

Synthesis of Various Functional Block Copolymers via Controlled Ring Opening Metathesis Polymerization and the Subsequent Chemical Modifications

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Introduction

Block copolymers are regarded as an essential substance to produce a well-defined nano-scale structure which is the key element in nanotechnology.[1] As the necessities for more sophisticated nanostructures are increasing, now the scope of the 'traditional' simple block copolymers is expanding toward 'functional' block copolymers, which can endow advantages coming from both ordered nano-structure and functionalities. The recently developed living ring opening metathesis polymerization (ROMP) have allowed for design and synthesis of these more complicated and novel block copolymers due to their improved functional group tolerance and mild reaction conditions.

Here, we report on the synthesis of block copolymers that have various functional groups such as an electroactive group (ferrocene), alkyl or aryl groups by ROMP, and studied the scope and limitation of their chemical modification for generating more useful functional groups such as aryl diazonium salts.

Experimental

General ROMP Procedure. To a vial charged with Grubbs catalyst-bispyridine complex **6** (10.4 mg, 0.012mmol) in 2 ml of dry CH_2Cl_2 was added a solution of **2** (520 mg, 2.34 mmol) in 4 ml of dry CH_2Cl_2 under argon atmosphere at rt. After 30 min, an aliquot (~100 μL) of the solution was taken for GPC analysis and a solution of **5** (280 mg, 0.78 mmol) in 4 ml of dry CH_2Cl_2 was added via a syringe at rt. The resulting light brown solution was allowed to stir for 40 min at rt. The reaction was quenched by adding excess ethyl vinyl ether (EVE). The solution was dripped into methanol to precipitate the polymer. The resulting ivory colored precipitate was filtered, washed with methanol, and dried under vacuum for 4 h to give the polymer **8** (750 mg, 94%), $M_w = 40,759$ g/mol, $M_n = 38,662$ g/mol, PDI = 1.05 (by GPC using PS standards).

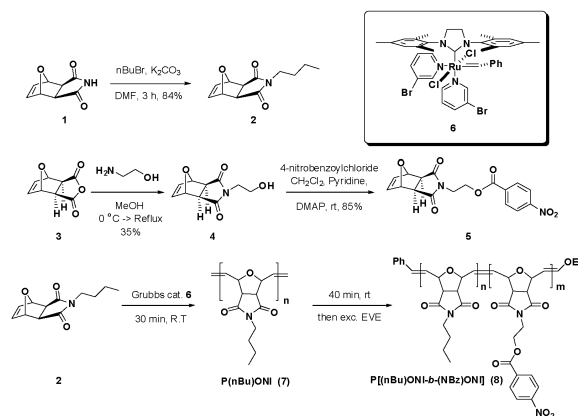
Hydrogenation of 8. 0.2 g of polymer **8** was dissolved in 20 ml of xylene in a reaction flask. To the solution were added *p*-toluene sulfonylhydrazide (0.8 g, 7.0 equiv. relative to the mole amount of the double bonds in the polymer) and a trace amount of 2,6-di-*tert*-butyl-4-methylphenol. The solution was degassed by bubbling argon gas for 10 min. The solution was gradually heated to 120 °C. At around 100 °C, a homogeneous solution resulted and nitrogen gas started to evolve. It was stirred for 3 h at 120 °C until the nitrogen evolution ceased. The solution was cooled to room temperature and dripped into methanol to precipitate the polymer. After filtration, the polymer precipitate was dissolved in THF and reprecipitated in methanol. The resulting polymer was dried in vacuo overnight at room temperature to give the reduced polymer **9** (180 mg, 90%). $^1\text{H-NMR}$ (300 MHz, CDCl_3); δ 8.26 (br, ArH), 8.15 (br, ArH), 4.54 (br, $-\text{CH}_2\text{OCOAr}$), 4.00–3.70 (br m, $-\text{NCH}_2\text{CH}_2\text{OCO}-$, $-\text{OCH}_2-$), 3.49 (br, $-\text{CH}_2\text{N}-$), 3.13 (br, $-\text{CH}_2-$), 1.99–1.74 (br, $-\text{CH}_2\text{CH}_2-$, backborn), 1.56 (br m, $-\text{CH}_2-$), 1.34 (br m, $-\text{CH}_2-$), 0.95 (br t, $-\text{CH}_3$).

