), N (11.65%), and S (13.34%), and the measured weight composition of the polymer was C (64.70%), H (9.97%), N (11.76%), and S (13.44%). This agreement between the calculated and measured elemental compositions for polymer (P12) confirmed that only one sulfur atom anchored to two nitrogen atoms is present in each repeating unit of the polymer. While, the thermal and mechanical properties of these polymers were not investigated, they were not prone to oxidation; in fact, no evidence of

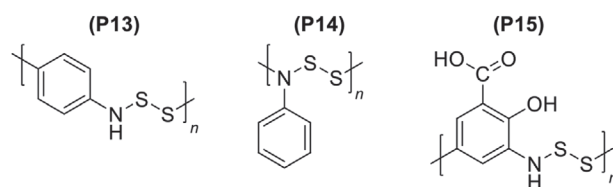
oxidation of the sulfur atoms was reported for the any of the aforementioned polymer samples.

2.3. Poly(aminodisulfide)s and Poly(diaminodisulfide)s

As one of the most intriguing dynamic covalent bonds featuring a simple redox chemistry, the disulfide bond, has a crucial importance not only in biochemistry,^[34] but also in polymer science.^[35] An extensive literature research is pointing out the advantages of the dynamic nature of the single disulfide bridges to explore adaptive self-sorting, self-healing, and degrading properties of various polymer materials in response to diverse stimuli (such as, redox conditions, thiol nucleophiles, heat, or light).^[36] While alkyl/aryl disulfide bonds are widely employed in organic synthesis and polymer chemistry, it is relevant to note that amino- and diaminodisulfide functional groups (Scheme 1, –S–S–N– and –N–S–S–N–, respectively) are very understudied in organic chemistry. In spite of that the study of polymers that contain either amino- or diaminodisulfide bond is still in its infancy, there is continuously growing interest toward the synthesis of these novel polymers. Henceforth, it is essential to emphasize some of the pioneering synthesis studies in sub-chapters focusing on each class separately: e.g., poly(aminodisulfide)s and poly(diaminodisulfide)s.

2.3.1. Poly(aminodisulfide)s

Poly(aminodisulfide)s, also known as poly(aza-disulfide)s are representatives of a rare and extraordinary class sulfur–nitrogen polymers, which were synthesized in early 1970s unprecedentedly by the reaction of aromatic amines (i.e., aniline) with sulfur monochloride (i.e., S₂Cl₂) (Scheme 5, (P13)).^[37] From one particular point of view, there was no evident report on the synthesis of small molecules possessing this unusual sulfur–nitrogen functional group up to 2018.^[38] Since, the construction of aza-disulfides is still a challenging transformation due to the high reactivity of –S–S– bond toward nucleophiles (such as amines). As on the other side, in the early 1970s, the synthesis of thermally stable poly(aminodisulfide)s was reported at considerably mild temperature range ($30 < T < 50\ ^\circ\text{C}$), with the liberation of HCl being the driving force for the reaction. The isolated polymers were crystalline with melting temperatures in the range of $182 < T_m < 189\ ^\circ\text{C}$, and displayed air stability up to 300–350 °C. Intriguingly, they were found to be paramagnetic. In fact, the concentration of the paramagnetic particles was 10^{18} – 10^{20} spin per g with a large electron displacement capacity, therefore these polymers behaved as polyvalent macroradical



Scheme 5. Examples of poly(aminodisulfide) derivatives (P13)–(P15) synthesized from aromatic amines with sulfur monochloride (i.e., S₂Cl₂).

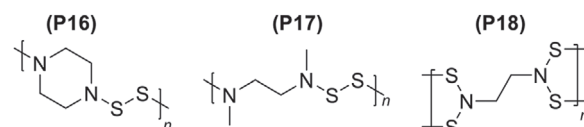
with auxiliary aromatic stabilization effect. As a result, this novel class of polymers was utilized as thermal stabilizers of vulcanized polyethylene by virtue of their excellent physico-chemical properties.^[29]

It took more than 40 years until Bowden and colleagues,^[39] demonstrated that the outcome of the reaction of aniline with S_2Cl_2 could be quite different, if the polymerization is performed in the presence of a base (such as triethylamine, (NEt_3)), at $-78\text{ }^\circ\text{C}$ (Scheme 5, (P14)). From a chemical structural perspective, (P14) with M_w of $4\,300\text{ g mol}^{-1}$ ($\bar{D} = 1.31$) was different in comparison to the one reported by Losev and colleagues, (P13).^[29] In fact, the conjugation of the macromolecular chain was through the inorganic aminodisulfide functional group, whereas the aromatic ring bonded to the nitrogen would allow the conjugation to be altered by varying the presence of functional groups. As a result, (P14) combined conductivity through inorganic functional groups with the ability to alter this conductivity by the presence of organic functional groups.

Another seminal report on the synthesis of poly(aminodisulfide) was based on the polymerization of 5-aminosalicylic acid (5-ASA) in the presence of S_2Cl_2 .^[40] The polymer ((P15) in Scheme 5) with a M_w of $\approx 2\,200\text{ g mol}^{-1}$, corresponding to an average of ten monomeric units, was characterized by UV absorbance spectrometry. Two absorption maximums at 241 and 286 nm with ϵ values of 49 200 and $94\,200\text{ M}^{-1}\text{ cm}^{-1}$, respectively, were in accordance with the UV spectrum of 5-ASA in 10% DMSO, which was also characterized by absorption maxima at 240 and 300 nm with ϵ values of 3 310 and $3\,470\text{ M}^{-1}\text{ cm}^{-1}$. Accordingly, implying the successful incorporation of 5-ASA within the poly(aminodisulfide) (P15).

2.3.2. Poly(diaminodisulfide)s

Generally, diaminodisulfide and its derivatives represented with the formula $R^2R^1N-S-S-NR^1R^2$ possess substantially low bond dissociation energies (for instance, 180 kJ mol^{-1} for the simplest diaminodisulfide $H_2N-S-S-NH_2$)^[41] in reference to diaryl and dialkyl disulfide bonds ($190\text{--}230$ and $250\text{--}290\text{ kJ mol}^{-1}$, respectively).^[42] Nevertheless, in spite of the low bond dissociation energy, molecules possessing disulfidediamine functional group are stable and readily handled at ambient temperature, as a result of the high stability of the respective thiyl radicals that are formed via catalyst free-thermally (or possibly photochemically) induced reversible dissociation. Thus, not surprisingly, diverse disulfidediamine derivatives, with first syntheses dating back to 1895,^[43] have been used as a thermally active crosslinking agents in the vulcanization of rubber, due to the facile homolytic cleavage of its $-S-S-$ bond at temperatures below $200\text{ }^\circ\text{C}$.^[44] The pioneering studies on the synthesis of polymeric diaminodisulfide derivatives (P16)–(P18), depicted in Scheme 6, was reported by Visco and colleagues in 1991.^[12] Diverse primary and secondary amines (such as ethylenediamine, 1,2-dimethylethylenediamine, piperazine, poly(ethyleneimine)) were reacted in the presence of S_2Cl_2 in chloroform (Scheme 6) to deliver polymers with unique redox features, thus as potential dynamic scaffolds. 4-dimethylaminopyridine (DMAP) was used in some particular reactions to scavenge the generated HCl. On one hand, the polymer (P17) synthesized

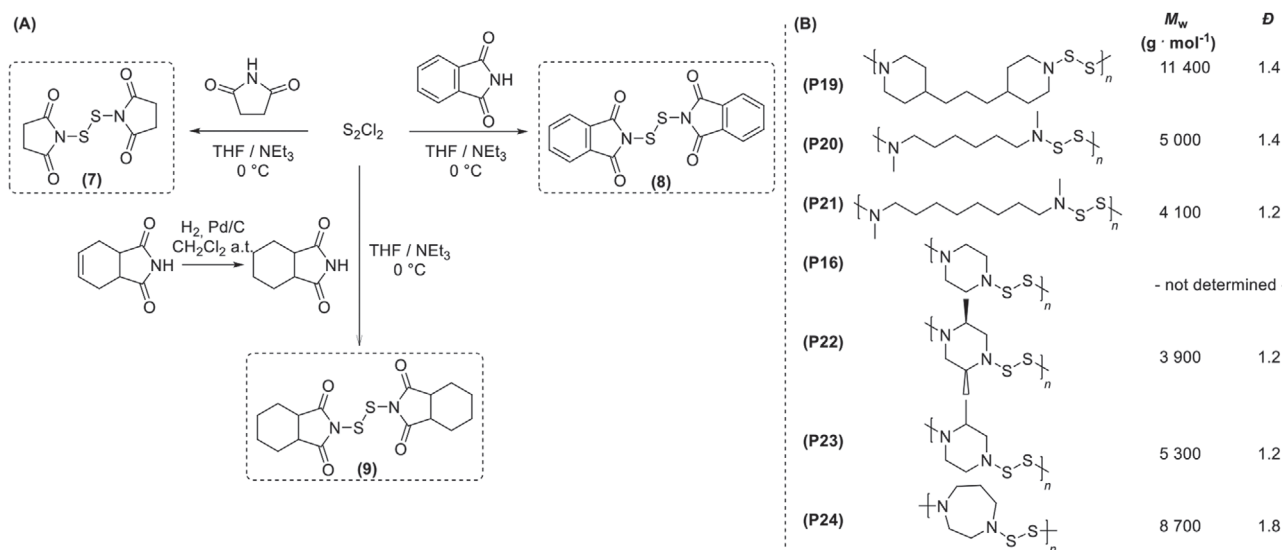


Scheme 6. Poly(diaminodisulfide) derivatives (P16)–(P18) synthesized from aliphatic diamines with sulfur monochloride (i.e., S_2Cl_2).

from ethylenediamine was labile under vacuum; on the contrary, elemental analysis clearly indicated the efficient synthesis of poly(diaminodisulfide)s (P16) starting from piperazine. While, the study failed to provide any complementary characterization of the reported poly(diaminodisulfide)s (P16)–(P18), crucially, it was disclosed that for the efficient synthesis of poly(diaminodisulfide)s, it is important wherever the diamine monomer is primary or secondary.

The first report dealing with the in-depth characterization of this class polymers was reported in 2012, in which polymerization reactions were based on the utilization of three different disulfidediamine transfer agents (e.g., dithiobiscinimide, dithiobisphthalimide and dithiobiscyclohexanedicarboximide, respectively, (7), (8), and (9) in Scheme 7A) as monomers.^[39] Whereas, the synthesis of (7) was straightforward, its purification was tedious, due to its limited solubility in common organic solvents, with an upper limit for solubility of 50 mg mL^{-1} in dichloromethane. Furthermore, the synthesis was accompanied by side products that were challenging to remove. Transfer agent (8) was synthesized in good yield and high purity, however, its solubility was more limited than (7), which in turn would hinder its usefulness in step-growth polymerizations. Eventually, dithiobiscyclohexanedicarboximide (9), a novel disulfur monomer, was developed, as shown in Scheme 7, and readily obtained by crystallization up to $>20\text{ g}$ without any limitation. The only drawback of this compound was that 18% of it decomposed in CD_3OD within 5 h.

Nevertheless, a library of different poly(diaminodisulfide)s (P16), (P19)–(P24) in Scheme 7B, respectively, were synthesized with moderate molecular weights ($3\,900 < M_w < 11\,400\text{ g mol}^{-1}$, $1.2 < \bar{D} < 1.8$). The polymerizations were performed in dichloromethane at ambient atmospheric conditions for 24 h with dithiobiscyclohexanedicarboximide (9), as the disulfide transfer agent monomer, and diverse secondary diamine derivatives. In similar manner to poly(sulfenamides), the dispersity, \bar{D} , values were lower than expected for step polymerizations for several possible reasons. For instance, polymers may have been fractionated in the isolation steps resulting in a loss of some low molecular weight polymer. In addition, the authors postulated that the choice of columns for the SEC analysis was not optimized for polymers with these molecular weights. Elemental analysis was attained to the polymer derived from N,N' -dimethyl-1,6-hexanediamine, (P20), in order to provide further evidence for the presence of disulfidediamine functional groups. The theoretical mass percentages (C, 57.3%; N, 10.3%; S, 23.5%; H, 8.8%) for the repeat unit closely matched the measured values, e.g., C, 55.3%; N, 9.7%; S, 23.1%; H, 8.5%. Thus, the analyzed elements accounted for 97% of the initial mass of the sample. The thermogravimetric analysis of (P20) revealed thermal stability at elevated temperatures, but with a sudden weight loss at $175\text{ }^\circ\text{C}$.

