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Diversified synthesis of poly(sulfonyl isourea)s by multicomponent polymerizations of isocyanides, sulfonyl azides, and alcohols/phenols†

Dongyang Fan,‡[a] Fenggang Chen,‡[a] Dong Wang, [ID][a] Ting Han*[a] and Ben Zhong Tang [ID] *[b]

Multicomponent polymerization (MCP) has become a powerful tool for the preparation of polymers with complex or well-defined structures. The development of MCPs that can take full advantage of the great diversity of monomer combinations is attractive but still remains challenging. Herein, we report a facile MCP method using isocyanides, sulfonyl azides, and alcohol/phenols as monomers, in which the monomer combination can be readily tuned to achieve the diversity-oriented synthesis of poly(sulfonyl isourea)s in excellent atom economy. By systematically optimizing the polymerization conditions and changing the functionalities and combinations of monomers, a series of heteroatom-rich polymers with sulfonyl isourea units and high molecular weights (M_w values of up to 120 500) were successfully prepared. All the obtained polymers exhibit good thermal stability, and the variation in polymer backbone structures led to an obvious difference in their morphological stability. This diversity-oriented MCP strategy may provide inspiration and new possibilities for the development of heterochain polymers with advanced functionalities.

Introduction

The development of new polymerization tools for the preparation of functional polymeric materials with novel structures and excellent properties is an important research topic in the field of polymer science. Most polymerizations are developed from small molecular organic reactions. Among various strategies, multicomponent reactions (MCRs) have attracted much attention in organic chemistry due to their high atom economy, simple operation, good functional group tolerance, and high efficiency.[1–5] Taking advantage of MCRs, polymer chemists have devoted great efforts to introducing them into the field of polymer synthesis. The derived multicomponent polymerization (MCP) strategies provide new possibilities for the efficient preparation of structurally complex and well-defined polymers from simple precursors.[6–12] In comparison with traditional homopolymerizations and two-component

polymerizations, one remarkable and unique advantage of MCPs is the excellent product diversity. By tuning the combinations of monofunctional and bifunctional monomers, a vast variety of polymer structures can be facilely generated by one MCP strategy.[11,13–16] However, the main focus of reported MCPs is still on the development of an MCP with a single type of monomer combination. There have been few studies that fully exploit the applicability of different monomer combinations to facilitate diversity-oriented polymer synthesis.

As a representative group of MCPs, MCPs based on triple-bond-containing monomers can yield polymers with conjugated linkers such as double bonds, triple bonds and aromatic heterocycles or special structural units.[17–25] The unique structures can impart attractive thermal, mechanical, optical, electrical, magnetic and biological properties to the polymers.[26–29] By combining the advantages of the classical click chemistry of copper-catalyzed alkyne–azide cycloadditions and MCP strategies, MCPs derived from the MCRs of alkynes and sulfonyl azides have become a powerful toolbox for the synthesis of heterochain or heterocyclic polymers.[25,30–35] For example, a series of MCPs of alkynes, sulfonyl azides, and nucleophilic reagents have been developed for the preparation of diverse polyamidines and polyimidates.[31,32] As depicted in Scheme 1A, MCPs based on alkynes and sulfonyl azides mainly work through the formation of ketenimine as the key intermediate to give heteroatom-rich target products. With amines as nucleophilic reagents, polyamidines can be readily

