6986 *Macromolecules* **2009**, *42*, 6986–6991
DOI: 10.1021/ma901302e

Macromolecules
ARTICLE

Poly(bisnorbornanediol)

Nai-Ti Lin, Sherng-Long Lee, Jian-Yuan Yu, Chun-hsien Chen,* Shou-Ling Huang, and Tien-Yau Luh*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106

Received June 17, 2009; Revised Manuscript Received July 17, 2009

ABSTRACT: Dihydroxylation of double-stranded poly(bisnorbornene) (**6**) with a ferrocene linker gives the corresponding poly(bisnorbornanediol) (**15**) diasteroselectively. The structures of polymers were characterized by spectroscopic means and STM images. Hydrolysis of **6** gives the corresponding isotactic single-stranded polynorbornene (**12**) having similar polydispersity and degree of polymerization as those of **6**. The STM image of the hydrogenated double-stranded polymer **13** clearly shows the double-stranded structure, and the spacing between two neighboring ferrocene linkers is 0.6 nm. In addition, poly(bisnorbornanediol) (**15**) forms ordered aggregation assembled via hydrogen bonding in both longitudinal and horizontal dimensions.

Introduction

Dihydroxylation of an alkene with osmium tetroxide offers a powerful arsenal to convert a hydrophobic substrate into a hydrophilic product.[1] In particular, the reaction can proceed in an asymmetric manner to give a diol in high enantioselectivity.[2] The use of this tactics for the synthesis of hydrophilic polymer has been sporadically explored.[3−8] Thus, bishydroxylations of polymers based on allyl-substituted glycidyl ethers,[3] methacrylate,[4] or glycolide[5] afford the corresponding water-soluble polymers. A similar strategy has been applied to the synthesis of pseudo-dendritic polyglycerols.[6] Double bonds on the main chain of the polymers such as poly(butane fumarate) can also be dihydroxylated.[7] Macromolecular compositions of C-glycoside analogues of ribofuranose polymers are obtained by dihydroxylation of polymers prepared by ring-opening metathesis polymerization (ROMP) of 7-oxanorbornene derivatives.[8]

We recently reported the first synthesis of DNA-like double-stranded polymers **1** and **2** by Grubbs I catalyst-mediated ROMP[9] of bis(norbornene) derivatives having a ferrocene linker **3** and **4**.[10,11] These rigid-rod polymers can exhibit helical, supercoil, or ladder morphology as revealed by scanning tunneling microscopy (STM).[10,11] ^{13}C NMR studies[12] of both single-stranded poly(norbornene)s and double-stranded **1** and **2** obtained by ROMP of the corresponding *endo*-*N*-arylpyrrolidine-fused norbornene derivatives catalyzed by Grubbs I catalyst suggest that the backbones of these polymers may adopt homogeneous tacticity.[10−12] The fused *N*-aryl heterocycle may offer a unique role for the stereoselective formation of trans double bonds with isotactic stereochemistry in these polymers.[10−12] Presumably, $\pi-\pi$ interactions between these pending aryl groups might take place during the course of the polymerization and would be responsible for stereoselectivity. Indeed, when the *N*-aryl pendant is replaced by the *N*-cyclohexyl group, poly(norbornene) **5** thus obtained contains a mixture of cis/trans double bonds (21/79) with poor selectivity on tacticity.[13]

As depicted in Figure 1, the face for each of the double bond toward the linker Y in a double-stranded polymer would be hindered. It is therefore envisaged that the addition reaction toward the double bonds would occur from the less hindered site. We now wish to report the first diastereoselective dihydroxylation of double bonds in DNA-like double-stranded poly(bisnorbornene)s.

*Corresponding authors: Fax (+886) 2-2364-4971; e-mail chhchen@ntu.edu. (C.-h.C.), twtyluh@ntu.edu.tw (T.-Y.L.).

Results and Discussion

In the beginning of this investigation, **1** or **2** was allowed to react with OsO_4 under Upjohn conditions (NMO/OsO_4/acetone)[14] or Narasaka conditions (NMO/OsO_4/$PhB(OH)_2$/DCM).[15] No desired dihdroxylation products were obtained, and the starting materials were not recovered. It is known that 4-aminobenzyl esters can easily be transformed into a quinone methide iminium ion intermediate under various conditions.[16] In addition, the ferrocene moiety in **2** might also undergo oxidation under these conditions.[17]

In order to avoid these unwanted side reactions, polymer **6** (M_n = 10 400, PDI = 1.3, corresponding to 13 repetitive units) was synthesized according to Scheme 1. It is noteworthy that **6** contains neither 4-aminobenzyl ester moiety nor electron-donating substituents on the ferrocene linker and would be expected to be stable under the oxidative dihydroxylation conditions. As shown in Figure 2a,b, the aromatic and ester carbonyl carbons of **6** and **11** in ^{13}C NMR spectra resonated at almost identical δ values. The ^{13}C NMR signal for the olefinic carbon shifted from δ 135.5 ppm in **11** to δ 131.4 ppm (overlapping with an absorption due to aromatic carbons ortho to the ester group as revealed by ^{13}C−H correlation spectrum[18]) in **6**. ^{13}C shifts of C_7[19] moved from δ 51.9 ppm in **11** to a broad peak around δ 36 ppm in **6**, the latter being characteristic for C_7 of poly(norbornene)s.[10−12,20] The other aliphatic carbons for **6** exhibited similar chemical shifts as those for **11**. The chemical shifts of protons on C_7 appeared at δ 1.8 and 1.4 ppm in the ^{1}H NMR spectrum of **6**. Given the simplicity of the ^{13}C NMR spectrum of **6** and the similarity between the spectra of **6** and **11**, polymer **6** could be highly symmetric. By comparing with the ^{13}C NMR spectra of related double-stranded poly(bisnorbornene)s,[10−12] the spectrum shown in Figure 2b is consistent with a double-stranded structure.[10,11,20]