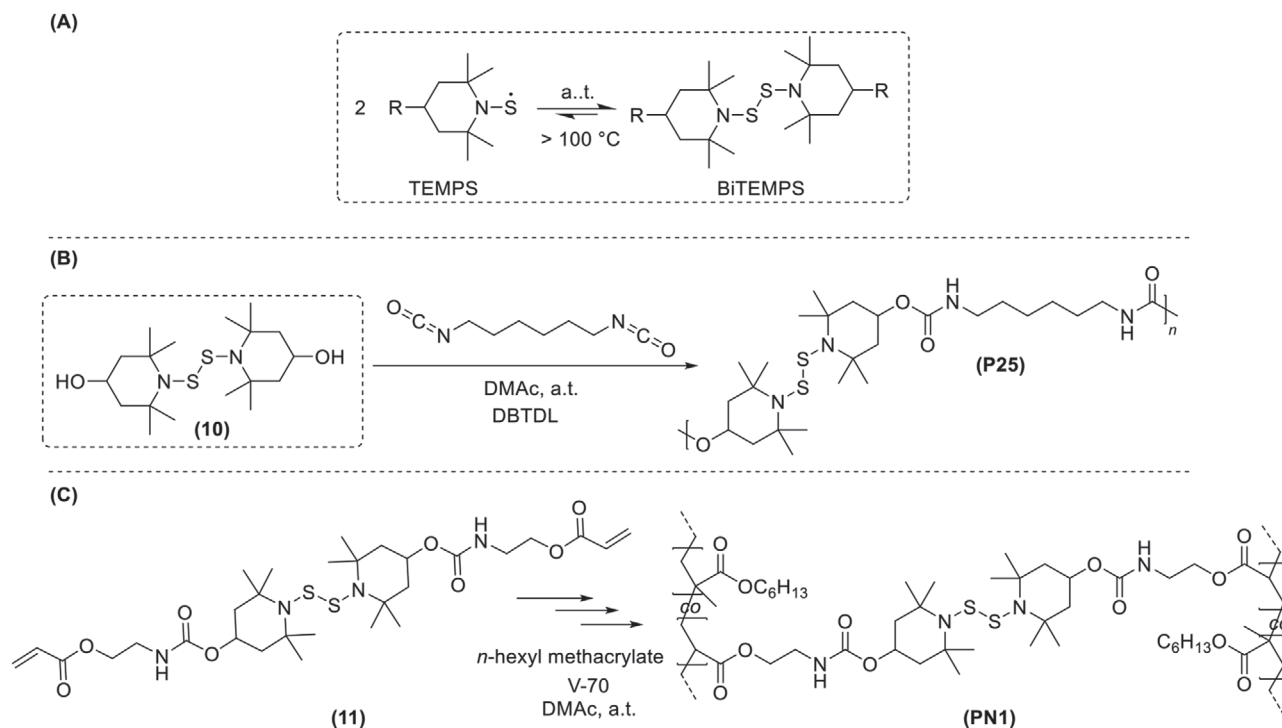


Scheme 7. A) The synthesis of three different disulfidediamine transfer agents (e.g., dithiobissuccinimide, dithiobisphthalimide and dithiobiscyclohexanedicarboximide, respectively, **(7)**, **(8)**, and **(9)**), further applied for the synthesis of poly(disulfidediamine). B) Poly(diaminodisulfide) derivatives (**P16**) and (**P19**)–(**P24**) synthesized from secondary aliphatic diamines with dithiobiscyclohexanedicarboximide (**9**) as the disulfide transfer agent monomer.

In a recent study, Otsuka and colleagues,^[45] enriched the toolbox of the monomers applicable for the synthesis of poly(diaminodisulfide)s by developing 2,2,6,6-tetramethylpiperidine-1-sulfanyl (TEMPS) dimers (e.g., BiTEMPS) as a new class of dynamic disulfide linkages. Furthermore, they demonstrated the utility of BiTEMPS as a functional component in linear and network polymer systems (**Scheme 8A**). While, the dimer derivatives of TEMPS were first reported by Bennett and coworkers in 1967^[46] to be thermally and reversibly dissociable under moderate heating, it took almost 50 years until BiTEMPS derivatives were recognized as dynamic constituents in various polymeric systems, by virtue of their unique redox features. Accordingly, bis(4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl) disulfide (BiTEMPS-OH, **(10)** in **Scheme 8B**) was designed as a versatile unit that can be easily modified at its OH groups to create a broad library of derivatives. Interestingly, the starting BiTEMPS-OH compound, which was successfully synthesized in 3 steps from commercially available compounds on a multi-gram scale, possessed sufficient air stability that in turn permits its facile use in atmospheric conditions and study its dynamic reactions without needing to exclude oxygen.

Respectively, polymer (**P25**) with M_n of $14\,900 \text{ g mol}^{-1}$ and unimodal molecular weight distribution ($\bar{D} = 1.8$) was first synthesized from BiTEMPS-OH and hexamethylene diisocyanate (HDI) using di-*n*-butyltin dilaurate (DBTDL) as the catalyst (**Scheme 8B**). Since, each repeating unit was tethered by the dynamic BiTEMPS linkage, the molecular weight of the polymer was thermally tunable through the exchange reaction according to the solution concentration without special care. Evaluation of the SEC data of a 0.5 wt% 1,4-dioxane solution of the polymer at $100 \text{ }^\circ\text{C}$ demonstrated a rapid shift of the original peak to the lower molecular weight region in 10 min, followed by gradual fragmentation, and subsequent degradation. SEC measurements showed a restoration of the polymer with the peak-top molecular weight $M_{\text{peak top}}$ of $25\,200 \text{ g mol}^{-1}$ (original: $27\,700 \text{ g mol}^{-1}$), once the degraded solution was concentrated to 10 wt% and then heated at $100 \text{ }^\circ\text{C}$.

In an additional experiment,^[47] the authors showed the a poly(hexyl methacrylate) network with BiTEMPS crosslinkers (**Scheme 8C**) exhibits outstanding healing and reprocessing properties. The BiTEMPS-containing poly(hexyl methacrylate) P(HMA-co-BTA) networks (**PN1** in **Scheme 8C**) were synthesized via the facile free-radical polymerizations using a BiTEMPS-containing cross-linker (**11**). The polymerization was carried out at temperatures $<30 \text{ }^\circ\text{C}$ in the presence of the low-temperature radical initiator V-70 to prevent the homolytic dissociation of BiTEMPS, which afforded a gel that is insoluble in common organic solvents. The chemical structures of these colorless, insoluble polymer network films, were easily characterized by de-cross-linking experiments via bond-exchange reactions with external low molecular-weight BiTEMPS compounds. Furthermore, a thermogravimetric analysis revealed comparable thermal decomposition temperatures ($275 < T_{d,5\%} < 315 \text{ }^\circ\text{C}$) for all networks, despite the differences in bond dissociation energy, which indicates that the incorporation of BiTEMPS moieties did not affect the thermal stability of the obtained materials in the temperature range examined. Swelling experiments and stress-relaxation measurements confirmed the readily inducible chain-exchanging properties based on the dissociation of BiTEMPS upon moderate heating ($120\text{--}140 \text{ }^\circ\text{C}$). External catalysts and special care to exclude atmospheric moisture or oxygen were not required, due to the high stability of the TEMPS radical mediators, which endows these network polymers with on-demand healability and reprocessability properties in the bulk. Furthermore, during the preparation of the this manuscript, another outstanding work of the same group was reported.^[48] Accordingly, BiTEMPS derivatives were employed as dynamic covalent bond (DCB) constituents within conditionally compatible two crosslinked polymeric systems (CLP), one decorated with DCB (BiTEMPS-MA, thus B-CLP in **Figure 2**) and the other one with conventional covalent bonds (PHBA-MA, thus C-CLP), to test their respective fusion, and therefore, reprocessing and recycling capabilities at the interface between the different CLPs. In



Scheme 8. A) Characteristic thermal and reversible dissociation of BiTEMPS dimers to TEMPS under moderate heating. B) Synthesis of BiTEMPS-incorporated linear polyurethane derivative (**P25**) from BiTEMPS-OH and hexamethylene diisocyanate (HDI) using di-*n*-butyltin dilaurate (DBTDL) as the catalyst. C) Synthesis of BiTEMPS-cross-linked poly(methacrylate) network (**PN1**) via the facile free-radical polymerization of hexyl methacrylate using a BiTEMPS-containing cross-linker (**11**), which endows these network polymers with on-demand healability and reprocessability properties in the bulk.

order to allow for the systematic study of the expected fusion behavior, two different vinyl monomers were utilized, e.g., hexyl methacrylate (HMA) and ethyl methacrylate (EMA), as HMA furnishes a typical elastic polymer, poly(HMA) (T_g of 6 °C), and EMA affords a typical plastic polymer, poly(EMA) (T_g of 92 °C). After applying the optimum fusion conditions, i.e., powdered CLPs were mixed [CLPpolyHMA/CLPpolyEMA = 2/1 (w/w)] and the mixed powder was placed in a mold and hot-pressed (120 °C, 6 MPa, 24 h), the samples were analyzed by swelling test and differential scanning calorimetry (DSC) measurement. The respective data demonstrated that two distinct CLPs were fused at the molecular level in bulk. Critically, the T_g values were independent of the mixing ratios, which showed that the fusion of the CLPs was limited to the interface, albeit that the profound interaction via the topological and chemical bonds

was sufficient to generate a self-standing film. By varying the mixing feed ratio of the two CLPs, the mechanical properties of the resulting fused samples could be also systematically tuned. For instance, with increasing feed ratio of EMA content, which induced plastic properties, the Young's modulus and fracture stress of the fused system increased, while the fracture strain decreased.

2.4. Poly(oxothiazene)s

Poly(oxothiazene)s, also regarded as poly(oxosulfur nitride)s, are class of polymers based on a backbone of alternating sulfur (VI) and nitrogen atoms with one variable and one "anchored" (oxygen) substituent on each sulfur atom, on which respectively

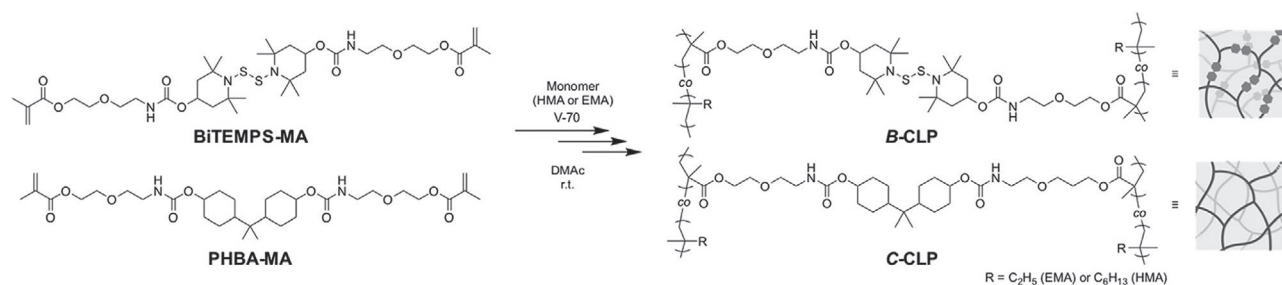
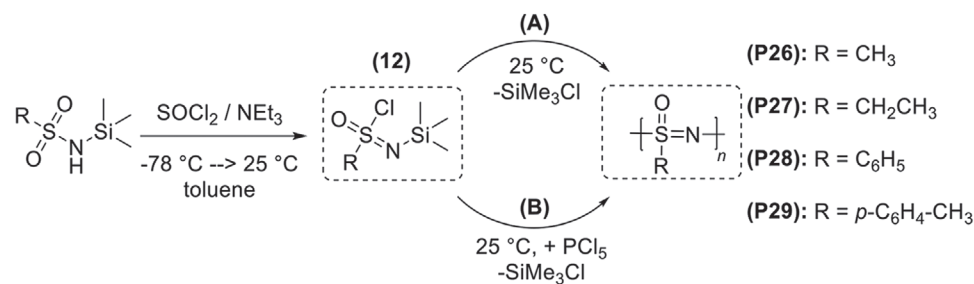


Figure 2. Synthesis of CLPs that contain BiTEMPS (B-CLPs) and of control CLPs with conventional covalent bonds (C-CLPs). Reproduced with permission.^[48] Copyright 2020, Wiley-VCH.



