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European Polymer Journal



journal homepage: www.elsevier.com/locate/europolj

A metal-free and air-tolerable insertion polymerization using sulfoxonium ylides as monomers

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ARTICLE INFO	A B S T R A C T			
<i>Keywords:</i> Insertion polymerization Metal-free Polythioethers Aromatic polyamines	Insertion polymerization represents a concise approach to construct carbon-heteroatom bonds in the main chain. Despite some momentous efforts have been devoted to transition-metal catalyzed insertion polymerization, the metal-free insertion polymerization remains elusive. Herein, the fascinating metal-free and air-tolerable insertion polymerization using sulfoxonium ylides as monomers has been disclosed, furnishing a plethora of polythioethers and aromatic polyamines with carbon-heteroatom bonds in the main chain (yield up to 99%, Mn up to 20100). The insertion polymerization features mild condition, easy operation and broad substrate scope. In addition, thermal analysis demonstrated the polymers exhibited good thermal properties.			

1. Introduction

Polymers containing carbon-heteroatom bonds in the main chain have emerged as one of the most pivotal class of polymers. Insertion reaction has been exploited as the robust and highly efficient approach for the construction of C-X bonds [1]. To date, some efforts have been devoted to insertion polymerization (Scheme 1a) [2-9]. Since the seminal work of rhodium-catalyzed O-H insertion polymerization of bis (diazo-carbonyl) compounds reported by Ihara in 2010, a series of diverse poly(ether ketone)s, poly(ester ether ketone)s and poly (β -keto enol ether)s were obtained accompanying simultaneous insertion of a ring-opened tetrahydrofuran [3-6]. Later on, they applied InCl₃ as catalyst to O-H insertion polymerization, while the number-average molecular weight of the polymer was moderate [7]. In 2017, a ruthenium-catalyzed N-H insertion polymerization of diazo-carbonyl monomers was achieved to deliver various aromatic polyamines in moderate to good yields [8]. Very recently, our group reported the enantioselective Cu-catalyzed Si-H bond insertion polymerization under mild conditions, providing the polyesters with high optical purity [9]. Despite of these significant achievements, there were still some substantial limitations. The catalysts of insertion polymerization mainly focused on transition-metals and diazo compounds as monomers of insertion polymerization were prone to self-aggregation, which impede the evolution of insertion polymerization. Hence, the search for a cheap and ease of handling reaction system is of much interest and significant importance for insertion polymerization.

The metal-free catalyst system is gradually employed in polymeric chemistry in recent years due to their lower cost and comparatively environmentally benignity [10-11], while the metal-free insertion polymerization is still in vacancy. Sulfoxonium ylides with characteristic of easy to protonation, could occur the substitution reaction [12]. Furthermore, the catalyst-free insertion of sulfoxonium ylides into aryl thiols has been reported by Burtoloso in 2016 [12a]. In addition, sulfoxonium ylides have merits covering convenience of use and good thermal stability [13]. Thus, we speculated monomer of sulfoxonium ylide would be the appealing alternative for insertion polymerization, and contribute to extending to a metal-free insertion polymerization. Our proposed polymerization pathway was as following: the first step was to protonate sulfoxonium ylide to give the intermediate A, then A could react with insertion monomer by displacing the DMSO and releasing H⁺ to complete the catalytic cycle. The chain propagation took place in the same pattern to achieve insertion polymerization. Accordingly, herein we report a metal-free and air-tolerable insertion polymerization of sulfoxonium ylides, furnishing a rich array of polymers with excellent yields and high molecular weights (yield up to 99 %, Mn up to 20100) (Scheme 1b). This approach provides a sustainable and concise way to construct carbon-heteroatom bonds in the main chain, covering polythioethers and aromatic polyamines.

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https://doi.org/10.1016/j.eurpolymj.2022.111578

Received 14 July 2022; Received in revised form 4 September 2022; Accepted 9 September 2022 Available online 14 September 2022 0014-3057/© 2022 Published by Elsevier Ltd.



Scheme 1. Insertion polymerization.

2. Results and discussion

Due to polymers containing C—N bonds in the main chain with vital performance [14], N—H insertion polymerization was studied firstly. According to mechanism analysis, our research was initiated with aromatic diamine **1a** and sulfoxonium ylide **2a** in the presence of diphenyl phosphate (acid 1) as protonic acid in DCM at 80 °C (Table 1, entry 1). As expected, N—H insertion polymerization took place to furnish aromatic polyamine **3a** in moderate molecular weight and yield. Considering the critical role of acids for selective N—H insertion polymerization, then we began to screen a variety of acids. For example,

Table 1Optimization of reaction conditions.



