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Newly Developed Multicomponent Polycondensation Involving Sulfur for the Successful Synthesis of Biobased Polythioureas

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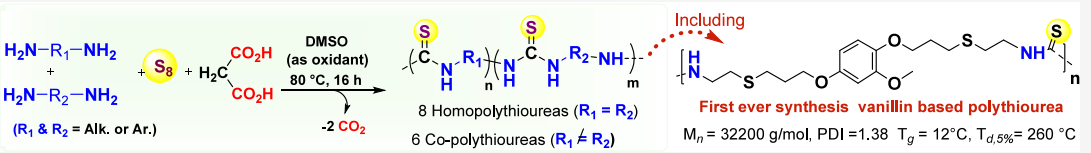

ABSTRACT: As an abundant byproduct of hydrodesulfurization in petroleum refining processes, elemental sulfur has become a major environmental concern due to its costly disposal and challenging storage. However, the development of synthetic and processing methods to convert elemental sulfur into useful chemicals has not been widely investigated. In this study, we report the development of a novel multicomponent polycondensation (MCP) involving sulfur, diamines, and malonic acid under mild conditions to produce polythioureas. A family of 13 polythioureas with high structural diversity (seven homopolymers and six copolymers) is successfully synthesized from seven commercially available diamines, achieving high yields (up to 96%) and high molar masses (up to 115 900 g/mol). In particular, we report the first ever synthesis of a new biosourced polythiourea from naturally abundant vanillin with good yield upon applying this newly developed MCP.

INTRODUCTION

Sulfur is a major byproduct in petroleum refinery and can be isolated as elemental sulfur (S_8) with an annual production of over 80 million tons,[1] thus yearly accelerating environmental problems such as high-cost disposal and challenging storage (flammability and microbial oxidation into SO_x and acidification). Thanks to its unique physical and chemical properties (polyallotropy, ambivalent acid/basic behavior, reversible polymerization, and catalytic activity), S_8 has been recognized as a valuable chemical agent for producing sulfur dioxide used in the pulp and paper industry, in bleaching,[2] and in the production of sulfuric acid[3] or sulfur-containing molecules[4,5] such as drug[6] and polymer materials.[3,7−9] However, its consumption is still negligible compared to its abundance. Therefore, it has been a long-standing global concern to develop an efficient and environmentally friendly economy based on large-scale valorization of S_8, such as a direct incorporation of sulfur into polymer chains for making high value-added materials used in different fields, i.e., medicines,[10] energy storage devices,[11−13] self-healing materials,[14,15] heat-resistant materials,[16] extraction of heavy metal ions[17,18] and dielectric materials,[19,20] *etc.* Additionally, it has been reported that the substitution of oxygen atoms in the polymer main chain by sulfur atoms enabled to improve not only the performances of these polymers[21−23] but also their solubility and processability (due to the weaker intermolecular H-bonds of sulfur counterpart).[24] For example, poly(butene trithiocarbonate) exhibits superior thermal, mechanical, and optical properties compared to the corresponding poly(butene carbonate)[22] and polythio(*p*-phenylene terephthamide) shows excellent solubility in common polar solvents such as DMSO and DMF while poly(*p*-phenylene terephthamide) is totally insoluble.[24] Although the use of sulfur in polymer chemistry has already dated back to the mid-19th century (vulcanization[25] and anionic copolymerization with polysulfides[26]), great effort toward the direct utilization of S_8 in the synthesis of high sulfur content polymers has witnessed significative progress only from the past decade. Such syntheses often involve high temperatures and lead to poorly soluble and ill-defined polymers.[27] Only few examples related to the direct use of S_8 to produce soluble polymers with well-defined structures have been reported.[28] Among them, multicomponent polymerizations (MCPs) based on highly efficient, operationally simple, highly atom economical, multicomponent reactions (MCRs) with large structural diversity and mild conditions offer great opportunities for direct sulfur utilization.[17,29−32] We have currently developed a versatile, atom-economy MCR involving S_8, amines, and malonic acid under mild conditions (no catalyst, low temperature, and open air atmosphere), leading to over 70 functional molecules