Scheme 9. Preparation of *N*-silylsulfonimidoyl chloride derivatives (**12**) and their in situ polymerization to deliver polymers (**P26**)–(**P29**).

also an alkyl or aryl group are tethered. Indeed, those polymers (**(P26)**–(**P29**) in **Scheme 9**), which were quite “hot” topic in 1960s, nowadays are considered as another less explored class of polymers decorated with sulfur–nitrogen bond within the main chain. Intriguingly, their chemical structures are presumably analogous to the industrially important polyphosphazenes.^[49] However, only a very limited number of well-characterized poly(oxothiazenes) have been described in the literature.^[50,51] As aforementioned, in the 1960s, poly(fluorooxothiazenes) and poly(aminoxothiazenes) had been reported as the products formed by the condensation of O–SF₄ with ammonia.^[52,53] In similar manner, poly(phenyloxothiazene) was reported to be synthesized from the condensation of either phenyl benzenesulfonimide or *N,N*-dimethylarenesulfonimidamides with arenesulfonyl chlorides.^[54,55] Clearly, little characterization data were provided to support the suggested polymer architectures in either of these cases. Only the solubility properties in solvents of high polarity, such as dimethyl sulfoxide (DMSO) or *N,N*-dimethylformamide (DMF) were mentioned. Aside, thermal characterization has revealed that *T*_g decreased as alkyl substituents increased in size; although considered unusual, it was postulated that this trend was analogous to the alkoxy phosphazenes. It took more than 30 years, until the first well-characterized examples were synthesized by the thermal condensation (e.g., 120–170 °C) of *N*-silylsulfonimidates (**(12)** in **Scheme 9**). Those polymerization attempts were in analogy to the synthesis of poly(phosphazene)s that is based on the phosphoranimine route.^[56] The reactions were performed either under catalyst-free conditions or catalyzed by Lewis acids and bases (e.g., BF₃Et₂O, AlCl₃, fluoride ion, and phenoxide ion), the elimination of trimethyl silyl ether being the driving force for the polymerizations. Alternatively, “silyl-free” sulfonimidates were employed as monomers. Since the elimination products were simple alcohol derivatives (such as methanol) with considerably low boiling temperatures, in comparison to the trimethyl silyl ethers, thus the reaction temperatures were lowered with 20–40 °C (i.e., 85–120 °C). Importantly, the rate of the polymerization was approximately two orders of magnitude faster, and resulting in polymers with relatively high molecular weight (6000 < *M*_n < 230000 g mol⁻¹). Complementary spectroscopic characterization (e.g., SEC or NMR data) methods were attained to prove the purity of the obtained products. Noteworthy, thermal characterization via DSC demonstrated that no clear melting transition has been observed with any of the polymers, which is in line with the polymers being essentially atactic. As a bottleneck, the above-mentioned methods faced several limitations, such as long reactions times (>96 h)

at high reaction temperatures (up to 160 °C) under catalyst-free conditions compared to reactions in the presence of Lewis acids catalysts, in which the reaction temperature was set to ≈120 °C. Furthermore, a lack of molecular weight control was another limitation, hence occasionally polymers with bimodal molecular weight distribution and high dispersity, i.e., *D* up to 21, were isolated.

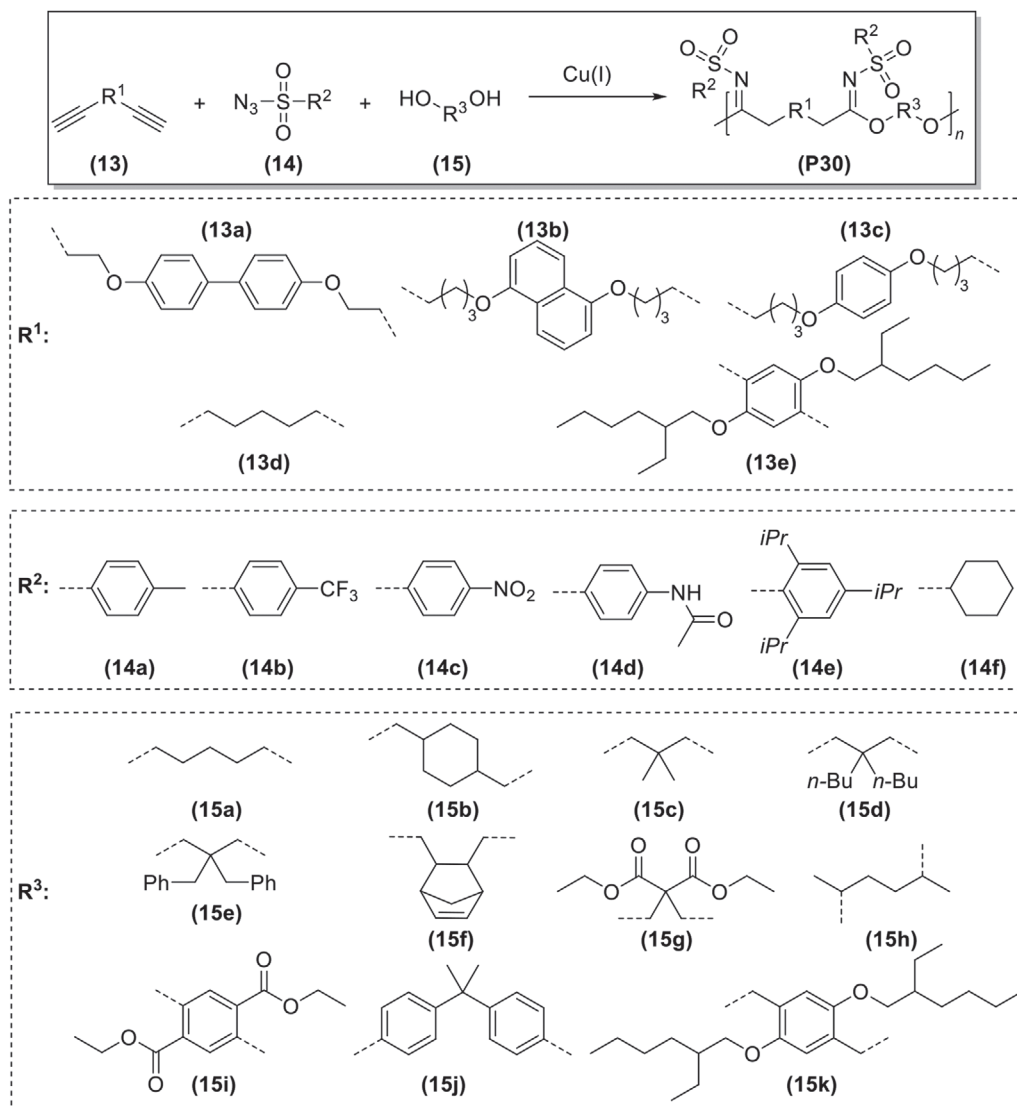
To address those limitations, an in situ Lewis acid (e.g., PCl₅) catalyzed polycondensation of *N*-silylsulfonimidoyl chlorides (**(12)**) was postulated as a potential novel reaction pathway (**Scheme 9**, methods **(A)** and **(B)**).^[57] This method was conducted at ambient temperature, and macromolecules (**(P26)**–(**P29**) of high molecular weight and low *D* values (10000 < *M*_w < 30000 g mol⁻¹, and 1.2 < *D* < 1.6) were isolated, accompanied by the formation of the condensation byproduct, Me₃SiCl. Interestingly, the properties of the poly(oxothiazene)s prepared by this method differed markedly compared to the materials prepared from the polycondensation reactions based on *N*-silylsulfonimidates or silyl-free analogues. In other words, the polymers prepared by the latter developed method possessed good solubility in both polar and apolar solvents, with unique thermal behavior. DSC analysis of the resulting materials revealed differences in the properties of the polymers formed at ambient temperature in comparison to those synthesized previously at elevated temperatures. For instance, on one hand, in the case of methyl substituted poly(oxothiazene), (**(P26)**), the observed *T*_g (41 °C) was significantly lower than the corresponding material formed at reactions performed at elevated temperatures, i.e., *T*_g = 55–65 °C. In similar manner, replacing the methyl group with aromatic side chains resulted (e.g., (**P28**)) also in a decrease of 20–30 °C in the *T*_g. It was possible that this difference reflected a variation in the tacticity of the polymers formed by the two different methods, which would result in different packing effects in the two materials. Aside, the differences in *T*_g could be attributed to the differences in the molecular weight distributions that arise from the different synthetic approaches. On the other hand, in stark contrast, *T*_g values for the ethyl substituted poly(oxothiazene) derivative (**(P27)**), formed by the two different methods, were in the similar temperature range, i.e., 29–33 °C.

2.5. Poly(sulfonylimidate)s

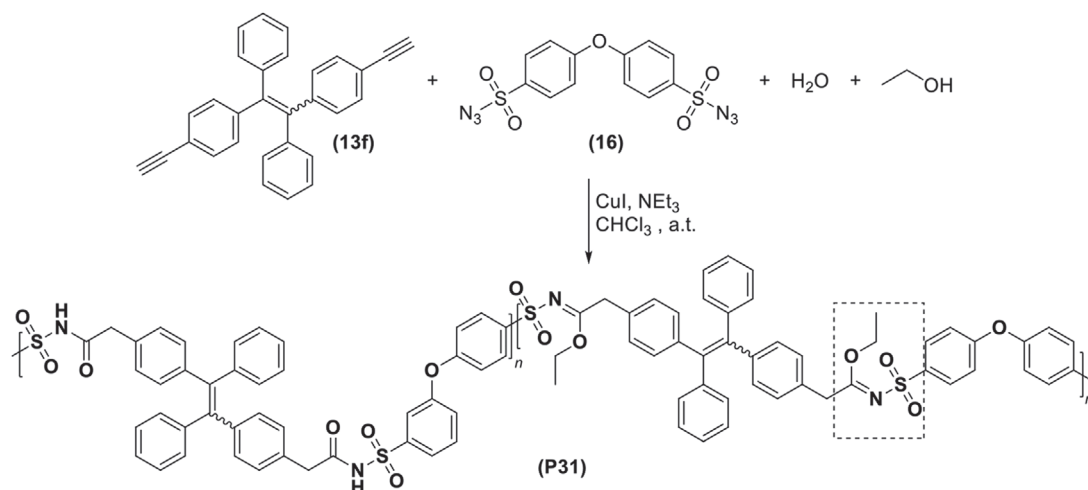
The synthesis of sulfonylimidates,^[58] i.e., sulfur analogues of imidates,^[59] gained considerable interest since they find spread applications as important pharmacophores, potential

bioactive compounds possessing sulfur–nitrogen bonds.^[60] In addition, sulfonylimidates have the potential to be useful as prodrug.^[61] In similar manner, sulfonylimidates have been also recognized as useful synthetic building blocks by virtue of their potent nucleophilicity, in similar way as esters.^[62] Thus, sulfonylimidate formation has been often viewed as a way to activate the otherwise relatively inert or unreactive amide equivalents.^[63] Recently, polymer chemists have devoted great efforts on developing methods to prepare poly(sulfonylimidate)s, given the wide existence of sulfonylimidate derivatives in synthetic chemistry. Generally, the synthesis of conventional poly(imidate)s is limited to two-component step-growth polymerizations using diols and moisture-sensitive imidoyl chlorides,^[64] since the imidate formation itself is quite challenging. On the contrary, the pioneering studies on the preparation of poly(sulfonylimidate)s are based on the copper (I) catalyzed multicomponent reaction of diynes (**13**), sulfonyl azides (**14**), and diols (**15**) (Scheme 10).^[65]

Multicomponent polymerizations (MCPs)^[66] based on multicomponent reactions have been recognized as a highly efficient process for making complex polymer structures by using orthogonally reactive monomers. MCPs display a series of advantages such as high efficiency, mild reaction conditions, atom economy, and operational simplicity, and thus are representing a powerful novel and efficient approach for the preparation of functional polymers. Accordingly, Choi and coworkers^[65] synthesized a library of 24 different poly(sulfonylimidate)s (depicted with the general chemical structure of (**P30**)) with moderate to high molecular weights ($9500 < M_w < 33\,500 \text{ g mol}^{-1}$, $1.43 < \bar{D} < 2.98$). The MCPs of readily available and bench stable monomers (e.g., diynes, sulfonyl azides, and diols) (Scheme 10) were performed at ambient temperature in the presence of 10.0 mol% CuI, as catalyst, and NEt₃, as accelerator, for 48 h in order to reach high polymerization yields. Minimizing water contamination was key to achieving the successful MCP of poly(sulfonylimidate)s.