5						• •
1	DCM	Acid 1	80	8600	1.78	81
2	DCM	Acid 2	80	5400	1.45	29
3	DCM	Acid 3	80	3500	2.09	57
4	DCM	TsOH·H ₂ O	80	6300	2.29	47
5	DCM	MeSO ₃ H	80	6600	2.23	60
6	Toluene	Acid 1	80	13600	2.89	51
7	EA	Acid 1	80	13300	2.73	42
8	THF	Acid 1	80	4900	1.71	36
9	CHCl ₃	Acid 1	80	7800	2.10	79
10	DCM	Acid 1	50	13000	2.61	75
11	DCM	Acid 1	110	4200	2.20	49
12	DCM	-	50	-	-	-

 $^{\rm a}Reaction$ conditions: 1a (0.15 mmol), 2a (0.15 mmol), acid (20 mol%), T $^{\rm o}C$, solvent (0.5 mL), 36 h.

^b Determined by GPC with RI.

^c Isolated yields.

when acid 2 was used, the aimed aromatic polyamine 3a was obtained in 29 % yield with Mn value of 5400 and PDI of 1.45 (entry 2). Replacing organic acid with more strong acid (TsOH·H₂O or MeSO₃H) resulted in a slight decrease on the reactivity and value of molecular weight (entries 4-5). Acid 1 proved to be the most suitable catalyst in terms of yield and molecular weight. In pursuit of higher molecular weight and better vield, other solvents of N-H insertion polymerization were next evaluated. However, things went contrary to our wishes that the results were not satisfactory. Toluene and EA gave higher molecular weight albeit with poor yields (entries 6-7). Switching the solvent to THF, only trace amounts of polymer 3a was obtained (entry 8). Pleasingly, lowering the temperature to 50 °C dramatically improved insertion polymerization performance, affording 3a in Mn of 13000 and 75 % yield (entry 10). Consistent with premise, no reaction occurred in the absence of acid, which confirmed that the acid catalyst was an inevitable parameter for concise N-H insertion polymerization (entry 12). Therefore, the optimal reaction conditions were finally established: Acid 1 (20 mol%) as the catalyst, DCM as the solvent, and the polymerization temperature of 50 °C

The scope of the metal-free N-H insertion polymerization was illustrated in Scheme 2. To our delight, this protocol was suitable to a series of commercially available inexpensive aromatic diamines 1a-1c with monomer 2a after slightly modified polymerization conditions. For example, the organocatalytic N-H insertion polymerization produced the aromatic polyamines 3b and 3c in moderate yields and molecular weight. Then, the substrate scope of sulfoxonium ylides for organocatalytic N-H insertion polymerization was studied by reaction with aromatic diamine 1a. By varying the tethering length between the ester group moiety, the corresponding aromatic polyamines 3d and 3e were synthesized in good to excellent yields (85 % and 90 %) and comparable values of molecular weight (14100 and 17100) respectively. Moreover, both electron-withdrawing (Cl) and electron-donating (Me) substituents on the para or meta position of the phenyl ring were tolerated, and all of these monomers were converted to the target aromatic polyamines 3f-3h in moderate yields and molecular weight.

Having successfully developed a metal-free N—H insertion polymerization, expanding the type of X-H insertion polymerization was the next goal. Polymers containing sulfur elements can enhance the material with intriguing performance, such as metal adsorption, high refractive index and complete recyclability [15]. From economic and



Scheme 2. Substrate scope of N-H insertion polymerization.

environmental perspectives, S—H insertion polymerization would be a promising and atom-economic complement to constructing sulfur-rich polymers [16]. To the best of our knowledge, no example of S—H insertion polymerization has been reported. Thus, the attention was turned to the S—H insertion polymerization.

Owing to the thiophenol with enough acidity to protonate sulfoxonium ylide, it contributed to carrying out a catalyst-free and airtolerable S-H insertion polymerization. In the initial study, the S-H insertion polymerization of 1,4-benzenedithiol 4a with sulfoxonium ylide 2a was performed in dichloromethane at 40 °C without additional catalyst. To our delight, polythioether 5a could be obtained, albeit with lower Mn value (3400) and yield (14 %) (Table 2, entry 1). Then, a systematic solvent screening was carried out (entries 2-8). It was found that the effect of solvents was a vital parameter to polymerization. Strong polar aprotic solvents such as CH₃CN and DMSO failed to deliver polythioether 5a (entries 2-3). Switching the solvent to THF, EA or toluene showed little improvement on Mn value and yield (entries 4-6). Notably, using the solvent which was insoluble for monomers, the better vield and Mn could be obtained, although the reason remains to be clarified. For example, the solvents hexane and cyclohexane yielded the desired polythioether 5a in Mn of 10600 and 14800 (entries 7-8), respectively.