[a]*Center for AIE Research, Guangdong Provincial Key Laboratory of New Energy Materials Service Safety, College of Materials Science and Engineering, Shenzhen University, Shenzhen, Guangdong 518060, China. E-mail: hanting@szu.edu.cn*
[b]*School of Science and Engineering, Shenzhen Institute of Aggregate Science and Technology, The Chinese University of Hong Kong, Shenzhen (CUHK-Shenzhen), Guangdong 518172, China. E-mail: tangbenz@cuhk.edu.cn*
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‡These authors contributed equally to this work.
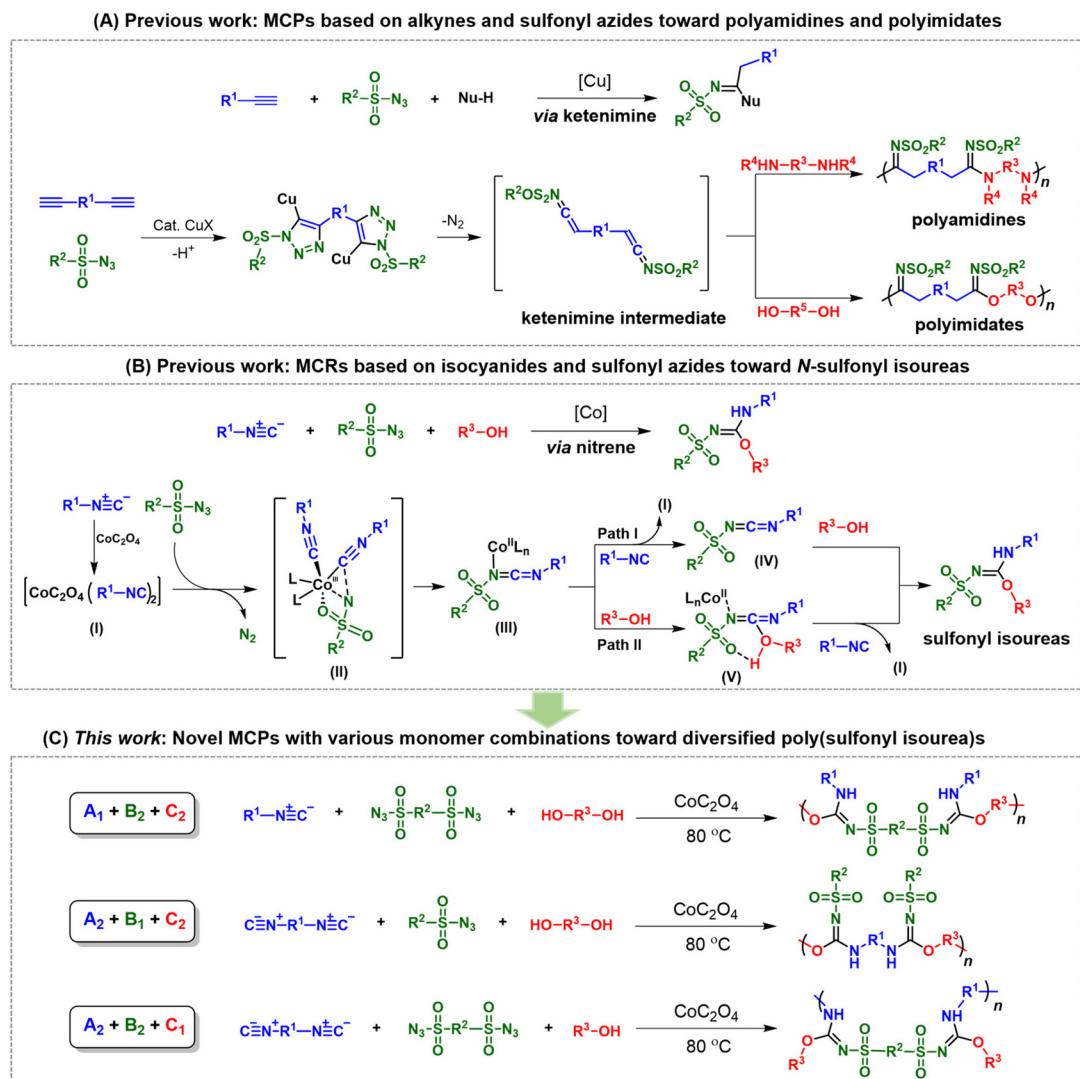
Scheme 1 (A) Multicomponent polymerizations (MCPs) based on alkynes and sulfonyl azides; (B) multicomponent reactions (MCRs) based on iso-cyanides and sulfonyl azides toward *N*-sulfonyl isoureas; (C) MCPs reported in this work with various monomer combinations.

generated.[32] When alcohols were employed as nucleophiles, polyimidates were produced with high efficiency.[31]

Apart from acetylenic monomers, isocyanides, another class of triple-bond-containing monomers, have also been introduced to MCPs as highly reactive monomers.[22,24,36] They are capable of reacting with almost any type of reagent such as electrophiles, nucleophiles and even free radicals to construct heterocyclic and spirocyclic compounds with the C=N unit in polymer backbones. The high reactivity of isocyanide substrates greatly reduces the harsh requirements for synthetic conditions, which makes them widely used in the preparation of heteroatom-rich compounds and pharmaceutical molecules. Classical isocyanide-based MCPs mainly include Passerini three-component polymerizations and Ugi multicomponent polymerizations.[13,22,37–40] In recent years, some fascinating MCPs with isocyanide and sulphur or selenium as monomers have also been developed to synthesize multifunctional heteroatom-rich polymers in a facile, economical and highly efficient

manner.[41–46] However, despite the attractive merits of click-type MCPs and isocyanide-based MCPs, MCPs with both iso-cyanides and sulfonyl azides as monomers have rarely been reported.