Hydrolysis of **6** under anhydrous hydroxide conditions[21] followed by Otera−Nozaki esterification[22] gave single-stranded isotactic **12** with all double bonds in trans configuration in 66% yield (M_n = 3700, PDI = 1.3, corresponding to 13 repetitive

 Published on Web 07/31/2009

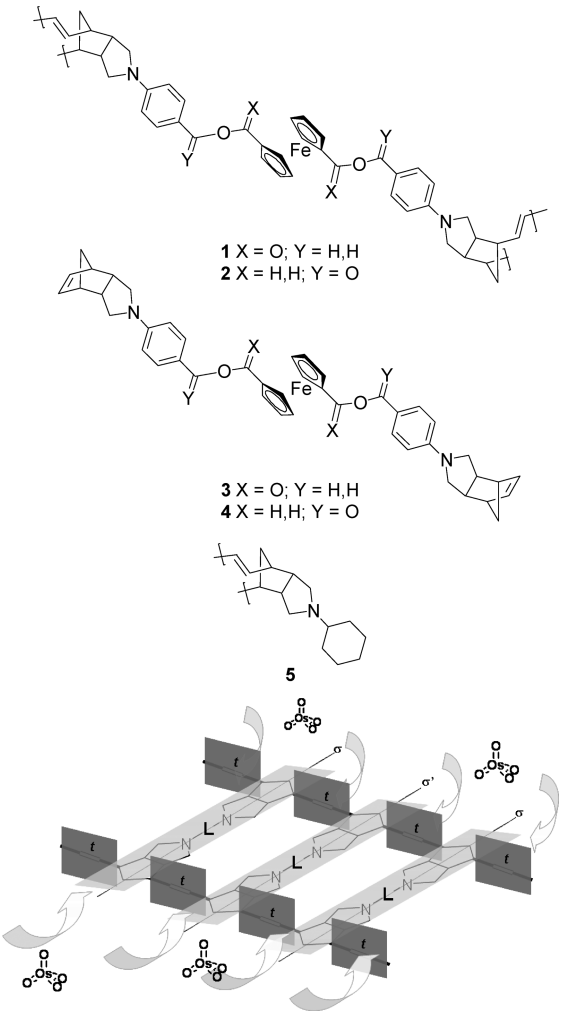
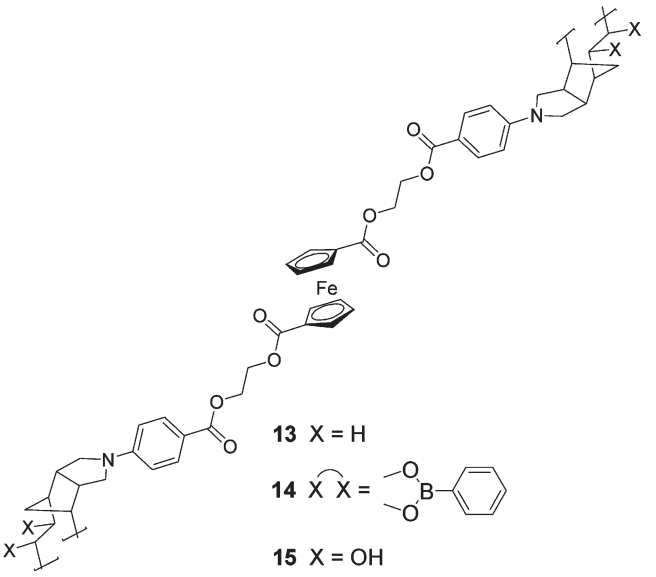


Figure 1. Schematic representation of stereoselective dihydroxylation of poly(bisnorbornene)s (σ,σ': symmetric planes; *t* = trans double bond, L: linker).

units).[12] The narrow dispersity of **12** and similar degree of polymerization of **12** and **6** further suggest that the poly(norbornene) backbones in **6** should have similar chain length. These results provided additional evidence for the double-stranded structure of **6**.

Polymer **6** was treated with $TsNHNH_2$ (Scheme 1) in refluxing chlorobenzene[12a,23] for 12 h to give the corresponding hydrogenated polymer **13** (M_n = 11 400, PDI = 1.3 corresponding to 14 repetitive units). The signal at δ 5.4 ppm in the ^{1}H NMR spectrum of **6** disappeared in that of **13**. As shown in Figure 2c, the ^{13}C NMR absorptions of **13** at the high field are significantly perturbed in comparison with those of **6**. The STM image of **13** on highly oriented pyrolytic graphite (HOPG) showed that **13** had a rodlike structure with a width for each of the polymers about 2.8 nm (Figure 3a). Each of the monomeric layers can be clearly observed on the images, and the average spacing between two neighboring monomeric units was about 0.6 nm. These results were comparable with the images of related polymers reported previously[10,11,19] and therefore consistent with the double-stranded nature of **13** and, hence, **6**.

