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Synthesis and Characterization of Diazonium Containing Block Copolymers *via* Controlled Ring Opening Metathesis Polymerization (ROMP) and the Subsequent Chemical Modification

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Summary: 7-Oxanorbornene-5,6-dicarboximide derivatives bearing either an alkyl- or a nitrophenyl group were prepared and these monomers were subjected to the controlled ring opening metathesis polymerization (ROMP). The resulting polymer, poly[*N*-(*n*-butyl)-7-oxanorbornene-5,6-carboximide-*b*-*N*-(2-(4-nitrobenzoyl)ethyl)-7-oxanorbornene-5,6-dicarboxiimide] P(BuONDI-*b*-NbONDI) (**8**), showed good molecular weight and narrow polydispersity control (PDI < 1.1). The alkene and the nitrophenyl groups in the block copolymer were selectively reduced using tosyl hydrazide and ammonium sulfide, respectively. The resulting aryl amines in the block polymer were then oxidized to the corresponding diazonium salts by treatment with nitrosyl tetrafluoroborate. The presence of the diazonium groups was verified by IR and cyclic voltammetry (CV), and also by several chemical reactions which are unique for diazonium salts.

Keywords: diazonium salt; functional block copolymer; ring opening metathesis polymerization (ROMP)

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 the 'functional' block copolymers, which can endow advantages coming from both the ordered nanostructure and the functionality of the polymer. The recently developed controlled polymerization methodologies such as atom transfer living radical polymerization (ATRP), nitroxide mediated radical polymerization (NMP), reversible addition-fragmentation transfer polymerization (RAFT), and living ring opening metathesis polymerization (ROMP) have allowed for design and synthesis of more complicated and novel block copolymers due to their improved functional group tolerance and mild reaction conditions.[2–4] So far, numerous studies on the synthesis of functional polymers containing conventional groups such as halide, alcohol, carboxylic acid, amine, and heterocycles were reported.[5] However, introduction of a novel functional group such as an aryl diazonium salt has not been achieved, while it is one of the most useful intermediates in organic synthesis. Nucleophilic aromatic substitution of an aryl diazonium salt by various nucleophiles such as hydroxides, halides, cyanides, azides, alkenes, and arenes is readily achievable.[6] Most of all, the feature that one electron reduction of aryl diazonium salt by electrochemical process can provide

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the highly reactive aryl radical species allows for functionalization of chemically inert surfaces such as glassy carbon (GC),[7,8] single-walled carbon nanotube (SWNT),[9–11] semiconductors,[12,13] and metals.[14,15] So far, modification of these inert surfaces was achieved only by using simple uni-molecular aryl diazonium salts, and the corresponding modification with polymeric diazonium salts has not been reported. If one can obtain aryl diazonium containing polymers and use them for the inert surface modification, he or she can endow the surface with more sophisticated functionalities and properties by introducing proper functional groups to the polymer from the beginning.

In this report, we describe the synthesis of block copolymers having nitrophenyl groups in one block by controlled ROMP, and its chemical modification to provide aryl diazonium salt containing block copolymers. We studied the scope and limitation of their chemical modification for generating more useful functional groups such as amine, and aryl diazonium salt.

Experimental Part

Materials and Characterization

All commercially obtained solvents and reagents were used without further purification except as noted below. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Dry methylene chloride was obtained by distilling from calcium hydride. ^{1}H-NMR and ^{13}C-NMR spectra were obtained using a Varian Gemini-300 (300 MHz for ^{1}H, and 75 MHz for ^{13}C) spectrometer. Elemental analyses were performed by the Organic Chemistry Research Center at Sogang University using a Carlo Erba EA 1180 elemental analyzer. IR spectra were obtained using a Thermo-Nicholet Avartar-330 IR spectrometer with a single-bounce ATR (Ge crystal) accessory (Smart MIRacle). Polymer molecular weights were estimated using a Sykam GmbH GPC system equipped with a Sykam S1122 HPLC pump, a S5200 autosampler, a S3580 differential RI and a S3210 UV/VIS detectors, and three Jordi Gel DVB GPC columns (500 Å, 1000 Å, 10 000 Å, 300 mm × 7.8 mm). Cyclic voltammetric experiments were recorded using a CHI 900 potentiostat (CH instrument Co. Int.) with a glassy carbon working electrode (3 mm diameter), a platinum wire counter electrode and an Ag/AgCl reference electrode. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (0.1 M) was used as the supporting electrolyte. UV-visible absorbance spectra were obtained by an Agilent 8453 UV-visible spectrometer. Atomic force microscopy (AFM) measurements were carried out using a Digital Instrument Nanoscope IV-A in a height mode.