Recently, Ji *et al.* reported a cobalt-catalyzed MCR of isocya-nides, sulfonyl azides, and alcohols for the preparation of *N*-sulfonyl isoureas (Scheme 1B).[47] This MCR has the advantages of high efficiency, wide substrate scope and ease of operation. Unlike the MCRs of alkynes and sulfonyl azides, and nucleophilic reagents, the reaction mechanism of this isocya-nide-based MCR involves nitrene as the key intermediate. First, the cobalt complex activates two isocyanide molecules to form intermediate I. Then, the sulfonyl azide substrate releases one molecule of N_2 and coordinates with intermediate I *via* transition state II to afford the reactive intermediate (III, nitrene) with the N=C=N structure. There exist two paths in the following procedure. In path I, intermediate III reacts with isocyanide to give intermediate IV, which is then attacked by

the alcohol to give the target molecule. In path II, intermediate III coordinates with alcohol to form intermediate V, which then undergoes exchange with isocyanide to form the final product. The mechanism of this MCR is relatively lucid and the structure of the product is well-defined. The produced sulfonyl isoureas exhibit the structural features of both amidines and imidates. The introduction of such structures into polymer backbones may impart the corresponding polymers with the properties and functionalities of both polyamidines and polyimidates.

Inspired by this MCR, herein we developed a novel MCP strategy with isocyanides, sulfonyl azides and alcohols/phenols for the preparation of poly(sulfonyl isourea)s (Scheme 1C). To take full advantage of the facile monomer tunability of this MCP, we thoroughly explored the possibility of this MCP for diversity-oriented polymer synthesis. The combination of isocyanide, sulfonyl azide, and alcohol/phenol monomers with different functionalities resulted in the realization of three routes of MCPs ($A_1 + B_2 + C_2$, $A_2 + B_1 + C_2$, and $A_2 + B_2 + C_1$), which greatly improved the diversity of polymerization products. The MCPs displayed relatively good tolerance to different functional groups and all polymerizations can be carried out under mild conditions. The obtained heteroatom-rich poly(sulfonylisourea)s exhibited molecular weight (M_w) values of up to 120 500 g mol^{-1}, with isolated yields ranging from 25% to 87%. All of the resulting polymers displayed good solubility and thermal stability.

Results and discussion

Polymerization

To advance MCPs for the efficient synthesis of poly(sulfonyl isourea)s, a series of isocyanide, sulfonyl azide, and alcohol/phenol monomers were systematically designed and synthesized based on the literature.[14,48,49] The readily available compounds 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (**1a**), 4,4′-oxydibenzenesulfonyl azide (**2a**), and hexane-1,6-diol (**3a**) were selected as model monomers to optimize the polymerization conditions in the combination "$A_1 + B_2 + C_2$".

Initially, polymerization was conducted in air using DCE at 80 °C with 10 mol% CoC$_2$O$_4$ and a monomer concentration of [**2a**] = 0.2 M for 24 hours. The monomer feed ratio of **1a**, **2a**, and **3a** was 2 : 1 : 1. Under such polymerization conditions, the product with an M_w of 8700 g mol^{-1} was obtained in only 21% yield. To enhance both yield and molecular weight, various solvents were tested (Table 1, entries 1–5). The results with THF were similar to those with DCE, while using a small amount of polar toluene, the molecular weight was increased, but the yield was reduced to 12%. Polymerization in DMF led to undesired products, while MeCN, a solvent with higher polarity, yielded slightly better results than DCE and a significantly improved molecular weight. Therefore, MeCN was selected as the optimal solvent. Further optimization focused on catalyst loading (Table 1, entries 5–8). The yield and molecular weight increased continuously as the amount of CoC$_2$O$_4$ was increased to 30 mol% and remained constant when the loading was further increased to 40 mol%. Additionally, no enhancement in yield or molecular weight was observed when the monomer concentration was increased (Table 1, entries 9 and 10). Considering both activity and cost, 30 mol% CoC$_2$O$_4$ with a 0.2 M monomer concentration was chosen for further optimization.