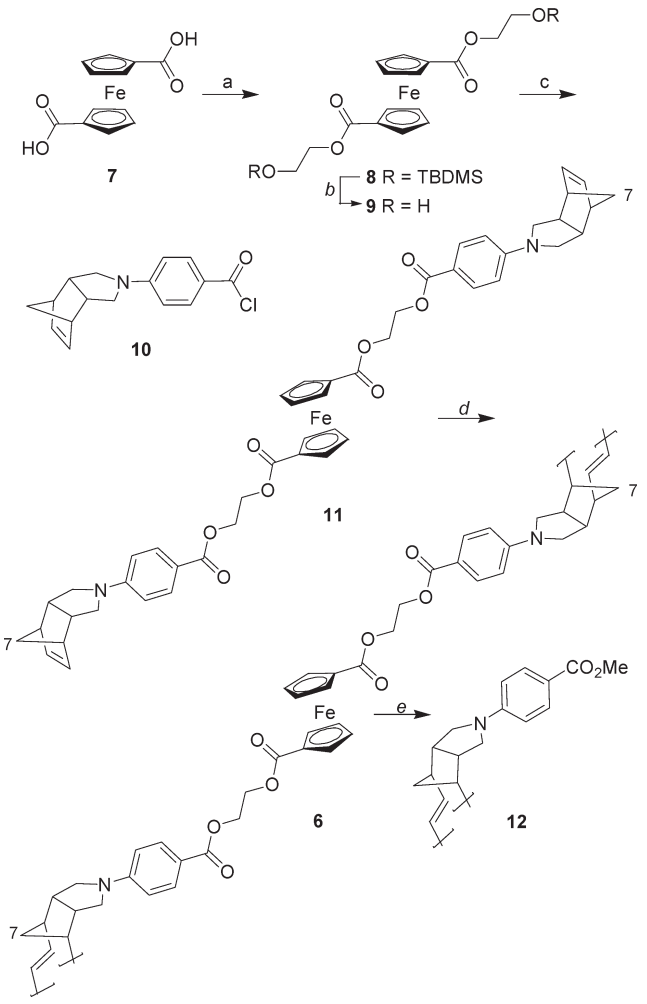
The oxidation potentials against the ferrocene/ferrocenium couple for **6** and **11** in CH_2Cl_2 were 540 and 580 mV, respectively, which were higher than those of the linkers in **2**.[17] It is believed that the ferrocenyl moiety in **6** would remain intact under the catalytic OsO_4 dihydroxylation conditions.[1,2] The modified Narasaka procedure[15] ($NMO/OsO_4/PhB(OH)_2/DCM/MgSO_4$) using slow addition protocol[24] was employed to convert **6** into the corresponding phenylboronic ester **14** (M_n = 13 800, PDI = 1.4 corresponding to 13 repetitive units) in 87% yield.[18] It is noteworthy that the presence of $MgSO_4$ was essential for this dihroxylation reaction in order to maintain the anhydrous conditions for the reaction.[15] The ^{1}H NMR spectrum of **14** showed that the signal for the olefinic protons around δ 5.4 ppm in **6** has disappeared, indicating a complete transformation into the corresponding cyclic boronic ester **14**.[18] The peaks in both ^{1}H and ^{13}C NMR spectra of **14** exhibited significant broadening, implying that there might be conformational isomers in **14**. The peaks at 127.8, 131.5, and 134.8 ppm in the ^{13}C NMR spectrum were assigned to be the carbons of the phenyl substituent on boron, and the two carbonyl absorptions at 166.6 and 170.2 ppm were clearly identified.



The boron moieties in **14** were removed via transesterfication[25] with 3 equiv of pentaerythritol in the presence of aqueous sodium hydroxide to give polyol **15** in essentially quantitative yield. The infrared spectrum of **15** showed a broad peak at 3450 cm^{-1}, indicating the presence of hydrogen-bonded hydroxyl group(s).[18] No double bond signals (δ 5.4 ppm) in DMSO-d_6 in the ^{1}H NMR spectrum were present at all in **15**.[18] The ^{13}C NMR spectra for **15** in pyridine-d_5 and in DMSO-d_6 are shown in Figure 2d. Again, the carbon chemical shifts of **15** were relatively sharp, and the signals for the linker and the aliphatic carbons of **15** occurred at similar δ values as those for **6**. These results suggest that **15** may be essentially a single diastereomer, and hence, the dihydroxylation reaction may occur stereoselectively. The signals for the carbons where the hydroxyl group is attached may overlap with those of ferrocenyl carbons (around δ 73 ppm).[26] Polyol **15** was sparing soluble in common organic solvents such as chloroform, acetone, ethyl acetate, or THF but soluble in more polar solvents (e.g., DMF, DMSO, or pyridine).

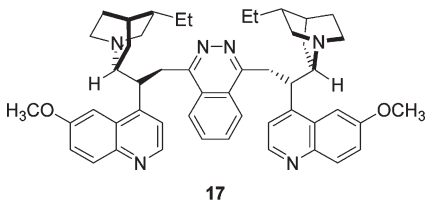
As shown in Figure 1, the double-stranded polymer **6** or the like (e.g., **1** and **2**) would have a symmetric plane for each of the monomeric unit. Since the central part of a double-stranded polymer such as **6** is occupied by the ferrocene linker, the dihydroxylation reaction would occur from the two less hindered outside faces of the double-stranded polymer. As such, the reaction may likely give the corresponding dihydroxyl adduct in meso form, since the two double bonds on the cyclopentane ring in each of the monomeric unit are in a *cis* relationship. When chiral auxiliary **17** was introduced, the dihydroxylation reaction

Scheme 1. Synthesis and Hydrolysis of Double-Stranded Polymer 6[a]



[a] Conditions: (a) $(COCl)_2$, then $HOCH_2CH_2OTBDMS$, 80%; (b) TBAF, 88%; (c) **10**, Et_3N, 72%; (d) $(Cy_3P)_2Cl_2Ru{=}CHPh$, 92%; (e) $KOBu^t$, H_2O (2 equiv), then CsF, MeI, 66%.

under the same conditions as described above afforded the corresponding boronic ester which was hydrolyzed to give the corresponding polyol **15′**. Polymer **15′** showed identical spectroscopic properties as those of **15**, and the optical rotation for **15′** was negligibly small ($[\alpha]_D^{25} = -1.2$). There would be essentially no chiral induction under Sharpless asymmetric dihydroxylation conditions.[24]



The STM morphological image of **15** on HOPG showed two-dimensional aggregation (Figure 3b). The average length of **15** on STM image was 7.5 nm, which corresponds to about 13 repetitive units for each polymer. The nominal width of polyol **15** in the aggregate is about 3.2 nm. The rodlike structure suggests that the basic skeleton of the polymers remain double stranded upon dihydroxylation reaction. In other words, the double-stranded nature may be preserved throughout this oxidation process.

