

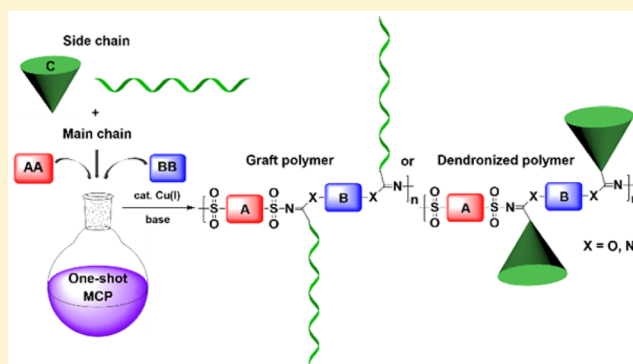
Diversity-Oriented Polymerization: One-Shot Synthesis of Library of Graft and Dendronized Polymers by Cu-Catalyzed Multicomponent Polymerization

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S Supporting Information

ABSTRACT: Graft and dendronized polymers have attracted much attention in the polymer community, and there have been significant efforts to develop better synthetic methods. Herein, we report the highly efficient synthesis of graft and dendronized polymers by using Cu-catalyzed multicomponent polymerization (MCP). Based on diversity-oriented synthesis, we prepared a library of various graft and dendronized polymers from combinations of three types of monomers (mono-functionalized alkynes, bis-sulfonyl azides, and diamines/diols) that are bench stable and readily accessible. After reaction optimization, 54 samples of high-molecular-weight graft and dendronized polymers were prepared, the MCP method allowing simultaneous manipulation of the structures of both the main chains and the side chains. Moreover, because of the severe steric hindrance of the side chains, these polymers adopted extended conformations, as shown by the large shape parameter in solution. Also, the extended morphology of the single polymer chains was directly visualized by atomic force microscopy and transmission electron microscopy in the solid state. Most importantly, this diversity-oriented polymerization became possible because of highly step-economical and efficient one-step MCP, paving the way toward the easily tunable synthesis of graft and dendronized polymers.



1. INTRODUCTION

Graft and dendronized polymers are a special class of macromolecules containing linear polymers or dendrons as side chains. These sterically bulky side chains repel each other, such that the polymer main chains adopt enthalpically favored extended conformation, leading to worm-like structures or cylindrical nano-objects.¹ Their one-dimensional structure produces hundreds of nanometer-long macromolecules covered with bulky side chains, which opens up numerous potential applications in nanoscale electronics² or biomaterials.³ However, constructing precisely defined microstructures of these complex macromolecules in order to utilize them as high-performance materials remains a challenge because synthetic methods to put together all the monomers needed to form main chains and bulky side chains in an efficient and orthogonal manner are highly limited. Especially, finding the right reactions to overcome steric congestion of repeat units and bulky side chains to produce high-molecular-weight polymers with high selectivity is a demanding task.

Generally, graft and dendronized polymers are prepared by three synthetic methods: “graft-to”, “graft-from”, and “graft-through”. The “graft-to” method⁴ introduces the final side chains, either long polymer chains or large dendrons, directly to the preformed main backbone (Figure 1a). Click chemistry is widely used for this approach, where side chains are coupled

directly onto the grafting site of the polymer backbone.⁵ However, high steric congestion between repeat units hinders perfect grafting of the bulky side chain, and this may leave a significant number of defects. A more popular method is the “graft-from” method (Figure 1b),⁶ where the bulky side chains are grown from the preformed main chains either by polymerization [e.g., atom transfer radical polymerization (ATRP)] or by coupling small dendrons one by one. Because small molecules are attached to the polymer main chain, higher grafting densities and easier purification of the final products are the main advantage of this method. However, the final polymers may still have some defects from incomplete coupling, chain transfer, or cross-linking, which results in broad dispersity in the side chains. Also, in most cases, the actual synthesis requires multiple steps and a significant amount of time.

The last method is the “graft-through” method or “macro-monomer approach” (Figure 1c),⁷ where monomers containing the final linear polymers or dendrons undergo polymerization such as ATRP,⁸ reversible addition–fragmentation chain-transfer polymerization (RAFT),⁹ ring-opening metathesis polymerization (ROMP),¹⁰ or polycondensation.¹¹ Although

