Cu(I)-Catalyzed Heterogeneous Multicomponent Polymerizations of Alkynes, Sulfonyl Azides, and NH₄Cl

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ABSTRACT: Nitrogen-containing polymers are a group of fascinating materials, which are usually prepared from nitrogen-containing organic monomers produced from NH₃ gas or aqueous solution of ammonia. The direct utilization of safe, clean, convenient, and inexpensive inorganic NH₄Cl salt as a nitrogen source for the construction of functional polymers is highly desired but challenging. Multicomponent polymerizations, with their strong designability, structural diversity, high efficiency, simple procedure, and environmental benefit, have been proven to be powerful tools to efficiently convert simple monomers to complex polymer materials. In this work, Cu(I)-catalyzed multicomponent polymerizations of alkynes, sulfonyl azides, and NH₄Cl are developed, utilizing simple inorganic NH₄Cl salt to serve as a monomer for the preparation of functional poly(sulfonyl amidine)s. The heterogeneous polymerization goes smoothly at room temperature in CH₂Cl₂/tetrahydrofuran, which is also applicable to a range of different monomer structures, affording seven poly(sulfonyl amidine)s with high yields (up to 96%) and high molecular weights (up to 47,100 g/mol). Unique functionalities such as photophysical properties and metal ion detection can be introduced to the poly(sulfonyl amidine)s either from monomer structures or the in situ generated product structures, rendering them as selective and sensitive fluorescence sensors for Ru³⁺. This multicomponent polymerization showed high synthetic efficiency with environmental and economic benefit, which has opened up a feasible synthetic method of using inorganic NH₄Cl salt instead of organic amines, isocyanates, nitriles, or nitrides to construct nitrogen-containing polymers, demonstrating a promising synthetic approach for the synthesis of advanced functional polymer materials.

INTRODUCTION

Nitrogen-containing polymers, ranging from natural macromolecules including polypeptides, proteins, DNA, and RNA to synthetic polymers such as polyamines, polyamides, polyimides, polyureas, polyurethanes, polyaminals, polyimides, and cationic polyelectrolytes, are a large group of fascinating materials with adjustable mechanical, electrical, and coordination properties, which are widely applicable in noble metal extraction, photoluminescence (PL), elastomers, solar cells, bioimaging, CO₂ capture, self-healing materials, and photo-responsive materials. Nitrogen-containing synthetic polymers are generally prepared from nitrogen-containing organic small molecular monomers or precursors such as amines, isocyanates, isocyanides, and nitriles, the generations of which usually involve the amination reaction with ammonia gas or the aqueous solution of ammonia at harsh conditions including high pressure and elevated temperatures, causing operational inconvenience and potential danger. Compared with NH₃ gas and the aqueous solution of ammonia, the inorganic NH₄Cl salt, a natural source known as sal-ammoniac, is a more convenient, safer, and cleaner nitrogen source, which is easy to qualify and operate. While NH₄Cl is utilized as the additive to assist many reactions, the direct utilization of NH₄Cl as the building block of polymer materials is highly desired but rarely reported, probably because of the poor solubility of NH₄Cl in common organic solvents. Few organic reactions have been mentioned to realize amination using NH₄Cl as an alternative to ammonia to afford amines and primary amides. However, the direct incorporation of NH₄Cl in polymer synthesis remains challenging. With the recent trend in polymer chemistry of using simple molecules in nature such as H₂O, CO₂, S₈, and O₂ to directly serve as monomers for the construction of functional polymers, it is of great research interest to develop feasible synthetic approaches to directly convert NH₄Cl to nitrogen-containing polymers with unique structures and advanced functionalities.

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Direct conversion from NH₄Cl to poly(sulfonyl amidine)

Yields up to 96%

Mw up to 47,100 g/mol

Ru³⁺ detection

R = aryl, alkyl

Heterogeneous Multicomponent Polymerization

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and regulating material properties.\textsuperscript{34} Compared with conventional polymerizations, MCPs can provide a simpler procedure to construct diversified polymers with complex structures from three or more monomers in the one-pot procedures, featuring advantages of high efficiency, simple procedure, structural diversity of products, high atom economy, and environmental friendliness.\textsuperscript{35} With efforts from polymer chemists in the past decade, a great number of MCPs have been developed, including isocyanide-based Passerini three-component polymerizations and Ugi four-component polymerizations.\textsuperscript{36,57} Alkyne-based A\textsuperscript{3}-polycouplings.\textsuperscript{38} Cu(I)-catalyzed alkyne and sulfonyl azide-based MCPs,\textsuperscript{39} elemental sulfur-based MCPs,\textsuperscript{40,41} MCPs of activated alkynes,\textsuperscript{42,43} multicomponent tandem polymerizations of alkynes,\textsuperscript{44,45} the organic ammonium salt NH\textsubscript{4}OAc-involving Hantzsch multicomponent condensations,\textsuperscript{46,47} and so forth. These MCPs have emerged as powerful tools for the construction of polymer materials with unique chemical, sequential, or topological structures\textsuperscript{48} and high-performance advanced functionalities.