As shown in Figure 3b, these polymers may aggregate via hydrogen bonding. It is interesting to note that the lengths of the polymers along the horizontal direction appeared to be similar. Since each of the hydrogen bonding may contribute ca. 3 kcal/mol stabilization energy, full usage of all available hydroxyl groups on the polymeric backbones for such hydrogen bonding may offer a possible rationale for the formation of the images shown in Figure 3b.[27] Interestingly, Yashima and co-workers recently reported that oligomers derived from *m*-terphenyl-based oligomeric strands form sequence- and chain-length-specific complementary double helices.[28] As can be seen from Figure 3b, polymer **15** in the aggregate are assembled in staggered form along the longitudinal direction. Presumably, the hydrogen bonding may also be formed between the terminal diols and the carbonyl group in the ester linkers as shown in Figure 3c.[29]

Conclusion

In summary, we have demonstrated for the first time the diastereoselective dihydroxylation of double bonds in hydrophobic double-stranded poly(bisnorbornene) **6** to give the corresponding hydrophilic polyol **15**. The double-stranded structure remains unchanged during the course of the oxidation process. This protocol would provide a useful route for the synthesis of hydrophilic double-stranded DNA-like polymers. The morphological behavior of **15** suggests that the polymers are likely to exhibit superstructures via intermolecular hydrogen bonding. Further studies on the structure−property relationships of hydroxylated double-stranded polymers are in progress.

Experimental Section

General. Melting points were uncorrected. All ^1H and ^{13}C NMR spectra were recorded on a Varian 400 Unity Plus spectrometer (400 MHz) or a Bruker Advance-500 MHz FT-NMR spectrometer (500 MHz) using $CDCl_3$, D_2O, or pyridine-d_6 as solvent at ambient temperature using internal TMS standard unless otherwise specified. IR spectra were recorded using Avatar 360 E.S.P Thermo Nicolet spectrophotometer. GPC was performed on a Waters GPC instrument equipped with Waters 1515 HPLC pump using Waters 2414 refractive index detector. Polymer (∼5 mg) in THF (0.1 mL) was filtered through a 0.5 μm filter, and 20 μL of the sample was injected into Waters Styragel HR4, Styragel HR3. Styragel HR2 columns with oven temperature at 40 °C using standard polystyrene samples (1.17×10^5−996 Da) for calibration. Waters Empower HPLC/GPC network software was used for data analyses.

1,1′-Bis[2-(*tert*-butyldimethylsilyloxy)ethothycarbonyl]ferrocene (8). To a suspension of **7** (1.0 g, 3.6 mmol) in CH_2Cl_2 (15 mL) was added slowly oxalyl chloride (1.4 g, 11 mmol). The mixture was stirred at rt for 1 h and then evaporated in vacuo to remove solvent and excess amount of oxalyl chloride. The resulting residue was dissolved with CH_2Cl_2 (10 mL) and then transferred into a round-bottomed flask containing Et_3N (1.5 g, 14.8 mmol), 2-(*tert*-butyldimethylsilyloxy)ethanol[30] (1.3 g, 7.4 mmol), and CH_2Cl_2 (10 mL). The mixture was cooled at 0 °C under a N_2 atomosphere and stirred at rt for 10 h. The resulting mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (50 mL). The organic layer was washed with brine (100 mL × 2), dried ($MgSO_4$), filtered, and evaporated in vacuo. The residue was chromatographed on silica gel (ether/hexane 1:4) to afforded **8** as an orange oil (1.7 g, 80%). IR: ν (cm^{-1}) 2953, 2929, 2856, 1718, 1463, 1275, 1257, 1150, 1126, 1105, 957, 834, 775. ^1H NMR (400 MHz, $CDCl_3$): δ 0.10 (s, 12 H), 0.91 (s, 18 H), 3.88−3.92 (m, 4 H), 4.26−4.30 (m, 4 H), 4.40 (t, J = 2.0 Hz, 4 H), 4. 84 (t, J = 2.0 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −5.0, 18.4, 25.9, 61.3, 65.8, 71.5, 72.6, 73.0, 170.1. HRMS (FAB): calcd $C_{28}H_{46}FeO_6Si_2$: 590.2182; found: 590.2174.

