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Cyclopolymerization To Synthesize Conjugated Polymers Containing Meldrum's Acid as a Precursor for Ketene Functionality

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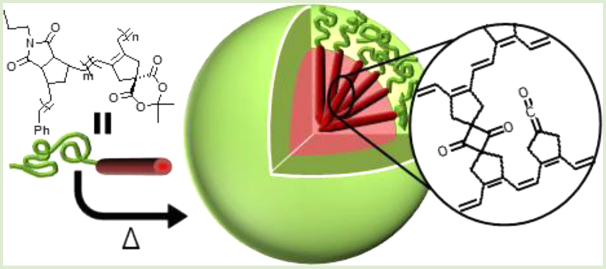
Ⓢ *Supporting Information*

ABSTRACT: Recently, the importance of Meldrum's acid has been reinvestigated because it serves as a great precursor for ketene generation by thermolysis. In this study, we synthesized conjugated polymers containing Meldrum's acid via controlled cyclopolymerization using a third-generation Grubbs catalyst. To avoid the solubility issue, copolymerization with soluble monomers was successfully used to provide various random and block copolymers containing Meldrum's acid in the conjugated backbone. Interestingly, when a polyacetylene derivative containing Meldrum's acid was incorporated into the second block of the diblock copolymers, highly stable core–shell supramolecules spontaneously formed during the polymerization via in situ nanoparticlization of conjugated polymer. This direct fabrication of nanostructures without requiring any post-treatments was due to the strong π–π interactions and the insolubility of the polyacetylene segment leading to the formation of core in situ. Moreover, thermolysis of Meldrum's acid to generate ketene in the conjugated polymer core was monitored by IR, and its consecutive cycloaddition to afford the cross-linked core improved the stability of the supramolecules.



Conjugated polymers such as polyacetylene (PA) have been extensively investigated over the past five decades because of interest in their electric and optical properties,[1] which has opened up the new field of polymer electronics.[2] PA, the simplest conducting polymer, unfortunately suffers from extremely low solubility and processability, which have limited its applications. To increase its solubility and processability, various substituents have been introduced to the PA backbone. One of the most powerful synthetic strategies for the preparation of soluble and functionalized PA derivatives is the cyclopolymerization of 1,6-heptadiyne derivatives via olefin metathesis.[3] Among many reported catalyst systems, Schrock and Buchmeiser reported the pioneering results of cyclopolymerization of the 1,6-heptadiyne derivatives using well-defined catalysts.[4,5] Recently, our group reported highly efficient living cyclopolymerization of 1,6-heptadiyne derivatives using a user-friendly third-generation Grubbs catalyst, which selectively generated five-membered ring structures.[6] Furthermore, this polymerization allowed for the synthesis of block copolymers with various structures.[7]

Since the first synthesis by Meldrum in 1908,[8] Meldrum's acid derivatives have been exploited in organic chemistry for their unique properties: the high acidity of the methylene proton and their use as precursors to highly electrophilic ketenes which can be produced from flash vacuum pyrolysis of the Meldrum's acid functionality.[9] Recently, Hawker reported the mild preparation of ketenes from polymers containing Meldrum's acid, and these ketenes were used to cross-link the polymer or introduce various functional groups to the polymer chain.[10,11] This strategy was also applied to the synthesis of polyester from a monomer containing Meldrum's acid.[12] Further development of the synthesis of conjugated polymers containing Meldrum's acid should broaden the applications of the chemistry of Meldrum's acid and the ketenes that can be generated upon its thermolysis. Herein, we report the synthesis of conjugated polymers containing Meldrum's acid by cyclopolymerization using a third-generation Grubbs catalyst. We demonstrate that living polymerization allowed for random and block copolymerization and discuss investigations of the self-assembly behavior of the diblock copolymers and their thermolysis to generate ketenes (Scheme 1).

