

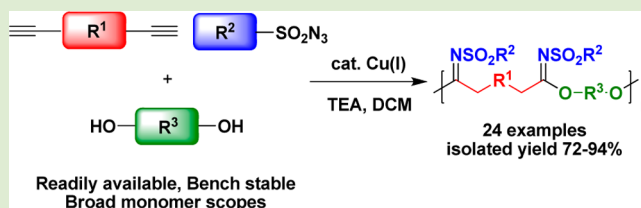
# Preparation of a Library of Poly(*N*-sulfonylimidates) by Cu-Catalyzed Multicomponent Polymerization

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**S** Supporting Information

**ABSTRACT:** Efficient synthesis of polyimidates has been a great challenge because of the difficulty of imidate bond formation and limited substrate scope. Here, we describe a successful method for the synthesis of various poly(*N*-sulfonylimidates) using Cu-catalyzed multicomponent polymerization (MCP). Minimizing water contamination in the polymerization, which results in low-molecular-weight oligomers, allows various combinations of three types of monomers (diynes, sulfonyl azides, and diols) that are bench stable and readily accessible, providing access to a library of polyimidates. Moreover, the formation of polyimidates is highly selective over the conventional click reactions. Most importantly, this report demonstrates a successful MCP that overcomes the drawbacks of previous MCP methods showing narrow monomer scope and producing low-molecular-weight polymers.



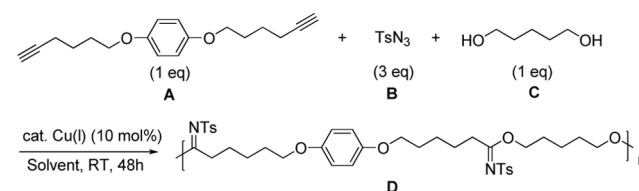
Multicomponent polymerization (MCP) based on multicomponent reactions is a highly efficient process for making complex polymer structures by using orthogonal reactivities among monomers. While typical polycondensations use two types of monomers (A and B), MCP uses three or more types of monomers (A, B, and C) and can easily expand the dimension of monomer combinations, making accessible a library of polymers. Various reactions such as the Cu-catalyzed three-component reaction,<sup>1</sup> Passerini reaction,<sup>2</sup> Mannich reaction,<sup>3</sup> and A<sup>3</sup> coupling<sup>4</sup> have been applied to MCP.<sup>5</sup> As a result, polyester,<sup>6</sup> poly(ester amide),<sup>7</sup> polyether,<sup>8</sup> poly(ester ether ketone),<sup>9</sup> polyurethane,<sup>10</sup> polythiourethane,<sup>11</sup> and poly(*p*-phenylenevinylene)<sup>12</sup> have been synthesized by MCP based on a step-growth mechanism. However, in spite of the versatility of MCP, many of the systems show narrow monomer scope and yield low-molecular-weight polymer because of side reactions and low conversions.

To overcome the previous drawbacks of MCP, our group chose a Cu-catalyzed three-component reaction and recently demonstrated a successful MCP to prepare a library of high-molecular-weight poly(*N*-sulfonylamidines) from diynes, sulfonyl azides, and diamines.<sup>13</sup> If diols are used as alternative nucleophiles, polyimidates will be formed by an analogous Cu-catalyzed MCP. Polyimidates have attracted our attention because of their particular heat resistance<sup>14</sup> and use in resin materials.<sup>15</sup> In addition, the Chapman rearrangement of polyimidates has produced novel polyamides.<sup>16–18</sup> However, only a handful of examples of polyimide synthesis have been reported because imidate formation itself is quite challenging.<sup>19</sup> For this reason, the previous synthesis of polyimidates has been limited to two-component step-growth polymerizations using diols and moisture-sensitive imidoyl chlorides. Therefore, a new efficient method for preparing various polyimidates with broad monomer scope is welcomed, especially if MCP is possible with

readily available monomers. Herein, we report a versatile method used to prepare a library of poly(*N*-sulfonylimidates) by Cu-catalyzed MCP from various diynes, sulfonyl azides, and diols.