Synthesis of P(BuONDI-*b*-NbONDI) (8)

To a vial charged with a solution of Grubbs catalyst-bispyridine complex **6** (10.4 mg, 0.012 mmol) in CH_2Cl_2 (2 mL) was added a solution of BuONDI **2** (520 mg, 2.34 mmol) in CH_2Cl_2 (4 mL) under argon atmosphere at rt. After 30 min, an aliquot (~100 μL) of the solution was taken for GPC analysis and a solution of NbONDI **5** (280 mg, 0.78 mmol) in CH_2Cl_2 (4 mL) 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 precipitates were filtered, washed with methanol, and dried under vacuum for 4 h to give the block copolymer P(BuONDI-*b*-NbONDI) (**8**) (750 mg, 94%). $M_w = 40{,}759$ g/mol, $M_n = 38{,}662$ g/mol, PDI = 1.05 (by GPC using PS standards). ^{1}H-NMR (300 MHz, $CDCl_3$); δ 8.19 (br, ArH), 8.07 (br, ArH), 6.08 (br s, $-C\underline{H}$ $C\underline{H}-$), 5.91 (br s, $-C\underline{H}$ $C\underline{H}-$), 5.78 (br s, $-C\underline{H}$ $C\underline{H}-$), 4.98 (br s, $-OC\underline{H}CH-$), 4.46 (br s, $-OC\underline{H}CH-$), 4.33 (br s, $-C\underline{H}_2OCOAr$), 3.88 (br s, $-NC\underline{H}_2CH_2OCOAr$), 3.47~ 3.32 (br m, $-C\underline{H}_2N-$, $-COC\underline{H}-$), 1.55 (br m, $-C\underline{H}_2-$), 1.32 (br m, $-C\underline{H}_2-$), 0.93 (br t, $-C\underline{H}_3$).

Hydrogenation of P(BuONDI-*b*-NbONDI)

Polymer P(BuONDI-*b*-NbONDI) (**8**) (0.2 g) 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 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 at 120 °C for 3 h until the evolution of nitrogen stopped. The solution was cooled to room temperature and dripped into methanol to precipitate the polymer. After filtration, the polymer precipitates were redissolved in THF and reprecipitated with methanol. The resulting polymer was dried in vaccuo overnight at room temperature to give the reduced polymer **9** (180 mg, 90%). ^{1}H-NMR (300 MHz, $CDCl_3$); δ 8.26 (br, Ar$\underline{H}$), 8.15 (br, Ar$\underline{H}$), 4.54 (br, –C$\underline{H}_2$OCOAr), 4.00~3.70 (br m, –NC$\underline{H}_2$CH$_2$OCO–, –OC$\underline{H}$–), 3.49 (br, –C$\underline{H}_2$N–), 3.13 (br, –C$\underline{H}$CO–), 1.99~1.74 (br, –C$\underline{H}_2$C$\underline{H}_2$–, backbone), 1.56 (br m,–C$\underline{H}_2$–), 1.34 (br m, –C$\underline{H}_2$–), 0.95 (br t, –C$\underline{H}_3$).

Nitro Group Reduction of Polymer 9

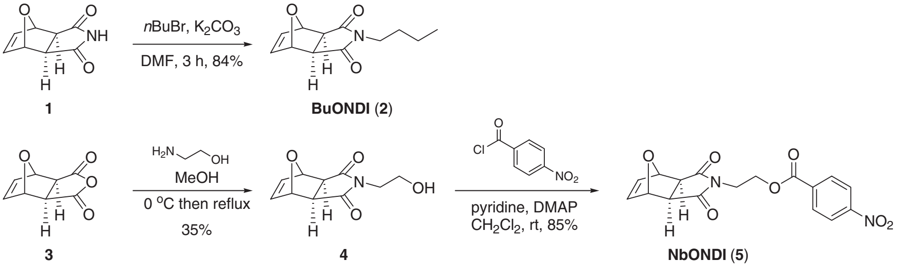
Olefin reduced polymer **9** (100 mg) was dissolved in THF (1 mL) in a culture tube. To the solution was added 0.5 mL of ammonium sulfide solution (60% aqueous solution, >5 equiv.). The resulting reddish brown solution was allowed to stir for 3 h at room temperature. After 3 h, the solution was dripped into methanol to precipitate the polymer. It was redissolved in THF purified by reprecipitation in methanol. After filtration, the polymer was dried under vacuum overnight (80 mg, 80%). ^{1}H-NMR (300 MHz, DMSO-d_6); δ 7.56 (br d, Ar$\underline{H}$), 6.57 (br d, Ar$\underline{H}$), 5.91 (br s, ArN$\underline{H}_2$), 4.29 (br s, –C$\underline{H}_2$OCOAr), 4.00~3.70 (br m, –NC$\underline{H}_2$CH$_2$OCO–, –OCH–), 3.49 (br m, –C$\underline{H}_2$N–), 3.13 (br m, –C$\underline{H}$CO–), 1.85~1.60 (br, –C$\underline{H}_2$C$\underline{H}_2$–, backbone), 1.44 (br m,–C$\underline{H}_2$–), 1.19 (br m, –C$\underline{H}_2$–), 0.85 (br t, –C$\underline{H}_3$).

