Macromolecules

Ruthenium-Catalyzed Cascade Metathetical Cyclopolymerization of Bisnorbornenes with Flexible Linkers

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Supporting Information

ABSTRACT: Treatments of bisnorbornenes tethered by a flexible linker (triethylene glycol, tetramethylene moiety, or crown ether) with the first generation of Grubbs catalyst give the corresponding single-stranded polybisnorbornenes via cascade metathetical cyclopolymerization (CMCP). The structures of these polymers were proved by spectroscopic means, MALDI-TOF mass spectrometry, gel permeation chromatography, and dynamic light scatterings as well as by chemical degradation via hydrolysis followed by esterification. The presence of *N*-aryl pendants to connect the norbornene moiety and the flexible linker is crucial for the success of such CMCP process. Presumably, intramolecular $\pi - \pi$ interactions between the pending aryl groups may take place to direct the ring closure process. Substrates without such *N*-aryl



pendants give a mixture of single- and double-stranded polynorbornenes in addition to cross-linking polymers.

INTRODUCTION

Olefin metathesis offers a powerful arsenal in organic and polymer syntheses.^{1–3} Cascade ring closure metatheses (RCM) are particularly useful for the ingenious construction of complex polycyclic natural products.^{2,3} A combination of ring-opening metathesis polymerizations (ROMP) with hydrogenation, atom transfer radical polymerizations,⁵ chain transfer reactions,⁶ insertion polymerization,⁶ or other related processes⁷ furnishes a versatile route for the preparation of functionalized polymers. Radical-initiated or metal-catalyzed cyclopolymerizations of α,ω -dienes⁸ or -diynes⁹ are well documented. To the best of our knowledge, no direct cascade metathetical cyclopolymerization of a bis-cycloalkene has been reported. One of the main obstacles may arise from the cycloreversion of the Chauvin's metallocyclobutane intermediate^{1,10} which can proceed via either ring-closure or ring-opening metathesis leading to a cycloalkene or a polymer. Thermodynamic factors, inter alia, are known to control such ring-chain equilibria.^{1h} Release of ring strain is commonly employed to create an enthalpically favored process for ROMP, whereas RCM would entropically prevail. It is therefore envisaged that a two strained cycloalkenes linked by a flexible tethers could undergo cascade metathetical cyclopolymerization (CMCP) process to give the corresponding cyclopolymerization product, when such thermodynamic aspects are considered.

ROMP of bis-cycloalkene 1 by a metallocarbene initiator followed by quenching with an olefin could lead to three different kinds of polymers 2, 4, and 6 (Scheme 1). Branched random polymer 2 would be expected, if no specially designed substrate 1 is employed. It is worth noting that polymer 2 thus obtained may have more than two sets of end groups. On the other hand, bis-cycloalkene 1 having a rigid linker would form the corresponding double-stranded ladderphane 4, if some kinds of interactions between the linkers could control the orientation of the incoming 1 during the course of the polymerization process. In this regard, the two cycloalkene moieties would undergo polymerization independently via an intermediate like 3. Hence, 4 would contain two sets of end groups. Indeed, bisnorbornenes 8 having a ferrocene, an oligoaryl, or a rigid alicyclic linker can polymerize in the presence of the first-generation Grubbs catalyst [(Cy₃P)₂Cl₂Ru=CHPh, 7] to give doublestranded DNA-like ladderphanes 9.11-16 It is noteworthy that the presence of the endo-N-arylpyrrolidine group in the linker in 8 is essential to control the isotactic stereochemistry and trans double bond selectivity in the polymerization process under these conditions.^{11–14,17}

The third possibility would involve a ring-opening metathesis of a cycloalkene in 1 followed by an intramolecular RCM with the second cycloalkene moiety in 1 to give a new carbene intermediate 5 that would react with another molecule of 1 leading to cyclopolymerization product 6. In this regard, only one set of end groups would be expected in 6. A flexible linker connecting two cycloalkene moieties would be essential to enable conformational equilibrium which may bring two cycloalkene moieties to close proximity so that RCM might take