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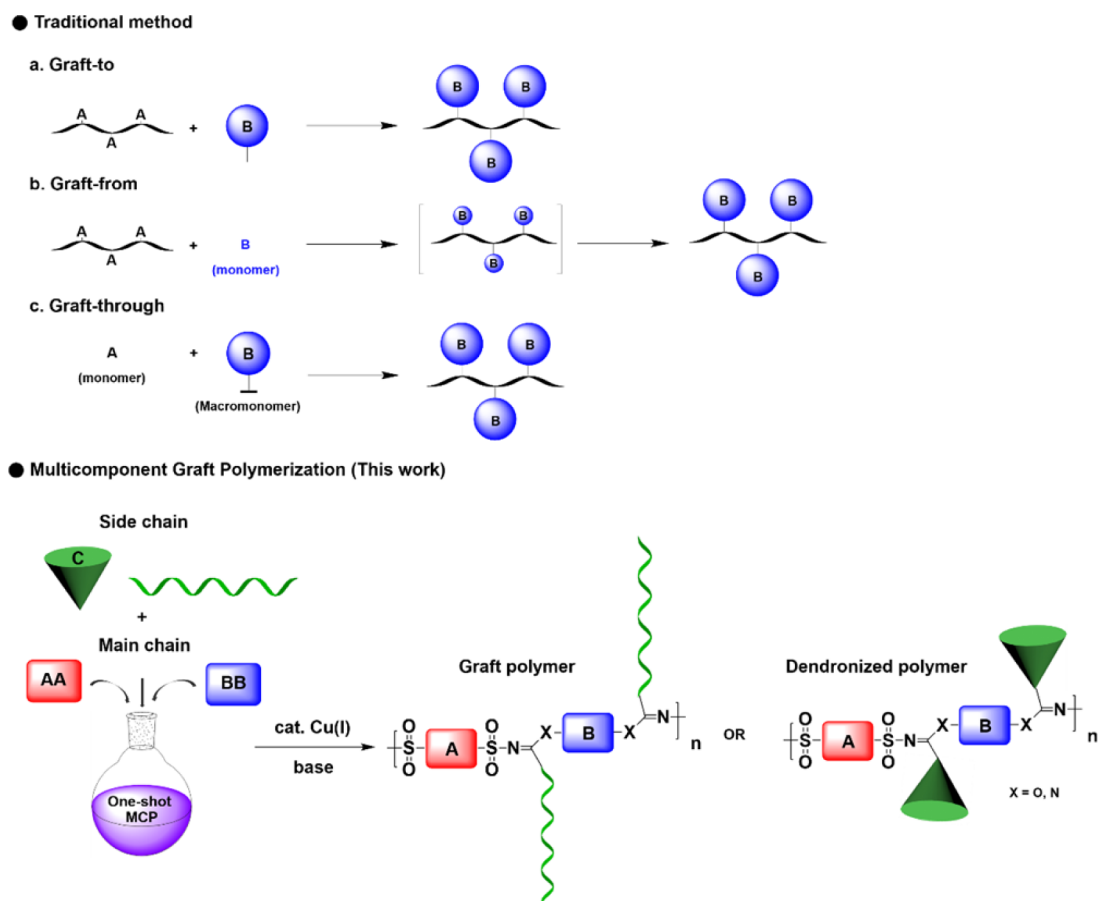
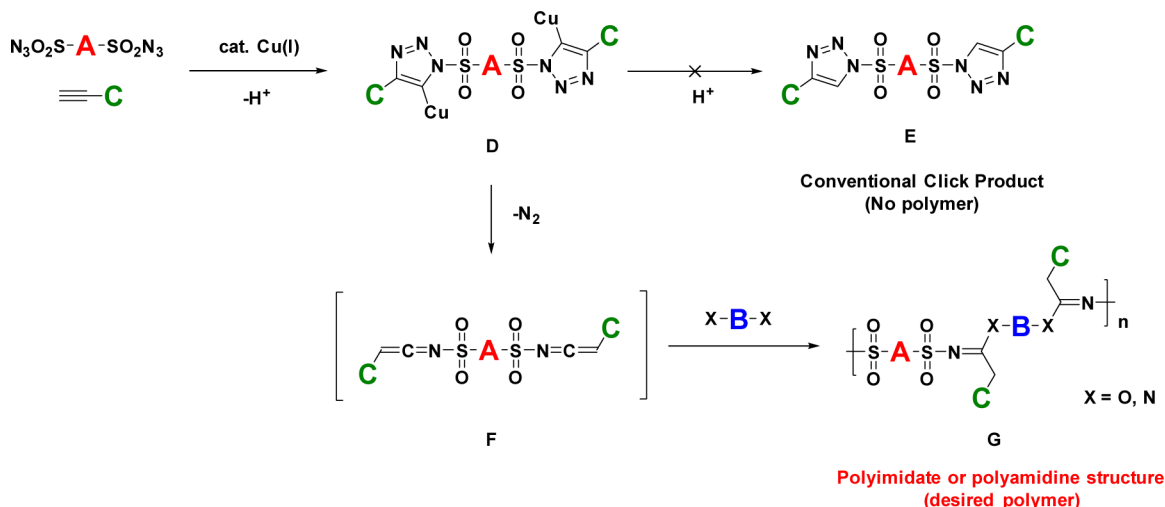


Figure 1. One-shot graft and dendronized polymerization by Cu-catalyzed MCP.

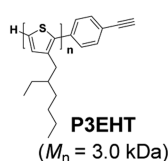
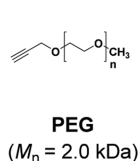
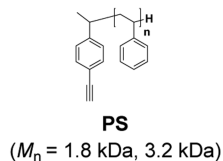
Scheme 1. Mechanism of One-Shot Graft and Dendronized Polymerization by Cu-Catalyzed MCP



this approach allows for the preparation of polymers with perfect polymer architecture, the biggest challenge is still to overcome the large steric hindrance of macromonomers in order to produce high-molecular-weight polymers. All three methods commonly require long reaction times, lengthy synthetic steps, and repeated purification from large excess amounts of monomers. As a result, obtaining a library of such complex polymers or diversity-oriented polymerization has been particularly challenging because of the narrow substrate scope.

Recently, multicomponent polymerization (MCP) based on multicomponent reactions has attracted much attention because it provides access to highly diverse polymer structures prepared from three or more monomers (A, B, and C, Scheme 1).^{12–18} Still, the biggest challenge is to find the right reactions to prepare high-molecular-weight polymers with high selectivity and wide monomer scope. In this regard, our group reported highly efficient Cu-catalyzed MCP from alkynes, sulfonyl azides, and nucleophiles to produce defect-free and well-defined high-molecular-weight poly(*N*-sulfonylamidines)¹⁹ and