Synthesis of Aryl Diazonium Block Copolymer 11

Amine polymer **10** (30 mg) and nitrosyl tetrafluoroborate (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 for 40 min at 0 °C. After 40 min, the mixture was dripped into hexane to precipitate the polymer. The resulting diazonium salt functionalized block copolymer **11** was dried under vacuum (22 mg, 73%). ^{1}H-NMR (300 MHz, DMSO-d_6); δ 8.81 (br d, Ar$\underline{H}$), 8.37 (br d, Ar$\underline{H}$), 4.45 (br s, –C$\underline{H}_2$OCOAr), 4.00~3.70 (br m, –NC$\underline{H}_2$CH$_2$OCO–, –OCH–), 3.49 (br, –C$\underline{H}_2$N–), 3.13 (br, –C$\underline{H}_2$–), 1.85~1.60 (br, –C$\underline{H}_2$C$\underline{H}_2$–, backbone), 1.44 (br m,–C$\underline{H}_2$–), 1.20 (br m, –C$\underline{H}_2$–), 0.85 (br t, –C$\underline{H}_3$).

Results and Discussion

Since aryl diazonium salt itself is an ionic species which is chemically too labile, direct polymerization of aryl diazonium salt monomer is infeasible. Therefore, we planned to use a nitrophenyl group as a precursor for aryl diazonium salt. The nitrophenyl groups can be converted to the corresponding aryl diazonium salts by the sequential chemical reactions which include reduction to aryl amine and the subsequent treatment of the resulting amine with nitrosonium ion. Syntheses of the required monomers are illustrated in Scheme 1. Alkylation of *exo*-7-oxanorbornene-5,6-dicarboximide (**1**) with *n*-butyl bromide under basic conditions (K_2CO_3 in DMF) provided the desired monomer *exo*-*N*-butyl-7-oxanorbornene-5, 6-dicarboxiimide (BuONDI) (**2**) in 84% yield.[16] Oxanorbornene diimide **1** was readily available by the Diels-Alder reaction of furan and maleimide with high *exo* selectivity.[17] Nitrophenyl group functionalized monomer, *exo*-*N*-[2-(4-nitrobenzoyl)-ethyl]-7-oxanorbornene-5, 6-dicarboxiimide



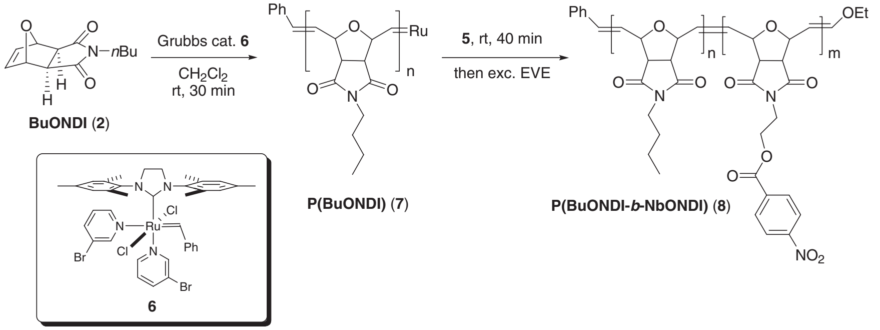
Scheme 1.
Synthesis of oxanorbornene class monomers, BuONDI (**2**) and NbONDI (**5**).