To synthesize the conjugated polymer containing Meldrum's acid functionalities, we prepared a 1,6-heptadiyne monomer (**1**) via simple alkylation of Meldrum's acid. Initially, cyclopolymerization of **1** was carried out in tetrahydrofuran (THF) with a molar feed ratio of **1** to Grubbs catalyst **A** of 50:1. The polymer, poly(**1**), precipitated out as a dark red solid in high yield but was insoluble in organic solvents such as chloroform and THF.[13] Because of the insolubility of the polymer, no further characterization by ^{1}H NMR and size-exclusion chromatography (SEC) was possible.

As a strategy to prepare soluble conjugated polymers containing Meldrum's acid, we attempted random copolymerization of **1** with soluble monomers **2** and **3** using catalyst **A** (Scheme 2). First, random copolymerization of **1** and **2** via cyclopolymerization was carried out to yield poly(**2**)-*ran*-poly(**1**). A second copolymer was synthesized via cyclo-

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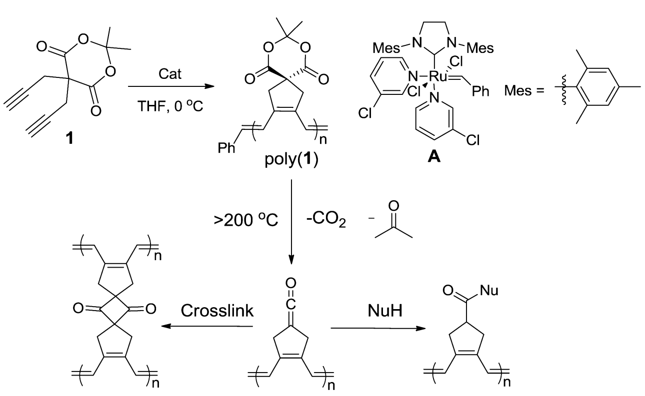
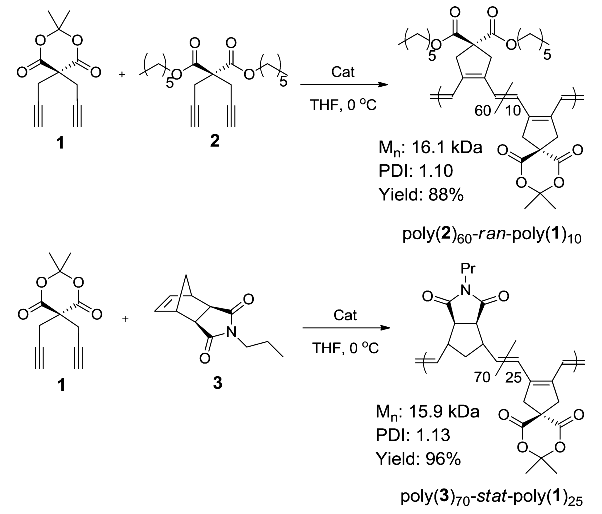
Scheme 1. Synthesis of the Conjugated Polymer Containing Meldrum's Acid and Its Post-Modification by Thermolysis



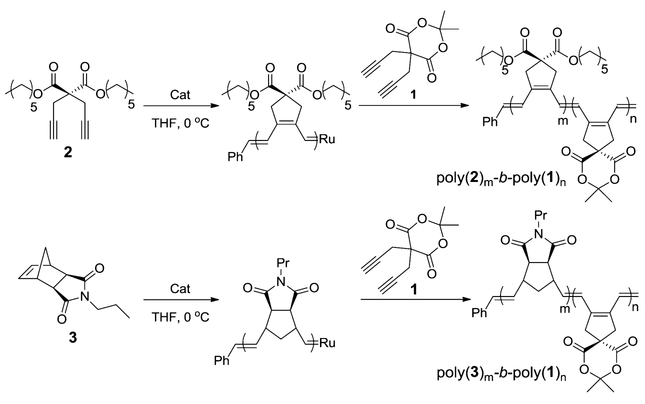
Scheme 2. Cyclopolymerization for the Synthesis of Random Copolymers Containing Meldrum's Acid



