

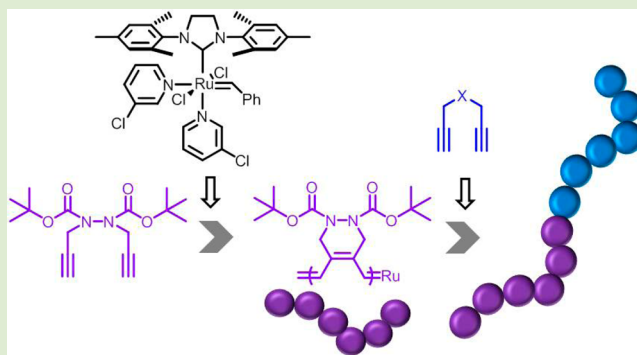
N-Containing 1,7-Octadiyne Derivatives for Living Cyclopolymerization Using Grubbs Catalysts

Jung-Ah Song, Seongeon Park, Taek-Soo Kim, and Tae-Lim Choi*

Department of Chemistry, Seoul National University, Seoul 151-747, Korea

S Supporting Information

ABSTRACT: Synthesis of a new class of conjugated polyenes containing N-heterocyclic six-membered rings was demonstrated via cyclopolymerization of N-containing 1,7-octadiyne derivatives using Grubbs catalysts. Successful cyclopolymerization was achieved by introducing protecting groups to the amines in the monomers. Moreover, a hydrazide-type monomer containing a di-*tert*-butyloxycarbonyl group (**6**) promoted the living cyclopolymerization to give poly(**6**) with a controlled molecular weight and narrow dispersity. This living polymerization allowed us to prepare various conjugated diblock copolymers using poly(**6**) as the first block.



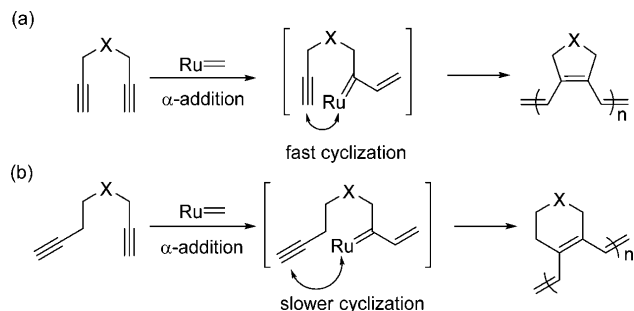
Cyclopolymerization of diyne derivatives via olefin metathesis is a powerful method for producing conjugated polyenes. In its early stages, ill-defined catalysts such as Ziegler–Natta, MoCl_5 , and WCl_6 were used.^{1,2} Then, with the development of well-defined Schrock catalysts, the microstructure of the resulting polymers and living cyclopolymerization were thoroughly studied.^{2,3} Recently, the introduction of air- and moisture-tolerant Ru-based Grubbs-type catalysts has expanded the scope and utility of this cyclopolymerization.^{4–7} Furthermore, their high regioselectivity toward α -addition on terminal alkynes yields conjugated polymers containing either cyclopentene or cyclohexene repeat units by the cyclopolymerization of 1,6-heptadiyne^{4,5,7a} or 1,7-octadiyne derivatives,^{3b,6} respectively (Scheme 1). In particular, by using a highly active third-generation Grubbs catalyst,⁸ we reported on the versatile living cyclopolymerization of 1,6-heptadiyne derivatives,^{4a,b} as well as 1,7-octadiynes.^{6b,c} However, we observed that the cyclopolymerization of the 1,7-octadiyne derivatives was challenging because the longer distance between

the two alkynes resulted in a slower cyclization than that of 1,6-heptadiyne derivatives (Scheme 1).^{6b} In our recent report, faster propagation of the 1,7-octadiyne derivatives was achieved by introducing sterically bulky substituents to enhance the cyclization by a Thorpe–Ingold effect.^{6c} Nevertheless, the cyclopolymerizations of these 1,7-octadiynes were still slow. Our next strategy to speed up the cyclization is to bring the two alkynes closer together by introducing a nitrogen atom because the C–N bond is shorter (1.47 Å) than the C–C bond (1.54 Å).

Among the previously reported nitrogen-containing diyne monomers, the cyclopolymerization of dipropargyl ammonium salts has been the most investigated.^{2,7,9} There have also been several studies on the cyclopolymerizations of dipropargyl amine by MoCl_5 , WCl_6 ,⁹ and Schrock-type^{3b,7a,c} catalysts. However, only one example for the cyclopolymerization using Grubbs-type^{7b} catalysts was reported because the strong coordination of free amines to the metal center tends to poison the catalysts.^{7c} In particular, the cyclopolymerization of 1,7-octadiyne derivatives containing nitrogen has not been reported. Herein, we report the successful cyclopolymerization of various 1,7-octadiyne derivatives containing a nitrogen at the 4-position or two nitrogens at the 4,5-positions with a proper choice of protecting groups. Furthermore, the living cyclopolymerization of 1,2-di-*tert*-butyloxycarbonyl-1,2-dipropargyl hydrazine (**7**) is achieved.