Excess isocyanide may enhance polymerization based on the mechanism of small molecules.[47,50,51] As depicted in Scheme 1B, reactive intermediate I was formed by combining CoC$_2$O$_4$ with two isocyanide monomers, though this process was slow and challenging. Thus, a surplus of isocyanide might

Table 1 Optimization of the multicomponent polymerization of A_1, B_2 and C_2 ^{a}

Entry	Solvent	CoC$_2$O$_4$ (mol%)	[**2a**] (M)	[**1a**] : [**2a**] : [**3a**]	Yield (%)	M_n ^{b} (g mol^{-1})	M_w ^{b} (g mol^{-1})	$Đ$ ^{b}
1	DCE	10	0.2	2 : 1 : 1	21	6800	8700	1.3
2	THF	10	0.2	2 : 1 : 1	20	7700	8900	1.2
3	Toluene	10	0.2	2 : 1 : 1	12	10 300	13 300	1.3
4	DMF	10	0.2	2 : 1 : 1	UD^c	—	—	—
5	MeCN	10	0.2	2 : 1 : 1	24	9800	12 500	1.3
6	MeCN	20	0.2	2 : 1 : 1	48	10 200	13 100	1.3
7	MeCN	30	0.2	2 : 1 : 1	58	10 600	14 000	1.3
8	MeCN	40	0.2	2 : 1 : 1	57	10 700	14 000	1.3
9	MeCN	30	0.3	2 : 1 : 1	45	10 400	13 400	1.3
10	MeCN	30	0.4	2 : 1 : 1	48	10 600	13 200	1.3
11	MeCN	30	0.2	3 : 1 : 1	68	13 300	17 200	1.3
12	MeCN	30	0.2	4 : 1 : 1	75	11 800	15 300	1.3
13	MeCN	30	0.2	5 : 1 : 1	55	12 400	15 600	1.3

^{a} The polymerizations were carried out at 80 °C for 24 h under air. ^{b} Estimated by gel permeation chromatography (GPC) with DMF containing 0.05 M LiBr as the mobile phase on the basis of a linear polystyrene calibration. Dispersity ($Đ$) = M_w/M_n. ^{c} Product with undesired and unidentified structures.

be necessary to produce sufficient intermediate I for stoichiometric balance with the sulfonyl azide monomer. Results in entries 11–13 of Table 1 showed that increasing the ratio of **1a** improved the polymerization efficiency. When the monomer ratio of [**1a**]:[**2a**]:[**3a**] was 4:1:1, the yield increased to 75% with an M_w of 15 300 g mol^{-1}. Further increasing the ratio led to a noticeable decrease in yield. Consequently, the optimal monomer ratio for the polymerization reaction was established as 4:1:1. In summary, the optimal conditions for this MCP are conducting the polymerizations in MeCN at 80 °C for 24 h in air in the presence of 30 mol% CoC$_2$O$_4$ with a monomer ratio of **1a**:[**2a**]:[**3a**] = 0.8:0.2:0.2.

Based on the optimized conditions, we explored the monomer scope. Various disulfonyl azides, isocyanides, and alcohols/phenols were used in the polymerizations (Table S1, entries 1–4†). Polymerization did not occur with monomer **1b**, probably due to activation of the C–H bonds adjacent to the isocyanide group under the polymerization conditions, which led to a side reaction rather than polymerization. Monomer **1c**, which has steric hindrance adjacent to the isocyanide group, resulted in polymer **P1c2a3a** with a molecular weight (M_w) of 19 900 g mol^{-1} and a yield of 44%. When the aliphatic monomer **1d** containing a morpholine structure was employed, polymer **P1d2a3a** was obtained with a yield of 62% and an M_w of 15 500 g mol^{-1}. However, both polymers exhibited lower purity. We then examined the scope of sulfonyl azide monomers. Monomer **2b** yielded a gelatinous product (Table S1, entry 5†). Even under adjusted polymerization conditions, such as shorter reaction time, the target polymer remained insoluble, indicating the high reactivity of monomer **2b**. The use of monomer **2c**, which contains flexible alkoxy chains, produced unidentified byproducts (Table S1, entry 6†). Finally, we examined the reactivity of the third component. In addition to the aliphatic diol **3a**, the reactivity of diphenol was also explored using monomer **3b** (Table S1, entry 7†). The polymerization reaction could proceed smoothly to give **P1a2a3b**.

Structural characterization

To gain insight into the structures of the synthesized polymers, model compound **model-1** was prepared according to Scheme S1,† in accordance with the reported literature.[47] The structure of **model-1** was fully characterized using high-resolution mass spectrometry (HRMS), NMR techniques (Fig. S1 and S2†), and FT-IR spectroscopy (Fig. 1D).