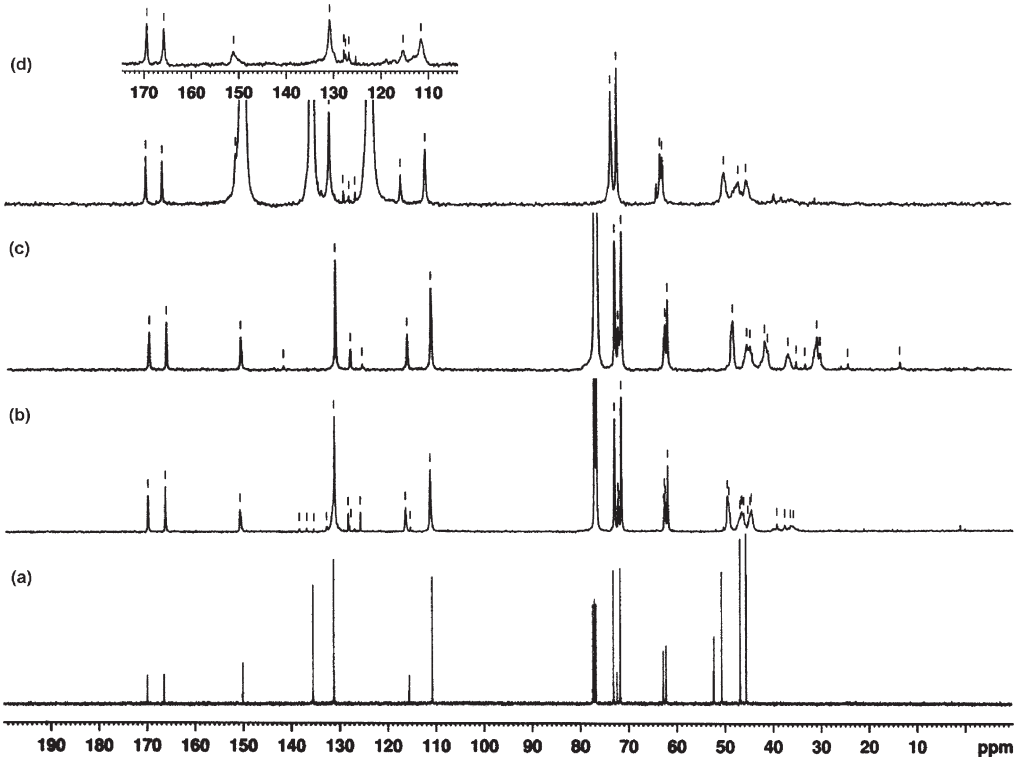


Figure 2. ^{13}C NMR spectra of (a) **11** in $CDCl_3$ and (b) **6** in $CDCl_3$. The residual signals at δ 126.0, 128.2, 128.5, 131.2, 135.7, and 137.1 ppm were assigned as the styryl end group and δ 115.5 and 138.6 ppm the ethylene end group. (c) **13** in $CDCl_3$. The residual signals at δ 33.2, 35.1, 125.8, 128.2, and 142.2 ppm may be attributed to the phenylethyl end group and δ 13.3 and 24.3 ppm the ethyl end group. (d) **15** in pyridine-d_5; inset: partial ^{13}C NMR spectrum of **15** in DMSO-d_6. The residual peaks at δ 126.7, 127.4, and 127.8 ppm may be due to the phenyl end group and δ 65.5 ppm (in DMSO-d_6) the hydroxymethyl end group.

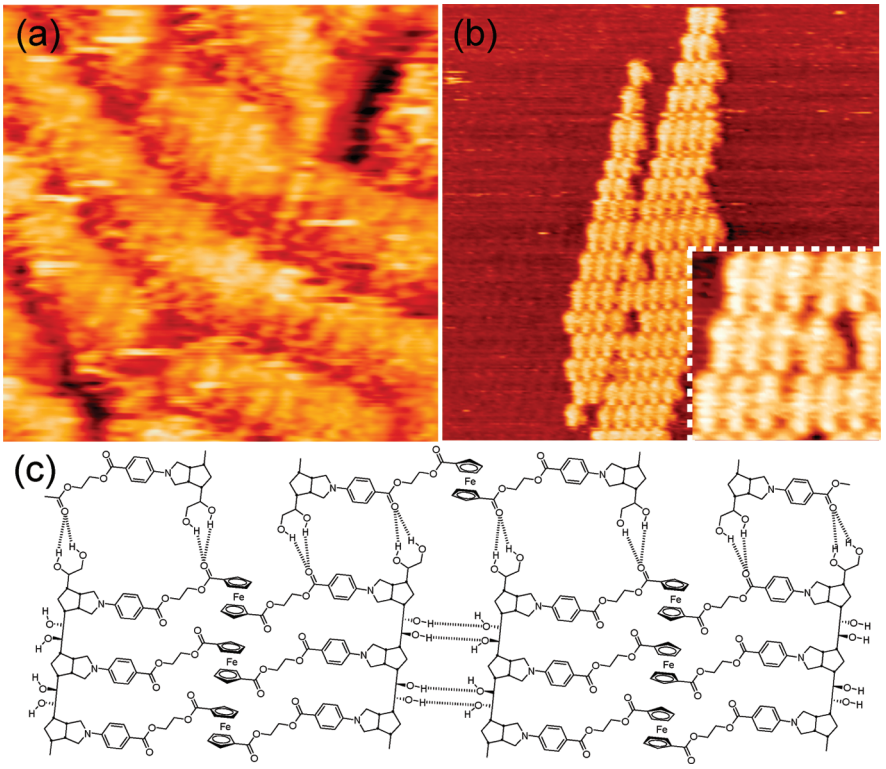


Figure 3. (a) STM images of **13** on HOPG (image size: 11 nm × 11 nm), E_{bias} = 1.2 V, $i_{tunneling}$ = 50 pA. (b) STM images of **15** on HOPG (108 nm × 108 nm), E_{bias}: 0.98 V, $I_{tunneling}$: 49 pA; inset: 24 nm × 24 nm. (c) Schematic representation of the aggregation of **15**.

1,1′-Bis[2-(hydroxy)ethothycarbonyl]ferrocene (9). To a solution of **8** (1.3 g, 2.2 mmol) in THF (5 mL) was added TBAF (1.0 M THF solution, 5 mL). The mixture was stirred at rt for 2 h and then evaporated in vacuo. The residue was chromatographed on silica gel (EtOAc) to afforded **9** as an orange solid (700 mg, 88%); mp 76−78 °C. IR: ν (cm^{-1}) 3436, 2951, 1710,

1465, 1378, 1279, 1148, 1078, 1032, 927, 833, 773. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.06 (br, 2 H), 3.90−4.00 (br, 4 H), 4.37−4.42 (m, 4 H), 4.48 (br t, J = 1.6 Hz, 4 H), 4.82 (br t, J = 1.6 Hz, 4 H). ^{13}C NMR (100 MHz): δ 61.2, 66.5, 72.1, 72.5, 170.9. HRMS (FAB): calcd $C_{16}H_{18}FeO_6$: 362.0453; found: 362.0488.