Nitro Group Reduction. polymer **8** (100 mg) was dissolved in THF (1 ml) in a culture tube. To the above solution was added 0.5 mL (>5 equiv.) of $(\text{NH}_4)_2\text{S}$. The resulting solution was allowed to stir for 3 h at room temperature. After 3 h, the solution was in methanol to precipitate the polymer. The polymer was dissolved in THF and reprecipitated in methanol. The polymer was dried in vacuum overnight (80 mg, 80%).

Preparation of Diazonium Salts: Amine polymer (30 mg) and nitrosyltetrafluoroborate (16 mg, 0.14 mmol) were dissolved in dry CH_3CN (2 mL) under argon atmosphere at 0 °C. The resulting solution was allowed to stir at 0 °C for 40 min. After 40 min, the polymer was precipitated in hexane. The diazonium salt containing block copolymer was dried in vacuum (22 mg, 73%)

Results and discussion

N-Butyl 7-oxanorbornene derivative **2** was prepared from maleimide-furan Diels-Alder adduct **1** by alkylation with *n*-BuBr in DMF in 84% yield. Another 7-oxanorbornene derivative **5** that contains a *p*-nitrobenzoyl group was prepared starting from anhydride **3** in two steps. The resulting two monomers were sequentially subjected to ROMP by using bis(3-bromopyridine) ligated Grubbs catalyst **6** [2] to give the block copolymer **8** (Scheme 1). These polymers were obtained with good molecular weight and low polydispersity (PDI) control (1.03–1.07).



Scheme 1. Synthesis of block copolymer **8**.

Having the nitrobenzoyl group containing block copolymer **8** in out hand, we have performed various chemical modifications of the polymer as summarized in Figure 1. The double bonds in the polymer backbone could be selectively reduced by using *p*-toluene sulfonyl hydrazide to give polymer **9**. Treatment of **9** with ammonium sulfide reduced the nitrobenzene group to aniline and this polymer formed cylindrical micelles, which is different from the spherical micelle of polymer **8**, as checked by AFM. The aniline group could be transformed to diazonium salt and the resulting polymer **12** was electrochemically active being deposited on a glassy carbon electrode efficiently. The presence of the diazonium salts in **12** could be also confirmed by treating with diethylaminobenzene, which formed diazo group containing diblock copolymer **11**.

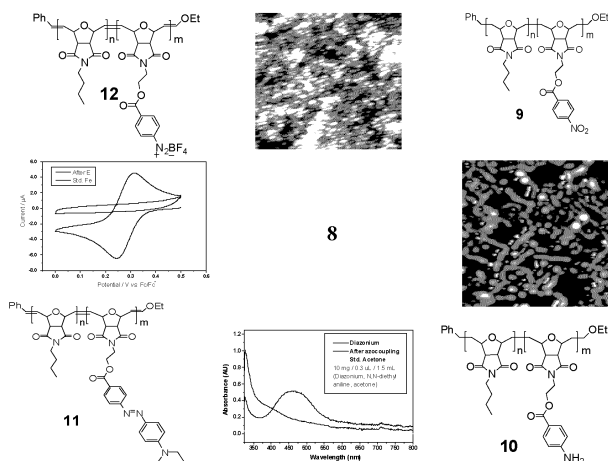


Figure 1. Chemical modifications of polymer **8**.

Conclusions

We have synthesized functional block copolymers by living ROMP with good molecular weight and polydispersity control and demonstrated several chemical modification of the polymers yielding useful functional groups such as amine, diazonium salt, and diazo benzene.

References

- [1] Hamly, I. W. *Nanotechnology* **2003**, *19*, R39.
- [2] Choi, T. L.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2003**, *42*, 1743.