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Controlled Cyclopolymerization of 1,5-Hexadiynes to Give Narrow Band Gap Conjugated Polyacetylenes Containing Highly Strained Cyclobutenes

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ABSTRACT: For decades, cyclopolymerization of α, ω -diyne derivatives has been an effective method to synthesize various soluble polyacetylenes containing five- to seven-membered rings in the backbone. However, cyclopolymerization to form four-membered carbocycles was considered impossible due to their exceptionally high ring strain (~30 kcal/mol). Herein, we demonstrate the successful cyclopolymerization of rationally designed 1,5-hexadiyne derivatives to afford various polyacetylenes containing highly strained cyclobutenes in each repeat unit. After screening, Ru catalysts containing bulky diisopropylphenyl groups promoted challenging four-membered ring cyclization efficiently from various monomers, enabling the synthesis of high molecular



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weight (up to 40 kDa) polyacetylenes in a controlled manner. Furthermore, living polymerization allowed for block copolymer synthesis by combining with ring-opening metathesis polymerization as well as block copolymerization of two different 1,5-hexadiyne monomers to give a fully conjugated polyacetylene. These new polymers unexpectedly showed much narrower band gaps than conventional substituted polyacetylenes by >0.2 eV. Interestingly, computational studies showed much smaller bond length alternation in the conjugated backbone containing cyclobutenes, resulting in highly delocalized π electrons along the polymer chain and lower band gaps.

■ INTRODUCTION

Cyclopolymerization (CP) of α, ω -divne derivatives is a powerful tool for preparing substituted polyacetylenes.¹⁻³ Early studies regarding CP used ill-defined catalysts, including Ziegler-Natta, MoCl₅, and WCl₆ catalysts,⁴⁻⁷ until the first breakthrough by the Schrock group and later by the Buchmeiser group demonstrating living CP using well-defined Mo-based olefin metathesis catalysts.⁸⁻¹¹ Subsequently, the utility of CP broadened when user-friendly Ru-based catalysts were shown to promote living CP.^{12–19} Extensive studies have been conducted using 1,6-heptadiyne monomers, yielding fiveor six-membered rings (in a random or highly regioselective fashion) in the conjugated backbone via α -^{10,12–19} or β addition,^{9,20-24} respectively. Moreoever, recent studies have expanded the scope of CP where 1,7-octadiyne²⁵⁻³¹ and 1,8nonadiyne derivatives³² were used to successfully produce polyacetylenes containing six- and seven-membered rings via α -addition (Scheme 1). However, in contrast to the cyclization to form thermodynamically stable five- to seven-membered rings, which is relatively easy, cyclization to make cyclobutenes is far more challenging due to their extremely high ring strain energy (29.5 kcal/mol),³³ making the process thermodynamically disfavored. Therefore, cyclobutenes are rather excellent monomers for ring-opening metathesis polymerization

 $(ROMP)^{34-44}$ or tandem ring-opening/ring-closing (or cross-metathesis) reactions.⁴⁵⁻⁴⁹

Then we were intrigued by the reports of CP of 1,2diethynyldisilane derivatives, which produced random copolymers containing both four- and five-membered rings using nonregioselective Mo catalysts.^{50–52} Unfortunately, this polymer containing a disilane group on the four-membered ring decomposed readily in air. Furthermore, Campagne et al. succeeded in preparing challenging cyclobutenes by a ringclosing enyne metathesis reaction using an α -selective Hoveyda–Grubbs catalyst at high dilution.⁵³ However, the efficiency was very poor with the maximum turnover number below 2 at 40 °C or between 2 and 5 even under microwave conditions, thereby rendering this process seemingly impossible to apply to polymerization. Regardless, inspired by these earlier studies,^{50–53} we envisioned that CP of properly designed 1,5-hexadiyne derivatives (ensuring the Thorpe–

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Scheme 1. α -Selective Cyclopolymerization of α, ω -Diynes, and Strain Energies of Cycloalkenes Depending on Ring Size



Ingold effect to facilitate cyclization) would be possible to yield planar poly(cyclobutenylene vinylene). In addition, by transforming two alkynes to a much more stable conjugated 1,3,5triene, this process (converting two π -bonds to two σ -bonds) may overcome the energetic cost of the high ring strain energy of cyclobutene, while the resulting conjugated cyclobutenes with large substituents would be stable against any secondary metathesis processes such as chain transfer or ROMP. Herein, we demonstrate the successful CP of 10 different 1,5-hexadiyne monomers to afford polyacetylenes containing cyclobutenes with perfect selectivity (promoted by α -selective Grubbs catalysts), and their intriguing optoelectronic properties were discussed based on experimental and computational studies.