polymerization of **1** and ring-opening metathesis polymerization (ROMP) of **3**. This, in fact, produced statistical copolymer, poly(**3**)-*stat*-poly(**1**), with a measured reactivity ratio of $r_1 = 0.7$ and $r_3 = 2.5$ (see the Supporting Information for details). In both cases, soluble random copolymers were obtained in high isolated yields at 0 °C within 2 h, and ^{1}H NMR analysis showed that the actual incorporated composition matched well with the monomer feed ratios (Figure S1). Fully conjugated copolymer poly(**2**)-*ran*-poly(**1**) was successfully obtained by random cyclopolymerization, and this was confirmed by UV analysis (Figure S2a). However, the UV analysis clearly revealed that poly(**3**)-*stat*-poly(**1**) showed a blue-shifted absorption spectrum because the copolymer prepared by ROMP and cyclopolymerization contained a large segment of nonconjugated polymer with only a small polyacetylene segment resulting in short conjugation length (Figure S2b). In both cases, a narrow polydispersity indice (PDI) below 1.13 determined by the SEC analysis suggested that all three monomers were successfully copolymerized by the living polymerization mechanism.

With the successful random copolymerization of **1** in the living polymerization manner, we attempted the synthesis of diblock copolymers containing poly(**2**) or poly(**3**) as the first block and poly(**1**) as the second block (Table 1). During the synthesis of poly(**2**)-*b*-poly(**1**) (entry 1), there was no clear change in color upon the addition of **1** after the synthesis of the first block of poly(**2**). In contrast, during the synthesis of poly(**3**)-*b*-poly(**1**) (entries 2 and 3), a drastic color change to dark red occurred after the addition of **1**. In all cases, as **1** was consumed, the viscosity of the solution drastically increased, suggesting that there was a large increase in the molecular weights of the products. After simple precipitation, the diblock copolymers were obtained in high isolated yields, and they were soluble in various organic solvents such as THF, dichloromethane, and chlorobenzene. However, ^{1}H NMR analysis of these block copolymers revealed no signals corresponding to poly(**1**) and only showed signals corresponding to the homopolymers of **2** or **3**, even though the cyclopolymerization of **1** as the second block occurred with full conversion (Figure S3). These two observations indicated that polymerization-induced self-assembly[14] occurred during block copolymerization to afford supramolecules consisting of the insoluble

Table 1. Block Copolymerization of Poly(1) with Poly(2) and Poly(3)



entry	comonomer	[comonomer]:[**1**]:[**A**]	$M_{n,m}$[a] (kDa)	PDI_m[a]	$M_{n,s}$[b] (kDa)	PDI_s[b]	yield[c] (%)
1	**2**	50:25:1	483.4	1.25	18.5	1.12	99%
2	**3**	66:25:1	122.1	1.18	14.5	1.08	98%
3	**3**	100:50:1	352.6	1.57	29.0	1.03	94%

[a]Values corresponding to the micelle. [b]Values corresponding to the polymer single chain determined by SEC eluted by THF and calibrated using polystyrene (PS) standards. [c]Isolated yields after purification.

poly(1) block as the core and the soluble poly(2) or poly(3) block as the shell. SEC analysis of the block copolymers showing two sets of traces strongly supported this idea; major traces with much higher molecular weights ($M_{n,m}$ in Table 1) than expected for the single chain of diblock copolymers ($M_{n,s}$ in Table 1) corresponded to the supramolecules containing the poly(1) core (Figure 1). The fact that the majority of the diblock copolymers maintained their structures as supramolecular adducts even under the high shear force condition of SEC pressure[15] indicated that the supramolecules were highly stable in solution as a result of strong $\pi-\pi$ interactions in the conjugated polymer core as well as the insolubility of the second block.

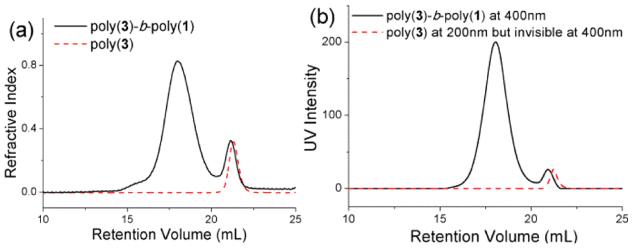


Figure 1. (a) $CHCl_3$ SEC traces of poly(3) and poly(3)-*b*-poly(1) determined using an RI detector. (b) SEC traces of poly(3)-*b*-poly(1) determined using UV detectors. From the SEC analysis with UV detection, we concluded that the minor traces corresponded to the single polymer chain of the diblock copolymers which had a slightly shorter PA chain.[16].