Monomer 11. To a solution of **9** (500 mg, 1.4 mmol) and NEt_3 (560 mg, 5.5 mmol) in CH_2Cl_2 (10 mL) was added **10** (790 mg, 2.9 mmol) in CH_2Cl_2 (6 mL) at 0 °C. The mixture was gradually warmed to rt and stirred for 10 h. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (CH_2Cl_2/hexane 4:1) to afford **11** as an orange solid (840 mg, 72%); mp 172−175 °C. IR ν (cm^{-1}): 3055, 2961, 2851, 1706, 1604, 1524, 1473, 1378, 1266, 1179, 1145, 1102, 827, 768, 726. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.49 (d, J = 8.2 Hz, 2 H), 1.59 (d, J = 8.2 Hz, 2 H), 2.88−3.00 (m, 8 H), 3.02−3.10 (m, 4 H), 3.20−3.30 (m, 4 H), 4.34 (t, J = 2.0 Hz, 4 H), 4.48−4.56 (m, 8 H), 4.81 (t, J = 2.0 Hz, 4 H), 6.12 (t, J = 1.6 Hz, 4 H), 6.35 (d, J = 9.0 Hz, 4 H), 7.88 (d, J = 9.0 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.3, 46.6, 50.4, 52.0, 61.9, 62.6, 71.6, 72.2, 73.0, 110.7, 115.5, 131.2, 135.5, 150.2, 166.5, 170.0. HRMS (FAB) calcd $C_{48}H_{48}FeN_2O_8$: 836.2760; found: 836.2748.

Polymer 6. To a solution of **11** (500 mg, 0.6 mmol) in CH_2Cl_2 (25 mL) stirred under a N_2 atmosphere was treated with a solution of Grubbs I catalyst (120 mg, 0.15 mmol) in CH_2Cl_2 (5 mL). After stirring for 90 min at rt, ethyl vinyl ether (3 mL) was added, and the mixture was stirred for 10 min. The resulting solution was concentrated, and the polymer was precipitated in Et_2O/EtOAc (50: 50 mL) as a yellowish solid (460 mg, 92%). IR ν (cm^{-1}): 2943, 2852, 1710, 1605, 1523, 1463, 1378, 1266, 1180, 1146, 1102, 1051, 963, 925, 828, 768, 697. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20−1.52 (br, 2 H), 1.64−2.00 (br, 2 H), 2.50−3.50 (brm, 16 H), 4.10−4.90 (brm, 16 H), 5.00−5.50 (br, 4 H), 6.26−6.66 (br, 4 H), 7.86−8.04 (br, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.5, 46.6, 49.5, 62.0, 62.5, 62.7, 71.6, 71.7, 72.1, 72.2, 73.0, 111.3, 116.3, 125.8, 128.3, 131.2, 150.7, 166.3, 169.9. GPC (THF): M_n = 10 400, PDI = 1.3. Anal. Calcd for $C_{592}H_{592}Fe_{12}N_{24}O_{96}$:[30a] C, 69.31; H, 5.77; N, 3.27. Found: C, 67.90; H, 6.04; N, 2.78.

Hydrolysis of 6. Under a N_2 atmosphere, to a slurry of KO^{t}Bu (800 mg, 7.1 mmol) in THF (5 mL) and water (18 mg, 1 mmol) was added at rt a solution of **6** (100 mg, containing 0.5 mmol equiv of the ester group) in THF (5 mL). After stirring at rt for 12 h, the mixture was poured into water and extracted with ethyl acetate (100 mL). The aqueous layer was separated and neutralized with HCl (1 M) at 0 °C to afford a brown precipitate (50 mg), which was directly used for the next reaction without further purification.

A mixture of the brown precipitate (50 mg, 0.15 mmol), CsF (33 mg, 0.2 mmol), and MeI (56 mg, 0.4 mmol) in DMF (2 mL) was stirred at rt for 10 h. The mixture was poured into water (50 mL) and extracted with CH_2Cl_2 (50 mL). The organic layer was separated, washed with brine (50 mL × 2), and dried ($MgSO_4$). The solvent was evaporated in vacuo, and **12** was precipitated in MeOH (20 mL) as a grayish solid (27 mg, 66% overall yield from **6**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20−1.52 (br, 1 H), 1.60−2.00 (br, 1 H), 2.58−3.10 (br, 4 H), 3.10−3.58 (br, 4 H), 3.70−4.05 (br, 3 H), 5.18−5.60 (br, 2 H), 6.24−6.70 (br, 2 H), 7.60−8.00 (br, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.5, 35.9, 37.4, 39.8, 44.4, 46.4, 49.4, 51.3, 111.4, 117.0, 131.2, 131.6, 150.7, 167.3. GPC (THF): M_n = 3700, PDI = 1.3.

Reduction of 6. To a solution of **6** (50 mg, 0.06 mmol) in chlorobenzene (15 mL) under a N_2 atmosphere was added *p*-toluenesulfonylhydrazide (445 mg, 2.4 mmol) at rt. After stirring at 130 °C (bath temperature) for 12 h, the solution was cooled, filtered, and concentrated. Polymer **13** was precipitated in MeOH (50 mL) as a yellowish solid (43 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.75−2.15 (brm, 16 H), 2.50−2.96 (br, 4 H), 2.96−3.50 (br, 8 H), 4.20−5.00 (brm, 16 H), 6.24−6.70 (br, 4 H), 7.66−8.20 (br, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 30.0, 30.2, 30.8, 35.1, 36.8, 41.1, 41.7, 44.8, 45.4, 48.4, 62.0, 62.5, 71.6, 72.3, 73.0, 111.5, 116.4, 128.2, 131.3, 151.1, 166.6, 170.2. GPC (THF): M_n = 11 400, PDI = 1.3.