RESULTS AND DISCUSSION

First, polymerization of simple 1,5-hexadiyne was attempted using a second-generation Hoveyda–Grubbs catalyst (Ru1) in tetrahydrofuran (THF), but disappointingly, it showed almost no CP reactivity (Table S1). To accelerate cyclization, tetrasubstituted meso-3,4-dimethylhexa-1,5-diyne-3,4-diol (M1) was used to induce the Thorpe-Ingold effect, and 58% of the product was isolated as an insoluble purple solid (typical color for substituted polyacetylenes produced by α selective CP) presumably due to short side chains and diol functionality lowering the solubility (Table 1, entry 1). Encouraged by this initial success, benzyl groups were attached to both alcohols to enhance solubility, but disappointingly, no reaction was observed, presumably due to excessive steric congestion (Table S1). Subsequently, monobenzyl-substituted M2 was prepared from M1 (meso form), and its polymerization yielded a soluble reddish-purple polymer P2 containing alcohol despite the low conversion (42% even at 50 °C, M/I = 30, entry 2), but its diastereomer prepared from the racemate form showed no reactivity (Table S1). Instead of using Ru1 containing the conventional mesityl (Mes)-substituted Nheterocyclic carbene (NHC), switching to the more stable Ru2 containing a 2,6-diisopropylphenyl (Dipp) group⁵⁴ significantly enhanced the polymerization efficiency to 69% conversion (entry 3). Finally, using bulkier substituents than

a benzyl group, such as the triethylsilyl (TES, M3) and *tert*butyldimethylsilyl (TBS, M4) groups, excellent conversions (>99%) were obtained to afford P3 and P4 with high M_n s of up to 22 kDa (entries 4 and 5). Revisiting the challenging tetrasubstituted monomer based on M1, a cyclic benzylidene acetal substituent was introduced to restrict bond rotation and reduce steric crowding. While polymerization of M5 having *syn:anti* = 1:1.7 mixture was rather sluggish with 47% conversion and a low M_n of 4 kDa even at 70 °C (entry 6), M6 with >99% *anti* stereoisomer showed much higher reactivity to give >99% conversion and M_n of 16.1 kDa (entry 7). This is presumably because of the faster cyclization or easier approach of catalyst to the alkynes when the phenyl group was present at the sterically less hindered *anti* position to the alkynes.

Despite the initial success, monomer design for tetrasubstituted M1-M6 was rather limited because the polymerization efficiency was sensitive to a certain stereochemistry, thereby resulting in different reactivity of diastereomers. Therefore, to broaden the monomer scope, we designed 3,3disubstituted 1,5-hexadiyne monomers (M7-M11) as the catalyst would easily approach to the less hindered alkyne at the 5 position, yielding a head-to-tail sequence. Furthermore, these monomers would still show sufficient Thorpe-Ingold effect due to the bis-substitution at the 3,3 position and would be free from the diastereomeric issue because of the single stereogenic center at the 3 position. Indeed, using Ru2, polymerization of undecyl- and TBS-substituted monomer (M7) at 50 °C yielded the blue-colored polymer P7 with 8.7 kDa in 70% conversion (M/I = 30, entry 8), and M8 containing a sterically bulkier triisopropylsilyl (TIPS) group significantly improved the polymerization efficiency to give >99% conversion and a high $M_{\rm n}$ of 20 kDa (entry 9). Benzylsubstituted monomers with TBS (M9) and TIPS (M10) groups also showed high reactivity to give >99% conversion and $M_{\rm n}$ s of 15–16 kDa (entries 10 and 11). It seems that the bulkier groups in both catalysts (Mes < Dipp) and monomers improved polymerization by suppressing catalyst decomposition (Figure S1)¹⁶ and by enhancing the cyclization due to the Thorpe–Ingold effect.^{28,2}