Polymer macromonomers



Dendronized macromonomers

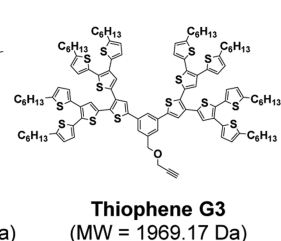
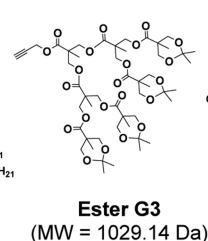
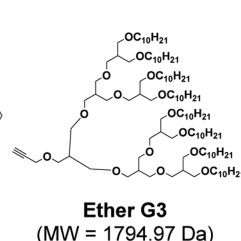
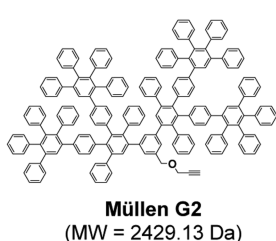
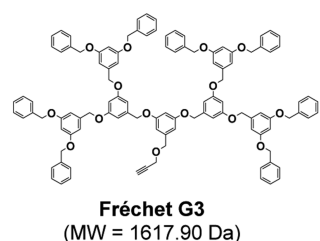
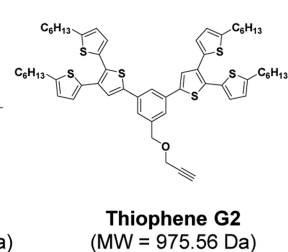
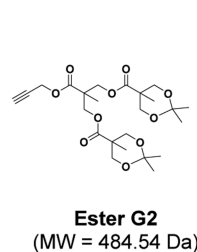
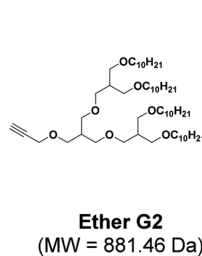
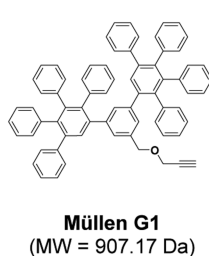
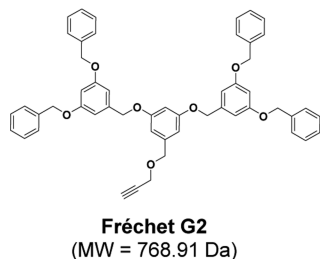
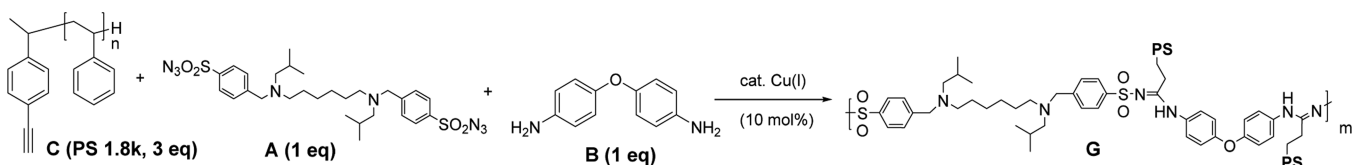


Figure 2. Mono-functionalized macromonomers.

Table 1. MCP Optimization for a Model Polymer^a

entry	catalyst	solvent	base	temp (°C)	M_n (MALLS) ^b	PDI ^b	DP ^c
1	CuCl	DMF	TEA	70	42.0k	1.39	9.6
2	CuCl	DMF	TEA	110	84.9k	1.44	19
3 ^d	CuCl	DMF	TEA	110	38.0k	1.17	8.7
4	Cu(ACN) ₄ PF ₆	DMF	TEA	110	87.8k	1.43	20
5	Cu(ACN) ₄ PF ₆	Tol/DMF	TOA	110	122.1k	2.03	28

^aFor more detail, please see Table S1. ^bAbsolute molecular weights (g/mol) determined by THF size-exclusion chromatography (SEC) using MALLS detector. ^cDegree of polymerization was determined by absolute molecular weight (MALLS) divided by MW of repeat unit. ^dSealed tube condition.

poly(*N*-sulfonylimidates),²⁰ and we demonstrated that diversity-oriented polymerization to provide a library of polymers was possible.


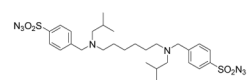
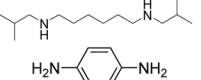


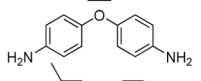


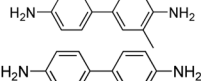

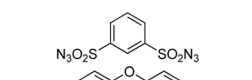


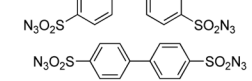


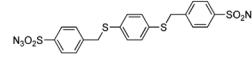



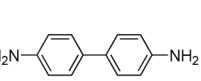


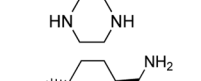

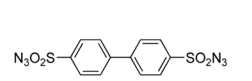
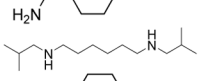


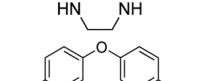


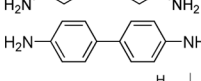


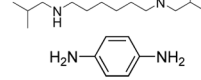

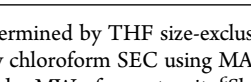
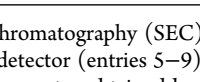

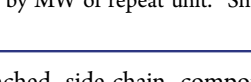
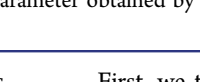

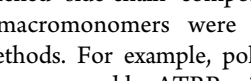
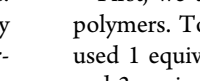

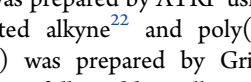
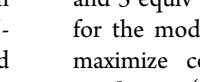

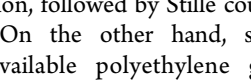
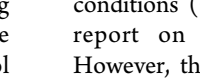

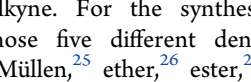
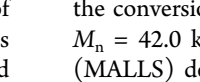
The versatility of MCP would greatly increase if it could provide a simple and efficient route to the synthesis of complex macromolecules such as graft and dendronized polymers. In fact, there was one example of utilizing MCP to produce graft polymers in two sequential steps reported by Li's group, who used Passerini polymerization to produce the main-chain polymer in the first step and then ATRP to grow side chains by the graft-from method.²¹ We envisioned that powerful MCP could provide an efficient and step-economical route for synthesizing a variety of complex polymer architectures by changing the polymer main chains and side chains simultaneously in a one-shot reaction. Herein, we report the first example of one-shot diversity-oriented polymerization to

prepare a library of more than 50 graft and dendronized polymers by Cu-catalyzed MCP.