Interestingly, the S—H insertion polymerization performed smoothly in neat, delivering the polythioether **5a** in 64 % yield with Mn of 12900 (entry 9). In view of economy and environment, a catalyst-free and solvent-free polymerization was the best option. Based on the above results, the main challenge was to improve the yield of polymerization. Varying the temperature to 80 °C, the efficiency of polymerization was significantly improved as the isolated yield increased from 64 % to 80 % (entry 11). When temperature was raised to 100 °C, it showed the comparable activity to 80 °C (entry 12). Satisfactorily, the yield and molecular weight of polythioether **5a** were sharply increased by employing 1.05 equiv of **2a** (entry 14). After comprehensive screening of the polymerization conditions, the fascinating S—H insertion polymerization performed smoothly in neat at 80 °C, delivering the polythioether **5a** in good yield, high molecular weight and narrow molecular

Table 2Optimization of reaction conditions.

	$ \begin{array}{c} $	$\xrightarrow{\text{Solvent, T °C, 24 h}} \left\{ S \xrightarrow{\text{Solvent, T °C, 24 h}}_{H O} \xrightarrow{\text{Solvent, T °C, 24 h}}_{H $					
Entry	Solvent	T (°C)	Mn ^b	$\mathbf{PDI}^{\mathrm{b}}$	Yield (%) ^c		
1	DCM	40	3400	1.53	14		
2	CH ₃ CN	40	-	-	-		
3	DMSO	40	-	-	-		
4	THF	40	4600	1.27	34		
5	EA	40	4900	1.41	40		
6	Toluene	40	2900	2.16	59		
7	Hexane	40	10600	2.08	66		
8	Cyclohexane	40	14800	2.51	68		
9	Neat	40	12900	1.79	64		
10	Neat	60	10900	2.11	70		
11	Neat	80	11100	1.93	80		
12	Neat	100	10100	1.93	83		
13 ^d	Neat	80	9600	1.95	70		
14 ^e	Neat	80	14800	2.08	95		

^aReaction conditions: **4a** (0.20 mmol), **2a** (0.20 mmol), solvent (0.5 mL), T $^{\circ}$ C, 24 h.

^b Determined by GPC with RI.

^c Isolated yields.

^d 4a (0.21 mmol).

^e **2a** (0.21 mmol).

weight distribution (entry 14).

With the optimal conditions in hand, we then focused on evaluating the generality of the catalyst-free S-H insertion polymerization (Scheme 3). The performance of different dithiols was first examined. This protocol was suitable for a plethora of commercial inexpensive source of aryl dithiols, furnishing the polythioethers 5a-5e with good vields, high molecular weight and narrow molecular weight distribution (Mn up to 20100 and yield up to 95 %). Regrettably, 1,4-phenylenedimethanethiol and aliphatic dithiols did not form the corresponding polythioethers even though in the present of acid catalyst. We further proceeded to investigate the catalyst-free S-H insertion polymerization of 4d with a series of sulfoxonium ylides 2. Considering the sulfoxonium ylides with differences in physical properties, the polymerization conditions were slightly modified and cyclohexane (0.5 mL) as solvent was added to promote yield and molecular weight. Then, a rich array of 2 with different chain length links could proceed smoothly, giving the aimed polythioethers 5f-5g with Mn value up to 10800 and yield up to 99 %. Besides, monomer 2d was also tolerated to furnish the polythioether 5h, regardless of its higher steric hindrance. Moreover, the monomers of sulfoxonium vlides containing electron-donating methyl group or electron-withdrawing chloro group on the aromatic ring were able to participate in catalyst-free S-H insertion polymerization, affording the corresponding polythioethers 5i-5k in excellent yields and high molecular weight. Furthermore, the catalyst-free S-H insertion polymerization could be extended to more sterically hindered monomer 2h with prolonged reaction time.

The NMR spectrum of representative polythioether **5a** was shown in Scheme 4. The aromatic proton signals of the polythioether **5a** were located 7.38–7.09 ppm. The characteristic peak of insertion polymerization (H_a) was at the range of 5.03–4.69 ppm. The CH₂CH₂ protons (H_b) in the main-chain appeared in 4.36–4.00 ppm. In ¹³C NMR spectrum of polythioether **5a**, the singlet at 169.9 ppm was identical to the typical carbonyl carbon of ester group. In addition, the singlet at 63.1 ppm was assigned to the characteristic carbon of insertion polymerization (C_a), and CH₂ carbon (*C_c*) was located at 55.9 ppm. Consequently, we confirmed a catalyst-free and air-stable S—H insertion polymerization was achieved.

On account of the first time to achieve S-H insertion



Scheme 3. Substrate scope of S-H insertion polymerization.