To test the synthesis of polyimidates by MCP, we initially polymerized monomers A, B, and C (Table 1) using the

**Table 1. MCP Optimization for a Model Polymer**



entry	catalyst	solvent	base	temp (°C)	additive (eq)	<i>M<sub>w</sub></i> (PDI) <sup>a</sup>
1	CuCl	DMF	TEA	70	None	6.2k (1.48)
2	CuCl	DMSO	TEA	70	None	5.9k (1.52)
3	CuI	CHCl <sub>3</sub>	TEA	RT	None	12.8k (2.35)
4	<b>CuCl</b>	<b>DCM</b>	<b>TEA</b>	<b>RT</b>	<b>None</b>	<b>16.6k (2.37)</b>
5	CuCl	DCM	TEA	40	None	8.5k (1.48)
6	CuCl	DCM	TEA	RT	TBTA (0.1)	6.5k (1.58)

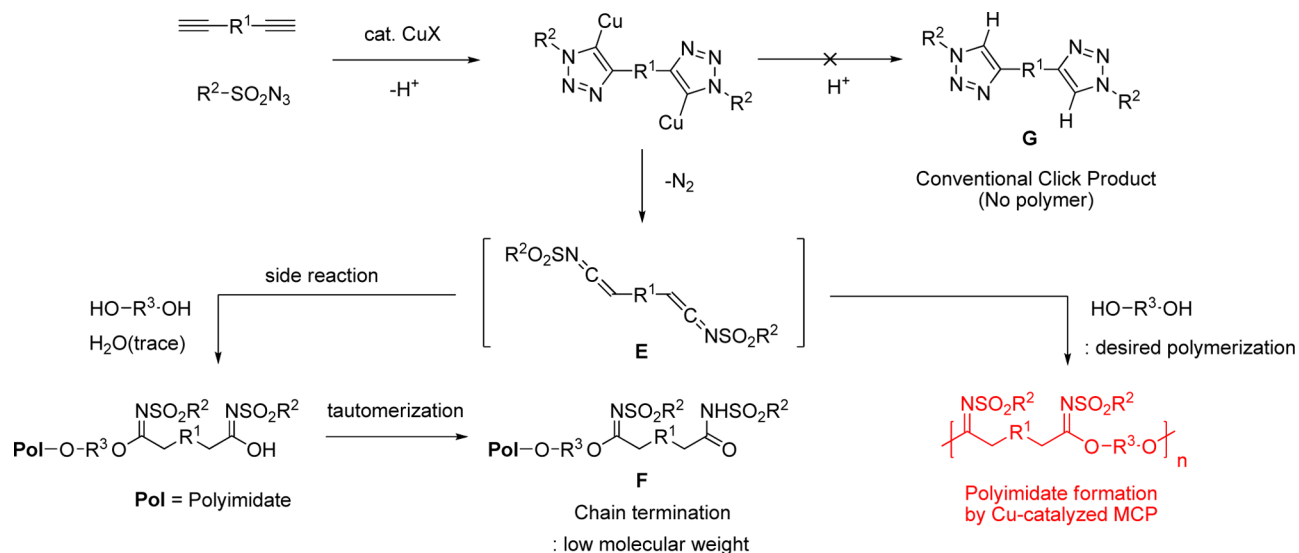
<sup>a</sup>Determined by THF size exclusion chromatography (SEC) calibrated by polystyrene standards.

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Scheme 1. Cu-Catalyzed Multicomponent Polymerization and Various Pathways Leading to Side Reactions



previously optimized conditions for the Cu-catalyzed MCP of polyamides<sup>12</sup> because the new nucleophiles, diols, show excellent nucleophilicity and solubility in *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). In contrast to those of polyamides, the weight-average molecular weight ( $M_w$ ) of the resulting poly(*N*-sulfonylimidate) **D** was very low (Table 1, entries 1 and 2).

We suspected that even small amounts of water in these hygroscopic polar aprotic solvents would compete with the bifunctional monomer, diol **C**, and once water reacted with the electrophilic keteneimine **E**, a key intermediate, it would terminate the polycondensation by forming *N*-sulfonyl amide **F** (Scheme 1 and Figure S1, Supporting Information).<sup>1d</sup> For this reason, we concluded that DMF and DMSO were not suitable solvents for polyimide synthesis by MCP.