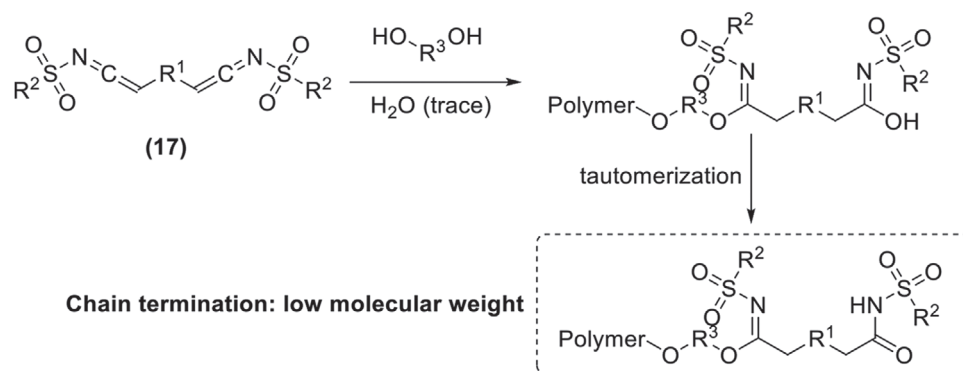
Scheme 10. Facile synthesis of poly(sulfonylimidate)s, e.g., (**P30**), based on the copper(I)-catalyzed multicomponent reaction of diynes (**13**), sulfonyl azides (**14**), and diols (**15**).



Scheme 11. One-pot, four-component polymerizations using diene (13f), disulfonyl azide (16), water, and ethanol as reactants to synthesize poly(sulfonylimidate) (P31).

Therefore, hygroscopic polar aprotic solvents (such as DMSO and DMF) were omitted, and dry chlorinated solvents (e.g., chloroform and dichloromethane), were found to be the best solvents for the synthesis of the targeted polymers. Rigid diynes or diols as monomers resulted in polymers with higher molecular weight compared to the flexible monomers, presumably because of the suppression of intramolecular cyclization. Whereas, the structures of the arylsulfonyl azides (14) did not have a significant effect on the MCP. Interestingly, phenolic diol monomers (e.g., (15i)-(15k)) with weak nucleophilicity were also suitable to be polymerized. Last but not at least, it is important to emphasize that the obtained polymers generally had high thermal stability with decomposition temperatures ranging from 233 °C to 307 °C.

Attracted by this pioneering example, Tang and colleagues,^[67] explored the feasibility of employing the above-mentioned MCP reaction for polymer synthesis in the presence of water as co-reactant (Scheme 11). Even though it was reported that even a small amount of water contamination is inevitably limiting the efficiency of the reaction, since water reacts with the electrophilic keteneimine intermediate, which in turn terminates the polycondensation by forming *N*-sulfonylamide (Scheme 12).



Scheme 12. Cu(I)-catalyzed multicomponent polymerization in the presence of trace amounts of water resulting in side reaction, i.e., chain termination, due to the fact that water reacts with the electrophilic keteneimine intermediate (17) to terminate the polycondensation by forming the *N*-sulfonylamide derivative.

polymerization. While, the optimum catalyst concentration was not playing a crucial role, the solvent exerted a strong effect on the reaction. In the former case, for instance, polymers with M_w value of 16 500 and 13 900 g mol^{-1} were obtained in the presence of 0.02 and 0.03 M of catalyst, respectively. While for the latter case, precipitation took place during the polymerization in THF, and gels were formed in 1,4-dioxane. Eventually, the polymerization proceeded with high efficiency in chlorinated solvents, chloroform and dichloromethane. The ratio of amide to sulfonylimidate units in the polymer was also readily modulated by controlling the feed ratio of water to ethanol, which was proven by detailed characterization via X-ray crystallography, fluorescence microscopy along standard spectroscopic techniques. Moreover, the obtained polymers showed a feature of aggregation-induced emission (AIE), since they emitted more intensely in the aggregate state than in the solution state due to presence of AIE-active moieties in the polymer chain. Importantly, since the adopted MCP fulfils some of the crucial requirements of “green chemistry,” such as high efficiency, good atom economy, simple operation, cheap monomers as well as high oxygen and moisture tolerance, this approach is meeting the requirements of “green chemistry.”

Encouraged by the above-mentioned fruitful achievements, Tang and colleagues,^[69,70] expanded the toolbox of Cu(I) catalyzed cycloaddition reactions between alkynes and sulfonyl azides toward the synthesis of fused heterocyclic polymers with advanced functionalities. Commercially available salicylic aldehyde (**18a**) or *ortho*-hydroxyacetophenone (**18b**) was reacted with diynes (**13**) and disulfonyl azide (**16**) in the presence of CuI and NEt_3 under nitrogen environment at ambient temperature to generate poly(sulfonylimidate)s (**P32**) integrated with fused heterocyclic unit of iminocoumarins (**Scheme 13**).^[69]

On the basis of the preliminary polymerization attempts with salicylic aldehyde (**18a**), DMAc was the most suitable solvent for high-efficiency compared to different common organic solvents, including tetrahydrofuran (THF), chloroform (CHCl_3) and DMSO. Following, the seminal work, polymers with the highest M_w and yield were obtained, i.e., 42 400 g mol^{-1} , and 91%, respectively. In similar way, the best polymerization result

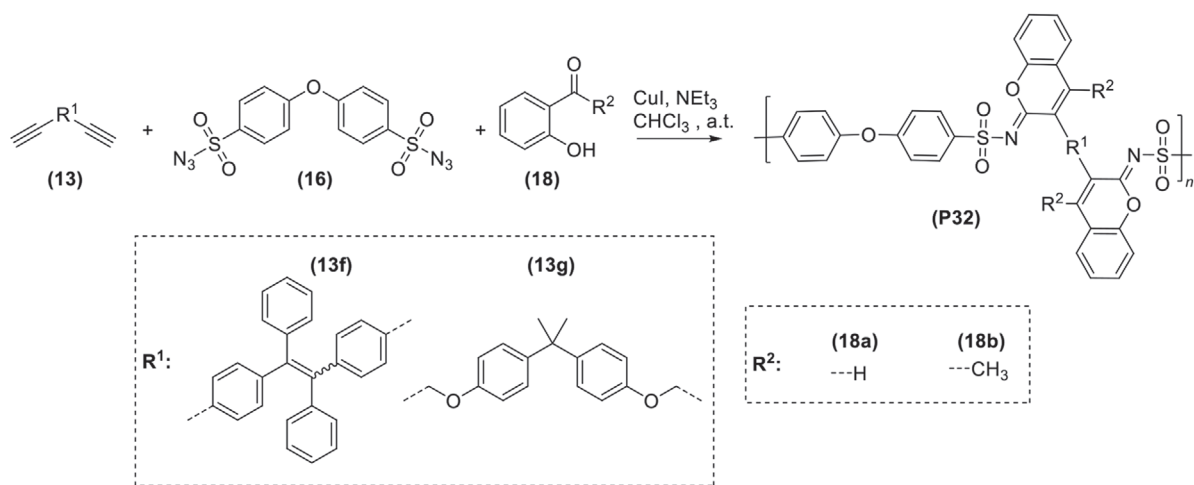
with M_w of 64 600 g mol^{-1} in 91% yield was achieved with a monomer concentration of $(\mathbf{13}) = (\mathbf{16}) = 0.40 \text{ M}$ and optimal feed ratio of $(\mathbf{13})/(\mathbf{16})/(\mathbf{18a}) = 1 : 1 : 2.2$, respectively. While, a polymer with M_w of 49 400 g mol^{-1} was obtained within 0.5 h, prolonging the reaction time to 1 h resulted in M_w of 64 600 g mol^{-1} . On the contrary, further extending the reaction time (i.e., more than 1 h) didn't have any crucial impact neither on the M_w nor the yield of the polymerization.

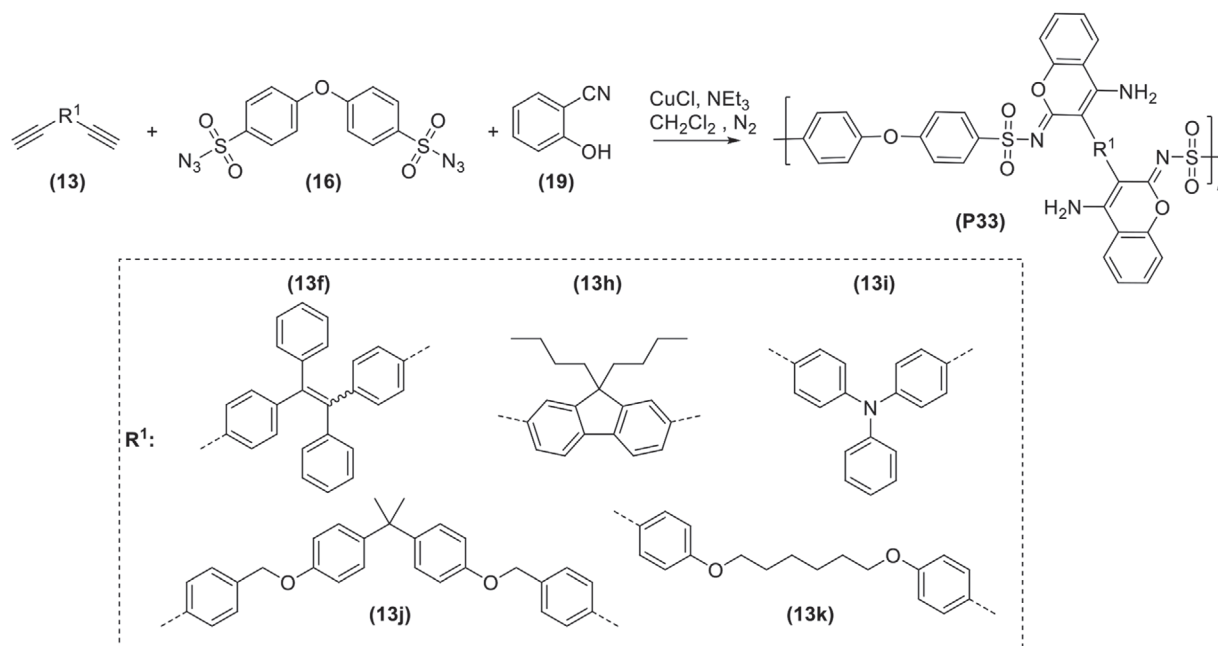
Replacing salicylic aldehyde by *ortho*-hydroxyacetophenone, (**18b**) in Scheme 13, under the optimized conditions, rapid gel formation was observed. In order to prevent the gel formation, and yield soluble macromolecules, the concentration of $(\mathbf{13}) = (\mathbf{16})$ was adjusted to 0.05 M with the constant feed ratio of monomers, i.e., $(\mathbf{13})/(\mathbf{16})/(\mathbf{18b}) = 1 : 1 : 2.2$, respectively. Thus, the broad applicability of this powerful and efficient polymerization was manifested by obtaining polymer with M_w of 50 200 g mol^{-1} .

Remarkably, the resulting polymers exhibited satisfactory morphological stability and outstanding film-forming ability along high thermal stability ($286 < T_{d,5\%} < 341 \text{ }^\circ\text{C}$, and $135 < T_g < 230 \text{ }^\circ\text{C}$). The polymer films also possessed outstanding refractive indices (1.9284–1.7734) in the visible and near-IR regions (400–893 nm), as a result of the highly polarized conjugated polymeric structures. Given the fact that abundant photosensitive groups were embedded in the polymer chain, the refractive index (n) values of polymer films were also easily modulated by UV treatment. For instance, the n values dropped to 1.6604–1.5849 from initial 1.9284–1.7734 with a decrease of 0.1282 at 632.8 nm after 15 min treatment with UV light, thus demonstrating proficient refractivity tunability.

In another effort, 2-hydroxybenzonitrile (**19**)^[70] was reacted with diynes (**13**) and disulfonyl azides (**16**) in the presence of CuCl and NEt_3 , as catalysts to generate iminocoumarin-containing poly(sulfonylimidate)s (**P33**) in **Scheme 14** with weight-average molecular weight (M_w) varying from 13 900 to 37 700 g mol^{-1} with unimodal distribution ($1.47 < D < 2.85$), and high yields (up to 96%).