Despite these monomers showing good reactivity with Ru2, all of the resulting polymers showed uncontrolled molecular weights with broad dispersities (1.56-2.07) due to the slow initiation from ether chelation. When the reaction of M8 with **Ru2** (M/I = 10 in THF- d_{8} , 0.25 M, 50 °C) was monitored via in situ NMR, slow initiation was observed, leaving >50% of the initial catalyst at the end of the reaction, resulting in a low k_i/k_p of 0.027 (Figure 1a). In contrast, similar to the widely used fast-initiating third-generation Grubbs catalyst (G3),⁵⁵ Ru3 containing 3-chloropyridine and NHC^{Dipp} ligands showed rapid initiation upon monomer addition, generating a large amount of propagating carbene (Figure 1b). Moreover, the carbene percentage remained high throughout polymerization (ca. 90%), confirming its high stability, especially compared to G3 (<60%, Figure S1). Notably, the propagation rate was approximately 8 times lower than that obtained using Ru2, presumably because the pyridine coordination to the propagating carbene (from Ru3, 18.74 ppm; Figure S2) significantly retarded CP compared to propagating carbene with weaker coordination of the putatively assigned olefin chelation⁵⁶ (from Ru2, 18.19 ppm; Figure S2). Therefore, Ru3 gave a higher k_i/k_p value of >4.4, at least 150 times larger. Encouraged by this kinetic data, the controlled polymerization

Table 1. Cyclopolymerization of the Various 1,5-Hexadiyne Derivatives



| entry | 101 | cat. | 101/1 | temp. (C) | conc. (IVI) | time (ii) | conv. (%) | yield (%) | M_n (KDa) | D |
|-----------------|-----|------|-------|-----------|-------------|-----------|-----------|-----------|-------------|------|
| 1 | M1 | Ru1 | 20 | rt | 0.5 | 14 | | 58 | | |
| 2 | M2 | Ru1 | 30 | 50 | 1.0 | 3 | 42 | | | |
| 3 | M2 | Ru2 | 30 | 50 | 1.0 | 3 | 69 | 35 | 2.3 | 1.85 |
| 4 | M3 | Ru2 | 30 | 50 | 1.0 | 3 | >99 | 76 | 21.6 | 1.80 |
| 5 | M4 | Ru2 | 30 | 50 | 1.0 | 3 | >99 | 56 | 19.5 | 1.56 |
| 6 | M5 | Ru2 | 30 | 70 | 1.0 | 4 | 47 | 35 | 4.1 | 1.67 |
| 7 | M6 | Ru2 | 30 | 70 | 1.0 | 4 | >99 | 94 | 16.1 | 1.88 |
| 8 | M7 | Ru2 | 30 | 50 | 0.5 | 4 | 70 | 69 | 8.7 | 1.68 |
| 9 | M8 | Ru2 | 30 | 50 | 0.5 | 4 | >99 | 86 | 19.7 | 1.61 |
| 10 | M9 | Ru2 | 30 | 50 | 0.5 | 4 | >99 | 98 | 15.1 | 1.91 |
| 11 | M10 | Ru2 | 30 | 50 | 0.5 | 3.5 | >99 | 99 | 16.2 | 2.07 |
| 12 | M8 | Ru3 | 10 | 50 | 0.5 | 1 | >99 | 58 | 3.9 | 1.29 |
| 13 ^d | M8 | Ru3 | 30 | 50 | 0.5 | 6 | 97 | 83 | 15.4 | 1.26 |
| 14 ^d | M8 | Ru3 | 50 | 50 | 0.5 | 15 | >99 | 90 | 28.5 | 1.36 |
| 15 ^d | M8 | Ru3 | 70 | 50 | 0.5 | 20 | 88 | 81 | 39.3 | 1.87 |
| 16 | M9 | Ru3 | 30 | 50 | 0.5 | 6 | >99 | 84 | 13.6 | 1.55 |
| 17 | M9 | Ru3 | 50 | 50 | 0.35 | 15 | >99 | 90 | 21.2 | 1.63 |
| | | | | | | | | | | |