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Scheme 1. Three Possible Reaction Paths for the Metathesis Polymerization of Bis-cycloalkene 1



place. Indeed, RCM is well documented for macrocycle syntheses.^{2e} In addition, the presence of heteroatoms in the nonconjugated diene starting material appears to be useful for efficient macrocyclizations.¹⁸ It is therefore envisaged that the third possibility shown in Scheme 1 would take place with bisnorbornene 10 having a flexible linker. As mentioned above, the presence of the endo-N-arylpyrrolidine moiety in 8 and related mononorbornene derivatives is crucial to control the stereoselectivity in single- and double-stranded polynorbornenes.^{11-14,17} Accordingly, incorporation of such aromatic pendant to connect the norbornene fragments in 10 with a flexible linker may furnish the syn conformer (syn-10), where some kind of interactions between aryl pendants might take place.¹⁹ Intramolecular RCM process may then occur leading to polymer 12 via intermediate 13. In this paper, we wish to report an unprecedented study on the metathetical cyclopolymerization of bisnorbornenes 10 with different kinds of aliphatic flexible linkers.

According to the strategy described in Scheme 1, reaction of **10** under metathesis conditions could afford either a double stranded ladderphane **11** or a cyclopolymerization product **12**. ROMPs of norbornene derivatives with 7 are known to be living.²⁰ Consequently, upon treatment with $100/n \mod \%$ of 7, if double-stranded ladderphane **11** were obtained, the polymer would be a 2n-mer containing two styrene end groups. Hydrolytic cleavage of **11** followed by esterification would give 2 equiv of single-stranded polymer **14a** that would also be a 2n-mer. However, the molecular weight of **14a** would be less than a half of that of **11**. On the other hand, if single-stranded polymer **12** were obtained from this reaction, the polymer would contain n repeat bisnorbornene units or 2n norbornene repetitive units with only one styrene end group. The number of norbornene unit in



14b, obtained by hydrolysis and esterification of 12, would be same as that of 12. In addition, the molecular weight of 14b should be compatible with that of 12. Accordingly, these two pathways can easily be differentiated by detailed analyses of the polymer and its degradation product.



RESULTS AND DISCUSSION

Single-Stranded Polybisnorbornene with Flexible Linkers. Triethylene glycol chain is flexible. It is therefore envisaged that such flexible linker would be suitable for CMCP process of bisnorbornenes. Bisnorbornene **10a** tethered with triethylene glycol was synthesized.²¹ Treatment of **10a** with 10 mol % of 7 in DCM followed by quenching with ethyl vinyl ether afforded polymer **12a** in 92% yield ($M_n = 7800$ and PDI = 1.2).²¹ This result suggests that **12a** could be either a single-stranded polybisnorbornene with 12 bisnorbornene repeats (or 24 norbornene repetitive moieties) or a double-stranded ladderphane^{13a} having 12 norbornene units per strand. Base-promoted hydrolysis of **12a** under Gassman conditions²² followed by esterification with EtI using Otera procedure²³ afforded the single-stranded polynorbornene **15a** ($M_n = 6700$ and PDI = 1.2) that corresponds to 24 repetitive norbornene units.^{17,21} The same number of repeat norbornene moieties in **12a** and **15a** indicates that **12a** should be a single-stranded polybisnorbornene derived from **10a**.



As mentioned before, a double-stranded ladderphane should have two pairs of end groups whereas a single-stranded polynorbornene should contain only one set of end groups. MALDI-TOF mass spectrometry would provide a useful tool to differentiate these two possibilities. When 7 is used as the catalyst and the reaction is quenched with ethyl vinyl ether, the polynorbornene thus obtained should contain both styrene and vinyl end groups. Hence, the molecular mass of the polymer would equal to the sum of the molecular mass of repeat norbornene units plus that of styrene. The MALDI-TOF mass spectrum²⁴ of **12a** with m/z values (M + H) for each of the individual major peaks and the simulated data are shown in Figure 1. It is worth noting that each of the prominent m/z



Figure 1. MALDI-TOF mass spectrum of **12a**. The simulated values $\{H + [PhCH + (molecular mass of$ **10a**) ×*n* $+ CH₂]\}$, where *n* is the number of repetitive units, are in parentheses.

peaks appeared to have one styrene end group that is consistent with a single-stranded polybisnorbornene.