On the contrary to the previous work, the best polymerization results were achieved with monomer concentration of





Scheme 14. Synthesis of fused heterocycle-containing (i.e., iminocoumarin) poly(sulfonylimidate) derivatives (**P33**) from 2-hydroxybenzonitrile (**19**) that were reacted with diynes (**13**) and disulfonyl azides (**16**) in the presence of CuCl and NEt₃.

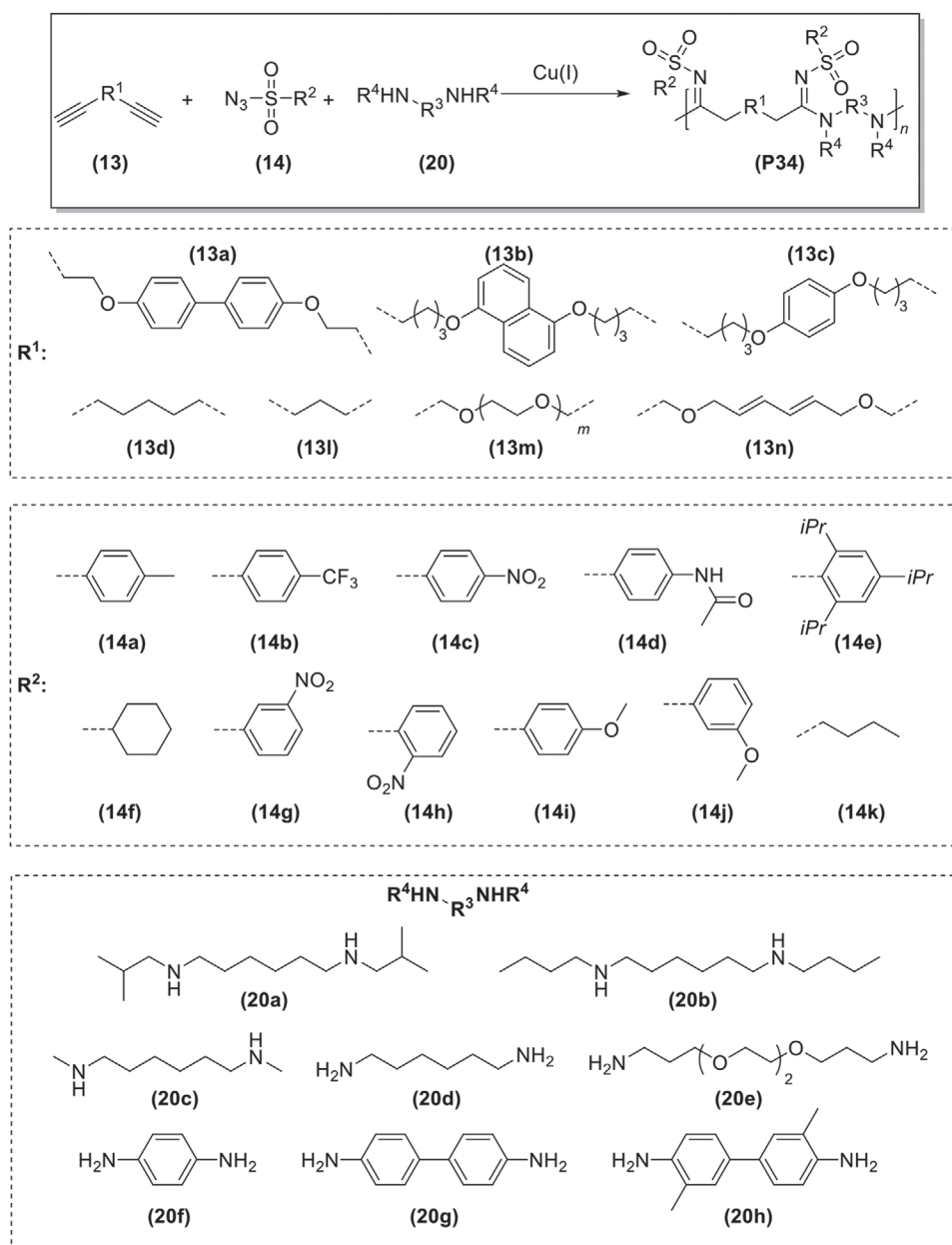
(**13**) = (**16**) = 0.05 M and optimal feed ratio of (**13**)/(**16**)/(**19**) = 1 : 1 : 2.5, respectively, at 40 °C in dichloromethane within 90 min. The presence of abundant and multiple types of intermolecular noncovalent interactions including hydrogen bonds and π - π stacking interactions in the macromolecules with high values of M_w , resulted in insoluble gel formation at higher monomer concentration (<0.05 M), longer polymerization time (<90 min), or higher polymerization temperature (<40 °C). Nonetheless, despite of the rigid conjugated fragments and hydrogen bonds, the poly(sulfonylimidate) (**P33**) exhibited satisfactory solubility in polar organic solvents such as DMSO and DMF. Furthermore, the high thermal stability of this class of polymers, with decomposition temperatures (T_d) at 5% weight loss ranging from 272 to 344 °C, was attained by thermogravimetric analysis.

2.6. Poly(sulfonylamidines)

Amidine functional group is known for its polar, structurally rigid, and hydrogen-bond-rich moiety. Further, in similar way to imidates,^[71] amidines are recognized as useful synthons to assemble complex molecules, and also as one of the most widely exploited moieties in medicinal chemistry. Alongside, recent research focus tends to favor the emergence of sulfonylamidines as bioactive pharmacophores, as numerous new synthetic methods have been developed to access these functional moieties. Given the fact that the carbon analogues, i.e., poly(amidine)s,^[72] have attracted great attention by virtue of their potential role as biomaterials, metallic conductors, and photo-sensitive semiconductors, along the endeavor to develop chemically diverse polymers possessing sulfur–nitrogen bonds tailored the synthesis of poly(sulfonylamidine)s. Accordingly, the three-component polymerization of diynes (**13**), sulfonyl azides (**14**),

and diamines (**20**) was explored by Choi and coworkers^[73] as first attempt to deliver 26 well-defined, defect-free high-molecular-weight poly(sulfonylamidine) derivatives ($4700 < M_n < 23\,500 \text{ g mol}^{-1}$ with $1.50 < D < 5.92$) with the generic chemical structure (**P34**). A toolbox of 26 different monomers [possessing diverse moieties such as alkyl, aryl, diene, and poly(ethylene glycol)] was utilized to demonstrate the broad substrate spectrum of this methodology (**Scheme 15**). Based on a series of optimizations, it was shown that the addition of excess NEt₃ (5 eq.) in the presence of CuCl as catalyst, and the use of DMF as a solvent were key factors to ensure efficient MCP. In similar manner, the stoichiometric ratio of the diyne (**13**) and the diamine (**20**) was also crucial, with monomer concentration of 1.0 M. Furthermore, excess of sulfonyl azide derivative (**14**) (3 equivalents) was essential in order to increase the conversion without limiting the molecular weight of the resulting poly(sulfonylamidine). Regardless of the structure, a broad scope of monomers including alkylsulfonyl azides, various aromatic sulfonyl azides containing electron-donating groups (–OMe, –NHCOMe), electron-withdrawing groups (–CF₃, –NO₂), or a sterically hindered group (–iPr) at various positions on the aromatic ring, were successfully employed in the MCP. Importantly, high reaction temperatures, i.e., 70 °C, ensured high conversion of the polymerization reaction. Critically, the polymerization suffered of side reactions such as the formation of cyclic poly(amidines), which was reduced by incorporating long or rigid moieties into the diyne (**13**) or diamine (**20**) monomer.

Inspired by the successful preparation of a library of poly(sulfonylamidine)s from diynes, sulfonyl azides, and diamines through Cu(I) catalyzed MCP, Tang^[74] and colleagues extended the MCP from diamines to monomer with asymmetric center (i.e., amino ester) as depicted in **Scheme 16**. Accordingly, this was the first report on the versatile preparation of chiral

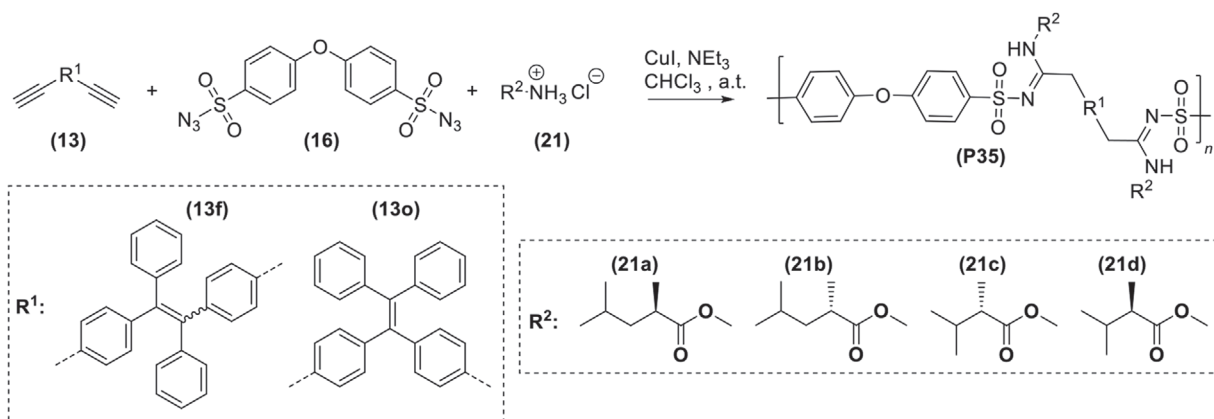


Scheme 15. One-pot facile synthesis of poly(sulfonylamidine) derivatives, e.g., (P34), based on the copper(I)-catalyzed multicomponent reaction of diynes (13), sulfonyl azides (14), and diamines (20).

poly(sulfonylamidines) (P35) by Cu(I) catalyzed MCP from various diynes (13), disulfonyl azides (16), and amino esters (21) (such as *L*-leucine methyl ester hydrochloride, *D*-leucine methyl ester hydrochloride, *L*-valine methyl ester hydrochloride, and *L*-alanine methyl ester hydrochloride).

CHCl₃ was identified as the most suitable solvent for the polymerization, which was performed at ambient temperature within 24 h. Thus, soluble polymer with the highest $M_n = 15400 \text{ g mol}^{-1}$ and in the highest yield (79%) was isolated under the following conditions: monomer concentration of (13) = (16) = 0.20 M and optimal feed ratio of (13)/(16)/(21) = 1 : 1 : 2.4, respectively, in the presence of 20 mol% CuI and 0.40 M NEt₃. Further diluting the concentration of diyne to 0.10 M or even 0.05 M at a constant

monomer ratio, produced polymers with good solubility, albeit in diminished isolated yields (61–70%) and molecular weights (M_n of $\approx 8000 \text{ g mol}^{-1}$). On the contrary, insoluble gels were formed quantitatively when the polymerization was carried out at a relatively high monomer concentration of 0.60 M for diyne, i.e., (13). In general, the polymerization reaction was very efficient with loadings of 20 mol% CuI, and could be performed in short reaction time (e.g., 6 h) to result in high molecular weight polymers (M_n of $\approx 13000 \text{ g mol}^{-1}$) with unimodal distribution (\mathcal{D} of 1.8) in favorable yields. Critically, reducing the CuI amount dramatically decreased the efficiency of the polymerization reaction. For instance, in the presence of 10 mol% CuI, a polymer with M_n of 6100 g mol^{-1} (\mathcal{D} of 1.7) was obtained.