The initial attempt to cyclopolymerize an amide-protected monomer **1** with third-generation Grubbs catalyst **I** gave the desired polymer in 65% yield in 2 h (Table 1, entry 1). This

Scheme 1. Cyclopolymerization of 1,6-Heptadiyne (a) and 1,7-Octadiyne (b)

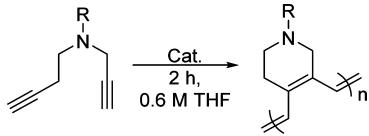


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Table 1. Cyclopolymerization of 1–3



entry	monomer	cat.	[M]/[I]	temp. (°C)	M_n (kDa) ^a	\bar{D} ^a	conv. (%) ^b	yield (%) ^c
1	1	I	50	rt	11	2.36	76	65
2	2	II	50	50	19	2.14	99	91
3 ^d	2	II	100	50	22	2.10	87	64
4	3	II	50	rt	8	1.60	79	63

^aDetermined by THF SEC calibrated using polystyrene (PS) standards. ^bDetermined by crude ¹H NMR. ^cIsolated yields after purification. ^d1.2 M in THF.

was an improved result compared to the previous cyclopolymerization of a monosubstituted 1,7-octadiyne monomer (20% yield in 24 h).^{6b} Several N-containing monomers with other protecting groups also underwent successful cyclopolymerization. The cyclopolymerizations of a sulfonamide-containing monomer **2** with 2 mol % **I** yielded the corresponding polymer in 75% yield in 2 h. To further improve the yield, the same polymerization of **2** was repeated with thermally stable second-generation Hoveyda–Grubbs catalyst **II**¹⁰ at 50 °C, and the yield increased to 91% (Table 1, entry 2). **2** was the best monomer presumably because of the enhanced Thorpe–Ingold effect by the larger substituent.¹¹ When the monomer feed ratio increased to 100, the polymer was produced in 64% yield (87% conversion, Table 1, entry 3). Poly(**3**), containing the less basic free aniline moiety, was also prepared in 63% yield (Table 1, entry 4). In short, these N-containing monosubstituted monomers seemed to be better monomers than the monosubstituted 1,7-octadiyne monomers.

To confirm the microstructure of the polymers, we independently synthesized the monomeric product containing a six-membered ring via ene–yne metathesis reaction of **2** with ethylene gas (see Supporting Information (SI) for details). This model compound and poly(**2**) shared common chemical shifts in their ¹H and ¹³C NMR spectra. Other polymers showed similar peak patterns, confirming the regioselective cyclopolymerization via α -addition.

To examine the origin of the improved reactivity of these nitrogen-containing monomers over the previous monosubstituted 1,7-octadiynes, we monitored the kinetics of the cyclopolymerization of a nitrogen and a carbon-containing 1,7-octadiyne derivative with the same substituent (**4a** and **4b**, Figure 1) to see if the carbamate group showed any positive effect on the propagation over the ester group. The initial reaction rate of **4a** (0.16 min⁻¹) was relatively faster than that of **4b** containing the ester (0.12 min⁻¹), presumably because of shorter C–N bond length (Figure S1 and S2, SI). Furthermore, the conversion of **4a** showed a steady increase over time, whereas no further conversion of **4b** was observed after 8 min. This result implied that the lifetime of the propagating carbene was longer for **4a** than **4b**, presumably because the more electron-rich carbonyl group on the carbamate of **4a** stabilized the propagating carbenes more effectively than the ester carbonyl in **4b**.^{4a,12} In short, the origins of the improved cyclopolymerization of **4a** over **4b** seemed to be the shorter distance between the two alkynes on **4a** and the longer lifetime of the propagating carbene. However, it seemed impossible to further increase the reactivity of these N-containing monomers