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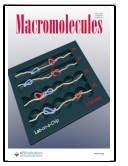
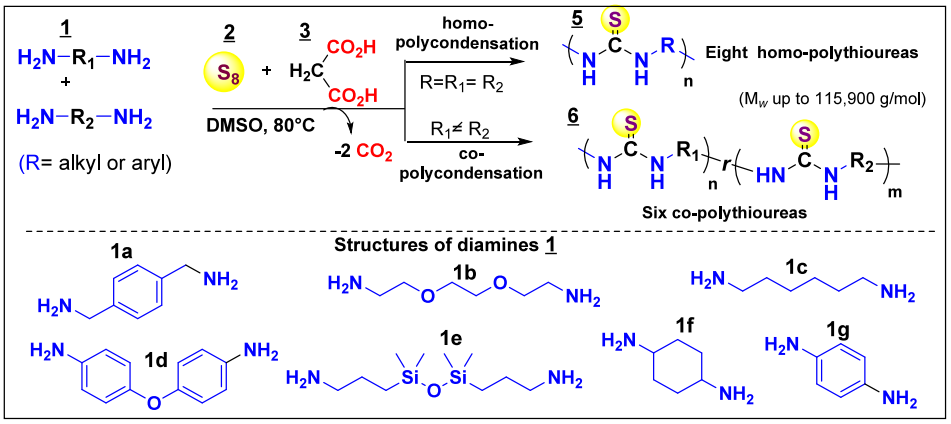
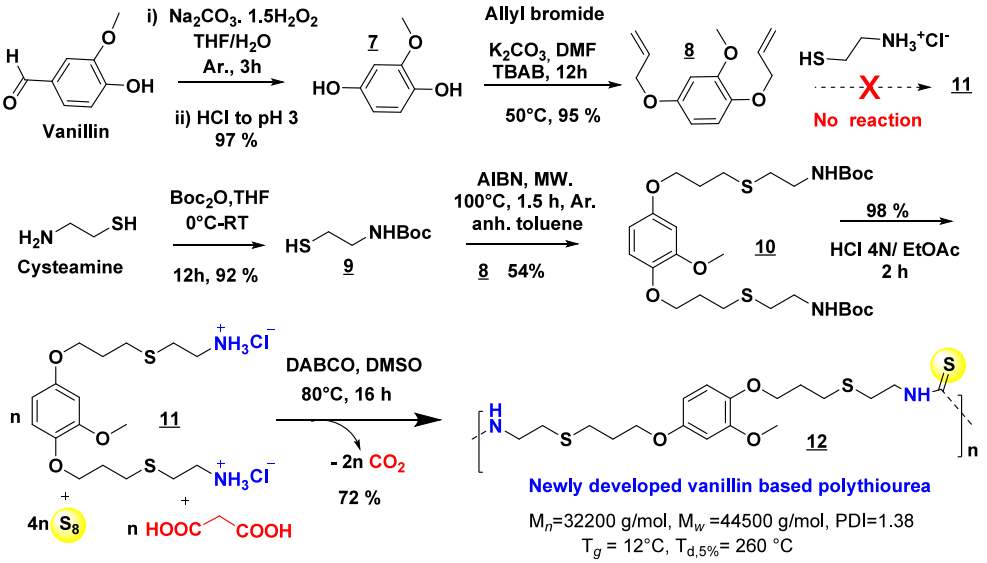


Scheme 1. Multicomponent (Co)polymerizations of Diamines, Elemental Sulfur, and Malonic Acid



Scheme 2. Strategy for the Successful Synthesis of Biosourced Polythiourea



including thioureas, thioamides, and *N*-heterocycles with excellent yields.[33] It is worthy of note that this novel MCR can be employed not only in the context of aliphatic amines but also in the case of weakly basic aromatic amines. The most significant advantage of this novel MCR is its potential to facilitate industrial-scale sulfur conversion by enabling the substitution of toxic, hazardous, and flammable reagents, including carbon disulfide, diisothiocyanate, and thiophosgene, which are currently employed in conventional methodologies[20,30,34] with malonic acid, a nontoxic, readily available, inexpensive, stable, and eco-friendly reagent. Additionally, malonic acid has been exploited for the first time as a C_1 synthon via didecarboxylation[33] instead of its well-known utilization as a C_2 synthon via monodecarboxylation.[35] For further valorizing this new sustainable MCR in different sectors of material sciences, we herein report its successful application in MCP for the synthesis of 14 different polythioureas including eight homopolymers and six copolymers simply by replacing monoamines by diamines. This newly developed MCP (Scheme 1) is much simpler than other reported MCPs that require at least two different types of monomers not always commercially available and difficult to prepare from toxic, hazardous, and flammable reagents.[17,29] Eight diamines, including seven commercially available diamines (Scheme 1) and one biosourced readily prepared from naturally abundant vanillin (Scheme 2), were used in this work. The successful preparation of both homo- and copolythioureas provides an easy way to effectively construct polythioureas, especially the biobased one, with great structural diversity and diverse potential applications.[11,36,37]

RESULTS AND DISCUSSION

Catalyst-Free MCPs of S_8, Diamines, and Malonic Acid. To extend the reported MCR to the synthesis of polythioureas via MCP of sulfur, diamines, and malonic acid, commercially available 1,4-phenylenedimethanamine **1a** was selected as the representative monomer (Scheme 1). The MCP of **1a**, sulfur **2**, and malonic acid **3** was first conducted at 80 °C for 16 h in DMSO with an initial diamine concentration of 2 M under an open air condition. When a strict theoretical monomer loading molar ratio [**1a**]:[**2**]:[**3**] = 1:1:1 (best molar ratio for polycondensation) was applied, polythiourea **5a** with M_w = 40 800 g/mol and M_n = 31 400 g/mol (PDI = 1.3) was isolated in 40% yield (entry 1, SI Table 2). It is noteworthy mentioning that DMSO used in this reaction played not only the role of solvent but also as an oxidizing agent thanks to its specific activating effect on sulfur; i.e., no reaction occurred when the DMSO was replaced by any other solvents, including