(NbONDI) (**5**), was prepared in 85% yield by treatment of *exo-N*-(2-hydroxyethyl)-7-oxanorbornene-5,6-dicarboximide (**4**) with 4-nitrobenzoyl chloride in the presence of pyridine and 4-dimethylaminopyridine (DMAP). Hydroxyethyl functionalized oxanorbornene **4** was obtained from *exo*-7-oxanorbornene-5,6-dicarboxylic anhydride **3** by the reaction with 2-hydroxyethyl amine in 35% yield.[18]

With these monomers in our hand, the successive ROMP of the two monomers was performed. Living ring opening metathesis polymerization of BuONDI (**2**) was readily achieved by adding 3-bromopyridine modified Grubbs catalyst **6** at room temperature. This 3-bromopyridine ligated Grubbs catalyst is known to exhibit a higher propagation/initiation rate ratio compared to the tricyclohexylphosphine ligated analogs, thereby giving a much narrower molecular weight distribution.[19]

Molecular weights of BuONDI block were determined by GPC with polystyrene standards and those of the second block (NbONDI block) were determined by ^{1}H-NMR comparing the peak integration against the first block peaks (Table 1). Although the molecular weights of several runs show some deviations from the theoretical ones, the resulting block copolymers showed fairly narrow polydispersities (PDI<1.1). This is probably due to partial deactivation of the growing ruthenium carbene species during the polymerization.

As for the next step, we investigated whether it is possible to reduce the nitro groups and olefins in the block copolymers through hydrogenation using Pd/C catalyst and hydrogen gas. However, several hydrogenation attempts even under vigorous conditions (120 psi hydrogen pressure) failed, and only starting material was



Scheme 2.
Synthesis of nitrophenyl group containing block copolymer P(BuONDI-*b*-NbONDI) (**8**) via ROMP.

Table 1.
Molecular weight data of P(BuONDI-*b*-NbONDI) (**8**).

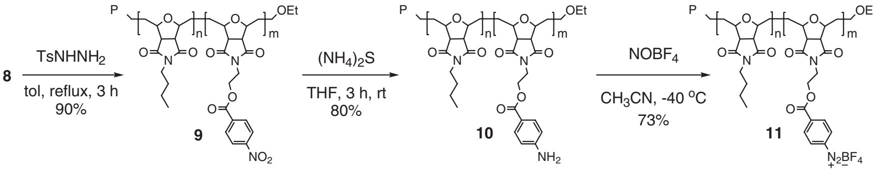
Entry	BuONDI block			NbONDI block				
	M/C[a]	$M_{n,\ theor}$[b] $\times 10^3$	$M_{n,\ GPC}$[c] $\times 10^3$	M/C[a]	$M_{n,\ theor}$[b] $\times 10^3$	$M_{n,\ NMR}$[d] $\times 10^3$	PDI[c]	Yield[e]
		g/mol	g/mol		g/mol	g/mol	$[M_w/M_n]$	[%]
1	100	22.1	28.4	50	17.9	41.1	1.07	75
2	100	22.1	33.2	50	17.9	34.7	1.05	87
3	100	22.1	16.7	33	11.8	11.0	1.03	77
4	200	44.3	28.6	33	11.8	22.3	1.07	71
5	200	44.3	34.4	33	11.8	23.4	1.05	90

[a] Monomer to catalyst mole ratio;
[b] Theoretical number average molecular weight, M_n, based on the initial monomer to catalyst ratio (M/C);
[c] Determined by GPC using polystyrene standards;
[d] Calculated by ^{1}H-NMR integration compared to the intensities of BuONDI peaks;
[e] Yield of product isolated by precipitating into methanol.

recovered. Therefore, we searched for a homogenous and mild reducing reagent, and finally found that *p*-toluene sulfonyl hydrazide[20] was the choice. This reagent selectively reduced the double bonds in the polymer backbone and the nitro groups remained untouched to give polymer **9** (Scheme 3). The backbone-reduced block copolymer **9** was characterized by ^{1}H-NMR (Figure 1). The vinyl protons at 5.7~6.3 ppm and the protons at 2,5-positions of the furan rings at 4.5 and 5.5 ppm completely disappeared while the aromatic protons at 8.0~8.4 ppm remained after the reaction. Treatment of polymer **9** with ammonium sulfide[21] in THF at room temperature then reduced the nitrophenyl groups to anilines giving polymer **10**. The aromatic peaks appearing at 8.0~8.4 ppm in polymer **8** shifted to 6.6 and 7.6 ppm after the reaction, which implies that the nitrophenyl groups were reduced to anilines. Finally, the amine containing block copolymer **10** was modified to diazonium salt containing block copolymer **11** by treatment with nitrosyl tetrafluoroborate ($NOBF_4$) in acetonitrile at −40 °C.