Figure 1. Plots of conversions and carbene changes monitored by in situ ¹H NMR during the polymerization of **M8** (M/I = 10) in THF- d_8 (0.25 M, 50 °C) using (a) **Ru2** and (b) **Ru3**. (c) Plot of M_n vs M/I and corresponding D values for **P8** synthesized by **Ru3**.

of **M8** was attempted by varying the M/I ratio from 10 to 50 and obtained **P8** with M_n ranging from 4 to 29 kDa according to the M/I ratio and relatively narrow dispersities between 1.26 and 1.36 (entries 12–14; Figure 1c). From polymerization at M/I = 70, a maximum M_n up to 40 kDa was achieved with a turnover number of 62, despite the broad dispersity (entry 15). Polymerization of **M9** with **Ru3** also showed a proportional increase of M_n up to M/I = 50 (entries 16 and 17). All of the polymer structures were characterized by ¹H, ¹³C, and 2D NMR, supporting an all-*trans* olefin stereochemistry and head-to-tail regioselectivity in the polymer backbones (Figures S3–S8).

Furthermore, block copolymers of polyacetylenes containing cyclobutenes were successfully synthesized through combina-



Figure 2. Syntheses of block copolymers by combining CP of M8 with ROMP of (a) M11 and (b) M12 as well as (c) by sequential CP of M8 and M10.

tion with living ROMP. First, a norbornene derivative (M11, 30 equiv) was polymerized by Ru3 at room temperature, and addition of M8 (15 equiv) to the same reaction pot at 50 °C resulted in successful block copolymerization, as demonstrated by a clear shift of SEC traces with increasing $M_{\rm n}$ from 8.4 to 18.0 kDa and a narrow dispersity of 1.11 (Figure 2a). In addition, from the fact that olefin chelation allowed the living polymerization of endo-tricyclo-[4.2.2.0^{2,5}]deca-3,9-diene derivatives even with relatively slow-initiating ether-chelated catalysts, 56-58 the living polymerization of M12 (25 equiv) was carried out by Ru2 to afford the first block with $M_{\rm p}$ of 6.6 kDa and D of 1.06. Subsequent addition of M8 (25 equiv) at 50 °C produced another block copolymer having an $M_{\rm p}$ of 18.1 kDa with a narrow dispersity of 1.22 (Figure 2b). More importantly, block copolymerization via sequential addition of two 1,5-hexadiyne monomers M8 (15 equiv) and M10 (15 equiv) to a **Ru3** solution resulted in the complete shift of SEC traces from 5.5 (D = 1.29) to 16.9 kDa (D = 1.45), demonstrating the livingness of this polymerization to form cyclobutenes (Figure 2c).

Compared to the previous CP cases, 14,16,28 a higher temperature (50 °C) was required to obtain high conversions due to slow propagation (Figure S9). Again, this demonstrates the challenges in cyclopolymerization forming thermodynamically unstable cyclobutenes. Nevertheless, as designed, chain

transfer reaction or other side reactions such as ROMP did not occur under this condition (Figure S10), presumably due to the steric repulsion between bulky groups near the propagating species and the polymer backbone.