Scheme 4. NMR spectra analysis of polythioether 5a.

polymerization, thermal properties of some representative polythioethers **5** were investigated under nitrogen atmosphere using TGA and DSC (Scheme 5). Thermogravimetric analysis was conducted by heating the polythioethers **5** from room temperature to 500 °C at 10 °C/ min under N₂ atmosphere, indicating polythioethers **5** with different chain length links showed similar T₅₀ values. And the thermal decomposition temperatures of polythioethers **5** at 5 % weight loss were in the range of 182–307 °C. In contrast to polythioether **5d**, T₅ value of the polythioether **5g** was much higher, which probably caused by monomer **2c** with long chain length link. All of polythioethers **5** exhibited glass transition temperatures via DSC, and Tg values varied from 9.3 to 33.3 °C. These results showed that the tested polythioethers **5** exhibited good thermal stability.

3. Conclusions

In summary, we have successively developed a metal-free and airtolerable insertion polymerization using sulfoxonium ylides as monomers. This protocol offered an efficient and sustainable avenue to



Scheme 5. Thermal analysis of polythioethers 5.

construct carbon-heteroatom bonds in the main chain, across a broad range of polythioethers and aromatic polyamines with high molecular weight and narrow molecular weight distribution. Of note, this approach enabled the first catalyst-free S—H bond insertion polymerization. Additional work will mainly focus on the O—H insertion polymerization and synthesis of optically active polymers via insertion polymerization.

4. Experiments

4.1. Reagents and instrumentation

All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Solvents were treated prior to use according to the standard methods. ¹H NMR and ¹³C NMR spectra were recorded at room temperature in CDCl₃ on 400 MHz instrument with TMS as internal standard. Flash column chromatography was performed on silica gel (200-300 mesh). The heat source for all heating reactions is the oil bath, unless otherwise noted. Highresolution mass spectrometry (HRMS) was measured on an electrospray ionization (ESI) apparatus using the time-of-flight (TOF) mass spectrometry. The GPC was performed on a Waters 1515 chromatography system equipped with Agilent PL1110 column using THF as the eluent (35 °C, 1 mL/min). Polystyrene standards were used for calibration. DSC was performed on a DSC Instruments 204 HP calorimeter (purge gas: nitrogen, flow rate: 20 mL/min, ramp rate: 10 °C/min, temperature range: -100 to 300 °C). TGA was performed on a STA instrument 449 F3 thermogravimetric analyzer (purge gas: nitrogen, flow rate: 20 mL/min, ramp rate: 10 °C/min, temperature range: 25 to 500 °C).

4.2. Procedure for synthesis of monomers



The monomer of sulfoxonium ylides **2** could be synthesized from diazo compounds according to the known literature procedures [12,17], Among them, all of which are new compounds. The starting material diazo compounds **S2** are the known compounds and could be conveniently synthesized according to the known procedures [9].

Path A: A mixture of dirhodium tetraacetate (2 mol%, 106.0 mg) and dimethyl sulfoxide (10 mL) were placed in a dried Schlenk tube under nitrogen atmosphere. The mixture was stirred at 75 °C for 5 min. Then, a solution of diazo compound **S2a** (12 mmol, 4.200 g) in dimethyl sulfoxide (100 mL) was added dropwise to the Schlenk tube and the reaction was stirred at 75 °C for 24 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and diluted with water (50 mL). Then the mixture was extracted three times with dichloromethane (60 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate and filtered. The volatiles were removed under the reduced pressure. The residue was purified by column chromatography on silica gel using dichloromethane/ methanol (70/1) as eluent to afford the monomer of sulfoxonium ylide **2a**.

The pure monomer of sulfoxonium ylide **2a** could be further purified through recrystallization with hexanes/dichloromethane.

Using the above analogous experimental procedures, monomers of sulfoxonium ylides **2b-2h** could be conveniently prepared.

Path B: A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **S2b** (0.5 mmol, 203.2 mg) and dimethyl sulfoxide (DMSO, 4 mmol, 284 μ L) in dry DCM (2 mL) under a nitrogen atmosphere. The reaction mixture was then stirred for 22 h at room

temperature under LED (456 nm, 40 W). After the completion of the reaction, the reaction mixture was diluted with water (2 mL). Then the mixture was extracted three times with dichloromethane (5 mL \times 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate and filtered. The volatiles were removed under the reduced pressure. The residue was purified by column chromatography on silica gel using dichloromethane/methanol (70/1) as eluent to afford the monomer of sulfoxonium ylide **2b**.

Using the above analogous experimental procedures, monomers of sulfoxonium ylides **2c**, **2e** and **2f** could be conveniently prepared.