Polymeric Boronic Ester 14. To a mixture of OsO_4 (4.5 mg, 0.02 mmol), NMO (245 mg, 1.8 mmol), $PhB(OH)_2$ (66 mg, 0.55 mmol), and $MgSO_4$ (500 mg) in CH_2Cl_2 (10 mL) was added over a period of 10 h via a gastight syringe controlled by a syringe pump a solution of **6** (150 mg, 0.18 mmol) in CH_2Cl_2 (4 mL). The tip of the syringe needle was immersed in the reaction mixture. After further stirring for 3 h at rt, the resulting mixture was filtered and the filtrate was washed with aqueous $Na_2S_2O_3$ (10%, 100 mL). The organic layer was separated, filtered, and concentrated in vacuo. The residue was triturated with EtOAc (100 mL), and the solid was collected as **14** as a yellow solid (166 mg, 87%). IR ν (cm^{-1}): 2951, 2863, 1709, 1604, 1521, 1377, 1360, 1267, 1182, 1147, 1102, 1027, 911, 768, 730. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.90−3.98 (brm, 20 H), 4.00−5.10 (brm, 20 H), 6.30−6.90 (br, 4 H), 6.90−7.70 (br, 8 H), 7.70−8.30 (br, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 44.5, 48.6, 62.3, 71.6, 72.1, 73.0, 82.6, 112.1, 125.9, 127.8, 131.4, 134.8, 149.3, 151.3, 166.6, 170.2. GPC (THF): M_n = 13 800, PDI = 1.4.

Poly(bisnorbornanediol) (15). To a solution of **14** (100 mg, 0.09 mmol) in CH_2Cl_2 (10 mL) and Et_2O (2 mL) was added pentaerythritol (73 mg, 0.54 mmol) and aqueous NaOH (1.0 M, 6 mL) at rt. After stirring for 30 h, the organic solvent was evaporated in vacuo to give a yellow precipitate which was filtered and washed with water (30 mL) and triturated with EtOAc (30 mL) to afford **15** as a yellowish solid (82 mg, 99%). IR ν (cm^{-1}): 3397, 2951, 1701, 1603, 1521, 1376, 1271, 1183, 1103, 769. ^{1}H NMR (500 MHz, pyridine-d_5): δ 1.40−1.70 (br, 2 H), 1.70−2.10 (br, 2 H), 2.60−3.10 (br, 8 H), 3.10−3.50 (br, 8 H), 4.30−4.50 (br, 4 H), 4.60−4.90 (br, 8 H), 4.90−5.20 (br, 8 H), 6.60−6.90 (br, 4 H), 8.10−8.40 (br, 4 H). ^{13}C NMR (125 MHz, pyridine-d_5): δ 39.8, 45.6, 46.5, 47.2, 50.2, 63.1, 63.6, 64.3, 72.7, 73.9, 112.6, 117.7, 132.4, 151.9, 167.3, 170.7. ^{13}C NMR (125 MHz, DMSO-d_6): δ 43.5, 48.4, 62.2, 71.2, 72.1, 72.7, 111.5, 115.3, 126.7, 127.4, 127.8, 130.8, 151.0, 165.7, 169.3. Anal. Calcd for $C_{592}H_{644}Fe_{12}N_{24}O_{148}\cdot 24H_2O$:[30b] C, 61.41; H, 5.78; N, 2.90. Found: C, 59.66; H, 6.35; N, 2.41.

STM (Scanning Tunneling Microscopy) Characterization. The polymer sample was taken into $CHCl_3$, and the mixture was sonicated for 10 min and filtered through PTFE membrane (pore size 0.5 μm) before being subject to STM studies. An aliquot of 10 μL $CHCl_3$ of **15** was casted on freshly cleaved HOPG (Advanced Ceramics, ZYH grade). The film was then vacuum-dried (~30 min, 0.1 Torr) to remove trace amount of solvent. STM measurements were carried out with a Picoscan (4500, Agilent Technologies) equipped with a low-current converter suitable for operation under high tunneling impedance. The STM probes were commercially available Pt/Ir tips (PT, Nanotips, Veeco Metrology Group/Digital Instruments). The typical imaging conditions of bias voltage and tunneling current ranged from 0.15 to 1.5 V and from 10 to 300 pA, respectively. The microscope was housed in a chamber where dry N_2 was purging throughout the experiments and the humidity was lower than 2%.

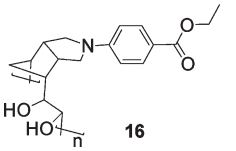
Electrochemistry Measurements. A potentiostat with conventional three-electrode system Pt disk (diameter = 3 mm) as the working electrode, Ag/Ag^+ as the reference electrode and Pt wire as the counter electrode was employed for the differential pulse experiments using 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the electrolyte. The system was purged with Ar for at least 10 min before experiments. The concentration of polymer was 10^{-3} M in CH_2Cl_2, and the potentials were referenced to the redox potential of ferrocene/ferrocenium (Fc/Fc^+).