2. RESULTS AND DISCUSSION

As shown in Scheme 1, Cu-catalyzed MCP, which, in fact, is an extension of Cu-catalyzed azide–alkyne cycloaddition (CuAAC), initially produces the electron-deficient triazole, D, by cycloaddition between A and C. This, then, releases nitrogen gas to give electrophilic keteneimine (F) without any formation of a click product (E). This allows nucleophilic addition of B to construct the desired polymer structure (Scheme 1, G, and Supporting Information, Figure S1). In the work reported here, we used bis-sulfonyl azides, diamines (or diols), as AA- and BB-type monomers for the formation of the polymer main chain, while a macromonomer (C) containing various dendrons or linear polymers terminated by easily accessible alkyne func-

Table 2. Synthesis of Various Graft Polymers

Entry	Macromonomer	Bis-sulfonyl azide	Diamine	M_n (MALLS) ^a	PDI ^a	DP ^b	α^c	Yield
	PS (1.8k)			1.80k	1.04	18		
1	PS 	1a 	2a 	113.4k	1.19	26	0.90	77%
2	PS 	1a 	2b 	76.8k	1.39	18	0.95	82%
3	PS 	1a 	2c 	122.1k	2.03	28	0.88	78%
4	PS 	1a 	2d 	123.8k	1.50	29	0.94	86%
5	PS 	1a 	2e 	463.4k	1.67	111	1.13	88%
6	PS 	1b 	2e 	223.4k	1.27	55	0.78	69%
7	PS 	1c 	2e 	140.4k	1.50	34	0.90	75%
8	PS 	1d 	2e 	113.6k	1.30	28	1.09	74%
9	PS 	1e 	2e 	357.8k	2.00	84	0.67	70%
	PS (3.2k)			3.20k	1.08	32		
10	PS 	1a 	2e 	347.3k	1.83	48	1.18	78%
11	PS 	1a 	2f 	148.3k	1.36	21	1.01	75%
12	PS 	1a 	2g 	183.0k	1.24	26	1.01	71%
13	PEG (2.0k) 	1d 	2a 	75.2k	1.34	17	0.85	86%
14	PEG (2.0k) 	1d 	2f 	49.8k	1.10	11	0.89	82%
15	PEG (2.0k) 	1d 	2c 	111.8k	1.12	25	0.86	85%
16	PEG (2.0k) 	1d 	2e 	270.1k	1.10	60	0.88	88%
17	P3EHT (3.0k) 	1a 	2a 	112.0k	1.43	16	0.74	70%
18	P3EHT (3.0k) 	1a 	2b 	124.4k	1.52	19	0.80	72%

^aAbsolute molecular weight was determined by THF size-exclusion chromatography (SEC) using MALLS detector (entries 1–4, 10–18). Absolute molecular weight was determined by chloroform SEC using MALLS detector (entries 5–9). ^bDegree of polymerization was determined by absolute molecular weight (MALLS) divided by MW of repeat unit. ^cShape parameter obtained by Mark–Houwink–Sakurada plots from SEC–viscometry analysis.

tional groups formed the branched side-chain components. Various mono-functionalized macromonomers were easily prepared by well-established methods. For example, polystyrene (PS)-terminated by alkyne was prepared by ATRP using an initiator containing silyl-protected alkyne²² and poly(3-(2'-ethyl)hexylthiophene) (P3EHT) was prepared by Grignard metathesis (GRIM) polymerization, followed by Stille coupling of phenylacetylene moiety.²³ On the other hand, simple alkylation of commercially available polyethylene glycol (PEG) afforded PEGylated alkyne. For the synthesis of dendronized polymers, we chose five different dendrons containing alkynes (Fréchet,²⁴ Müllen,²⁵ ether,²⁶ ester,²⁷ and thiophene types²⁸) with two different sizes for the generation for each dendron. Altogether, 10 dendronized macromonomers having molecular weights from 500 Da to 2.4 kDa were prepared (Figure 2).

First, we tested whether MCP was feasible to produce graft polymers. To screen for optimal polymerization conditions, we used 1 equiv of bis-sulfonyl azide (A), 1 equiv of diamine (B), and 3 equiv of polystyrene macromonomer (C, $M_n = 1.8$ kDa) for the model study; 3 equiv of macromonomer was used to maximize conversion. The initial attempt used the same conditions (CuCl, DMF at 70 °C) optimized in our previous report on the synthesis of poly(*N*-sulfonylamidines).¹⁹ However, the reaction mixture became very viscous, and thus the conversion was relatively low, yielding a graft polymer with $M_n = 42.0$ kDa measured by multi-angle laser light scattering (MALLS) detection, which translates to a degree of polymerization (DP) of 9.6. (Table 1, entry 1) To increase the polymerization efficiency, the reaction temperature was increased to 110 °C, above the glass transition temperature (T_g) of PS to improve the stirring condition. The DP was thus