Ethane-1,2-diyl bis(2-(dimethyl(oxo)- λ^6 -sulfanylidene)-2-phenylacetate) (2a): 3.866 g, 72 % yield, white solid, mp 118–119 °C, new compound, R_f = 0.25 (dichloromethane/methanol 25/1). ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.27 (m, 8H), 7.26–7.19 (m, 2H), 4.27 (s, 4H), 3.28 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 165.4, 133.7, 132.8, 128.5, 127.0, 70.4, 61.6, 43.5. HRMS Calculated for C₂₂H₂₇O₆S₂ [M + H]⁺ 451.1244, found: 451.1220.

Hexane-1,6-diyl bis(2-(dimethyl(oxo)- λ^6 -sulfanylidene)-2-phenylacetate) (2b): Path A: 2.212 g, 45 % yield; Path B: 122 mg, 48 % yield, white solid, mp 157–158 °C, new compound, R_f = 0.26 (dichloromethane/methanol 25/1). ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.26 (m, 8H), 7.26–7.20 (m, 2H), 3.99 (t, *J* = 6.7 Hz, 4H), 3.39 (s, 12H), 1.58–1.41 (m, 4H), 1.32-1.20 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 166.5, 133.7, 132.7, 128.4, 127.0, 70.4, 63.0, 43.3, 29.0, 25.7. HRMS Calculated for C₂₆H₃₅O₆S₂ [M + H]⁺ 507.1870, found: 507.1826.

Nonane-1,9-diyl bis(2-(dimethyl(oxo)- λ^6 -sulfanylidene)-2-phenylacetate) (2c): Path A: 2.033 g, 40 % yield; Path B: 69 mg, 25 % yield, white solid, mp 99–100 °C, new compound, R_f = 0.22 (dichloromethane/methanol 25/1). ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.27 (m, 8H), 7.26–7.20 (m, 2H), 4.02 (t, *J* = 6.7 Hz, 4H), 3.41 (s, 12H), 1.60–1.45 (m, 4H), 1.29–1.16 (m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ 166.5, 133.7, 132.8, 128.4, 127.0, 70.4, 63.2, 43.3, 29.5, 29.2, 29.2, 26.1. HRMS Calculated for C₂₉H₄₁O₆S₂ [M + H]⁺ 549.2339, found: 549.2336.

1,4-Phenylenebis(ethane-2,1-diyl) bis(2-(dimethyl(oxo)-λ⁶-sulfanylidene)-2-phenylacetate) (2d): 2.561 g, 61 % yield, white solid, mp 209–210 °C, new compound, $R_f = 0.32$ (dichlorome- thane/methanol 25/1). ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.19 (m, 10*H*), 6.97 (s, 4H), 4.23 (t, J = 6.3 Hz, 4H), 3.29 (s, 12H), 2.82 (t, J = 6.5 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 136.7, 133.8, 132.6, 129.1, 128.4, 127.1, 70.5, 63.9, 43.1, 35.2. HRMS Calculated for $C_{30}H_{35}O_6S_2$ [M + H]⁺ 555.1870, found: 555.1867.

Ethane-1,2-diyl bis(2-(4-chlorophenyl)-2-(dimethyl(oxo)- λ^6 -sulfanylidene)acetate) (2e): Path A: 1.316 g, 69 % yield; Path B: 42 mg, 16 % yield, white solid, mp 215–216 °C, new compound, R_f = 0.24 (dichloromethane/methanol 25/1). ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.25 (m, 4H), 7.24–7.16 (m, 4H), 4.24 (s, 4H), 3.34 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 165.2, 134.7, 132.8, 131.1, 128.6, 69.0, 61.6, 43.5. HRMS Calculated for C₂₂H₂₅Cl₂ O₆S₂ [M + H]⁺ 519.0464, found: 519.0451.

Ethane-1,2-diyl bis(2-(dimethyl(oxo)-λ⁶-sulfanylidene)-2-(*p*-tolyl)acetate) (2f): Path A: 1.197 g, 25 % yield; Path B: 103 mg, 43 % yield, white solid, mp 224–225 °C, new compound, $R_f = 0.58$ (dichloromethane/methanol 25/1). ¹H NMR (400 MHz, CDCl₃) δ 7.17 (d, *J* = 8.0 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 4H), 4.25 (s, 4H), 3.29 (s, 12H), 2.33 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 165.6, 136.9, 133.7, 129.5, 129.3, 69.9, 61.6, 43.4, 21.3. HRMS Calculated for C₂₄H₃₁O₆S₂ [M + H]⁺ 479.1557, found: 479.1553.