Acknowledgment. We thank the National Science Council and the National Taiwan University for support. We also express our special thanks to Professor K. Barry Sharpless for stimulating discussions.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra and the GPC results for all new compounds (polymers). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Schröder, M. *Chem. Rev.* **1980**, *80*, 187–213.
(2) Kolb, H. C.; Vannieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483–254.
(3) Wurm, F.; Nieberle, J.; Frey, H. *Macromolecules* **2008**, *41*, 1909–1911.
(4) París, R.; De La Fuente, J. L. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3538–3549.
(5) Leemhuis, M.; Akeroyd, N.; Kruijtzer, J. A. W.; van Nostrum, C. F.; Hennink, W. E. *Eur. Polym. J.* **2008**, *44*, 308–317.
(6) Haag, R.; Sunder, A.; Stumbé, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 2954–2955.
(7) Hao, Q. H.; Yang, J.; Li, Q. B.; Li, Y.; Jia, L.; Fang, Q.; Cao, A. M. *Biomacromolecules* **2005**, *6*, 3474–3480.
(8) Meier, S.; Reisinger, H.; Haag, R.; Mecking, S.; Mulhaupt, R.; Stelzer, F. *Chem. Commun.* **2001**, 855–856.
(9) (a) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100–110. (b) Hamilton, J. G. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; Vol. *3*, pp 143−179.
(10) For a review, see: Luh, T.-Y.; Yang, H.-C.; Lin, N.-T.; Lin, S.-Y.; Lee, S.-L.; Chen, C.-h. *Pure Appl. Chem.* **2008**, *80*, 819–829.
(11) (a) Yang, H.-C.; Lin, S.-Y.; Yang, H.-C.; Lin, C.-L.; Tsai, L.; Huang, S.-L.; Chen, L.-W. P.; Chen, C.-h.; Jin, B.-K.; Luh, T.-Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 726–730. (b) Yang, H.-C.; Lin, S.-M.; Liu, Y.-H.; Wang, Y.; Chen, M.-M.; Sheu, H.-S.; Tsou, D.-L.; Lin, C.-H.; Luh, T.-Y. *J. Organomet. Chem.* **2006**, *691*, 3196–3200. (c) Yang, H.-C.; Lee, S.-L.; Chen, C.-h.; Lin, N.-T.; Yang, H.-C.; Jin, B.-K.; Luh, T.-Y. *Chem. Commun.* **2008**, 6158–6160.
(12) (a) Lin, W.-Y.; Wang, H.-W.; Liu, Z.-C.; Xu, J.; Chen, C.-W.; Yang, Y.-C.; Huang, S.-L.; Yang, H.-C.; Luh, T.-Y. *Chem. Asian J.* **2007**, *2*, 764–774. (b) Lin, W.-Y.; Murugesh, M. G.; Sudhakar, S.; Yang, H.-C.; Tai, H.-C.; Chang, C.-S.; Liu, Y.-H.; Wang, Y.; Chen, I.-W. P.; Chen, C.-h.; Luh, T.-Y. *Chem.—Eur. J.* **2005**, *12*, 324–330.
(13) Wang, H.-W.; Liu, Z.-C.; Chen, C.-H.; Lim, T.-S.; Fann, W.; Chao, C.-K.; Yu, J.-Y.; Lee, S.-L.; Chen, C.-h.; Huang, S.-L.; Luh, T.-Y. *Chem.—Eur. J.* **2009**, *15*, 5719–5728.
(14) (a) Van Rheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973–1976.(b) Van Rheenen, V.; Cha, D. Y.; Hartley, W. M. *Org. Synth.* **1988**, Collect. Vol. *6*, 342−348.
(15) (a) Iwasawa, N.; Kato, T.; Narasaka, K. *Chem. Lett.* **1988**, 1721–1724. (b) Gypser, A.; Michel, D.; Nirschl, D. S.; Sharpless, K. B. *J. Org. Chem.* **1998**, *63*, 7322–7327. (c) Sakurai, H.; Iwasawa, N.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2585–2594.
(16) Lai, Y.-Y.; Lin, N.-T.; Liu, Y.-H.; Wang, Y.; Luh, T.-Y. *Tetrahedron* **2007**, *63*, 6051–6055.
(17) (a) Lin, C.-L.; Yang, H.-C.; Lin, N.-T.; Hsu, I.-J.; Wang, Y.; Luh, T.-Y. *Chem. Commun.* **2008**, 4484–4486. (b) The oxidation potentials for the ferrocene moiety in 1 and 2 were 475 and 95 mV, respectively, against the ferrocene/ferrocenium redox pair. The aminobenzyl and aminobenzoate groups in 2 showed irreversible electrochemical oxidation at 475 and 620 mV, respectively.
(18) See the Supporting Information.
(19) Numberings for norbornenes are used here.
(20) Lin, N.-T.; Lin, S.-Y.; Lee, S.-L.; Chen, C.-h.; Hsu, C.-H.; Hwang, L.-P.; Xie, Z.-Y.; Chen, C.-H.; Huang, S.-L.; Luh, T.-Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 4481–4485.
(21) (a) Gassman, P. G.; Hodgson, P. K. G.; Balchunis, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 1275–1276. (b) Gassman, P. G.; Schenk, W. N. *J. Org. Chem.* **1977**, *42*, 918–920.
(22) Sato, T.; Otera, J.; Nozaki, H. *J. Org. Chem.* **1992**, *57*, 2166–2169.
(23) (a) For a review, see: Pasto, D. J.; Taylor, R. T. *Org. React.* **1991**, *40*, 91–155. (b) Nang, T. D.; Katabe, Y.; Minoura, Y. *Polymer* **1976**, *17*, 117–120.
(24) Wai, J. S. M.; Marko, I.; Svendsen, J. S.; Finn, M. G.; Jacobsen, E. N.; Sharpless, K. B. *J. Am. Chem. Soc.* **1989**, *111*, 1123–1125.
(25) Matteson, D. S.; Man, H. W. *J. Org. Chem.* **1996**, *61*, 6047–6051.
(26) The absorptions for the CHOH carbons in single-stranded poly(norbornandiol) (**16**) were found at δ 72.7.



16

(27) Diols are known to form hydrogen bonding with another diol in solid. For example: Salem, B.; Suffert, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 2826–2830.
(28) Ito, H.; Furusho, Y.; Hasegawa, T.; Yashima, E. *J. Am. Chem. Soc.* **2008**, *130*, 14008–14015.
(29) Examples are known on the hydrogen bonding between a diol moiety and a carbonyl group of an ester in solid. For example: Kelly, T. R.; Cai, X.; Tu, B.; Elliott, E. L.; Grossmann, G.; Laurent, P. *Org. Lett.* **2004**, *6*, 4953–4956.
(30) McDougal, P. G.; Rico, J. G.; Oh, Y.-I.; Condon, B. D. *J. Org. Chem.* **1986**, *51*, 3388–3390.
(31) (a) Calculation based on a 12-mer with two styrene and two vinyl end groups. (b) Calculation based on the product with complete dihydroxylation of all double bonds in a 12-mer **6** with two styrene and two vinyl end groups plus 24 water molecules because polymer **15** may be hygroscopic.