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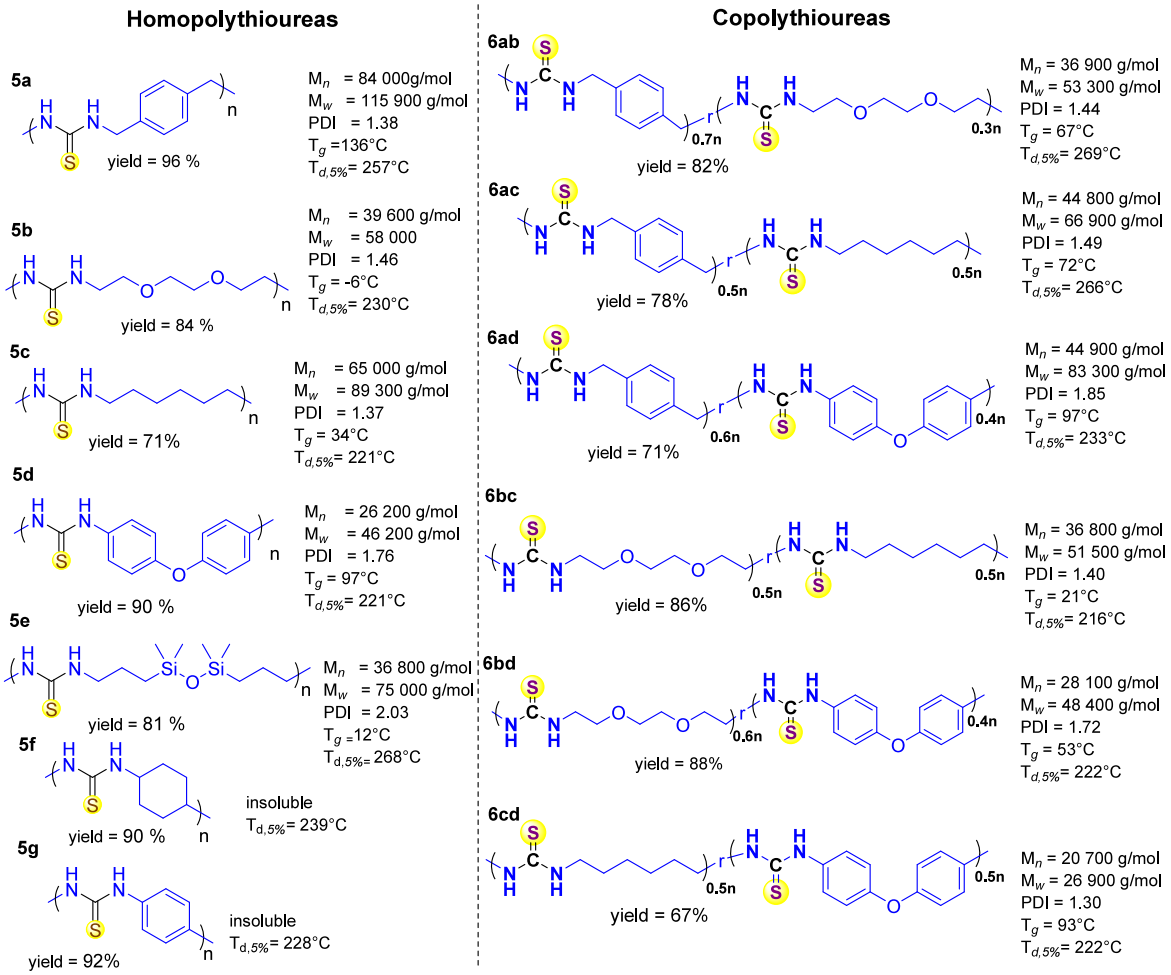

Figure 1. Chemical structures of homopolythioureas **5** and copolythioureas **6**.