Ethane-1,2-diylbis(2-(dimethyl(oxo)-λ^6-sulfanylidene)-2-(m-tolyl)acetate) (2 g): 0.802 g, 42 % yield, white solid, mp 188–189 °C,new compound, $R_f = 0.58$ (dichloromethane/methanol 25/1). ¹H NMR(400 MHz, CDCl₃) δ 7.17–7.11 (m, 2H), 7.08 (s, 2H), 7.06–6.96 (m, 4H),4.23 (s, 4H), 3.22 (s, 12H), 2.28 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ165.4, 138.0, 134.4, 132.6, 130.8, 128.4, 128.0, 70.5, 61.6, 43.4, 21.5.HRMS Calculated for C₂₄H₃₁O₆S₂ [M + H]⁺ 479.1557, found: 479.1553.Ethane-1,2-diylbis(2-(dimethyl(oxo)-λ⁶-sulfanylidene)-2-

(naphthalen-2-yl)acetate) (2h): 1.028 g, 19 % yield, white solid, mp 198–199 °C, new compound, $R_f = 0.58$ (dichloromethane/methanol 25/1). ¹H NMR (400 MHz, CDCl₃) δ 7.86–7.59 (m, 8H), 7.53–7.28 (m, 6H), 4.28 (s, 4H), 3.18 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 165.4, 133.5, 132.3, 131.9, 131.6, 130.5, 128.0, 127.8, 127.6, 126.1, 126.0, 70.8, 61.6, 43.3. HRMS Calculated for $C_{30}H_{31}O_6S_2$ [M + H]⁺ 551.1557, found: 551.1530.

4.3. Procedure for organocatalytic N-H insertion polymerization



Typical procedure: To an oven-dried 10 mL reseatable Schlenk flask equipped with a magnetic stir bar was charged diphenyl phosphate (0.03 mmol, 7.5 mg), monomer of aromatic diamine **1a** (0.15 mmol, 27.6 mg), monomer of sulfoxonium ylide **2a** (0.15 mmol, 67.6 mg) and dichloromethane (0.5 mL) under air. The flask was heated at 50 °C for 36 h. After the polymerization, the reaction mixture was cooled to room temperature, and the aromatic polyamine **3a** was purified by the precipitation method.

The polyamine **3a** was soluble in dichloromethane and insoluble in methanol, so these two solvents were used in the precipitation process. The reaction mixture was first homogenized by the addition of as low as possible amount of dichloromethane (1.0 mL). Then cold methanol (20 mL) was added portionwise until it turned to a biphasic mixture. The top layer was taken out, and the bottom solid layer was washed with methanol two times until it gave a dark brown solid polymer. The resulting aromatic polyamine **3a** was dried to a constant weight.

Using the above analogous experimental procedures, the aromatic polyamine **3b-3h** could be conveniently prepared and characterized by ¹H NMR, ¹³C NMR, GPC, TG and DSC.

Aromatic polyamine (3a): 54 mg, 75 % yield, dark brown soft solid. ¹H NMR (400 MHz, CDCl₃) δ 7.48–7.37 (m, 4H), 7.32–7.22 (m, 10H), 6.64–6.37 (m, 4H), 5.23–4.60 (m, 4H), 4.42–4.12 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 171.7, 144.5, 137.4, 131.3, 129.1, 128.6, 127.3, 127.3, 113.8, 63.0, 60.8, 60.7.

Aromatic polyamine (3b): 35 mg, 58 % yield, dark brown soft solid. ¹H NMR (400 MHz, CDCl₃) δ 7.42–7.33 (m, 4H), 7.26–7.13 (m, 6H), 6.51–6.19 (m, 4H), 4.93–4.74 (m, 2H), 4.45 (s, 2H), 4.30–4.05 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 138.8, 137.8, 128.9, 128.4, 127.3, 115.3, 62.8, 61.7.

Aromatic polyamine (3c): 50 mg, 68 % yield, colorless solid. ¹H NMR (400 MHz, CDCl₃) δ 7.44–7.35 (m, 4H), 7.31–7.23 (m, 6H), 6.82–6.66 (m, 4H), 6.57–6.35 (m, 4H), 4.97–4.82 (m, 2H), 4.71 (s, 2H), 4.38–4.04 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 171.7, 150.3, 141.6, 137.4, 129.0, 128.6, 127.3, 127.3, 119.6, 114.5, 63.0, 62.9, 61.3, 61.2.

Aromatic polyamine (3d): 68 mg, 85 % yield, dark brown soft solid. ¹H NMR (400 MHz, CDCl₃) δ 7.53–7.44 (m, 4H), 7.34–7.23 (m, 10H), 6.69–6.45 (m, 4H), 5.39–4.50 (m, 4H), 4.12–3.94 (m, 4H), 1.50–1.35 (m, 4H), 1.12–0.93 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 172.0, 144.6, 138.0, 131.2, 128.9, 128.4, 127.3, 127.2, 113.8, 65.6, 61.0, 28.3, 25.2.