In the IR spectrum of polymer **11** was found a peak at 2293 cm^{-1}, which is the critical signature of aryl diazonium salt. In addition, treatment of the diazonium containing block copolymer **11** with diethylaminobenzene in THF resulted in color change from light yellow to dark orange, which was caused by the formation of diazo dyes in the polymer (Scheme 4). UV-Vis spectral changes before and after the reaction are illustrated in Figure 2 along with the photographs of the solutions.

In addition, electrochemical property of aryl diazonium block copolymer **11** was also investigated by cyclic voltammetry (CV) as shown in Figure 3. Sweeping the potential between 0.3 to −1.7 V vs. Ag/AgCl showed irreversible reduction peak of aryl diazonium salt at an onset potential of −1.2 V, and repetitive scanning resulted in diminished reduction peaks (inset in Figure 3). This indicates that the polymer was successfully deposited on the glassy carbon



Scheme 3.
Chemical modification of P(BuONDI-*b*-NbONDI) (**8**).

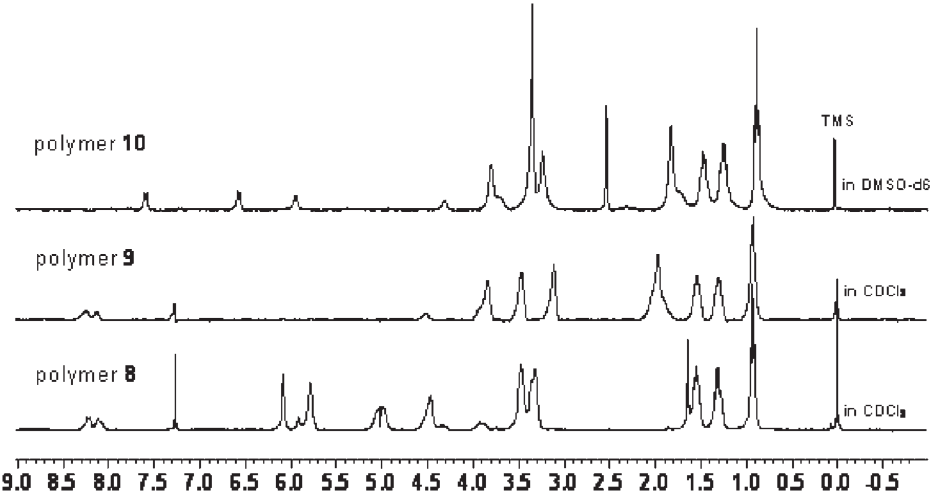
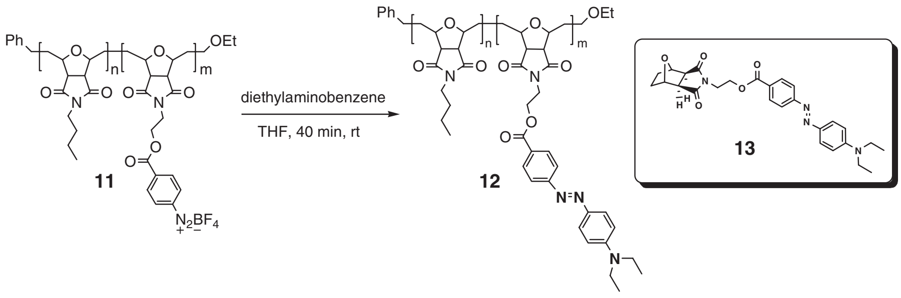


Figure 1.
^{1}H-NMR spectra of polymers **8**, **9**, and **10**.

(GC) electrode surface. After the modification, the surface grafted electrode was subjected to cyclic voltammetry of $Fe(CN)_6^{3-}$. While the bare GC electrode shows distinct redox peaks of $Fe(CN)_6^{3-}$ (dotted line in Figure 3), the surface grafted GC electrode showed no peak. From these CV experiments, it was concluded that polymer **11** was indeed functionalized with aryl diazonium salts and electrochemically active for electrode modification.