DMF (SI Table 1). To further confirm the oxidizing role of DMSO in this MCP, neat polymerization was also carried out. As expected, no polymerization took place even at 100 °C. To increase the molar mass distribution of the polymers, various reaction parameters were optimized, including sulfur molar ratio, monomer concentration, and temperature. Starting with the molar ratio of sulfur, according to previously reported sulfur-based MCPs, an excess of sulfur is beneficial for both yields and molar mass distribution of the MCP.[29,30,38,39] A similar trend was also observed in this new MCP, i.e., when higher molar ratios of sulfur were applied ([**1a**]:[**2**]:[**3**] = 1:2:1 or 1:3:1 or 1:4:1 for entries 2, 3 and 4, SI Table 2), both the yield and M_w increased significantly and the best result (polymer with M_w = 99 400 g/mol, 83% yield, and PDI = 1.38) was observed with the monomer feeding ratio [**1a**]:[**2**]:[**3**] = 1:4:1 (SI Table 2, entry 4). However, a larger excess of sulfur loading ([**1a**]:[**2**]:[**3**] = 1:5:1 and 1:6:1 for entries 5 and 6, respectively) not only decreased M_w but also increased the polydispersity, probably due to the high viscosity of the reaction mixture. Based on the optimized molar ratio of [**1a**]:[**2**]:[**3**] = 1:4:1, the concentration of monomer diamine **1a** was then screened from 1 to 4 M (SI Table 3). Although it has been known that a high monomer concentration is beneficial to the polycondensation, a significant decrease in M_w (from 99 400 to 70 700 g/mol) and in yield (from 83 to 45%) was observed when the concentration of [**1a**] was increased from 2 to 4 M. The highly viscous polymerization solution (heterogeneity) of the reaction mixture caused by the very low amount of DMSO used may inhibit the complete conversion of the monomer to polymer. Surprisingly, a slight dilution of **1a** from 2 to 1.3 M led to the polymer with the highest molecular mass distribution M_w = 115 900 g/mol with PDI = 1.38 (SI Table 3, entry 2), while further dilution of [**1a**] to 1 M resulted in a drop of M_w down to 75 100 g/mol. Therefore, the best concentration [**1a**] = 1.3 M was used for the final and decisive temperature screening step in the range of 50 to 100 °C (SI Table 4). It can be concluded that the lowest temperature at which polymerization could occur was 60 °C, and the best result (M_w = 115 700 g/mol, PDI = 1.38, and yield = 96%) was observed when the reaction was carried out at 80 °C. Indeed, the M_w of the polymer product always decreased regardless of the change in temperature, i.e., below 80 °C (entries 2 and 3, SI Table 4), both the yield and M_w of the product decreased to 68% and 23 400 g/mol, respectively, probably due to the poor solubility of the ammonium salt formed from diamine and malonic acid, and above 80 °C (entries 5 and 6, SI Table 4), the M_w of the product was slightly decreased to 87 600 g/mol as compared to that obtained at 80 °C (115 900 g/mol), while the yield was not much affected. Surprisingly, the polymerization at a high temperature (100 °C) resulted in a narrower molar mass polymer distribution (polydispersity index: PDI = 1.23 vs 1.38 at 80 °C), likely due to the better solubility of sulfur in the reaction mixture at high temperatures.

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Finally, the kinetic study for MCP of **1a** was followed by ^{1}H NMR and by SEC. Both of these techniques showed that the conversion of the monomer was complete after 16 h (SI Figure 2 and SI Table 5). Beyond this reaction time, a slight increase in the M_w of the polymer product (from 115 900 to 122 000 g/mol after 24 h) together with a slight decrease in M_n (from 84 000 to 83 555 g/mol) and thus a slightly broader PDI (1.46 vs 1.38) was observed. A further increase in the reaction time (to 48 h) resulted in a slight decrease in both M_w and M_n of the polymer product (down to 110 000 and 80 600 g/mol, respectively), probably due to the inaccuracy of the SEC machine. Therefore, the optimized reaction time of 16 h was used for this MCP and thus the optimized conditions for this MCP are monomer feeding molar ratio [**1a**]:[**2**]:[**3**] = 1:4:1, diamine concentration [**1a**] = 1.3 M, 80 °C for 16 h.

Following the successful use of malonic acid as a source of thiocarbonyl in the preparation of polythiourea **5a**, we explored the scope of diamine monomers for obtaining the structural diversity of polymer products. Seven different commercially available aliphatic and aromatic diamines **1a**−**1g** were investigated (Scheme 1). Homopolymerization and copolymerization between these diamines were also carried out using the optimized conditions found above, namely, 80 °C, 16 h, and monomer molar feeding ratio [**1b**−**1g**]:[**2**]:[**3**] = 1:4:1 (Scheme 1). All homopolymerizations proceeded smoothly and rapidly to produce seven homopolymers **5a**−**5g** with good to excellent yields of 71−96% and high M_w of 46 200−115 900 g/mol, demonstrating general monomer applicability and high efficiency of this MCP (Scheme 1 and Figure 1). Five of these homopolymers (**5a**−**5e**) are soluble in highly polar solvents such as DMF and DMSO, while the two remaining (**5f** and **5g**) are insoluble in all solvents, probably due to their very rigid structure caused by cyclohexane and benzene rings, respectively, as part of the polymer chain as well as their dense network of intra/inter H-bond interaction between thiourea groups within the same polymer chain or between different ones. In the case of copolymerization, six combinations between different diamines allowed the preparation of six copolythioureas **6ab**, **6ac**, **6ad**, **6bc**, **6bd**, and **6cd** with good yields ranging from 67 to 88% and M_w ranging from 26 900 to 83 300 g/mol. Among all synthesized polymers, the homopolymer **5a** presents the highest M_w = 115 900 g/mol and M_n = 84 000 g/mol with a rather narrow polydispersity (PDI = 1.38).

Interestingly, in our previous MCR work,[33] a basic catalyst such as DABCO was used for aromatic amine substrates. On the other hand, aliphatic amines are more basic and their reaction could proceed without the addition of a catalyst. In the present work, the reaction with aliphatic diamines could be carried out in the same way without a basic catalyst. When the polymerization was carried out with aromatic diamine diaminodiphenyl ether **1d** for the synthesis of polymers **5d**, **5g**, **6ad**, **6bd**, and **6cd**), we found that the reaction could proceed without a basic catalyst. Considering the structure of these diamine substrates, the presence of an electron-donating group in the *para* position of the amino groups could increase the basicity and could be the determining factor for such a difference in reactivity compared with other aromatic amines.