Table 3. Synthesis of Various Dendronized Polymers

Entry	Macromonomer	Bis-sulfonyl azide	Diamine / Diol	M_n (MALLS) ^a	PDI ^a	DP ^b	α^c	Yield
1	Fréchet G2	1a	2a	91.3k	1.17	39	1.06	73%
2	Fréchet G2	1a	2f	572.0k	1.10	249	1.04	79%
3	Fréchet G3	1f	2a	209.1k	1.27	53	1.16	70%
4	Fréchet G3	1a	2a	353.7k	1.23	87	1.03	71%
5	Fréchet G3	1b	2a	143.3k	1.18	39	1.14	65%
6	Fréchet G3	1c	2a	364.7k	1.23	96	1.19	77%
7	Fréchet G3	1d	2a	211.2k	1.12	56	1.16	81%
8	Fréchet G3	1e	2a	94.0k	1.41	24	0.94	75%
9	Fréchet G3	1b	2b	507.5k	1.36	141	1.19	65%
10	Fréchet G3	1c	2b	301.6k	1.97	82	0.96	70%
11	Fréchet G3	1d	2b	463.4k	1.66	125	1.38	73%
12	Fréchet G3	1a	2h	125.7k	1.25	32	0.73	66%
13	Fréchet G3	1a	2i	210.5k	1.34	53	0.81	71%
14	Fréchet G3	1a	2d	782.1k	1.14	194	1.22	78%
15	Fréchet G3	1a	2b	1041k	1.39	265	1.06	79%
16	Müllen G1	1a	2j	69.1k	1.16	27	0.84	71%
17	Müllen G1	1a	2k	184.2k	1.59	70	0.87	78%
18	Müllen G1	1a	2g	86.9k	1.15	35	1.03	73%
19	Müllen G1	1a	2f	106.8k	1.39	43	0.70	72%
20	Müllen G1	1f	2k	41.0k	1.36	16	1.14	81%
21	Müllen G2	1a	2j	58.4k	1.35	11	0.96	84%
22	Müllen G2	1a	2f	129.0k	1.47	24	1.00	82%
23	Müllen G2	1a	2e	66.9k	1.44	12	1.10	80%
24	Ether G2	1a	2a	51.1k	1.16	21	0.97	75%
25	Ether G2	1a	2h	47.9k	1.34	18	1.05	70%
26	Ether G2	1a	2b	197.2k	1.47	81	1.07	71%
27	Ether G2	1a	2f	53.5k	1.24	22	1.19	70%
28	Ether G3	1a	2f	68.9k	1.29	16	1.03	82%
29	Ether G3	1a	2e	61.8k	1.31	15	0.94	80%
30	Ester G2	1a	2l	57.6k	1.45	32	0.75	71%
31	Ester G2	1a	2m	32.8k	2.00	19	0.72	72%
32	Ester G3	1a	2n	99.8k	1.45	36	1.06	76%
33	Thiophene G2	1a	2a	44.7k	1.30	25	0.85	70%
34	Thiophene G2	1a	2k	147.7k	1.55	54	0.96	71%
35	Thiophene G3	1a	2a	125.2k	1.45	20	0.95	77%
36	Thiophene G3	1a	2k	65.7k	1.24	14	1.03	71%

^aAbsolute molecular weight was determined by THF size-exclusion chromatography (SEC) using an MALLS detector (entries 1–8, 12–36). Absolute molecular weight was determined by chloroform SEC using an MALLS detector (entries 9–11). ^bDegree of polymerization was determined by absolute molecular weight (MALLS) divided by MW of repeat unit. ^cShape parameter obtained by Mark–Houwink–Sakurada plots from SEC–viscometry analysis.

increased to 19 (Table 1, entry 2). On the other hand, the same condition but in a sealed tube lowered the DP because nitrogen evolution, one of the driving forces, decreased (Table 1, entry 3). Next, we examined other Cu(I) sources to increase the conversion, and we found that $\text{Cu}(\text{ACN})_4\text{PF}_6$ containing non-nucleophilic bulky counteranions showed slightly better results under the same conditions (Table 1, entry 4). Finally, tri-*n*-octyl amine (TOA) instead of TEA seemed to increase the conversion for graft polymerization, showing the highest DP of 28 (Table 1, entry 5), presumably by lowering the viscosity of total reaction mixture as a plasticizer effect. This graft polymer showed good stability against strong basic condition (hydrolysis) because not a significant reduction in the molecular weight was observed even after 24 h (Table S2).

With the optimized conditions in hand, we examined various combinations of bis-sulfonyl azides, diamines, and macromonomers to expand the monomer scope for the synthesis of graft polymers. Owing to the highly efficient and selective Cu-catalyzed MCP, we prepared a library of 18 graft polymers with high molecular weights and high yields, as summarized in Table 2. Also, one could investigate the conformation of these graft polymers in solution by obtaining shape parameter (α) from Mark–Houwink–Sakurada plots from SEC–viscometry analysis and learn how different combinations of monomers affected the α values. (for a sphere, $\alpha = 0$; for a random coil, $\alpha < 0.8$; for a rod-like structure, $0.8 < \alpha < 2.0$; for a perfect rod, $\alpha = 2.0$)

At first, we explored various diamines as nucleophiles and prepared various high-molecular-weight graft polymers containing 1.8k PS as a side chain. Their DP was 18–111 as estimated from the absolute molecular weight analyzed by MALLS (Table 2, entries 1–5). Both flexible alkyl diamines (2a) and aromatic diamines (2b–2d) produced graft polymers having similar DP values (Table 2, entries 2–4), whereas rigid and more nucleophilic benzidine (2e) produced a graft polymer with the highest DP value of 111 (Table 2, entry 5). In general, the shape parameter (α) seemed to increase when linear-shaped diamines were used instead of flexible or bent ones, implying that the polymer backbone became stiffer when rigid monomers were used (Table 2, entries 1 and 3 vs entry 5). Also, MCP using various bis-sulfonyl azides (1b–1e) and benzidine (2e) resulted in successful synthesis of graft polymers with DP = 28–84 (Table 2, entries 6–9). Again, using a more linear monomer combination seemed to give higher rigidity (Table 2, entry 8).