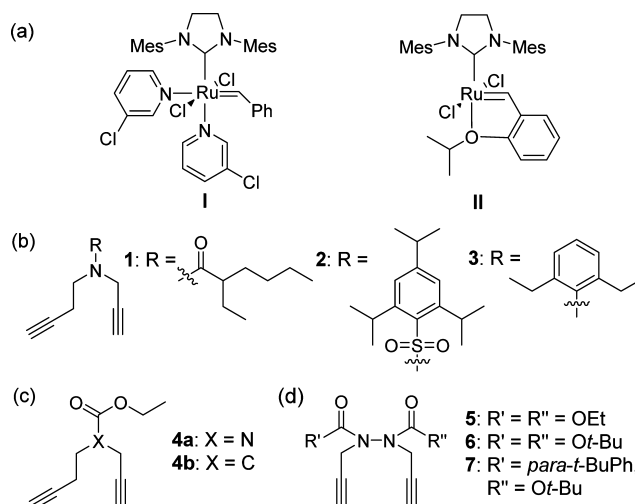


Figure 1. Structures of (a) catalysts (**I** and **II**), (b) the monomers containing protected amide and aniline functionalities (**1**–**3**), (c) the monomers used in the kinetic studies (**4a** and **4b**), and (d) hydrazide-type monomers (**5**–**7**).

with only a single substituent because of the lack of the Thorpe–Ingold effect.

To further enhance the reactivity of the cyclopolymerization of 1,7-octadiyne derivatives, we introduced two nitrogen atoms as bis-protected hydrazines (Figure 1). By using 2 mol % **I**, the cyclopolymerization of the hydrazide-type monomers was greatly accelerated compared to that of the previous monomers containing a single protected nitrogen (Table 2). First, the cyclopolymerization of **5**, containing diethoxycarbonyl hydrazine, was complete within 15 min, but the molar mass dispersity (\bar{D}) was slightly broad (1.42), presumably because of the occurrence of some chain-transfer reaction (Table 2, entry 1). To suppress the chain-transfer reaction, we designed a new monomer **6** with the bulkier di-*tert*-butyloxycarbonyl (di-*t*-BOC) group; **6** was completely converted within 5 min to give a polymer with a dispersity of 1.16 (Table 2, entry 2). This improved reactivity was comparable to that of 1,6-heptadiyne derivatives with catalyst **I**.^{4a} When one of the *t*-BOC groups in **6** was changed to the smaller *para*-*tert*-butylbenzoyl group (**7**), the reaction was complete within 30 min (Table 2, entry 3). Even though the reaction was slower than with **5**, it still maintained a faster rate than the previous monomers containing a single nitrogen. To check the possibility of living polymerization of **6**, the polymerization temperature was lowered to 10 °C as the optimized conditions,¹³ and we found that the molecular weights of poly(**6**) were directly

Table 2. Cyclopolymerization of Monomers 5–7

entry	monomer	[M]:[I]	temp. (°C)	time (min)	M_n (kDa) ^a	\mathcal{D} ^a	conv. (%) ^b	yield (%) ^c
1	5	50	rt	15	18	1.42	>99	88
2	6	50	rt	5	16	1.16	>99	90
3	7	50	rt	30	14	1.44	>99	95
4	6	25	10	30	9	1.12	>99	88
5	6	50	10	30	18	1.18	>99	95
6	6	75	10	60	27	1.25	>99	95
7	6	100	10	90	37	1.39	>99	94

^aDetermined by chloroform SEC calibrated using polystyrene (PS) standards. ^bDetermined by crude ¹H NMR. ^cIsolated yields after purification.

proportional to the [M]:[I] ratio; excellent control over the [M]:[I] from 25:1 to 100:1 and narrow dispersity were maintained (Table 2, entries 4–7 and Figure 2). The

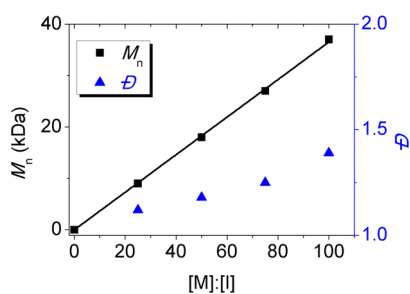


Figure 2. Correlation between M_n and [M]:[I] for poly(6).

microstructure of these polymers containing six-membered rings as repeat units was confirmed by ¹³C NMR analysis in the same way as the previous monosubstituted amine-type polymers (Figure S7, SI).

These conjugated polymers containing six-membered N-heterocyclic repeat units were analyzed by UV–vis spectroscopy. Their band gaps were approximately 2.3 eV with an onset around 550 nm, and λ_{\max} in chloroform was in the range of 440–450 nm for the polymers containing monosubstituted amines and 440–475 nm for the bis-substituted hydrazide-type polymers (Figure S4, SI). The lower λ_{\max} values in comparison to those of poly(dipropargylamines) with five-membered ring structures (480–600 nm)^{7d} suggested that the new polymers with six-membered N-heterocyclic structures adapted a less coplanar polymer conformation, resulting in a shorter conjugation length. The initial *cis/trans* ratio for poly(6) was 1/13, calculated by ¹H NMR. After 5 h of blue LED irradiation in THF-*d*₆, isomerization occurred, as confirmed by the disappearance of the signal for the *cis*-olefin (Figure S5, SI).¹⁴ Furthermore, this isomerized poly(6) showed an increased λ_{\max} from 467 to 482 nm because of the extended conjugation length as a result of the higher *trans*-olefin ratio (Figure S6, SI).