Design and Synthesis of a Novel Biobased Polythiourea. The successful application of the newly developed atom-economy MCR to sulfur-assisted MCP was validated on the homo/copolymerization of seven different commercially available diamines under mild reaction conditions (rather low temperature, open air, and no catalyst). To better valorize this MCP, replacing commercially available diamines issued from petroleum sources with those derived from renewable biomass would be an excellent solution to overcoming the depletion of natural resources. Therefore, the biobased diammonium **11** was designed and successfully synthesized in five steps with an overall yield of 44.9% from naturally abundant vanillin (Scheme 2). The key step of this strategy was to introduce two reactive double bonds as anchor points for further introduction of $-NH_2$ functions via the click thiol−ene reaction. To this end, the aldehyde function of vanillin was first converted into −OH simply by using sodium percarbonate as a strong oxidizing reagent under basic conditions (via a decarboxylation mechanism).[40] The di-*O*-allylation of the resulting methoxyhydroquinone **7** was carried out in quantitative yield simply by reaction with allyl bromide under mildly basic conditions at a low temperature (50 °C). The click thiol−ene reaction between the diallylated intermediate **8** and the protected cysteamine **9**, obtained in quantitative yield simply by Boc-protecting cysteamine, successfully afforded di-NHBoc vanillin **10** in 54% yield. Finally, Boc-deprotection of **10** with HCl solution (4 N) in ethyl acetate led to the desired vanillin-based diammonium **11** in quantitative yield. It is noteworthy that the synthesis of intermediate **8** has already been reported in the literature,[41] but under different reaction conditions, mostly much longer reaction times, *e.g.*, up to 7 days instead of a half day described in this work. Surprisingly, contrary to what has been reported in the literature,[41] the thiol−ene click reaction between the diallylated intermediate **8** and cysteamine hydrocholoride could not yield any trace of the final monomer diammonium **11** whatever the reaction conditions: in the presence or absence of a radical initiator, solvent nature (polar or apolar), UV irradiation or heating (classical heating or microwave irradiation). This explains the need for Boc protection of the amino group in cysteamine prior to the click thiol−ene reaction applied in this work.

Prior to be used in the MCP, the protonated diamine **11** was first converted into neutral diamine using 1,4-diazabicyclo[2.2.2]octane (DABCO), a cyclic tertiary diamine, as the dibase. Upon applying the optimized polymerization conditions found above (feeding molar ratio [**11**]:[**2**]:[**3**] = 1:4:1, 80 °C, 16 h), the MCP was carried out smoothly in DMSO in the presence of 1.05 equiv of DABCO. The desired pure vanillin-based polythiourea **12** was isolated in 72% yield as a viscous red oil after dialysis in deionized water (M_w = 44 500 g/mol, M_n = 32 200 g/mol, PDI = 1.38). To the best of our knowledge, this vanillin-based polythiourea has not been reported before.

All small intermediate molecules (**7**, **8**, **9**, **10**, and **11**) and almost all polythioureas (six homopolymers **5a**−**5e** including the biosourced one **12** and six copolymers **6ab**, **6ac**, **6ad**, **6bc**, **6bd**, and **6cd**) were well characterized by ^{1}H and ^{13}C NMR, FTIR, and MS (for small molecules) and SEC (for polymers) as detailed in the Supporting Information. In the case of homopolymers **5f** and **5g**, only IR and TGA analyses are available due to their insolubility in all solvents.

Characterization of Polythioureas. *^{1}H and ^{13}C NMR.* The newly developed biosourced polythiourea **12** was chosen as an example for structural characterization. The comparison of ^{1}H and ^{13}C NMR of this polymer and the diammonium monomer **11** as well as the intermediate Boc-protected diamine **10** is shown in Figure 2. Compared to the ^{1}H NMR