Aromatic polyamine (3e): 77 mg, 90 % yield, dark brown soft solid. ¹H NMR (400 MHz, CDCl₃) δ 7.56–7.47 (m, 4H), 7.34–7.18 (m, 10H), 6.69–6.37 (m, 4H), 5.45–4.55 (m, 4H), 4.17–3.99 (m, 4H), 1.59–1.43 (m, 4H), 1.21–1.01 (m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ 172.0, 144.6, 138.0, 131.2, 128.9, 128.3, 127.3, 127.2, 113.8, 65.9, 61.0, 29.4, 29.1, 28.5, 25.7.

Aromatic polyamine (3f): 77 mg, 94 % yield, dark brown soft solid. ¹H NMR (400 MHz, CDCl₃) δ 7.45–7.22 (m, 12H), 6.67–6.30 (m, 4H), 5.17–4.64 (m, 4H), 4.42–4.11 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 144.1, 135.9, 134.4, 131.5, 129.2, 128.7, 127.3, 113.9, 63.2, 60.2.

Aromatic polyamine (3g): 54 mg, 71 % yield, dark brown soft solid. ¹H NMR (400 MHz, CDCl₃) δ 7.37–7.23 (m, 8H), 7.13–7.00 (m, 4H), 6.67–6.27 (m, 4H), 5.32–4.59 (m, 4H), 4.41–4.12 (m, 4H), 2.28 (s, 3H), 2.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.8, 144.5, 138.4, 134.4, 131.3, 129.7, 127.3, 127.2, 113.8, 63.0, 60.4, 21.3.

Aromatic polyamine (3h): 44 mg, 58 % yield, dark brown soft solid. ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.05 (m, 12H), 6.70–6.33 (m, 4H), 5.40–4.51 (m, 4H), 4.40–4.08 (m, 4H), 2.29 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 171.8, 144.6, 138.8, 137.4, 131.3, 129.4, 128.9, 127.9, 127.3, 124.5, 113.8, 63.0, 62.9, 60.9, 60.8, 21.6.

4.4. Procedure for catalyst-free S—H insertion polymerization



Typical Procedure: To an oven-dried 10 mL resealable Schlenk flask equipped with a magnetic stir bar was charged the monomer of aryl dithiol **4a** (0.2 mmol, 28.4 mg) and monomer of sulfoxonium ylide **2a** (0.21 mmol, 94.6 mg) in neat under air. The flask was heated at 80 $^{\circ}$ C (sand bath temperature) for 24 h. After the polymerization, the reaction mixture was cooled to room temperature, and the polythioether **5a** was purified by the precipitation method.

The polythioether **5a** was soluble in dichloromethane and insoluble in methanol, so these two solvents were used in the precipitation process. The reaction mixture was first homogenized by the addition of as low as possible amount of dichloromethane (1.0 mL), then cold methanol was added portionwise (20 mL) until it turned to a biphasic mixture. The top layer was taken out, and the bottom solid layer was washed with methanol two times until it gave a white solid polymer. The resulting polythioether **5a** was dried to a constant weight and characterized by ¹H NMR, ¹³C NMR, GPC, TG and DSC.

Using the above analogous experimental procedures, the polythioethers **5d** and **5e** could be conveniently prepared.

For the synthesis of polythioethers (**5b**, **5c**, **5f-5l**), cyclohexane (0.5 mL) as solvent was needed during the catalyst-free S—H insertion polymerization.

Polythioether (5a): 83 mg, 95 % yield, colorless foamy solid. ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.25 (m, 10H), 7.24–7.09 (m, 4H), 5.03–4.69 (m, 2H), 4.16 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 135.1, 133.7, 132.7, 132.6, 132.6, 128.9, 128.6, 127.9, 63.1, 55.9.

Polythioether (5b): 54 mg, 62 % yield, colorless soft solid. ¹H NMR (400 MHz, CDCl₃) δ 7.47–7.25 (m, 10H), 7.25–6.91 (m, 4H), 4.77 (s, 2H), 4.15 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 136.2, 135.2, 134.7, 134.6, 132.0, 131.9, 129.5, 128.9, 128.7, 63.1, 55.9.

Polythioether (5c): 85 mg, 83 % yield. colorless soft solid. ¹H NMR (400 MHz, CDCl₃) δ 7.45–7.33 (m, 12H), 7.31–7.25 (m, 6H), 4.98–4.83 (m, 2H), 4.31–4.08 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 139.8, 139.7, 135.3, 133.2, 132.9, 132.8, 128.9, 128.7, 128.6, 127.6, 63.1, 63.1, 56.0.

Polythioether (5d): 102 mg, 84 % yield, colorless foamy solid. ¹H NMR (400 MHz, CDCl₃) δ 7.43–7.22 (m, 14H), 6.91–6.75 (m, 4H), 4.92–4.69 (m, 2H), 4.36–4.09 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 157.3, 135.9, 135.8, 135.4, 131.1, 128.8, 128.7, 128.5, 127.5, 119.8, 119.5, 63.0, 56.7.