Living cyclopolymerization provides a convenient method to prepare various conjugated block copolymers.⁴ Previously, 1,7-octadiyne derivatives were only used as the second monomer for block copolymerization using a Grubbs catalyst because of their relatively low reactivity;^{6b,c} when 1,7-octadiyne derivatives were used for the first block, the final block copolymers were always contaminated by small amounts of their homopol-

ymers.¹⁵ However, various diblock copolymers could be prepared with the highly reactive poly(6) as the first block (Figure 3). The block copolymerization of 6 and 7 with catalyst

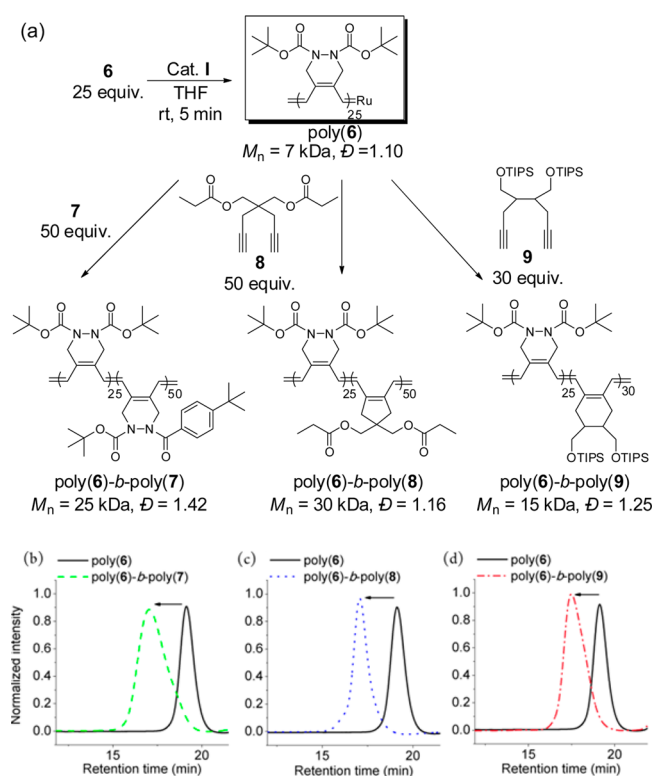


Figure 3. (a) Diblock copolymerization of 6 and various diyne derivatives. SEC traces of homopolymer poly(6) and diblock copolymers: (b) poly(6)-*b*-poly(7), (c) poly(6)-*b*-poly(8), and (d) poly(6)-*b*-poly(9).

I produced, for the first time, a block copolymer consisting of two different six-membered heterocycles. Furthermore, block copolymerizations of 6 and 1,6-heptadiyne 8 produced diblock copolymer poly(6)-*b*-poly(8) containing blocks of six-membered heterocycle and five-membered carbocycle repeat units. Lastly, a 4,5-disubstituted 1,7-octadiyne monomer¹⁵ was used as a second block to give poly(6)-*b*-poly(9) containing blocks of six-membered heterocycle and six-membered carbocycle repeat units. The microstructures of these block copolymers were verified by size-exclusion chromatography (SEC), which

showed the complete shifts of the traces from the initial poly(**6**) to higher molecular weight regions (Figure 3(b)–(d)) while maintaining their narrow dispersities (Figure 3).

In conclusion, we demonstrated the synthesis of new conjugated polymers consisting of various six-membered N- or N,N'-heterocyclic repeat units via regioselective cyclo-polymerization of nitrogen-containing 1,7-octadiyne derivatives. Introducing protecting groups and bulky substituents led to improved cyclopolymerization results compared to those observed in the case of the corresponding all-carbon monomers. Using ^1H NMR kinetic studies, we concluded that the N-containing monomers gave higher conversion because of the shorter C–N bond length and the stabilizing effect on the propagating carbene. By introducing the hydrazide group, the reactivity increased greatly, and we could achieve the living cyclopolymerization of monomer **6** to produce conjugated polymers with controlled molecular weights and narrow dispersities. This living polymerization allowed the synthesis of various diblock copolymers with poly(**6**) as the first block, and this expanded the monomer scope for block copolymerization. This work demonstrates that the introduction of a heteroatom effectively increased the reactivity and utility of the cyclopolymerization.

■ ASSOCIATED CONTENT

● Supporting Information

Detailed experimental procedures, NMR data for new compounds and polymers, UV–vis spectra of polymers, kinetic data, and plots for molecular weight control. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tlc@snu.ac.kr.

Notes

The authors declare no competing financial interest.

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