Inspired by this MCR, NH\textsubscript{4}Cl was designed as the third-component monomer of the heterogeneous alkyne and sulfonyl azide-based MCP in this work, which served as the direct nitrogen source for the construction of N-unsubstituted poly(sulfonyl amidine). Despite the poor solubility of NH\textsubscript{4}Cl in the reaction solvent, the MCP proceeded smoothly and efficiently at mild conditions, affording polymers with high molecular weights, high yields, satisfying solubility, high thermal stability, and potential application as a fluorescent chemosensor for Ru\textsuperscript{3+}.

\section*{RESULTS AND DISCUSSION}

\subsection*{Multicomponent Polymerizations.} A NH\textsubscript{4}Cl solid was directly used as a monomer to investigate the feasibility of the Cu(I)-catalyzed MCP of diyne, disulfonil azide, and NH\textsubscript{4}Cl. The MCP of fluorene-containing diyne 1a, aromatic disulfonil azide 2a, and NH\textsubscript{4}Cl 3 was first carried out in CH\textsubscript{2}Cl\textsubscript{2} at room temperature (\textdegree{}C) under a nitrogen atmosphere in the presence of CuI and Et\textsubscript{3}N (Scheme 1). KOH was added to accelerate the reaction by reacting with NH\textsubscript{4}Cl to generate ammonia and avoid the production of H\textsuperscript{+} that may inhibit the generation of the ketenimine intermediate.\textsuperscript{59} After 18 min, an insoluble precipitate was formed in CH\textsubscript{2}Cl\textsubscript{2} in 75\% yield, which was partially soluble in dimethylformamide (DMF) with a high molecular weight (M\textsubscript{w}) of 42,500 g/mol for the soluble portion. The high reactivity in CH\textsubscript{2}Cl\textsubscript{2} has led to the formation of polymer products with high M\textsubscript{w} and poor solubility, which were then coated on the undissolved NH\textsubscript{4}Cl solid, causing large molecular weight dispersity. The MCP was then conducted in different solvents, as shown in Table S1. While no polymer could be obtained in polar solvents such as DMF, dimethylacetamide, and dimethyl sulfoxide (DMSO), a polymer with good solubility and a M\textsubscript{w} of 17,200 g/mol was produced in 69\% yield after reaction in tetrahydrofuran (THF) for 1 h. To balance the reaction efficiency and product solubility, CH\textsubscript{2}Cl\textsubscript{2}/THF mixtures with the volume ratio tuned from 1/2 to 3/1 were investigated as solvents, and the optimal result was afforded in CH\textsubscript{2}Cl\textsubscript{2}/THF (v/v, 3/1), generating a soluble polymer with a M\textsubscript{w} of 24,400 g/mol in 93\% yield after 40 min.

The study of the loading ratios of CuI and KOH suggested that the optimal polymerization result was obtained in the presence of 20 mol\% of CuI and 2 equivalents of KOH referenced with the diyne monomer 1a (Table S2). While excess amount of NH\textsubscript{4}Cl 3 was beneficial to the MCP, the study of the monomer loading ratio of 1a and 2a revealed that the strict 1:1 ratio of 1a and 2a was crucial to obtain a soluble...
polymer with high yield, whereas higher $M_w$ could be afforded with the sacrifice of solubility when a slightly excess amount of disulfonyl azide 2a was adopted (Table S3).

The monomer concentration effect of the MCP was then studied in CH$_2$Cl$_2$/THF (v/v, 3/1) with the fixed monomer loading ratio of [1a]/[2a]/[3] = 1:1:3 (Table S4, entry 1–6). When the concentrations of 1a or 2a were increased from 0.05 to 0.20 M, the $M_w$ was gradually increased from 10,000 to 33,800 g/mol, and the yield was increased from 43 to 96%.

Further increase of the monomer concentration led to gelation. Moreover, the time course of the MCP suggested that the polymer started to form in 10 min, a large amount of insoluble precipitate was agglomerated after 60 min, and the optimal polymerization time was determined to be 40 min (Table S4, entry 7–9) (Scheme 1).