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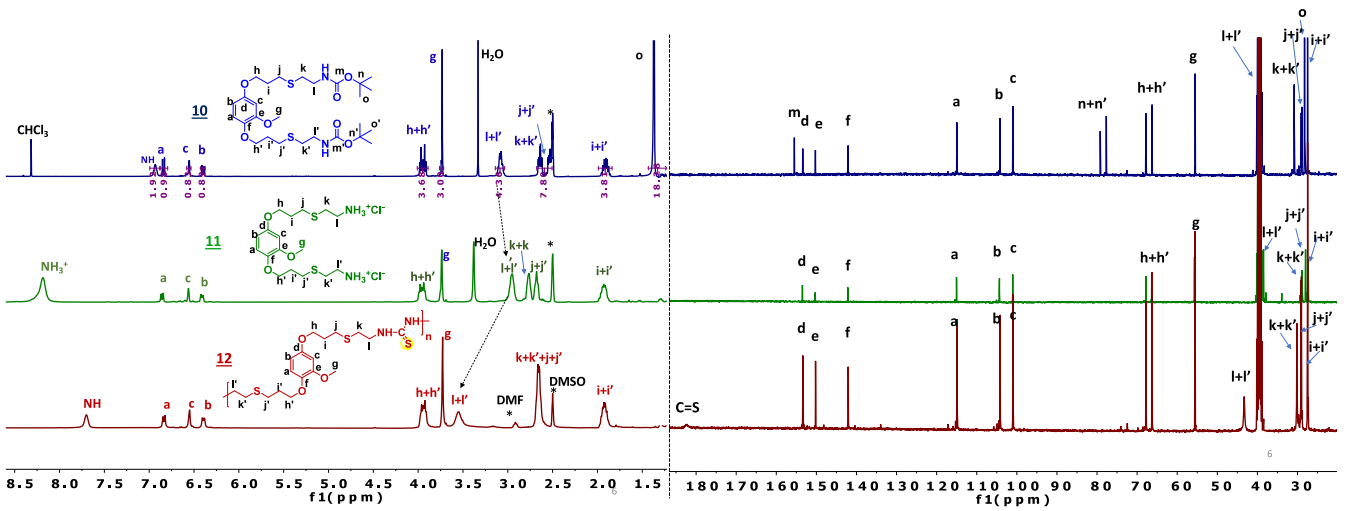

Figure 2. Comparison of ^{1}H NMR (left) and ^{13}C NMR (right) spectra in DMSO-d_6 at 25 °C of **10**, **11**, and **12**.

spectrum of Boc-protected diamine **10**, that of diammonium **11** clearly shows the absence of 18 *t*-butyl protons at δ 1.35 ppm and the upfield shift (from δ 3.08 to 2.95 ppm) of $-CH_2$ protons next to NH as well as the appearance of the broad NH_3^+ resonance at δ ∼8.30 ppm, confirming the successful removal of protecting Boc groups. After polymerization, compared to the ^{1}H NMR spectrum of the starting diammonium **11**, that of the resulting biosourced polythiourea **12** shows the following: (i) the disappearance of the NH_3^+ peak, (ii) the downfield shift of $-CH_2$ protons next to NH (from δ 2.95 to 3.55 ppm), (iii) the merging of the two CH_2- peaks (k+k'and j+j') in monomer **11** at δ 2.77 and 2.68 ppm, respectively, into a single peak at δ 2.65 ppm due to the similar chemical environment of these two $-CH_2-$ groups in the polymer chain, and (iv) most importantly, the emerging of the new peak at δ 7.7 ppm, corresponding to the −NH proton of the newly formed thiourea group (Figure 2 left). Similarly, the ^{13}C NMR spectra of polymer **12** show the disappearance of the CH_2 protons next to NH_3^+ in monomer **11** at δ 38.47 ppm and the appearance of the new CH_2 peak next to the thiourea function at δ 43.3 ppm and, especially, the emerging of a new broad **C**=S peak at δ 182.4 ppm, again confirming the chemical structure of the biosourced polythiourea **12**.

For the 12 soluble polythioureas (among the 14 synthesized), the characteristic −NH− protons of thiourea groups appeared between δ 9.73−7.31 ppm in their ^{1}H NMR spectra, and the characteristic C=S peaks between δ 183.6−180.5 all emerged in their ^{13}C NMR spectra, confirming their polythiourea structures (SI Figures 37−70). Two remaining homopolymers **5f** and **5g** are completely insoluble in any organic solvents even at a high temperature, probably due to their very rigid structure with no flexible motion presented in the polymer chains, hence making it impossible to be characterized by standard techniques except FTIR and TGA.

ATR-FTIR. The comparison of the FTIR spectra of Boc-protected diamine **10** and diammonium **11** and polymer **12** clearly shows several characteristic bands, which are well assigned in Figure 3, in particular: (i) the stretching vibration of the C=O bond of the Boc-protecting group at about 1700 cm^{-1} in the spectrum of **10** is no longer present in that of **11** and (ii) the appearance of new bands from NH_3^+ moieties in **11**, including the stretching vibration (ν_{NH3+} ∼ 2760−3100 cm^{-1}) and the symmetric and asymmetric bending ($\delta_{s\text{-}NH3+}$ &

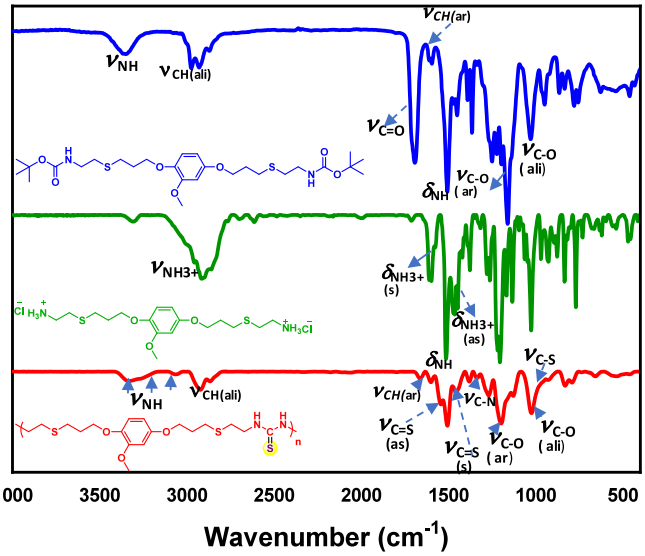

Figure 3. Comparison of the FTIR-ATR spectra of **10**, **11**, and **12**.