The characterization results of **P1a2a3a** were compared with those of **model-1** and the corresponding monomers, as illustrated in Fig. 1. The characteristic peaks associated with the N≡C and N$_3$ stretching vibrations at 2152 cm^{-1} and 2125 cm^{-1} for monomers **1a** and **2a**, respectively, nearly disappeared in both **model-1** and **P1a2a3a**. This observation indicated the consumption of isocyanide and azide by MCP.

^{1}H NMR analysis was performed to gain more detailed information about the polymer structure. As illustrated in Fig. 2A–E, the resonance peaks corresponding to the methyl and methylene groups of **1a** at positions "a" and "b" were
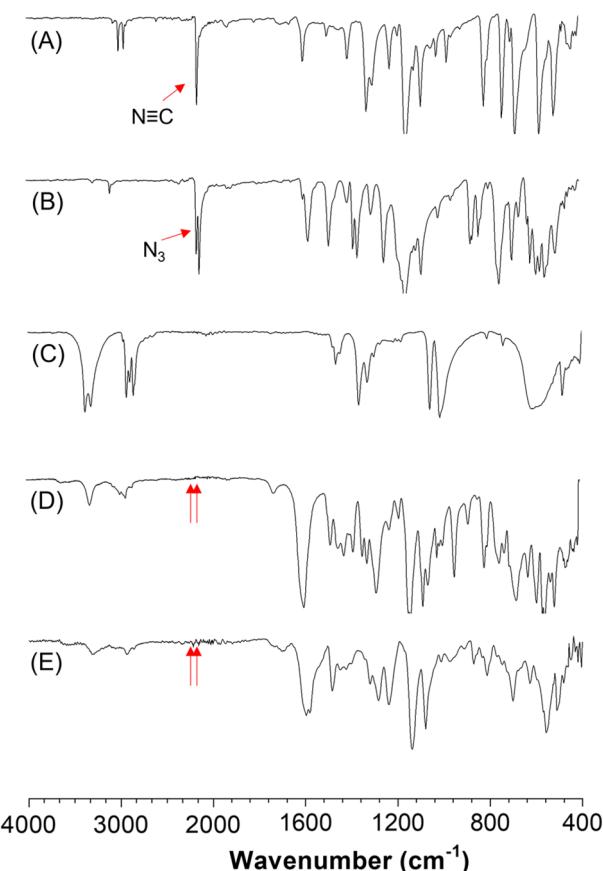
Fig. 1 IR spectra of (A) **1a**, (B) **2a**, (C) **3a**, (D) **model-1**, and (E) **P1a2a3a**.

observed in similar regions of the ^{1}H NMR spectra for both **model-1** and **P1a2a3a**. The OH proton (position "c") of monomer **1c** that resonated at δ 1.70 ppm disappeared, while the resonance peak of the proton at position "d" was shifted to low-field positions e and e′ after the reaction. New peaks at positions "f" and "f′" in the products were attributed to the NH protons of the sulfonyl isourea units. These observations confirm that polymerization successfully occurred and that new sulfonyl isourea structures were formed *via* the MCP processes.

The polymer structure was further validated through ^{13}C NMR analysis (Fig. 3A–E). The carbon associated with the isocyanide group ("a") in monomer **1a** disappeared after the reaction, while the methylene carbon ("b") was detected at similar positions ("c" and "c′") in both **model-1** and **P1a2a3a**. The signal at position "d" in **2a** was retained in **P1a2a3a** at position "e". The resonance peak at position "f" in **3a** shifted to lower fields, appearing at positions "g" and "g′" in **model-1** and **P1a2a3a**, respectively. Carbon signals corresponding to the newly formed imine groups ("h" and "h′") were detected in both **model-1** and **P1a2a3a**, indicating the formation of sulfonyl isourea groups. Similar features were observed in the NMR results of other polymers (Fig. S3–S5†), confirming that the MCP processes successfully produced the target polymers.
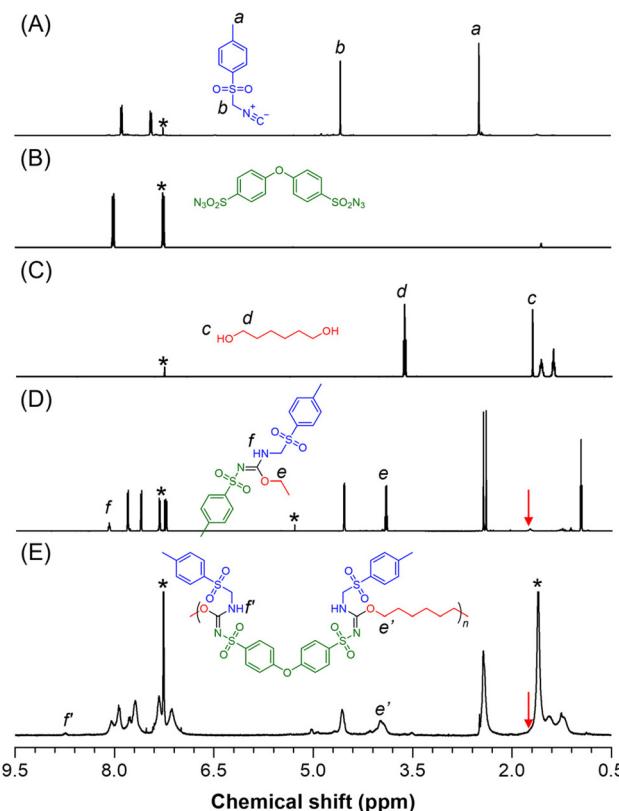
Fig. 2 ^{1}H NMR spectra of (A) **1a**, (B) **2a**, (C) **3a**, (D) **model-1**, and (E) **P1a2a3a** in CDCl$_3$. The solvent peaks are marked with asterisks.