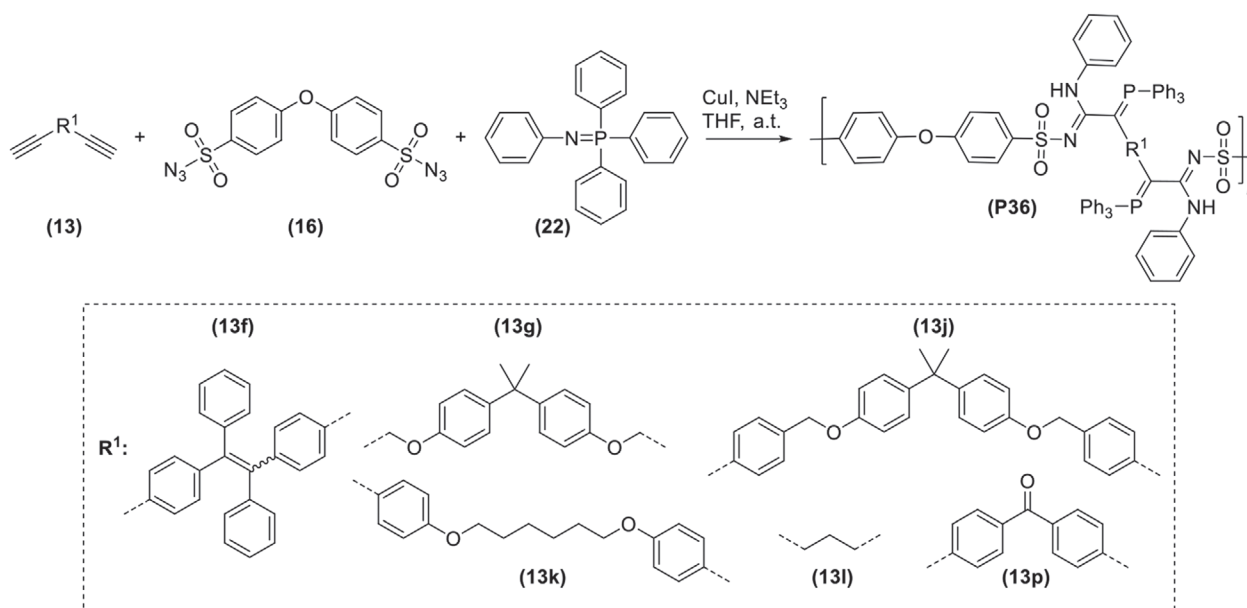
Scheme 16. Multicomponent polymerization of various diynes (**13**), disulfonyl azides (**16**), and amino esters (**21**) to obtain helical and luminescent polymer derivatives (**P35**).

Despite the highly aromatic backbone, interestingly, all the polymers possessed excellent solubility in common organic solvents. Accordingly, most of the polymers could be readily fabricated into uniform thin films by the spin-coating technique. Unfortunately, compared to their oxygen counter partners, i.e., poly(sulfonylimidate)s, the poly(sulfonylamidine) derivatives demonstrated lower thermal stability with 5% weight losses at temperature (T_d) ranging from 244 to 293 °C under nitrogen.

Nevertheless, circular dichroism (CD) signals associated with the positive Cotton effect, centered at ≈ 287 nm, were observed in the absorption region of the polymer backbones, indicating the chirality of the amino ester pendant was transferred to the polymer backbone. The thin films of these polymers possess high refractive index (n) values (1.72327–1.6419) in a wide wavelength region of 400–893 nm and low chromic dispersions (D down to 0.0247). Complementary, the sulfonyl and ester groups incorporated into the skeleton of the poly(sulfonylamidine)s

endowed these polymers with photosensitivity, which in turn enabled them to be fabricated into fluorescent photopatterns through the photolithography process. In fact, two-dimensional photoresist patterns with high resolution and sharp edges were observed under a fluorescence microscope.

In order to expand the toolbox toward the synthesis of poly(sulfonylamidine)s, the group of Tang intensively explored new reactant partners for the ketenimines (the intermediate product formed from the reaction of alkynes and sulfonyl azides), and has recently proposed a new reactant for the Cu(I) MCP, i.e., the commercially available iminophosphorane, e.g., (**22**).^[75] In fact, iminophosphorane is a reactant with bipolar nature whose MCR with alkyne and sulfonyl azide can generate unique poly(sulfonylamidine)s (**P36**), decorated with phosphorous moieties, under mild reaction conditions (**Scheme 17**). The best polymerization results were obtained when the MCP was carried out under nitrogen atmosphere in polar solvent



Scheme 17. Multicomponent polymerizations of alkynes, sulfonyl azides, and iminophosphorane (**22**) toward heteroatom-rich multifunctional poly(sulfonylamidine)s (**P36**).

(i.e., THF) at ambient temperature for 12 h in the presence of CuI (0.02 M) and NEt₃ (0.20 M). The monomer concentration was fixed at 0.1 M for feeding ratio of (13)/(16)/(22) = 1:1:2.5. In general, under these optimized polymerization conditions, a wide monomer scope including aromatic and aliphatic alkynes could be employed in the MCP together with aromatic sulfonyl azides and iminophosphorane, in order to generate polymers (with the generic chemical structure (P36)) with good to excellent yields of up to 92% and 14400 < M_w < 85600 g mol⁻¹ (1.58 < Đ < 3.16).

The polymer structures were characterized through the comparison of the conventional spectroscopic techniques such as IR as well as ¹H, ¹³C, and ³¹P NMR spectra of the monomers, model compounds, and the polymers. In similar manner, thermogravimetric analysis revealed satisfactory thermal stability (i.e., T_{d, 5%} ranging from 219–237 °C under nitrogen). The abundant heteroatoms and polarizable aromatic rings of these poly(sulfonylamidine)s endowed them not only with high *n* value in the range of 1.6287–1.8145, but also with a series of properties such as good solubility in polar solvents and good film-forming ability.

Attracted by the straightforward construction of quino-line structures via the MCRs of alkynes, sulfonyl azides, and 2-aminobenzonitrile (23),^[76] Tang and coworkers developed the efficient MCP of diynes, disulfonyl azides, and 2-aminobenzonitrile (22) to furnish aminoquinoline-containing poly(sulfonylamidine) derivative (P37). Under optimum conditions, a high molecular weight polymer (M_w of 32800 g mol⁻¹, Đ < 2.13) with reasonable high polymerization yield (82%) was isolated in 30 min (Scheme 18A).^[70]

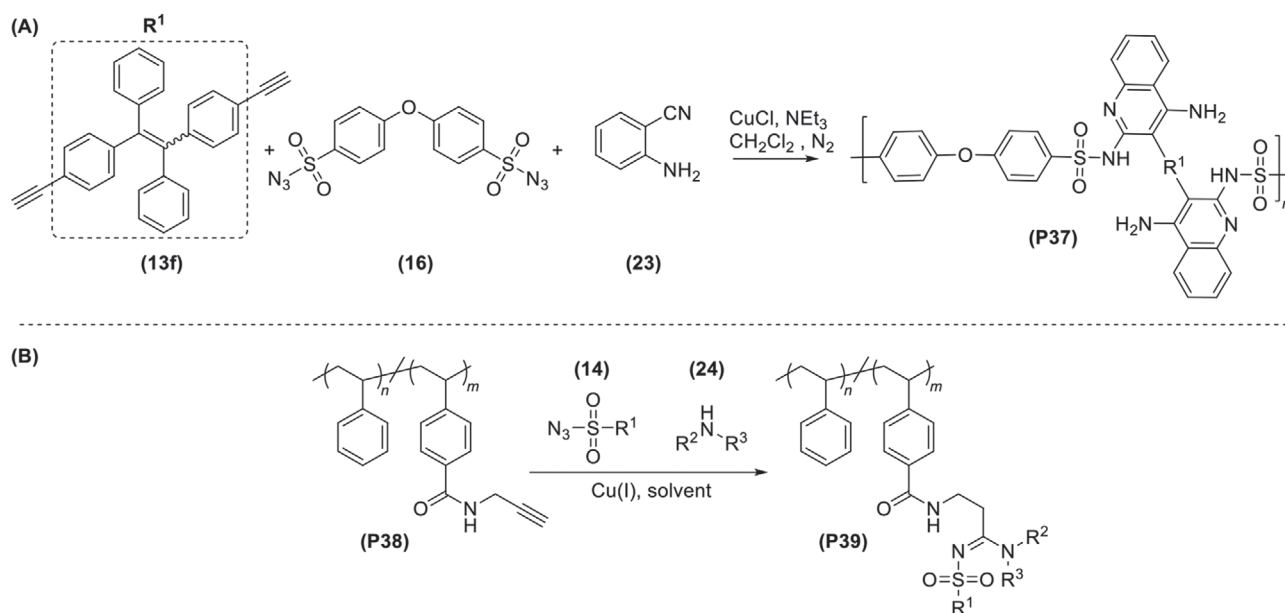
The group of Theato^[77] validated the synthetic utility of Cu(I) catalyzed MCR for a post-polymerization modification of polymers featuring acetylene moieties (e.g., (P38)) with sulfonyl azides (14) and amines (24) in the presence of a catalytic amount of Cu(PPh₃)₃Br (Scheme 18B) to yield the respective polymeric *N*-sulfonylamidine derivatives (P39).

3. Applications of Polymers with Sulfur–Nitrogen Bond

Compared to the limited number of S–N bond-containing molecules that life produces from the plentiful precursors available, the synthetic polymer chemist has evolved the ability to overcome the restriction on life's use of S–N chemistry, and developed methodologies to deliver polymers with very distinctive S–N structural groups, as it was comprehensively summarized in the previous section of the review. Nevertheless, the applications of those polymers have not been previously in-depth summarized. Indeed, considering the remarkable characteristics of these polymers that result from the unique chemical properties of the sulfur–nitrogen bond (e.g., its polar character and the multiple valence states of sulfur), a plethora of innovative applications are foreseen. Thus, a glimpse on the exciting applications of the current research involving biomedical applications, energy storage materials, metal-ion detection, and flame retardancy are outlined below.

3.1. Biomedical Applications

On one hand, by virtue of its wide chemical and structural functionality, the very rich S–N bond chemistry has been applied in various branches of industry (e.g., industrial materials, agrochemicals, etc.),^[78] However, given the fact that S–N bond chemistry is incompatible with essential segments of biochemistry, specifically with thiols, the sulfur–nitrogen bond rarely appears in natural molecules^[79] and macromolecules (e.g., proteins),^[79] b,c as there are only about 100 naturally abundant compounds that contain S–N bonds.^[80] In line with this, little research has been published on biochemistry involving S–N bond containing compounds (with an exception of *S*-nitrosothiols, utilized in



Scheme 18. A) The facile and efficient multicomponent click polymerization route mediated by Cu(I) to construct aminoquinoline-containing poly(sulfonylamidine) derivative (P37) with advanced functionalities. B) Schematic representation of the post-modification process based on a Cu-catalyzed three-component reaction to furnish polymeric *N*-sulfonylamidine derivatives (P39).

redox metabolism of the cell).^[81,82] Although, Nature has been avoiding to some extent *S*–*N* bond chemistry in light of the diversity, flexibility, and utilization of sulfur, the below mentioned examples shall illustrate the potential applicability of polymers decorated with *S*–*N* bond-containing functional moieties in the field of biomaterials.

On the other hand, biomaterials, which are recognized as a significant technology, are promising candidate adjuvants (a pharmacological or immunological agent that modifies the effect of other agent) to enhance vaccine efficacy.^[83] In fact, the use of vaccines to diseases (such as AIDS, malaria, and cancer) is broadened through adjuvant design. Thus, delivery systems based on polymeric particles have been considered promising candidates for vaccine delivery, because they possess pathogen-mimicking properties in terms of shape, size and morphology. The toolbox of polymer chemistry offers a variety of polymers that can be employed for the fabrication of these particles; however, most of those polymers fail to be biodegradable and biocompatible, and critically, the degradation by-products of these polymers are toxic. Motivated by these problems, Salem and colleagues developed polymer that possessed unique *S*–*N* bonds ((**P4**) in Scheme 2B), i.e., sulfenamide,^[84] and explored its utilization for the fabrication of microparticles, which in turn were applied as cancer vaccine delivery system. Intriguingly, in comparison to the most synthetic polymers (e.g., polyesters, polyamides, or polyamides amongst others) used to deliver pharmaceutical drugs in the body, these polymers decorated with sulfur–nitrogen bonds were stable in polar protic and aprotic solvents, but degraded rapidly when exposed to acidic conditions.

A water-in-oil-in-water single^[10] and double^[84]-emulsion solvent-evaporation methods were the method of choice for the fabrication of the microparticles. Importantly, in order to produce drug-loaded particles, fluorescein isothiocyanate (FITC)-dextran was used as a model hydrophilic compound. At the optimal formulation conditions, the external morphology of the poly(sulfenamide) based microparticles was examined by scanning electron microscopy in order to show the formation of smooth-surfaced spherical particles with low polydispersity. The microparticles had a net negative surface charge (–23 mV) as analyzed by a zetasizer, whereas, the drug encapsulation efficiency of the particles and the drug loading were found to be a function of the following parameters: i) drug molecular weight, ii) amount of FITC-dextran used in fabricating FITC-dextran-loaded microparticles, iii) concentration of poly(sulfenamide) and surfactant, and iv) volume of the internal and external water phases. FITC-dextran was found to be distributed throughout the poly(sulfenamide) microparticles, and its release profile the microparticles demonstrated gradual and continuous release over two weeks following an initial burst release. Last but not at least, confocal laser scanning microscopy was used to qualitatively observe the cellular uptake of poly(sulfenamide) microparticles and indicated localization of the particles mainly in the cell cytoplasm of human embryonic kidney-293 (HEK-293) cells, and to some extent, in the nucleus.