To minimize this termination reaction, dry solvents were investigated in the MCP (Table S1, Supporting Information), and chlorinated solvents, such as chloroform and dichloromethane (DCM), were found to be the best solvents for polyimide synthesis. Initially, we used the same conditions as for the synthesis of small-molecule imidates as reported by Chang's group<sup>1b</sup> and obtained **D** with a moderate molecular weight (Table 1, entry 3). Next, we examined several Cu(I) sources to increase the conversion (Table S1, Supporting Information), and among them, polymerization using 10 mol % CuCl in DCM at room temperature showed the best result (Table 1, entry 4). Although polymerization at room temperature took a long time (2 days), the result was better than when the polymerization was run at a higher temperature (Table 1, entry 5). Finally, triethylamine (TEA) was found to be the best base for this polymerization (Table S2, Supporting Information), and additives such as tris(benzyltriazolylmethyl)amine (TBTA), a ligand known to accelerate CuAAC,<sup>1c</sup> gave poor conversion<sup>12</sup> (Table 1, entry 6). By analyzing <sup>1</sup>H and <sup>13</sup>C NMR spectra of the resulting polymer **D**, the conventional click product **G**, formed by another side reaction that terminates polymerization (Scheme 1), was not observed (Figure S2, Supporting Information). This implied that the Cu-catalyzed MCP was successful because the initial triazole ring underwent a highly selective ring-opening reaction to form the reactive keteneimine **E**.<sup>1a,c</sup>

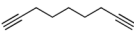

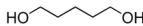
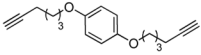
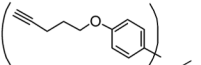
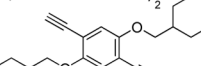
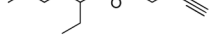
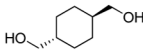

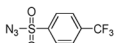

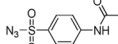
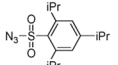
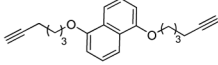
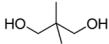
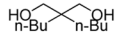
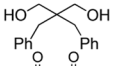
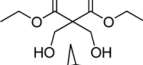
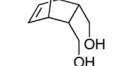
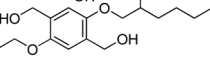
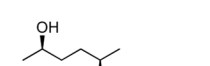
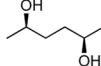
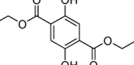
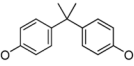
With the newly optimized conditions in hand, various types of diynes, sulfonyl azides, and diols were examined to expand the polymerization scope. Although diols are far less nucleophilic than diamines, we were able to synthesize a library of polyimides with  $M_w$  over 10k, and these results are summarized in Table 2. In general, employing rigid diynes or diols produced polyimides with higher molecular weight than when flexible linkers are used, presumably because of the suppression of intramolecular cyclizations.

We then explored other diynes. Polymerization was initially achieved with commercially available 1,8-nonadiyne, *p*-toluenesulfonyl azide, and 1,5-pentanediol, yielding a polyimide of moderate  $M_w$  (Table 2, entry 1). By introducing more rigid phenyl or biphenyl groups on diyne monomers, polymers with higher  $M_w$  were obtained (Table 2, entries 2 and 3). However, MCP of an even more rigid and reactive aromatic diyne (**1d**) gave a relatively low-molecular-weight polymer, presumably because the less stable diyne might have decomposed during the reaction causing a stoichiometric imbalance and resulting in lower conversion (Table 2, entry 4).

Next, we examined an assortment of sulfonyl azides for MCP by testing various arylsulfonyl azides containing an electron-withdrawing group [ $\text{CF}_3$  (**2c**),  $\text{NO}_2$  (**2d**)] and electron-donating group [ $\text{NHCOMe}$  (**2e**), 2,4,6-tris-*i*Pr (**2f**)] (Table 2, entries 7–10). Regardless of the electronics of the arylsulfonyl azide, various polyimides having moderate to high  $M_w$  up to 33.5k were obtained. The sterically hindered sulfonyl azide (**2f**) did not disturb nucleophilic addition of the diol, and the aliphatic azide (**2b**) was also shown to be a feasible monomer for MCP (Table 2, entries 6 and 10).