The typical concentration of bisnorbornenes **10a** for this metathetical cyclopolymerizations was 1.6 mM. Similar results were obtained when the concentration of **10a** was raised up to 8 mM.²¹ However, when higher concentrations of **10a** (40 or 80 mM) were used, gelation was observed within few minutes, and the polymers thus obtained were insoluble in organic solvents. Presumably, cross-linking might take place under these high concentration conditions.

In a similar manner, single-stranded polybisnorbornene **12b** $(M_n = 5300, \text{PDI} = 1.3)$ was obtained from the CMCP of **10b** with tetramethylene linkage upon treatment with 10 mol % of 7.²¹ This result suggests that the degree of polymerization of **12b** would be 18. Again, the MALDI-TOF mass spectrum²⁴ (Figure 2) showed that **12b** contains only one styrene end group and therefore is consistent with a single-stranded structure. Hydrolysis²² followed by esterification²³ of **12b** in a manner similar to that described above gave **15b** $(M_n = 4600, \text{PDI} = 1.2)$ corresponding to the 16 repetitive norbornene units. Similar



Figure 2. MALDI-TOF mass spectra and simulate values in parentheses {H + [PhCH + (molecular mass of **10b**) × n + CH₂]}, where *n* is the number of repetitive units of **12b**.

chain lengths between 12b and 15b indicate that 12b should be arisen from the CMCP of 10b.

Single-Stranded Polybisnorbornene with Diaza-18crown-6 Linker. Similar polymerization of 10c having 4,13diaza-18-crown-6 linker with 10 mol % of 7 afforded 12c in 90% yield. Gel permeation chromatographic (GPC) analysis²¹ indicates that 12c ($M_n = 6500$, PDI = 1.3) may have 18 repeating norbornene moieties and so was its corresponding hydrolysis– esterification product 15c ($M_n = 5000$, PDI = 1.2). The MALDI-TOF mass spectrum²⁴ of 12c with m/z values (M + Na) for each of the individual major peaks and the simulated data are shown in Figure 3. It is worth noting that each of the prominent m/z peaks



Figure 3. MALDI-TOF mass spectrum of **12c**. The simulated values $\{Na + [PhCH + (molecular mass of$ **10c**) ×*n* $+ CH₂]\}$, where *n* is the number of repetitive units} are in parentheses. Inset: expanded region from *m*/*z* 4500 to 4700.

appeared to have one styrene end group that is consistent with a single-stranded polybisnorbornene. The expanded region of m/z around 4550 is shown as an example in the inset in Figure 3. The m/z at 4525 and 4564 were attributed to the protonated and potassium incorporated peaks, respectively, whereas the major peak at 4549 would be the species complexed with a sodium ion. In addition, the small peak at 4653 could be arisen from a trace amount of the polymer containing two styrene end groups which could be a double-stranded-like polymer.

Double-Stranded Ladderphane with Diaza-19-crown-6 Linker. As mentioned above, MALDI-TOF experiments have

offered valuable structural information on single-stranded polybisnorbornenes **12**. In order to verify this viewpoint, doublestranded **19**, with 10 repeat nobornene units in each of the strands, was synthesized according to the replication protocol (Scheme 2).^{21,25} Hydrolysis of **19** ($M_{\rm p}$ = 7100 and PDI = 1.2)²²

Scheme 2. Double-Stranded Poly(bisnorbornene) via the Replication $\operatorname{Protocol}^a$



^aReaction conditions: (a) trifluoroacetic acid, DCM, 5 h; (b) 17, Et₃N, DCM, 10 h, 70% overall yield from 16; (c) 10 mol % 7, DCM, RT, 2 h, 95%.

followed by esterfication²³ afforded single-stranded decanorbornene **15d** (M_n = 2900 and PDI = 1.2). As shown in Figure 4, all peaks in the MALDI-TOF mass spectrum²⁴ of **19** contain two styrene end groups that are clearly different from those obtained from single-stranded polynorbornenes shown in Figures 1–3.