$\delta_{as\ NH3+}$ ∼ 1604 cm^{-1} and 1485 cm^{-1}), respectively, confirming the successful deprotection of Boc prior to be used in MCP. After polymerization, the IR spectrum of polymer **12** clearly shows the appearance of several new characteristic bands, especially: (i) three bands in the regions ∼1430−1600 cm^{-1}, ∼1260−1380 cm^{-1}, and ∼980−1070 cm^{-1} that can be ascribed to the mixed vibrations in thiourea functional groups, namely, the strong vibrational stretching (ν_{as} and ν_{s}) of the C=S bond, the stretching vibrations of the C−N bond (ν_{C-N}), and that of the C−S bond (ν_{C-S}), respectively.[42] Indeed, an unambiguous assignment of the C=S stretching seems to be possible only when the C=S group is attached to atoms other than nitrogen.[42] Moreover, the presence of three broad vibrational bands at ∼3350 cm^{-1}, ∼3247 cm^{-1}, and ∼3080 cm^{-1} can be attributed to different types of NH stretching vibrations of nonlinearly H-bonded thiourea units (tautomeric form)[43] due to the likely coexistence of different conformers *cis/trans* and *trans/trans* (estimated energy gap is 2.9 to 4.2 kJ mol^{-1}).[43] These FTIR features show that dense thiourea units, which tightly cross-link the polymer backbone chains through weak H-bonding interactions, induce little crystallization

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because the resulting H-bonded arrays are nonlinear and less ordered.[14,44]

Thermal Properties. The thermal properties of all of the as-synthesized polymers were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

TGA analysis of the biosourced polythiourea **12** shows the initial decomposition temperature at 5 wt % weight losses ($T_{d,5\%}$) at ∼260 °C under a nitrogen atmosphere, indicating a good thermal resistance (SI Figure 36). The TGA curves of all synthesized polythioureas are shown in the Supporting Information (SI Figures 22−36), and all $T_{d,5\%}$ found (ranging from 216 to 269 °C) are summarized in SI Table 7. Such a high thermal stability may be explained by the presence of the intramolecular and intermolecular hydrogen bonds among the abundant thiourea moieties.

The DSC profile on the second heating cycle of polymer **12** (SI Figure 21) shows no sharp peaks due to the crystallization in the temperature range from −20 to 200 °C at any scan rate from 1 to 10 °C/min, but only a broad peak corresponding to a glass transition (T_g) appeared at ∼ 12 °C. Despite its rather high molecular weight M_w 44 500 g/mol and a narrow molecular weight distribution (PDI = 1.38), this low T_g value implies a high amorphous fraction present in this vanillin-based polymer and can be explained by the presence of two flexible aliphatic chains bearing both ether and thioether functions in each. The DSC curves of all synthesized polymers (except for **5f** and **5g**) are shown in SI Figures 8−21, and all T_g values found (from −6 to 136 °C) are summarized in SI Table 6. Polymer **5a** shows the highest glass transition temperature (T_g = 136 °C), probably due to its highest crystalline fraction compared to others, while polymer **5b** exhibits the lowest T_g = −6 °C due to its highest amorphous fraction. Moreover, the significant difference in T_g between **5a** and **5b** can be attributed to the fact that the arene moieties are part of the main chain in the polythiourea **5a**, while only flexible ethylene glycol repeating fragments are present in polymer **5b.** It is worth noting that polythioureas are expected to have a lower T_g than their polyurea counterparts because H-bonds in thiourea functions form mostly nonlinear zigzag arrays that adopt both *cis/trans* and strained *trans/trans* conformations, while those in urea functions form linear arrays adopting only a *trans/trans* conformation.[14] Therefore, the high amorphous fraction in most polythioureas originates from such less ordered, nonlinear geometries of its H-bonded thiourea units. Finally, no glass transition temperature was observed for two insoluble polythioureas **5g** and **5f**, likely due to their very stiff structure caused by the rigid structures of cyclohexane and benzene rings, respectively, as part of their polymer chains as well as their dense network of intra/inter H-bond interaction between thiourea groups within the same polymer chain or between different ones. These two effects would induce a higher degree of crystallinity and thus highly limit the motion of their polymer chains (SI Figures 13 and 14).