Fig. 3 ^{13}C NMR spectra of (A) **1a**, (B) **2a**, (C) **3a**, (D) **model-1**, and (E) **P1a2a3a** in CDCl$_3$. The solvent peaks are marked with asterisks.

MCPs of other monomer combinations

Although the applicability of monomers for route A$_1$ + B$_2$ + C$_2$ was not fully satisfactory, the results still demonstrated the potential for multi-route polymerization. Consequently, we next investigated MCPs using the monomer combinations of A$_2$ + B$_1$ + C$_2$ (Table 2).

Initially, polymerization was performed using DCE as the solvent under the optimized conditions previously described. The first attempt of MCP yielded a product with a molecular weight (M_w) of 15 800 g mol^{-1} but only achieved a 20% yield (Table 2, entry 1). Due to this low efficiency, we subsequently explored variations in monomer ratios and solvents. Adjusting the monomer ratio to 1 : 3 : 1 resulted in a slight increase in yield, while using DCE as the solvent slightly improved the molecular weight (Table 2, entries 2–5). The low yield may be attributed to the significant steric hindrance of monomer **1e**, which likely impeded the efficient formation of diimide intermediates with sulfonyl azide monomers. Consequently, we employed the less hindered diisocyanide monomer **1f**, which led to a notable increase in yield to approximately 60% (Table 2, entry 6). Additionally, when ethylene glycol monomer **3c** was polymerized with **1f** and **2d**, both yield and molecular weight improved slightly (Table 2, entry 7). However, small amounts of impurities were detected in the structures of the resulting products. Detailed characterization data for this route are available in the ESI (Fig. S6–S10†).

Based on the reaction mechanism, the polymerization of difunctionalized isocyanide, difunctionalized sulfonyl azide, and alcohol (A$_2$ + B$_2$ + C$_1$) initially forms polymer main chains, which then react with the third component to generate branched chains. This process differs significantly from the previous two routes. Initial polymerization attempts under the optimal conditions of the first route yielded only 20% (Table 3, entry 1), with the formation of a large amount of orange insolubles. These insolubles, probably resulting from the reaction between isocyanide and sulfonyl azide, exhibited poor solubility in MeCN, which negatively impacted subsequent polymerizations. Switching solvents to DCE and DMF improved the solubility and subsequently the polymerization yields. In DCE, the yield of **P1f2a3d** increased to 76% with a molecular weight (M_w) of 120 500 g mol^{-1}, making DCE the optimal solvent (Table 3, entries 2 and 3). The yield of **P1e2a3d** reached 87% with a M_w of 78 300 g mol^{-1} (Table 3, entry 4). To explore the potential for fluorescence applications, we conducted MCPs with a TPE-containing phenolic monomer **3e** (Table 3, entries 5 and 6). Despite achieving a bright yellowish-green fluorescence, the polymer structure was incorrect. Even upon changing the solvent and other conditions, we failed to achieve the target product. The differences in electronegativity and chemical properties between phenols and alcohols may have contributed to the polymerization failure. Detailed characterization data for this route are available in the ESI (Fig. S10–S14†).