In concomitant study, microparticles based on another poly(sulfenamide) derivative, i.e., (**P3**), shown in Scheme 2B,^[22] were fabricated by using an oil-in-water single emulsion solvent evaporation methodology, to which drugs and fluorescent molecules, such as rhodamine, were incorporated into by

mixing them in the polymer/chloroform mixture prior to emulsification (**Figure 3**). The average size of the microparticles was 2.6 μm with a dispersity of 1.62 (**Figure 3B**). They were spherical in shape, had a smooth surface, and had a negative charge of –41 mV in PBS buffer at pH = 7.4. The slow degradation of poly(sulfenamide) to yield sulfinic acid caused negative charge, since the respective sulfinic acid was deprotonated and led to a negatively charged surface.

The degradation of the sulfenamide bond was rapid in water, whereas, these microparticles fabricated from poly(sulfenamide)s, exhibited different degradation profile based on the monomer used in its synthesis. For instance, in **Figure 3C**, microparticles of (**P3**) at various stages of degradation can be observed after incubation in acetate buffer (pH 4.0) for 14 days. Further, these microparticles were readily internalized by two different cell lines (e.g., murine dendritic cell line (i.e., JAWSII) and HEK293 cells) and their uptake was studied using confocal microscopy, which in turn revealed that this system has potential in immunological applications, especially in vaccine delivery and potential for gene therapy applications (**Figure 3D**). Indeed, confocal images clearly outlined that the microparticles were found on the interior of the cells, i.e., near the cytoplasm, hence indicating the phagocytosis of the microparticles by cells.

In similar manner to poly(sulfenamide)s, macromolecules possessing the unique diaminosulfide,^[31,85] functional group (e.g., (**P12**) in Scheme 4B) found application in the fabrication of microparticles as drug delivery vesicles (**Figure 4A**). As previously mentioned, the diaminosulfide functional group degraded several orders of magnitude faster than conventional ester bonds under acidic conditions, and thus revealed reasonable stability in water under neutral conditions.^[23] Hence, in their seminal work, Bowden and colleagues prepared microparticles according to a water-in-oil-in-water double emulsion-solvent evaporation method using poly(vinyl alcohol) as a surfactant. The particles, which surface charge was determined to be -11.6 ± 0.8 mV, were spherical in shape and possessed a smooth, nonporous surface. The z-average particle size, determined by dynamic light scattering, was 660 nm and consistent with the SEM micrograph shown in **Figure 4B**. While, being nontoxic toward HEK-293 cells, their successful internalization into the cells was demonstrated in **Figure 4C**. Indeed, these microparticles were co-loaded with antigen (ovalbumin) and adjuvant (cytosine–phosphate–guanosine motifs), which upon vaccination, displayed the capacity to generate detectable cell-mediated immune responses, as defined by increased levels of ovalbumin-specific cytotoxic T cell lymphocytes, and promoted increased survival of tumor challenged mice.^[85] Respectively, in this prophylactic setting the antitumor effect of these co-loaded microparticles was at least comparable with that achieved with co-loaded poly(lactic acid-co-glycolic acid) microparticles or adenovirus type 5 encoding ovalbumin, suggesting that vaccine delivery systems fabricated from poly(diaminosulfide)s may hold great promise in cancer therapy.

Iminocoumarin derivatives have been recognized as compounds with pharmacological properties,^[86] therefore, Tang and colleagues^[70] investigated the antibacterial property of 4-aminoiminocoumarin-containing poly(sulfonylimidate) fluorescent (**P33**) shown in Scheme 14, revealing that this unique class of polymer can be utilized in the inhibition of the growth of

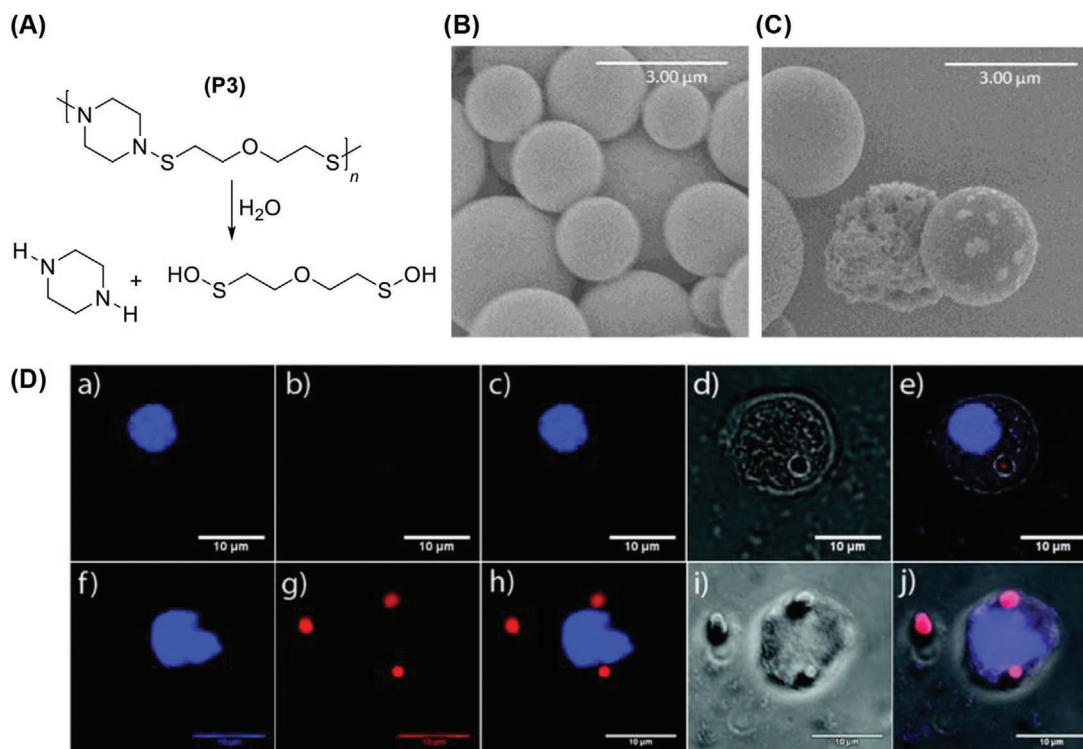


Figure 3. A) Degradation of poly(sulfenamide) (**P3**) in water to release an amine and sulfenic acids. B) Surface scanning electron microscopy image of microparticles fabricated at the optimal formulation conditions. C) A confocal image is depicting the presence of green fluorescent FITC-dextran loaded microparticles mainly in the cell cytoplasm of (HEK-293) cells, and to some extent, in the nucleus. D) Confocal microscopy images showing the uptake of microparticles fabricated from (**P3**) in Scheme 3, and loaded with rhodamine: a–e) are JAWSII immature dendritic cells, and f–j) are HEK293 cells; the nucleus of the cell was stained with 4',6-diamidino-2-phenylindole to appear blue and the rhodamine appeared red; in (d) and (i) the transmitted light images indicated the periphery of the cells and the location of the microparticles, while (e) and (j) are the merged images, which clearly outline the periphery of the cell, the location of the nucleus, and the microparticles to depict that the microparticles were found on the interior of the cells. Reproduced with permission.^[22] Copyright 2012, American Chemical Society.

bacteria such as *S. aureus*. The structure of poly(sulfonylimidate) endowed it unique interaction with *S. aureus*, thus enabling its accumulation around *S. aureus* and further inhibition on the growth of the bacteria. In fact, the calculated inhibition ratio reached 58% when *S. aureus* was incubated with 32×10^{-6} M of poly(sulfonylimidate) for 12 h.

In summary, although S–N bond-containing small molecule compounds are rare in life due to their inherent incompatible with the thiol containing compounds, which on the other hand, are central to life's metabolism, the abovementioned examples clearly imply the potential of the macromolecules anchored with diverse S–N bond containing functional groups in the field of biomedicine. Given the fact of the numerous developments in the area of polymer chemistry, we pursue for the selective expansion of polymers decorated with S–N bond-containing compounds compared to thiols, thus, in order to deliver exquisite materials that find broader applications in the field of biomedicine.

3.2. Metal-Ion Detection

Rapid and sensitive detection of heavy metal-ions, for example in environmental samples, is significant and challenging. Because of the severe risks for human health, though metals

are important to carry out cellular functions, the contamination of heavy metal ions in the environment has received increasing attention. Therefore, it is crucial to develop new materials for highly selective and sensitive detection of metal ions.

Aggregation-induced emission (AIE), polymers are extensively studied as fluorescent chemosensors for metal ion detection, owing to their high sensitivity, selectivity, and reliability.^[87] In similar manner, the heteroatom-rich nature of the polymers possessing diverse sulfur–nitrogen bonds attributes these macromolecules unique and specific properties (such as good solubility in polar solvents, good film-forming ability, satisfactory thermal stability, and high refractivity with small chromatic dispersions), thus they could serve as environmentally sensitive probes to visualize metal-ions. For example, Tang and coworkers,^[75] synthesized poly(sulfonylamidine) derivatives, decorated with phosphorous moieties, which were further utilized as ligand for platinum group metal ions, particularly palladium. As an generic example, they studied the nanoaggregates of the polymer (**P36**), in Scheme 17, based on (**13f**)/(**16**)/(**22**) [i.e., (**P36**)_{(13f)/(16)/(22)}] in DMSO/H₂O mixtures with 50 vol% water. Once the concentration of PdCl₂ was increased from 0×10^{-6} to 100×10^{-6} M, the photoluminescence (PL) intensity dramatically dropped (**Figure 5A**), respectively the Stern–Volmer plot of relative PL intensity (I_0/I) versus the Pd²⁺ concentration appeared

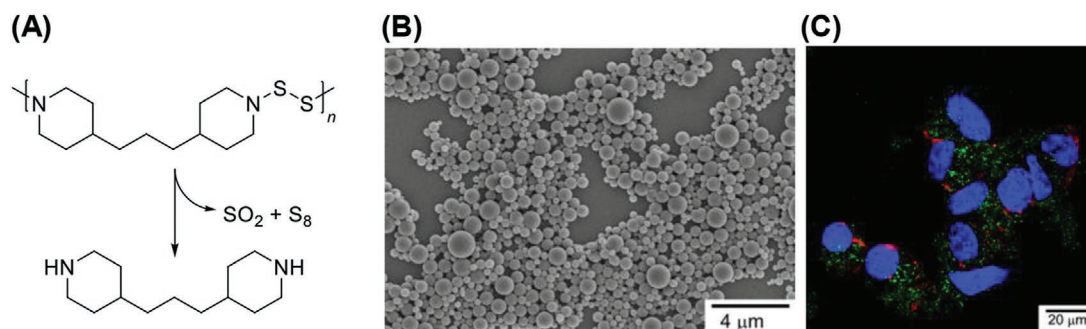


Figure 4. A) Degradation of poly(diaminosulfide) (**P12**) in water to release an amine and sulfur monoxide, which in turn possessed a half-life of seconds and decomposed to release SO_2 and elemental sulfur. B) SEM micrographs of microparticles fabricated from the polymer (**P12**) in Scheme 12. C) A laser scanning microscopic image, which shows HEK-293 cells that were exposed to microparticles loaded with FITC-dextran (green) for 24 h and then washed to remove microparticles that were not internalized into the cells. The nuclei of the cells are stained blue by 4',6-diamidino-2-phenylindole, and the cytoplasm/cell membranes are stained red by phalloidin. Thus, this image revealed that the microparticles were internalized into the cells. Reproduced with permission.^[31] Copyright 2012, American Chemical Society.

as a straight line with a large quenching constant of $207\,600\ \text{M}^{-1}$, thus revealing a detection of limit (LOD), which was calculated to be $2.4 \times 10^{-7}\ \text{M}$ (Figure 5B). This analysis has revealed the high sensitivity of this specific polymer (**P36**_{(13f)/(16)/(22)}) toward Pd^{2+} ions. Remarkably, when the PL spectra of (**P36**_{(13f)/(16)/(22)}) in 50 vol% aqueous mixture were studied in the presence of 16 different metal ions including Ru^{3+} , Rh^{3+} , Pd^{2+} , Pt^{4+} , Cr^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Ce^{3+} , and Pb^{2+} under the same condition for comparison, only Pd^{2+} showed reasonable fluorescence response, one more time proving the high selectivity of this fluorescent chemosensor (Figure 5C and D, respectively).