To investigate the monomer scope and enrich the structural diversity of the products, various aromatic diynes 1a–d, aliphatic diynes 1e–f, and aromatic disulfonyl azides 2a, 2b...
were designed as monomers to polymerize with NH₄Cl (Scheme 2A). The MCPs generally went smoothly under the optimal condition at room temperature in CH₂Cl₂/THF (v/v, 3/1) under a nitrogen atmosphere with 0.20 M of 1a–f and the monomer loading ratio of [1a–f]/[2a–b]/[3] = 1:1:3 (Chart 1 and Table S5). The aromatic diynes generally deliver better polymerization results compared with the aliphatic diynes, affording various poly(sulfonyl amidine)s with the Mn of 33,800−47,100 g/mol in 83−96% yields.

**Structural Characterizations.** The chemical structures of the MCP products were characterized by ¹H and ¹³C NMR and IR spectra, proving by the comparison of the corresponding spectra of polymer products with their monomers and small molecular model compound S (Scheme 2B). In the ¹H NMR spectrum of P1, the terminal alkyn proton peak at δ 4.20 from 1a was absent, and the aromatic proton peaks at δ 8.12 and 7.48 from monomer 2a were shifted to δ 7.76 and 7.05, respectively (Figure 1A–D). Most importantly, three new peaks emerged at about δ 8.81, 8.07, and 3.61 in the ¹H NMR spectrum of P1, corresponding to the newly generated N–H and C=N groups, respectively. Similarly, in the ¹³C NMR spectrum of P1, the resonances of terminal alkyn carbon of 1a at δ 81.1 and 84.2 were absent, the resonance peak of aromatic carbon adjacent to sulfonyl group in 2a at δ 160.3 shifted to δ 158.2, and two new peaks emerged at δ 168.2 and 42.6, in correspondence with the newly formed imine carbons and CH₂ carbons, respectively (Figure 1E–H). In the IR spectrum of P1, the C≡C and C=O stretching vibration bands of 1a at 2102 and 3303 cm⁻¹, respectively, and the N₃ stretching vibration bands of 2a at 2156 cm⁻¹ were absent, while two new absorption bands appeared at 3236−3415 and 1637 cm⁻¹, indicating the existence of newly formed N–H and C=N groups, respectively (Figure S1). For P2−P7, the characteristic ¹H NMR peaks at δ 8.61−8.90, 8.02−8.21, and 2.69−3.63 (Figure S2), the ¹³C NMR peaks at δ 167.3−168.8 and 36.9−42.7 (Figure S3) and the IR peaks at 3220−3450 and 1628−1645 cm⁻¹ all emerged (Figure S4), proving their expected poly(sulfonyl amidine) structures.

**Kinetic Study of the MCP.** To study the kinetic process of the MCP, the in situ Fourier transform infrared (FT-IR) spectra of the polymerization solution of 1a, 2a, and 3 before and after 60 min reaction, together with the CH₂Cl₂/THF solutions of 1a or 2a with the identical concentrations, are compared in Figure S5. The polymerization process was monitored under a nitrogen atmosphere at room temperature, with the focus on the resonance peaks at ~1637 and 1556 cm⁻¹ related to the stretching vibration of C=N and the in-plane bending vibration of N−H, respectively (Figure 2A). The plots of peak intensity versus polymerization time counting from the addition of triethylamine suggest that in the first 10 min, both peak intensities at ~1637 and 1556 cm⁻¹ increased rapidly, which were slowed down in the next 20 min, and precipitates were observed in solution and covered on the in situ IR detector. Rapid growth of the peak intensities was observed again after 30 min until saturation was reached in 1 h, accompanying the formation of a large amount of precipitates (Figure 2B,C). Furthermore, the absorbance band at 1376 cm⁻¹ from disulfonyl azide 2a disappeared after the polymerization, suggesting the consumption of the monomer.

**Solubility, Thermal Stability, and Refractivity.** The poly(sulfonyl amidine)s possess satisfying solubility in polar solvents such as DMF and DMSO, although they can hardly be dissolved in THF and dichloromethane, probably because of

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**Figure 1.** ¹H NMR spectra of (A) 1a, (B) 2a, (C) S, and (D) P1 in DMSO-d₆. ¹³C NMR spectra of (E) 1a, (F) 2a, (G) S, and (H) P1 in DMSO-d₆. The solvent peaks were marked with asterisks.
the existence of potential intermolecular hydrogen bonds among sulfonyl amidine groups. These polymers also enjoy high thermal resistance, and their thermogravimetric analysis (TGA) suggest that their decomposition temperatures at 5 wt % weight loss under a nitrogen atmosphere range from 239 to 298 °C (Figure 3A). Moreover, the rich heteroatoms and aromatic rings have endowed these poly(sulfonyl amidine)s with a high refractive index ($n$) value. The $n$ values of the spin-coated thin films of P1 and P3 were measured to be 1.6763−1.7367 in a wide wavelength region of 400−1700 nm, and their chromatic dispersions in the infrared region were 0.0022 (P1) and 0.0070 (P3), suggesting their higher refractive indices and lower chromatic dispersion compared with commercial optical plastics such as polycarbonates, poly(methyl methacrylate), celluloses, and polystyrene ($n = 1.49−1.59$) (Figure 3B and Table S6).