Table 2 Optimization and monomer scope of the multicomponent polymerization of A_2, B_1 and C_2 [a]

Entry	Polymer	Solvent	[1] (M)	[1]:[2]:[3]	Yield (%)	M_n [b] (g mol^{-1})	M_w [b] (g mol^{-1})	$Đ$ [b]
1	**P1e2d3a**	DCE	0.2	1:2:1	20	12 100	15 800	1.3
2	**P1e2d3a**	DCE	0.2	1:3:1	25	20 500	22 600	1.1
3	**P1e2d3a**	DCE	0.2	1:4:1	23	19 900	22 500	1.1
4	**P1e2d3a**	DMF	0.2	1:3:1	UD[c]	—	—	—
5	**P1e2d3a**	MeCN	0.2	1:3:1	26	19 500	21 100	1.1
6	**P1f2d3a**	DCE	0.2	1:3:1	60[d]	19 200	23 000	1.2
7	**P1f2d3c**	DCE	0.2	1:3:1	61[d]	19 900	24 700	1.2

[a] The polymerizations were carried out using CoC_2O_4 (30 mol%) at 80 °C for 24 h under air. [b] Estimated by gel permeation chromatography (GPC) with DMF containing 0.05 M LiBr as the mobile phase on the basis of a linear polystyrene calibration. Dispersity ($Đ$) = M_w/M_n. [c] Product with undesired and unidentified structures. [d] Product with the coexistence of the desired structure and impure structure.

Table 3 Optimization and monomer scope of the multicomponent polymerization of A_2, B_2 and C_1 [a]

Entry	Polymer	Solvent	[1] (M)	Amount of 3	Yield (%)	M_n [b] (g mol^{-1})	M_w [b] (g mol^{-1})	$Đ$ [b]
1	**P1f2a3d**	MeCN	0.2	0.5 mL	20	13 800	20 700	1.5
2	**P1f2a3d**	DCE	0.2	0.5 mL	76	36 300	120 500	3.3
3	**P1f2a3d**	DMF	0.2	0.5 mL	73	32 100	60 600	1.9
4	**P1e2a3d**	DCE	0.2	0.5 mL	87	44 000	78 300	1.8
5	**P1e2a3e**	DCE	0.2	0.5 M	UD[c]	—	—	—
6	**P1f2a3e**	DCE	0.2	0.5 M	Gel	—	—	—

[a] The polymerizations were carried out using CoC_2O_4 (30 mol%) at 80 °C for 24 h under an air atmosphere and a monomer molar ratio of [1] = [2] = 0.2 M. [b] Estimated by gel permeation chromatography (GPC) with DMF containing 0.05 M LiBr as the mobile phase on the basis of a linear polystyrene calibration. Dispersity ($Đ$) = M_w/M_n. [c] Product with undesired and unidentified structures.

Solubility and thermal properties

The prepared heteroatom-rich poly(sulfonyl isourea)s in this work all exhibit good solubility and can be dissolved in commonly used organic solvents such as DCM, CHCl$_3$, THF, DMSO, and DMF.