Next, we examined MCP using longer PS macromonomers with almost double the molecular weight ($M_n = 3.2$ kDa) and using rigid benzidine (2e) as a nucleophile. A high-molecular-weight graft polymer with DP = 48 was produced (Table 2, entry 10). Also, nucleophilic piperazine (2f) or primary amine (2g) successfully produced high-molecular-weight graft polymers with DP = 21 and 26, respectively (Table 2, entries 11 and 12).

Furthermore, we tested MCP for other macromonomers having different polymer structures and found that PEG ($M_n = 2.0$ kDa) was also a good macromonomer. Rigid biphenyl sulfonyl azide (1d) in combination with flexible diamine (2a) or piperazine (2f) afforded moderate-molecular-weight graft polymers with DP = 17 and 11, respectively (Table 2, entries 13 and 14, respectively). On the other hand, changing nucleophiles to rigid aryl diamines (2c and 2e) produced higher-molecular-weight polymers with DP = 25 and 60, respectively (Table 2, entries 15 and 16, respectively). These

graft polymers containing flexible PEG side chains showed α values higher than 0.8, implying that they adopted an extended conformation in solution (Table 2, entries 13–16).

Finally, the conjugated polymer P3EHT ($M_n = 3.0$ kDa) was a promising macromonomer for producing semiconducting graft polymers having moderate molecular weights with DP = 16 and 19 (Table 2, entries 17 and 18, respectively). From UV–vis analysis, these polymers showed maximum absorption at 443 and 451 nm, respectively, in the film state with an optical band gap of 2.18 eV (Figure S2, A). In short, using glassy and nonpolar polystyrene, polar PEO, and even semiconducting P3EHT as macromonomers, diversity-oriented synthesis of graft polymers was possible by the one-shot Cu-catalyzed MCP method.

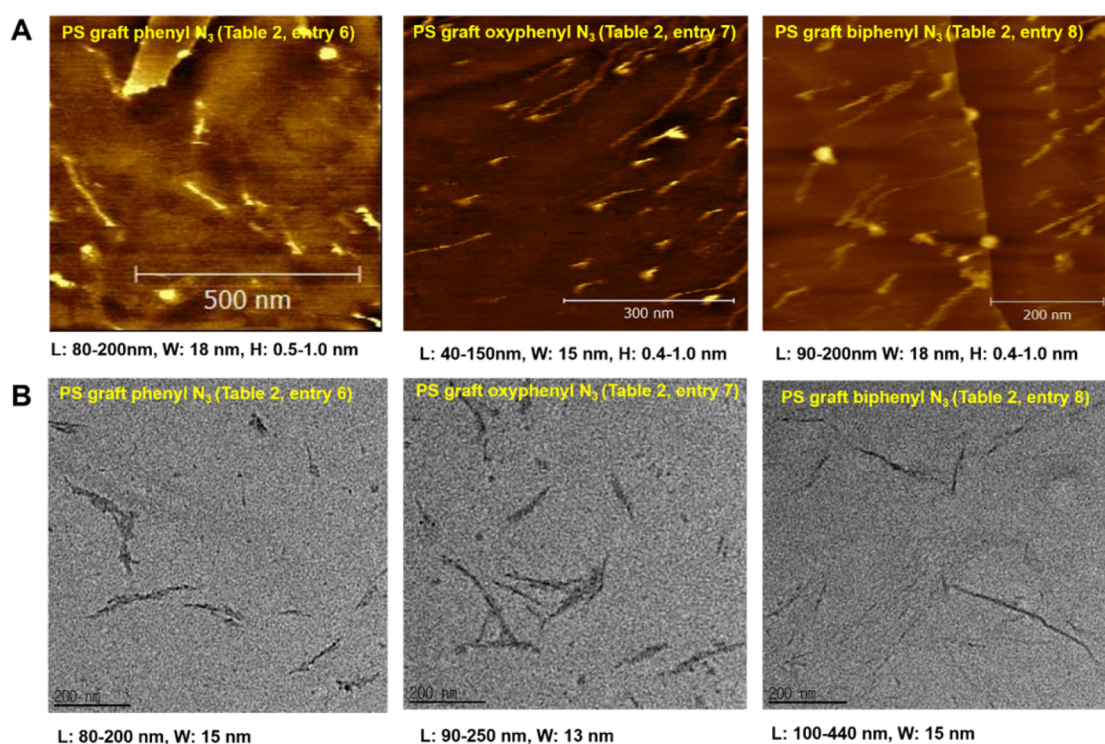
After successful preparation of the library of graft polymers, we extended this MCP method to the synthesis of dendronized polymers. Dendrons are interesting macromolecules because they have perfectly defined branching and show high solubility and low viscosity. Thus, there was no viscosity problem during the synthesis of dendronized polymers, and more readily accessible TEA was used instead of TOA as the optimized reaction condition.