To investigate the self-assembly in detail, structural information on these supramolecules was obtained using atomic force microscopy (AFM) and dynamic light scattering (DLS) analysis. For AFM imaging, a dilute solution of the polymers in chloroform was spin-coated onto mica, and via tapping mode, nanospheres with average width of 31.4 (±2) nm and height of 2.4 (±0.7) nm were vividly observed (Figure 2a). In addition, the three-dimensional side-view showed the typical flattened pancake shape of the nanospheres (Figure 2b). Next, DLS analysis providing size information revealed that the nanospheres had an average diameter of 45 nm in chloroform solution. The size of the nanospheres determined from the DLS analysis appeared to be larger than that obtained from the AFM images in solid state because of the solvation of the polymers in solution (Figure S4). Surprisingly, the spherical nanostructure was maintained even after heating the solution to 100 °C or sonicating it for 30 min. In short, all of these analyses strongly indicate that the diblock copolymers spontaneously self-assembled into stable spherical structures during polymerization. This is because the growing chain of the insoluble polyacetylene block containing the Meldrum's acid functionalities could no longer be solvated as a unimer and instead formed a spherical supramolecule to reduce the exposed area of the solvophobic PA segment. This process is noteworthy since it eliminates the need for any post-treatments, such as dialysis or changing the specific solvent composition,[17−19] which are essential for inducing the conventional self-assembly process. This direct fabrication of the stable nanosphere is possible because the $\pi-\pi$ interaction forming the core−shell nanostructure is strong enough to maintain the supramolecular adducts even under heating and the shear pressure conditions of SEC.

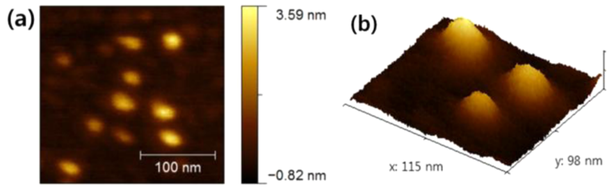


Figure 2. (a) AFM image of poly$(3)_{100}$-*b*-poly$(1)_{50}$ in height mode. The nanospheres had an average width of 31.4 (±2) nm and height of 2.4 (±0.7) nm. (b) Three-dimensional view of the block copolymer micelles.

With the successful copolymerization of 1, we next investigated the thermolysis of the various copolymers to monitor the decomposition of Meldrum's acid to ketene. Ketene formation temperatures (T_{kf}) of the statistical and diblock copolymers containing Meldrum's acid and the homopolymer of 1 were determined by the onset point in thermal gravimetric analysis (TGA). The clear drop in weight was attributed to the loss of acetone and CO_2 as the ketene was generated, and the observed weight percentages lost were in good agreement with the theoretically calculated weight losses. The T_{kf} of the copolymers (203 °C for random and 205 °C for block copolymers) were higher than that of the homopolymer (194 °C) (Figure 3a). Direct evidence of ketene formation was confirmed by infrared (IR) analysis of the films of the statistical and diblock copolymers. After heating the polymer samples at 220 °C for 5 min, the IR signal at 2111 cm^{-1} corresponding to