On the other hand, the film morphologies of block copolymers **8**, **9**, and **10** obtained from selective solvents (benzene for **8** and **9**, THF for **10**) were investigated by atomic force microscopy (AFM). A diluted solution of each polymer (0.5 wt%) in the designated selective solvent was spin-coated on a silicon wafer, and the surfaces were investigated by AFM. The images are shown in Figure 4. While P(BuONDI-*b*-NbONDI) (**8**) shows spherical micelles with an average diameter of ~60 nm and high regularity (A in Figure 4), backbone-reduced polymer **9** shows both spherical and cylindrical micelles with larger diameters (B in Figure 4). On the other hand, aryl amine functionalized polymer **10** presents coagulated spherical micelles (C in Figure 4), which is probably



Scheme 4.
Formation of diazo group containing block copolymer **12** by the reaction of block copolymer **11** with diethylaminobenzene. In the box is shown the structure of monomeric diazo compound **13** for UV-Vis spectra comparison shown in Figure 2.

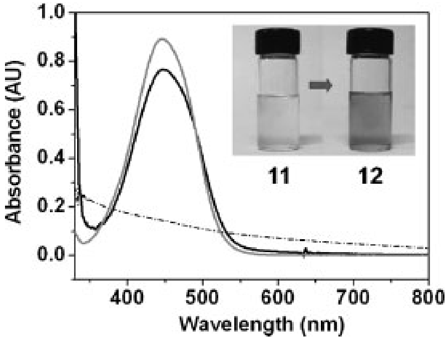


Figure 2.
UV-Vis spectra of diazonium containing block copolymer **11** (dashed line), diazo group containing block copolymer **12** (black), monomeric diazo dye **13** (dark grey). The inset represents the photographs of solutions of **11** and **12**.

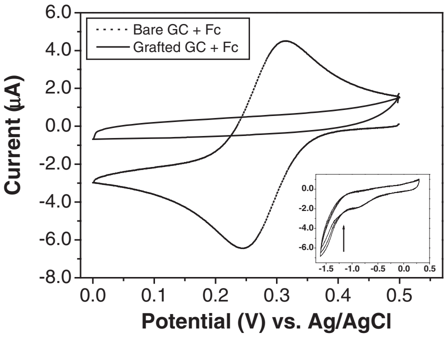


Figure 3.
Cyclic voltammograms of bare (dotted line) and polymer **11** modified glassy carbon electrodes (solid line) in 0.5 mM $Fe(CN)_6^{3-}$ in water (containing 0.1 M KNO_3). Inset: cyclic voltammograms of a glassy carbon electrode during the continuous cycling in a 0.5 mM diazonium functionalized block copolymer **11** solution in acetonitrile containing 0.1 M $TBAPF_6$. Scan rate was 50 mVs^{-1}.

due to the strong inter-micellar interaction caused by hydrogen bonding between amine and imide groups.

Conclusion

We have synthesized *n*-butyl and nitro group containing block copolymer, poly[*N*-(*n*-butyl)-7-oxanorbornene-5,6-carboximide-*b*-*N*-(2-(4-nitrobenzoyl)ethyl)-7-oxanorbornene-5,6-dicarboxiimide] P(BuONDI-*b*-NbONDI) (**8**), via ROMP with good molecular weight and polydispersity control (PDI = 1.03~1.07). Aryl diazonium functionalized block copolymer **11** was obtained by the sequential chemical modification of polymer **8** which includes olefin reduction by tosyl hydrazide, nitro group reduction with ammonium sulfide, and diazotiation with nitroso tetrafluoroborate. We believe that the synthetic protocol demonstrated in this work has provided an access to more sophisticated functional block copolymers which can have numerous applications in the future.

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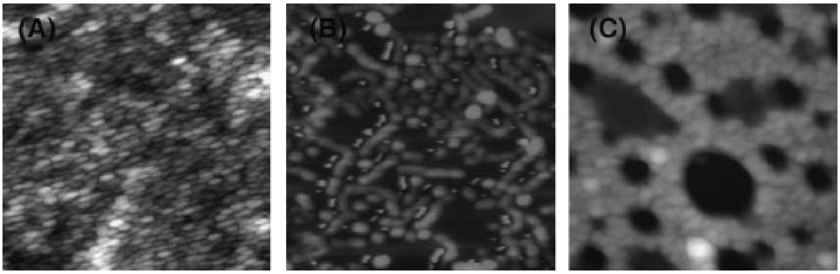

Figure 4.
AFM images (scan size is 1 μm × 1 μm) of polymer **8** (A), polymer **9** (B), and polymer **10** (C) on a silicon wafer.

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