Finally, we tested various diols to further expand the monomer scope. Monomers containing primary alcohols were found to be good substrates for MCP (Table 2, entries 13–16). Also, monomers containing cyclic (**3b**), bicyclic (**3g**), and aromatic diols (**3h**) were applicable to MCP (Table 2, entries 10, 17, and 18). Moreover, secondary diol (**3i**) was a suitable monomer for MCP, although secondary alcohol has been reported to afford the imidate product in moderate yield due to its steric hindrance (Table 2, entry 20).<sup>1b</sup> The broad monomer scope suggested that MCP showed excellent functional group tolerance (e.g., ester and alkene functionalities). Interestingly,

Table 2. Synthesis of Various Poly(*N*-sulfonylimidates)

Entry	Diyne	Sulfonyl azide	Diol	$M_w^a$	PDI <sup>a</sup>	Yield <sup>b</sup>
1	1a 	2a 	3a 	11.2k	1.93	89%
2	1b 	2a	3a	16.6k	2.37	82%
3	1c 	2a	3a	17.4k	1.83	87%
4	1d 	2a	3a	9.5k	2.02	76%
5	1b 	2a	3b 	12.8k	2.08	90%
6	1b	2b 	3b	10.7k	2.36	84%
7	1b	2c 	3b	11.6k <sup>c</sup>	1.43 <sup>c</sup>	80%
8	1b	2d 	3b	13.8k	1.73	93%
9	1b	2e 	3b	33.5k	1.52	90%
10	1b	2f 	3b	20.2k	2.02	92%
11	1a	2f	3b	26.3k	2.66	94%
12	1e 	2f	3b	32.2k	2.98	87%
13	1b	2f	3c 	15.1k	1.64	72%
14	1b	2f	3d 	28.9k	2.33	91%
15	1b	2f	3e 	19.7k	1.97	83%
16	1b	2f	3f 	17.6k	1.73	82%
17	1b	2f	3g 	19.4k	2.23	87%
18	1c	2f	3h 	11.6k	1.52	81%
19	1e	2f	3h 	17.3k	1.53	89%
20	1b	2a	3i 	10.9k	1.73	74%
21	1b	2f	3j 	13.3k	1.85	88%
22	1a	2f	3k 	12.7k	2.02	91%
23	1b	2f	3k	16.5k	2.01	93%
24	1e	2f	3k	16.3k	2.30	90%

<sup>a</sup>Determined by THF SEC calibrated using polystyrene standards (entries 1–7, 14, 15, 18–24). Determined by DMF SEC calibrated using poly(methyl methacrylate) standards (entries 8 and 9). Determined by CHCl<sub>3</sub> SEC calibrated using polystyrene standards (entries 10–13, 16, 17). <sup>b</sup>Isolated yield after precipitation into selected solvents. <sup>c</sup>0.9 equiv of diol was used.

despite their weaker nucleophilicity, monomers with bisphenols underwent successful MCP in the same manner as aliphatic diols (Table 2, entries 21–24). Specifically, several polyimidates were successfully prepared with commercially available bisphenol A (3k). Although it was previously reported that the yield of Cu-catalyzed three-component reactions in small-

molecule synthesis was only 61%,<sup>1b</sup> our optimized conditions for MCP of phenolic monomers (3j and 3k) showed efficient nucleophilic addition to keteneimines, affording a  $M_w$  up to 16.5k. The successful polymerization of phenolic monomers suggested that the rigidity of phenolic nucleophiles may play a positive role in the polymerization. However, since diols are

much weaker nucleophiles than diamines, the MCP to prepare polyimides is inevitably limited by even a small amount of water contamination (Table S3, Supporting Information), and this results in a lower conversion for the synthesis of polyimides compared with polyamidines.<sup>12</sup> Additionally, the longer reaction time is another downside of this MCP. Still, the decomposition temperatures of the resulting polyimides obtained by thermal gravimetric analysis ranged from 233 to 307 °C, showing good stability at high temperature (Table S4, Supporting Information).

In summary, we synthesized a library of poly(*N*-sulfonylimides) with moderate to high molecular weights via the Cu-catalyzed MCP of diynes, sulfonyl azides, and diols. Because of the mild conditions, we were able to prepare 24 different poly(*N*-sulfonylimides) from readily available and bench stable monomers (5 diynes, 6 sulfonyl azides, and 11 diols). Minimizing water contamination was key to achieving the successful MCP of poly(*N*-sulfonylimides).

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Experimental details, synthesis, optimization tables, characterization data (TGA, DSC, SEC traces etc.), and spectra of the compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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