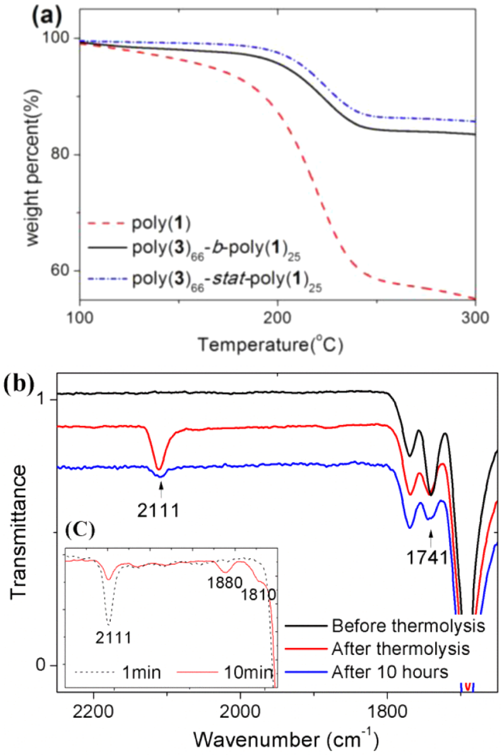


Figure 3. (a) TGA profiles of the homopolymer and copolymers. (b) IR spectrum of poly(3)-*b*-poly(1) to monitor ketene formation before and after thermolysis at 220 °C for 5 min. The growing signal at 2111 cm^{-1} corresponds to ketene formation, and the decreasing signal at 1741 cm^{-1} indicates decomposition of Meldrum's acid. (c) Infrared spectrum of poly(3)-*b*-poly(1) after heating at 240 °C for 1 and 10 min. New signals at 1810 cm^{-1} and 1880 cm^{-1} suggest the cross-linking of ketenes to afford cyclobutanedione moieties.

the ketene appeared,[10] and the signal at 1741 cm^{-1} corresponding to the ester of the Meldrum's acid functionality decreased. For poly(**3**)-*b*-poly(**1**), the signal for the thermally generated ketenes remained for more than 10 h under ambient conditions (Figure 3b). However, for poly(**3**)-*stat*-poly(**1**), the signal for the ketenes disappeared at a much faster rate. We believe that the increased ketene stability in the block copolymer could be attributed to its core−shell supramolecular structure. The poly(**3**) block would suppress the approach of external nucleophiles such as water to the core. Moreover, a well-stacked and solvophobic PA block in the core also prevented nucleophiles from attacking the ketenes. This observation implied that the polymer structures and morphology could be a determining factor for the stability of the ketenes.

Ketenes are known to undergo [2 + 2] cycloaddition to give cyclobutanedione[10] (Scheme 1). This reaction could be used to permanently cross-link the cores of the nanopspheres. This was achieved by thermolysis of poly(**3**)-*b*-poly(**1**) at 240 °C for 10 min. This was also monitored by IR analysis, which revealed the reduction in the ketene signal at 2111 cm^{-1} in addition to the appearance of new signals at 1880 cm^{-1} and 1810 cm^{-1} corresponding to cyclobutanedione (Figure 3c). To our knowledge, this is the first example of core−shell supramolecules containing a conjugated backbone cross-linked by ketenes generated in situ. Although the stable nanospheres were formed directly during the polymerization without post-treatment, this simple cross-linking of the core via heating provides an alternative strategy to photocross-linking or covalent cross-linking by a click reaction[20−22] to ensure an even higher stability of the nanoparticles.

In conclusion, we have prepared both soluble random and diblock copolymers containing conjugated polymer backbones with the Meldrum's acid functionality via controlled cyclopolymerization using a third-generation Grubbs catalyst. Diblock copolymers containing poly(**1**) as the second block spontaneously self-assembled in organic solvents to generate nanospheres via in situ nanoparticlization of conjugated polymer. Transformation of Meldrum's acid to ketenes occurred successfully by thermolysis at 220 °C resulting in highly stable spherical nanoparticles with cross-linked cores. These conjugated polymers containing ketenes could be potentially useful as electronic materials because they consist of semiconducting (and potentially conducting) cores with insulating shells.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, HR−MS data for monomer, ^{1}H NMR data for polymers, UV−vis spectra, and DLS analysis data for block copolymers. 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.

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(16) The polymers with high and low molecular weight fractions were separated by SEC, and their UV spectra were obtained (Figure S5). The spectrum for the low molecular weight fraction was slightly blue-shifted, but the second block might be long enough to form the core−shell adducts as there was no signals corresponding to the single polymer chain from DLS (Figure S4).

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