First, macromonomer containing popular and easily prepared second-generation Fréchet dendron was tested for MCP. Both flexible diamine (2a) and cyclic diamine (2f) produced high-molecular-weight dendronized polymers with DP = 39 and 249, respectively (Table 3, entries 1 and 2, respectively). Expanding to larger macromonomer containing more soluble third-generation Fréchet dendron allowed us to use various combination of bis-sulfonyl azides and diamines, and high-molecular-weight dendronized polymers with DPs ranging from 24 to 265 were obtained (Table 3, entries 3–15). Using rigid and linear monomers, MCP became more efficient presumably due to suppressed cyclization. Especially, as compared to other more flexible diamines, linear aromatic diamines (2b and 2d) produced very high-molecular-weight dendronized polymers with DPs above 100 and higher α values (Table 3, entries 5 vs 9, 7 vs 11, 12 vs 14, and 13 vs 15).

Next, we examined the possibility of another nonpolar Müllen-type dendron as a potential macromonomer. Notably, even the first-generation dendron has high molecular weight and high steric bulkiness (Figure 2, MW = 907.17 Da). For this reason, the resulting dendronized polymer showed lower solubility and lower conversion than Fréchet dendrons, producing moderate-molecular-weight polymers with DPs between 16 and 70 (Table 3, entries 16–20). For example, using a more soluble diamine containing longer alkyl chains (2j vs 2k) might have increased the DP from 27 to 70 (Table 3, entries 16 and 17). By introducing more nucleophilic diamine monomers (2f and 2g), polymers with high DPs of 35 and 43 were obtained (Table 3, entries 18 and 19). On the other hand, rigid bis-sulfonyl azide (1f) might result in lower DPs of dendronized polymers as compared to the case of using flexible bis-sulfonyl azide (1a), presumably due to the lower solubility of the polymer (Table 3, entries 17 vs 20).

On the other hand, attempts to use second-generation Müllen dendron as a macromonomer also produced dendronized polymers successfully, although their DPs were somewhat lower, between 11 and 24 (Table 3, entries 21 and 22), due to their extremely bulky side chains as compared to other dendrons (Figure 2, MW = 2429.13 Da). Still, Cu-catalyzed MCP was efficient enough to produce high-molecular-weight polymers of 58.4–129 kDa by overcoming

(1) PS Graft Polymers



(2) Fréchet Dendronized Polymers

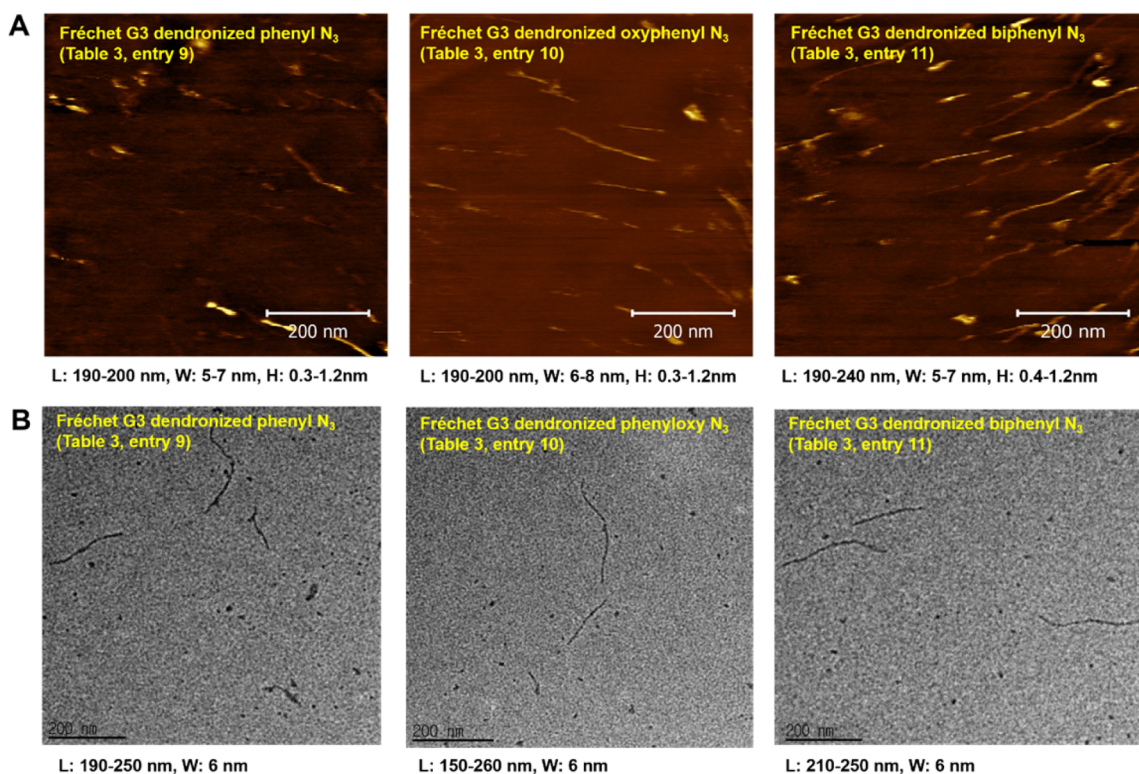


Figure 3. AFM (A) and TEM (B) images of graft and dendronized polymers.

huge steric hindrance during each coupling reaction. It seemed that those dendronized polymers became more rigid when the size of the dendrons increase. The shape parameter, α , of the dendronized polymers synthesized from the same combination

of bis-sulfonyl azide (**1a**) and diamines (**2f** and **2j**) increased from 0.84 to 0.96 and from 0.70 to 1.00, respectively, when a bigger macromonomer (second-generation Müllen dendron)

was attached (Table 3, entries 16 vs 21 and entries 19 vs 22, respectively).