Interestingly, polymers from 3,3-disubstituted monomers (P7-P10) showed a dark blue color in solution, implying absorption at longer wavelengths of the visible light spectrum. Indeed, UV-vis analysis indicated that P8 showed two vibronic peaks (strong indication of α -selectivity) with significantly higher λ_{\max} at 601 and 651 nm compared to those obtained from analogous polyacetylenes containing five-(P13, 552 and 594 nm)⁵⁹ and six-membered rings (P14, 487 nm)²⁶ prepared via CP of 1,6-heptadiynes and 1,7-octadiynes, respectively (Figure 3). To further understand the origin of the higher λ_{max} values (the highest λ_{max} for soluble substituted polyacetylenes),^{3,60} density functional theory (DFT) calculations were performed on model oligoacetylenes containing four- (A), five- (B), and six-membered carbocycles (C) with degrees of polymerization (DP) from 1 to 15 (Figure 4). $^{61-63}$ Bond length alternation (BLA),⁶⁴ the difference between the length of the central double bond ((x + y)/2) and the single bond (z), was calculated to be much smaller for A (4.5 pm with DP = 15) compared to those from **B** (6.1 pm) and **C** (7.9 pm; Figure 4a). In addition, consistent with experimental observations (**P8** = 1.78, **P13** = 1.98, **P14** = 2.23 eV; Figure 3),



Figure 3. UV-vis spectra of various polyacetylenes containing four-, five-, and six-membered rings.



Figure 4. Comparison of (a) bond length alternation (BLA) and (b) HOMO–LUMO gaps of model polyacetylenes with different ring sizes calculated by DFT using the B3LYP method and 6-31G(d) basis set (N = number of carbon atoms in the polyacetylene backbone). (c) Interpretation of the calculation results.

the calculated band gap decreased with smaller rings (A = 1.49, B = 1.78, C = 2.11 eV for DP = 15; Figure 4b). This unexpectedly smaller BLA and narrower band gap of A is likely due to the small bond angle of cyclobutene which induces more p-orbital character to the σ -bonding orbitals on the ring, favoring ca. 90° geometry, thereby forming a slightly longer

endocyclic double bond (x) compared to the analogous double bond of the cyclopentene model compound (A = 1.383, B =1.380 Å for DP = 15). More importantly, this should conversely increase the s-orbital character of the exocyclic single bonds (z), thereby shortening them (A = 1.421, B = 1.434 Å for DP = 15; Figure 4c). Therefore, the difference between the single (shortened) and the double bond (elongated) lengths decreased, leading to a reduction of the Peierls distortion of the polyacetylene backbone⁶⁴ and resulting in enhanced delocalization of π -electrons and a narrower band gap. Compared to P7-P10, polymers P3, P4, and P6 derived from tetrasubstituted monomers showed blueshifted absorption spectra (λ_{max} = 550–600 nm), presumably because the significant steric repulsion between the four substituents distorted the backbone and weakened the conjugation (Table S2, Figure S11). The highest occupied molecular orbital (HOMO) energies of P3-P10 were determined by cyclic voltammetry (from -5.12 to -5.34 eV), which were similar to or slightly lower than that of polyacetylene containing cyclopentenes (-5.14 eV; Figure \$13). Finally, thermal decomposition temperatures of the polymers ranged from 175 to 348 °C, as measured by thermogravimetric analysis (Figure S14).

CONCLUSION

In conclusion, successful cyclopolymerization of 1,5-hexadiyne derivatives was demonstrated using α -selective Grubbs catalysts, propagating by forming highly strained cyclobutenes in each repeat unit. To show the generality of this seemingly challenging cyclopolymerization, 10 different monomers were prepared and high molecular weight polymers up to 40 kDa were synthesized using Ru catalysts containing a bulky NHC^{Dipp} ligand. In addition, controlled polymerization was possible to give polymers with M_n linearly correlated to the M/ I ratios, exhibiting relatively narrow D. Eventually, block copolymers were prepared by combination with ROMP, and even the block copolymerization of two different 1,5-hexadiyne monomers was possible. These new polyacetylenes containing cyclobutenes showed surprisingly long-wavelength absorption, among the highest λ_{max} (the lowest band gap) reported for substituted polyacetylenes. DFT calculations shed light on the origin of the narrow band gaps of these conjugated polymers containing cyclobutenes, as their π electrons were highly delocalized due to short BLA between double and single bonds on the conjugated backbone. This study broadens the utility of the Grubbs catalysts for the synthesis of conjugated polymers and provides profound insights regarding the structureproperty relationships of conjugated polymers with different ring sizes in the backbone.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c07666.

Supplemental figures, experimental procedures, monomer and polymer structural characterization, and NMR spectra for new compounds (PDF)

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Notes

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