**Photophysical Properties and Fluorescence Detection of Ru$^{3+}$.** Unique functionalities such as photophysical properties and metal ion detection can be introduced to these poly(sulfonyl amidine)s from monomer structures or the in
situ generated product structures. The UV absorption spectra of P1−P7 were investigated in dilute DMSO solution (Figure S6). While the rest of the polymers possess no significant absorption peak beyond 300 nm, the fluorene-containing polymers P1 and P7 possess absorption maxima at 311 nm. Moreover, P3 with a tetraphenylethene moiety, a well-known aggregation-induced emission (AIE)-active fluorophore, possesses a broad absorbance peak at ∼316 nm. The PL spectra and fluorescence quantum efficiency of P3 were then investigated in DMSO/water mixtures with different water contents. As shown in Figure 4A,B, no emission could be observed from the DMSO solution of P3; however, when a poor solvent, water, was gradually added into DMSO solution, an emission peak emerged at 481 nm, reaching a maximum in 60 vol % aqueous mixture with the corresponding fluorescence quantum efficiency of 8.4% (Figure 4C). Further increase in water content in the solution led to a slight decline of emission intensity, probably because of the reduction of the effective concentration, resulting from the formation of precipitates with high water content.

Furthermore, the amidine groups in P3 can serve as a metal ligand which may selectively coordinate with Ru3+,62 delivering different fluorescence signals to realize sensitive fluorescence detection of Ru3+, which is crucial, considering that the extensive use of ruthenium in catalysts nowadays may increase the direct contact and exposure to humans and may cause severe damage to health.63 The PL spectrum of P3 in the DMSO/water mixture with 60 vol % water was tested in the presence of 14 different metal ions including Ag+, Au3+, Cd2+, Ce3+, Co2+, Cr3+, Fe3+, Gd3+, Mg2+, Mn2+, Ni2+, Ru3+, Zn2+, and Zr4+, respectively (Figure 5A). While the rest of the metal ions did not show obvious influence on the emission intensity, dramatic fluorescence quenching was observed for Ru3+ selectively. When the concentration of Ru3+ in the 60 vol % aqueous mixture of P3 was gradually increased from 0 to 20 μM, the PL intensity at 481 nm continuously decreased without any change in the spectral profile (Figure 5B). The Stern–Volmer plot of I0/I versus Ru3+ concentration demonstrated a linear relationship (Figure 5C). The quenching constant Ksv and the limit of detection (LOD) were calculated to be 3.1 × 10^5 M^-1 and 9.4 × 10^-8 M, respectively, suggesting high sensitivity of Ru3+ detection with the poly(sulfonyl amidine).

**CONCLUSIONS**

In this work, simple inorganic salt NH4Cl was designed as a monomer of alkyne and sulfonyl azide-based MCPs to directly serve as the nitrogen source of nitrogen-containing polymers. The MCPs proceeded conveniently and efficiently at mild
conditions at room temperature under the catalysis of CuI, converting NH₄Cl to imine moieties with high atom economy and affording poly(sulfonyl amidine)s with well-defined structures, high yields, high molecular weights, good solubility, thermal stability, and high refractivity. Furthermore, the poly(sulfonyl amidine)s enjoy metal coordination ability, which can be combined with other functionalities from the monomer such as fluorescence. For example, the tetraphenylethene-containing poly(sulfonyl amidine) features AIE property and selective coordination with Ru²⁺, which was proven to be a promising fluorescence chemosensor for Ru³⁺ with good selectivity and sensitivity. The MCP has demonstrated a feasible synthetic approach for the direct utilization of inorganic NH₄Cl salt in the construction of advanced functional nitrogen-containing polymer materials.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c02139.

Materials and instruments; synthetic procedures and characterization data; proposed reaction mechanism; polymerization condition optimization on solvent, concentration of CuI and KOH, and the monomer loading ratio on the MCP of 1a, 2a, and 3; synthesis, IR spectra, and UV–vis absorption spectra of P1–P7; ¹H and ¹³C NMR spectra of P2–P7; in situ FT-IR spectra of 1a and 2a in the CH₂Cl₂/THF solutions; polymerization solution with 1a, 2a, and 3 before and after 60 min reaction; and refractive indices and chromatic dispersions of thin films of P1 and P3 (PDF)

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**Notes**
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