More polar alkyl ether dendrons were also suitable macromonomers for MCP when reacted with various diamines. Because both second- and third-generation ether dendrons are liquid, the polymerizations were conducted at neat conditions to enhance the conversion. With the macromonomer containing second-generation alkyl ether dendron, MCP successfully produced high-molecular-weight polymers with DP = 18–81 (Table 3, entries 24–27). Among them, rigid and linear aryl diamine (2b) produced the highest-molecular-weight dendronized polymer presumably due to suppressed intramolecular cyclization (Table 3, entry 26). Attempts to use a larger macromonomer containing third-generation ether dendron, however, produced polymers with lower DPs of 15 or 16 because larger steric congestion and dilution caused by the larger volume of total reaction mixture would inevitably decrease the conversion (Table 3, entries 28 and 29).

We further examined other polar ester dendrons as macromonomers for MCP, but using diamines as nucleophiles failed because they underwent side reactions such as transamidation with ester functionality on the side chains and produced insoluble gels. Thus, we changed to much weaker nucleophiles, diols instead, which showed functional-group tolerance toward ester functionality. MCP successfully afforded dendronized polymers containing G2 and G3 esters by using the previously optimized conditions in dichloromethane at room temperature (Table 3, entries 30–32).²⁰ Similar to other cases, larger third-generation dendrons generally showed higher α values (Table 3, entry 32).

Lastly, we tested macromonomers containing thiophene dendrons to show that dendronized polymers containing conjugated side chains could be prepared by MCP as well. Indeed, the MCP produced high-molecular-weight polymers containing second-generation thiophene dendron with DP = 25 and 54 (Table 3, entries 33 and 34), whereas those containing larger third-generation thiophene dendron showed somewhat lower conversion, with DP = 20 and 14, similar to other cases (Table 3, entries 35 and 36). These dendronized polymers containing conjugated thiophene side chains showed optical band gaps of 2.85 eV (G2) and 2.53 eV (G3) (Figure S2, B).

Although the shape parameter, α , suggested that these graft and dendronized polymers would adopt extended chain conformation, more direct evidence would be more supportive. Thus, some of the graft and dendronized polymers were visualized by atomic force microscopy (AFM) and transmission electron microscopy (TEM) because of the large size of these complex macromolecules. Particularly, monomer combinations of rigid aryl diamine (2b and 2e) and aryl bis-sulfonyl azides (1b–1d) produced electron-rich aryl backbones, which allowed direct imaging by TEM without any staining (Figure 3). Indeed, single chains of graft polymers prepared from PS, benzidine (2e), and aryl bis-sulfonyl azides (1b, 1c, and 1d) showed extended conformation by AFM and TEM. From AFM imaging on a highly oriented pyrolytic graphite (HOPG) surface, the observed single chains showed lengths of 200 nm, widths of 15–18 nm, and heights of 0.5–1.0 nm. Because of the low height, getting high-resolution images by AFM was exceptionally challenging. However, TEM revealed better images with higher contrast showing similar lengths from 100 to 200 nm and widths of 13–15 nm [Figure 3, (1)].

Single chains of dendronized polymers consisting of Fréchet dendrons and aryl-rich main chains from bis-sulfonyl azides

(1b, 1c, and 1d) and diamine (2b) also exhibited extended conformation, as shown by AFM and TEM imaging (Table 3, entries 9–11). AFM showed that these polymers had lengths up to 200 nm, heights of 0.3–1.2 nm, and widths of 5–8 nm. Also, a similar range of lengths of 175–210 nm and widths of 6 nm were observed by TEM [Figure 3, (2)]. The width of dendronized polymers seemed to be lower than that of graft polymers because the side chains of dendronized polymers were obviously shorter.

Lastly, all these resulting graft and dendronized polymers showed great thermal stability, as supported by the high decomposition temperatures (T_d) obtained by thermal gravimetric analysis (TGA). The T_d of graft polymers ranged from 325 to 442 °C, whereas that of the dendronized polymers ranged from 312 to 419 °C (Table S3). A few exceptions were the dendronized polymers containing ester dendrons, whose T_d ranged from 251 to 260 °C. It seems that the ester linkages would be less stable at such high temperatures. All the graft and dendronized polymers except the PEGylated polyamides [Table 2, entries 13–16; melting temperature (T_m) = 52–55 °C] were shown to be amorphous without any melting transition as determined by differential scanning calorimetry (DSC).

3. CONCLUSION

In summary, we synthesized a library of high-molecular-weight graft and dendronized polymers with good yield by one-shot Cu-catalyzed multicomponent polymerization. Finding optimized conditions, such as using a more active catalyst, enhancing proper solubility, and lowering the viscosity of the reaction mixture, was the key to successful MCP. The biggest advantage of MCP was that the broad monomer scope enabled us to obtain various complex macromolecules by adjusting the compositions of the main chains and side chains simultaneously in one-shot synthesis. For example, one could tune various properties such as flexibility, polarity, and conjugation of both the main backbone and the side chains. Therefore, diversity-oriented polymerization became possible by extremely efficient and step-economical MCP. To demonstrate the power of this method, 54 different high-molecular-weight graft and dendronized polymers were prepared from 11 diamines, 3 diols, 6 bis-sulfonyl azides, and 14 macromonomers containing alkynes (4 linear polymers and 10 dendrons). However, one should choose monomer sets that are tolerable to amines and alcohols, because otherwise, selective MCP would not occur. Most of the polymers showed rigid conformation, with a shape parameter, α , larger than 0.8. Generally speaking, these α values seemed to increase with the incorporation of larger macromonomers, whereas the DP inevitably decreased due to steric congestion. From AFM and TEM imaging, we confirmed the extended conformation of the single-chain morphologies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04695.

Experimental details, synthesis, optimization tables, characterization data (TGA, DSC, SEC traces, etc.), and spectra of the compounds, including Tables S1–S3 and Figures S1 and S2 (PDF)

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Notes

The authors declare no competing financial interest.

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