The thermal properties of representative polymers were evaluated for each MCP route. Fig. 4A presents the specific structures and molecular weights of the polymers. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed to assess thermal and morphological stability. As shown in Fig. 4B, the thermal degradation temperature (T_d) at 5% weight loss of these polymers reached 220–278 °C. Among the polymers, **P1a2a3a** with long alkyl chains in the main chains and sulfonamide side chains showed the lowest T_d values. In contrast, **P1e2d3a**, which also contained alkyl chains in the main chains but had sulfonimide side chains, demonstrated excellent thermal stability with a T_d value of 274 °C. **P1e2a3d** and **P1f2a3d** with more rigid main chains and higher molecular weights showed
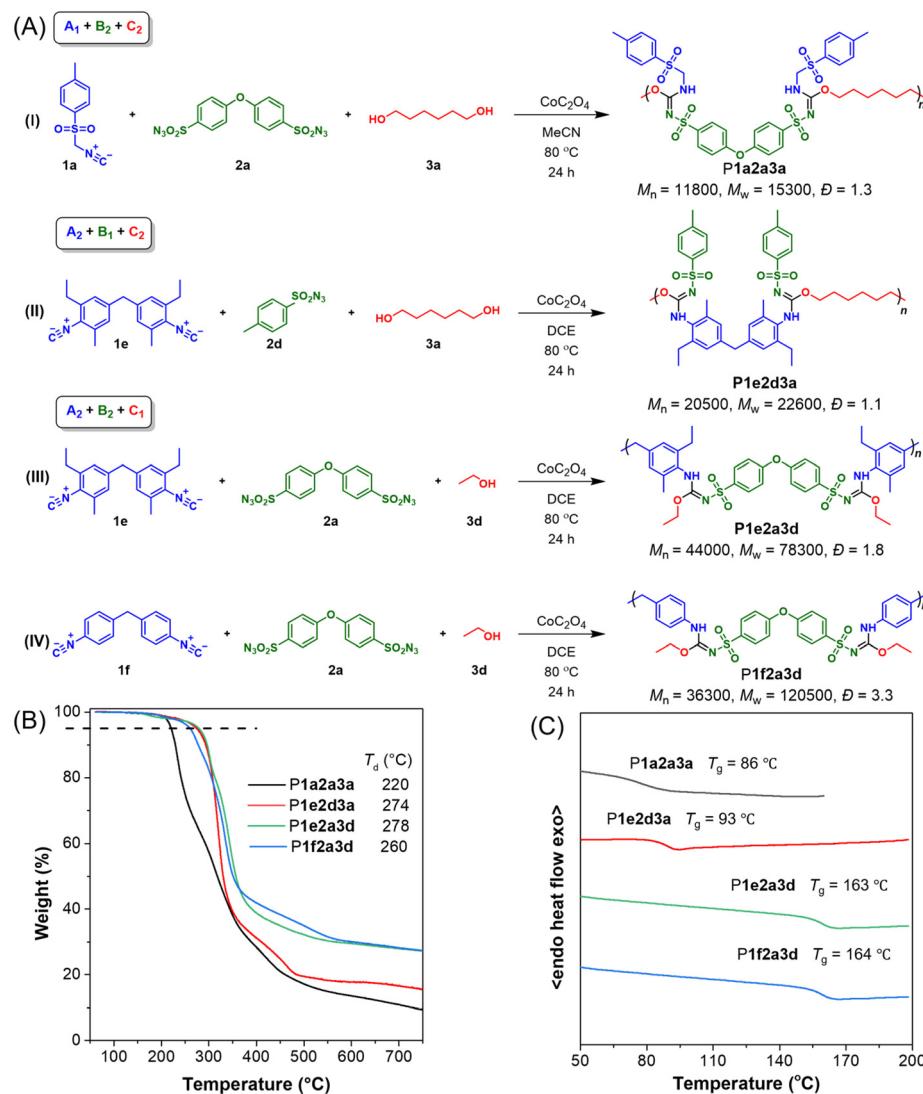
Fig. 4 (A) The specific structures and molecular weights of **P1a2a3a**, **P1e2d3a**, **P1f2a3d** and **P1e2a3d**. (B) TGA thermograms of polymers recorded under nitrogen at a heating rate of 10 °C min^{-1}. (C) DSC thermograms of polymers recorded under nitrogen during the second heating cycle at a heating rate of 10 °C min^{-1}.

superior thermal stability. It is worth noting that polymer structures greatly affect char residue values. In general, polymers with rigid structures and high molecular weights tend to exhibit higher char residue values. For example, **P1a2a3a** and **P1e2d3a**, which have flexible alkyl chains and low molecular weights, exhibited low char residue values of approximately 9% and 15% at 800 °C, respectively. In contrast, **P1e2a3d** and **P1f2a3d** with aromatic conjugated structures and high molecular weights exhibited a higher char residue value of around 27%. As shown in Fig. 4C, the glass transition temperature (T_g) of these polymers ranged from 86 °C to 164 °C. **P1a2a3a** and **P1e2d3a** had the lowest T_g values, attributed to the presence of long alkyl chains in their backbones, while **P1e2a3d** and **P1f2a3d** exhibited higher T_g values. This suggests that polymers with more rigid main chains have higher T_g values, and *vice versa*.

Conclusions

In summary, we have successfully developed a new MCP strategy of isocyanides, sulfonyl azides, and alcohols/phenols for the preparation of heteroatom-rich poly(sulfonyl isourea)s. Based on the facile preparation of the difunctionalized monomers, possible monomeric combinations are fully achieved to realize the diversity of polymer structures of MCPs. A series of poly(sulfonyl isourea)s with different main chains and branched chains were conveniently prepared under mild reaction conditions. The obtained polymers showed high M_w values of up to 120 500 g mol^{-1} with high yields of up to 87%. These polymers have good solubility, and thermal and morphological stability. It is foreseeable that the present MCP strategy could provide new inspiration and possibilities for the facile and efficient preparation of heteroatom-rich multifunc-

tional polymers and may facilitate the development of diversity-oriented polymerization strategies.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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