In another representative example, the fluorescence response of AIE-active poly(sulfonylimidate) (**P33**) derivative (i.e., (**P33**_{(13f)/(16)/(19)})) upon coordination with various metal ions was explored. Since the multiple heteroatoms and amino groups of poly(sulfonylimidate) may serve as metal ligands.^[70] Into the DMSO/ H_2O mixed solution of (**P33**_{(13f)/(16)/(19)}) with 50 vol% H_2O , different metal ions such as Ru^{3+} , Rh^{3+} , Pd^{2+} , Pt^{4+} , Cr^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Ce^{3+} , and Pb^{2+} were added. The fluorescence of (**P33**_{(13f)/(16)/(19)}) was selectively quenched upon the addition of Ru^{3+} , while no significant change was observed with any other metal ion. The control experiments with the mixture of different metal ions and Ru^{3+} also confirmed that the fluorescence quenching was only affected by Ru^{3+} , indicating high selectivity of the fluorescence detection of Ru^{3+} . In similar manner, it was observed that with increasing the concentration of RuCl_3 from 0 to $100 \times 10^{-6}\ \text{M}$, the emission intensity of (**P33**_{(13f)/(16)/(19)}) decreased, while keeping the spectral profile intact. Indeed, the emission of (**P33**_{(13f)/(16)/(19)}) and the absorption of RuCl_3 in DMSO/ H_2O mixture with 50 vol% water content overlapped at the wavelength range of 400–650 nm, indicating potential energy transfer from (**P33**_{(13f)/(16)/(19)}) to Ru^{3+} , which caused fluorescence quenching.

3.3. Flame Retardant Chemicals Based on Polymers with Sulfur–Nitrogen Bonds

The recent bushfires erupted in Australia^[88] have invoked, one more time, the scientific and public attention to the field of

flame retardant chemicals.^[89] Generally, flame retardancy can be attained by different physical and chemical mechanisms, thus, there is also a great variety in products, which can be used to achieve a lowering of the flammability of materials. In fact, considerable effort has been focused upon enhancing the char-forming efficiency of flame-retardants (FRs) by designing new intumescent systems. On one hand, sulfur-containing compounds have long been used as flame retardants, or as adjuvants, to boost the flame retardancy activity of other elements, especially phosphorus.^[89] On the other hand, recently, sulfenamides and polymers thereof, were evaluated as excellent flame retarding chemicals.^[19,24,90] The excellent flame retarding action of sulfenamide based polymers (for instance (**P7**) in Scheme 2C) on polypropylene, low density polyethylene and polystyrene was reported. Indeed, the small molecule and poly(sulfenamide) flame retardants enabled polypropylene films and fibers to self-extinguish even at a very low loading of 0.5–1.0 wt%. The sulfur–nitrogen bond of low basicity demonstrated stability at conventional polymer processing temperatures of polypropylene, but rapidly decomposed under fire conditions. The generated aminyl and sulfenyl radicals interrupted the radical processes otherwise leading to the fire propagation, hence exhibiting appropriate thermal properties as flame retardants for polypropylene. In similar manner, the potential of poly(sulfenamide)s as synergists with conventional halogen free-flame retardants were investigated, implying the suitability of poly(sulfenamide) derivatives as standalone flame retardant or as synergists with conventional flame retardants.^[90]

From the above results, it may be reasonably concluded that the polymers possessing S–N bond and its derivatives are excellent approach to obtain particularly active polymeric FRs combining the merits of sulfur and nitrogen atoms.

3.4. Energy Storage Applications

In the last three decades, numerous organosulfur compounds, which mainly cover disulfides, polysulfides, and thioethers, have been reported as possible cathode materials for organic rechargeable batteries.^[91] The pioneering

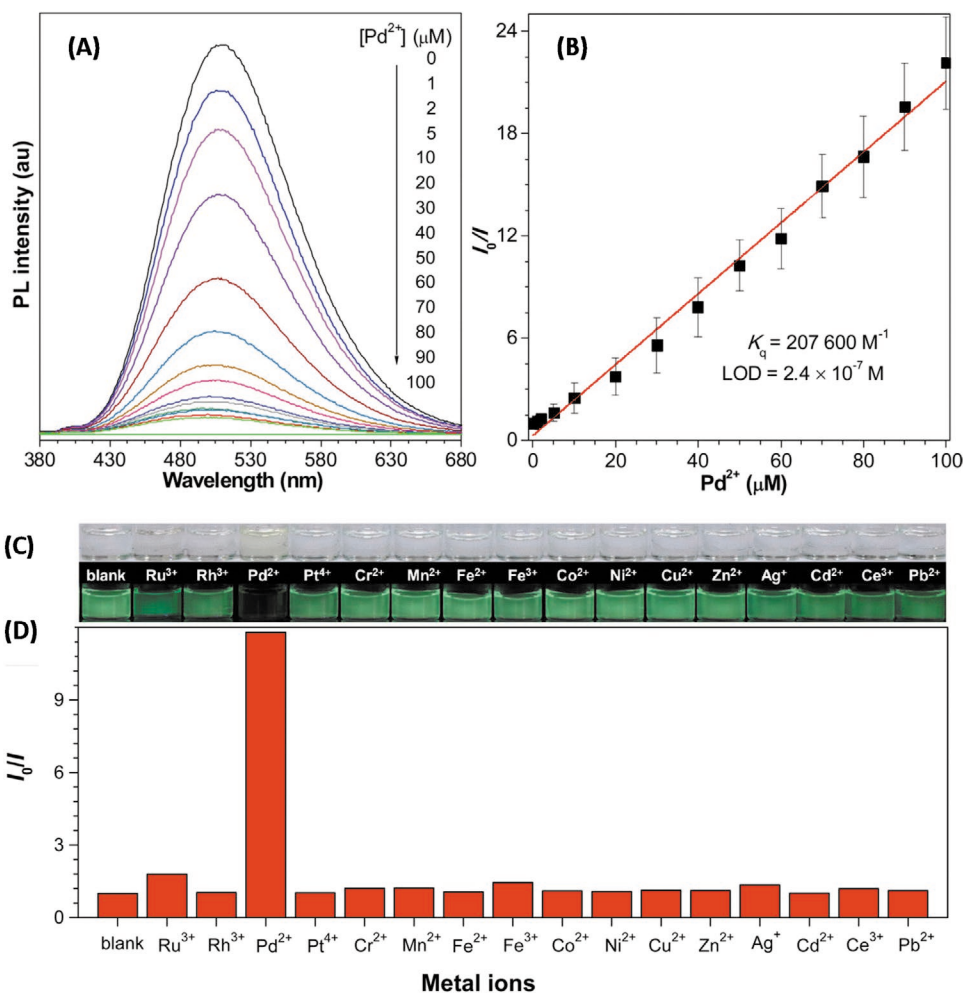


Figure 5. A) PL spectra of (**P36**_{(13f)/(16)/(22)}) in DMSO/water mixture with 50 vol% water in the presence of different amounts of Pd^{2+} . B) Stern–Volmer plot of relative intensity (I_0/I) versus the Pd^{2+} concentration. I_0 = PL intensity without Pd^{2+} (Concentration: $10 \times 10^{-6}\ \text{M}$). C) Images of (**P36**_{(13f)/(16)/(22)}) in DMSO/water mixtures with 50 vol% water containing different metal ions taken (upper) in daylight and (lower) under UV illumination. D) Relative intensity (I_0/I) of aqueous solution of (**P36**_{(13f)/(16)/(22)}) versus different metal ions. I_0 = PL intensity without metal ions, at concentrations of 10×10^{-6} and $50 \times 10^{-6}\ \text{M}$, respectively, for polymer (**P36**_{(13f)/(16)/(22)}) and metal ion. Reproduced with permission.^[75] Copyright 2017, American Chemical Society.

studies on organosulfur compounds in the field of energy storage dates back to late 90s, when Visco and coworkers^[12] introduced different poly(diaminodisulfide)s (e.g., (**P16**) and (**P18**) in scheme 6) as alternative electrode materials in high temperature battery systems such as Li-FeS_2 and $\text{Na-Na}_2\text{S}_x$. One-electron-transfer electrochemistry based on the cleavage and formation of $-\text{S}-\text{S}-$ bonds during discharge and charge, respectively, accounted for the rate-determining step, while the total number of transferred electrons in the overall reaction was two. Unfortunately, the cell configuration seemed sophisticated, and cyclic voltammetry results implied very poor kinetics of the redox reaction, due to the large separation between the cathodic and anodic peak potentials ($\Delta E_p = 1.25 - 1.63\ \text{V}$). As an additional intrinsic drawback, these organic materials operated at elevated temperatures (typically 80–130 °C). Nevertheless, these studies underpinned the plausibility of using poly(diaminodisulfide)s as cathodes in rechargeable lithium batteries, mainly due the fact that the

heteroatomic nature of the sulfur–nitrogen bond presented in each repeating unit of the polymer greatly accelerated the electrode kinetics.

30 years later, Bowden and colleagues^[39] fabricated a poly(aminodisulfide) derivative (**P14**) (Scheme 5) into a layered device to measure its current–voltage curve in the solid state. The cross-sectional area was $16.9 \times 10^{-3}\ \text{mm}^2$ and the thickness of the poly(disulfidediamine) was 40 nm. According to the current–voltage curve shown in Figure 6, the polymer demonstrated diode characteristics and was weakly electrically conducting. The conductivity between 9 and 10 V was estimated to be $4.73 \times 10^{-8}\ \text{S cm}^{-1}$. Whereas, this value was very low and similar to that of distilled water, it was comparable to values for other undoped polymers, such as polythiophene, polyaniline, and polyacetylene, which have conductivities of approximately 10^{-5} – $10^{-9}\ \text{S cm}^{-1}$. Besides, the impact of dopants on (**P14**) was briefly tested by exposing the device to iodine vapor for 5 min and then immediately measuring the conductivity. Indeed,

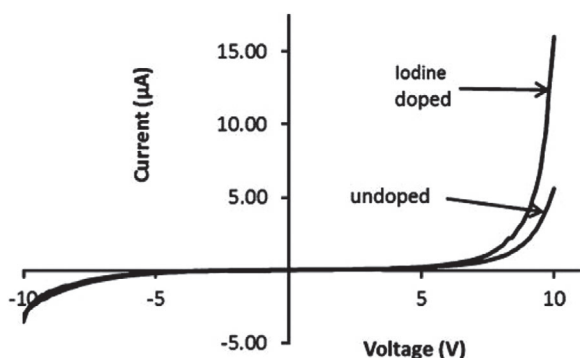


Figure 6. Current–voltage curve for polymer (P14), which reveals that (P14) possessed diode characteristics and was weakly electrically conducting. Reproduced with permission.^[39] Copyright 2012, American Chemical Society.

the iodine doping enhanced the electrical conductivity up to $2.85 \times 10^{-7} \text{ S cm}^{-1}$.

4. Conclusion and Outlook

With the aid of a series of synthetic breakthroughs in recent years, new chemistries suitable for the synthesis of various polymers containing S–N functional groups have been developed, and thus novel materials with interesting properties have been created. Nevertheless, some bottlenecks and challenges arising from the incompatibility between S–N bonds and thiols, resulting in the effective near exclusion of S–N chemistry from biochemistry, are example of a constraint. A constraint that could be resolved with the novel developments in the toolbox of polymer chemistry, by exploring, in a systematic way, mutually exclusive sets of chemical synthetic options to deliver the desired polymers and reveal valuable information for biomedical science. Ultimately, further research on these polymers is needed to boost and expand their applications. Indeed, polymers with sulfur–nitrogen bond can be considered as a sleeping beauty and (re)appear to be promising to new materials that combine the advantages of sulfur and nitrogen solely. Nevertheless, to endeavor polymers with sulfur–nitrogen bonds more streamlined, it is essential to harness an interdisciplinary combination of conventional synthetic methods drawn from organic, inorganic, and polymer chemistry, as well as fabrication and processing techniques to create new materials.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

poly(diaminodisulfide), poly(diaminosulfide), poly(oxothiazene)s, poly(sulfenamide), poly(sulfonylimidate)s, sulfur–nitrogen polymers

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