CONCLUSIONS

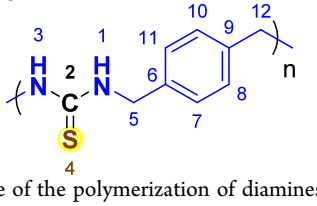
This study presents a straightforward one-step conversion of elemental sulfur to polythioureas via a catalyst-free MCP of sulfur, diamines, and malonic acid. This MCP offers a distinctive set of benefits including mild conditions, an open atmosphere, a diverse range of monomers (including aliphatic and weakly aromatic diamines), high efficiency, and atom economy. A family of 13 polythioureas with structural diversity (comprising seven homopolymers and six copolymers) was successfully prepared in high yields and with large molecular weights (up to 115 900 g/mol) from seven different commercially available diamines. Most notably, this novel polycondensation methodology enabled the first-time synthesis of a biosourced polythiourea from naturally abundant vanillin, with favorable yield. This newly developed MCP can provide an economical, convenient, and efficient tool for the direct conversion of elemental sulfur into functional materials. This offers a solution to the problems of sulfur storage and sulfur/mercury pollution, effectively addressing two issues simultaneously and ultimately benefiting both industry and the environment.

EXPERIMENTAL SECTION

Materials. Reagents were purchased from commercial suppliers and used as received without further purification: *p*-xylylenediamine **1a** (TCI), 2,2′-(ethylenedioxy)bis(ethylamine) **1b** (TCI), hexane-1,6-diamine **1c** (Sigma-Alrich), 4,4′-diaminodiphenyl ether **1d** (TCI), 3,3′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(propan-1-amine) **1e** (TCI), cyclohexane-1,4-diamine **1f** (TCI), 1,4-phenylenediamine **1g** (Sigma-Alrich), elemental sulfur **2** (Sigma-Alrich), malonic acid **3** (Sigma-Alrich), vanillin (Sigma-Alrich), sodium percarbonate (TCI), allyl bromide (ACBR), tetrabutylammonium bromide (ACBR), cysteamine (TCI), di-*tert*-butyl decarbonate (ACBR), azobis-(isobutyronitrile) (Sigma-Alrich), 1,4-diazabicyclo[2.2.2]octane (TCI).

Instruments. NMR spectra were recorded at 298 K utilizing a Bruker Ultrashield Plus 400 MHz NMR spectrometer with operating frequencies of 400 MHz (for ^{1}H) and 101 MHz (^{13}C) using either deuterated dimethyl sulfoxide d_6-DMSO or $CDCl_3$ (from Eurisotop) as solvents. FTIR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer using the attenuated total reflection (ATR) mode between 4000 and 450 cm^{-1} with an average of 32 consecutive scans and a resolution of 4 cm^{-1}. The molecular weights of precursor polymers were determined via size exclusion chromatography (SEC) in DMF as the eluent, and SEC analyses were conducted on a Shimadzu instrument equipped with mixed-C columns and RI detector. Molecular weight distribution (M_w/M_n) was calculated using polystyrene (PS) standards. GC-MS spectra were determined on an ion trap mass spectrometer (ThermoFisher Scientific, model: ITQ700, election energy: 70 eV). Thermogravimetric analyses were performed from 30 to 800 °C at 10 °C min^{-1} under an air atmosphere on a LABSYS evo instrument from Setaram. Differential scanning calorimetry measurements were carried out using a TA Instruments DSC25 from −50 to 150 °C at a heating rate of 10 °C/min to obtain the endothermic and exothermic phenomena resulting from the material during heating.

Polymerizations.



A typical procedure of the polymerization of diamines **1a**, **2**, and **3** is given below. Into a 10 mL Schlenk tube equipped with a magnetic stir bar were added *p*-xylylenediamine (1.36 g, 10.0 mmol, 1 equiv), elemental sulfur (1.28 g, 40.0 mmol, 4 equiv), malonic acid **3** (1.04 g, 10.0 mmol, 1 equiv), and finally 7.5 mL of DMSO. The solution was stirred at 80 °C for 16 h. Following the reaction, the unrefined mixture was dissolved using 3 × 3 mL of DMF, and the excess of sulfur was removed via filtration and subsequently precipitated with 400 mL of MeOH. Afterward, the polymer product (displaying an orange-yellow hue) underwent purification through a 48 h Soxhlet extraction with MeOH to obtain 1.71 g of pure pale-yellow solid powder polymer **5a** in 96% yield. M_n = 84 000 g/mol, M_w = 115 900 g/mol, M_w/M_n = 1.38, T_g = 136 °C, and $T_{d,5\%}$ = 257 °C. FTIR (ATR), ν (cm^{-1}): 3350 (ν_{NH}), 3257, 3054 ($\nu_{Csp2\text{-}H}$), 2917($\nu_{Csp3\text{-}H}$),

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1606 ($\nu_{C=C}$), 1539−1500 ($\nu_{C=S}$), 1343−1217 (ν_{C-N}), 830, 506. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.91 (s, 2H, −NH−), 7.23 (s, 4H, $H^{7+8+10+11}$), 4.64 (s, 4H, H^{5+12}) .^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 183.01(C=S), 137.86 (C^{6+9}), 127.26 ($C^{7+8+10+11}$), 46.89 (C^{5+12}) ppm. Other procedures can be found in the SI.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.5c00177.

Synthesis and characterization of all polymers and small molecules (IR and ^{1}H NMR, ^{13}C NMR spectra, TGA thermograms, and DSC profiles) (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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