Polythioether (5e): 106 mg, 85 % yield, colorless foamy solid. ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.35 (m, 4H), 7.31–7.25 (m, 6H), 7.21 (dd, *J* = 8.3, 2.9 Hz, 4H), 7.11 (dd, *J* = 8.4, 2.2 Hz, 4H), 4.83 (s, 2H), 4.34–4.07 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 170.0, 135.5, 135.1, 133.2, 133.2, 132.9, 131.4, 128.9, 128.6, 63.1, 56.0.

Polythioether (5f): 117 mg, 99 % yield, colorless foamy solid. ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.36 (m, 4H), 7.33–7.26 (m, 10H), 6.82 (d, J = 8.6 Hz, 4H), 4.80 (s, 2H), 4.03 (t, J = 6.6 Hz, 4H), 1.55–1.42 (m,

4H), 1.24–1.09 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 170.5, 157.2, 135.9, 135.7, 128.8, 128.7, 128.4, 119.4, 65.7, 57.2, 28.4, 25.4.

Polythioether (5g): 117 mg, 94 % yield, colorless foamy solid. ¹H NMR (400 MHz, CDCl₃) δ 7.43–7.36 (m, 4H), 7.33–7.26 (m, 10H), 6.83 (d, *J* = 8.6 Hz, 4H), 4.81 (s, 2H), 4.06 (t, *J* = 6.7 Hz, 4H), 1.61–1.49 (m, 4H), 1.26–1.10 (m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ 170.5, 157.2, 135.9, 135.7, 128.7, 128.7, 128.4, 119.4, 66.0, 57.2, 29.4, 29.1, 28.5, 25.8.

Polythioether (5h): 126 mg, 99 % yield, colorless foamy solid. ¹H NMR (400 MHz, CDCl₃) δ 7.42–7.34 (m, 4H), 7.32–7.23 (m, 10H), 6.96 (s, 4H), 6.80 (d, J = 8.5 Hz, 4H), 4.79 (s, 2H), 4.25 (t, J = 6.4 Hz, 4H), 2.79 (t, J = 6.9 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 170.3, 157.2, 135.7, 135.7, 129.1, 128.7, 128.7, 119.4, 66.2, 57.2, 34.6.

Polythioether (5i): 129 mg, 99 % yield, colorless foamy solid. ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.23 (m, 12H), 6.90–6.77 (m, 4H), 4.79–4.66 (m, 2H), 4.24 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 169.7, 157.4, 136.2, 134.5, 134.0, 130.1, 129.0, 127.0, 119.6, 63.1, 56.1.

Polythioether (5j): 103 mg, 93 % yield, colorless foamy solid. ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.27 (m, 4H), 7.27–7.22 (m, 4H), 7.12–7.02 (m, 4H), 6.91–6.77 (m, 4H), 4.96–4.68 (m, 2H), 4.32–4.04 (m, 4H), 2.29 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 170.3, 157.2, 157.2, 138.4, 135.7, 135.6, 132.3, 129.5, 128.6, 127.7, 119.5, 63.0, 56.5, 21.3.

Polythioether (5k): 102 mg, 92 % yield, colorless foamy solid. ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.26 (m, 4H), 7.22–7.12 (m, 6H), 7.11–7.04 (m, 2H), 6.91–6.75 (m, 4H), 4.86–4.70 (m, 2H), 4.33–4.04 (m, 4H), 2.29 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 170.3, 157.2, 138.5, 135.7, 135.7, 135.2, 129.3, 129.3, 128.7, 127.7, 125.7, 119.4, 63.0, 56.7, 21.5.

Polythioether (5l): 104 mg, 83 % yield, colorless foamy solid. ¹H NMR (400 MHz, CDCl₃) δ 7.75–7.58 (m, 8H), 7.49–7.34 (m, 6H), 7.25–7.12 (m, 4H), 6.79–6.59 (m, 4H), 5.00–4.81 (m, 2H), 4.40–4.13 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 157.2, 136.0, 136.0, 133.1, 128.7, 128.1, 128.0, 127.8, 126.6, 126.5, 126.1, 119.7, 119.4, 63.1, 57.0.

CRediT authorship contribution statement

Xiao-Qing Wang: Investigation, Visualization, Writing – original draft, Writing – review & editing. Yu-Qing Bai: Validation, Writing – original draft. Kun Wang: Validation. Bo Wu: Supervision, Validation, Writing – original draft, Writing – review & editing. Yong-Gui Zhou: Conceptualization, Supervision, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgment

Financial support from National Natural Science Foundation of China (21690074) and Chinese Academy of Sciences (DICP I202015) is acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2022.111578.

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