Dynamic Light Scattering and Intrinsic Viscosity Studies. Single- and double-stranded polynorbornenes derived from *N*-arylpyrrolidine-fused norbornenes are in general rodlike polymers as revealed by their scanning tunneling microscopic (STM) images.^{11–14} The lengths of these rod polymers could be closely related to the dimensions determined by dynamic light scattering (DLS) method.^{26,27} Single-stranded polynorbornene **21a**–**c** with all trans double bonds were prepared from **20** using different amount of 7.^{17b} Similarly, crown ether containing polymer **12c**' with 10 repeat norbornene moieties was synthesized from **10c** using 20 mol % of 7. A plot of hydrodynamic



Figure 4. MALDI-TOF mass spectrum of **19**. The simulated values $\{H + [(PhCH) \times 2 + (molecular mass of$ **10c** $) \times n + (CH₂) \times 2]\}$, where *n* is the number of repetitive units, are in parentheses.

diameters of 21a-21c against the number of repeat norbornene moieties (from GPC) gave a straight line, when the number of repeat units ranged from 10 to 50 (Figure 5a).²⁸ The hydrodynamic diameters of 12c and 12c' obtained by DLS were 10.4 and 5.8 nm, respectively. The DLS data for 12c and 12c' were used to fit onto the line in Figure 5a, and the number of repeat norbornene units obtained by this fitting was 18 and 10, respectively, which match nicely with those from the GPC results.²¹ The DLS results suggest that these polynorbornenes, whether single- or double-stranded, would have similar length as long as the numbers of repetitive norbornene units are the same. The DLS data offer additional evidence for the structures of these polymers, no cross-linking products being formed under these reactions conditions. The intrinsic viscosities $[\eta]$ of these polymers (12c, 12c', and 21) in CHCl₂ were also examined and the relationship between $[\eta]$ and the degree of polymerization is shown in Figure 5b.



Stereochemistry. The stereochemistry of **15** is worthy of comment. The ¹³C NMR spectrum of **15c** is compared with those of **21**^{17b} and **22**^{21,29} in Figure S6. The chemical shift for C_7^{30} appeared at δ 39.1 for **22** as a single peak, whereas those for **21** at δ 36.1 and 35.7 as two peaks.^{17b} In addition, the chemical shift for C_2 in **22** exhibits characteristic signal at δ 40.2, whereas there is no absorption in this region due to polynorbornene moieties with trans double bonds in **21**. The signals at δ 36.2 and 35.7 for **15c** were assigned to C_7 having neighboring trans double bond(s), whereas the peak at δ 39.9 in **15c** is consistent with the presence of cis double bonds. Apparently, the double-bond stereoselectivity in cyclopolymerization of bisnorbornenes **10** may not be as selective as those in the ROMP of **20**. Diimide reduction of **15c**, however, gave **23a** which showed identical spectroscopic properties to those of **23b**^{17b} and **23c**²⁹ obtained from a similar reduction of **21** and of **22**, respectively.

30 0.18 (b) (a) 21c(n=50) 21c(n=50) 0.16 Size (nm) determined by DLS Intrinsic Viscosity [ŋ] (dL/g) 0.14 20 0.12 21b(n=22) 0.10 21b(n=22) 120 0.08 21a(n=13) 21a(n=13)26 0.06 19 19 10 20 10 30 40 50 20 30 40 50 No. of repeat norbornene units by GPC No. of repeat norbornene units by GPC

Figure 5. (a) Plot of the sizes of 12, 19, and 21 determined by DLS against the degree of polymerization. (b) Relationship of the intrinsic viscosity of 12, 19, and 21 against the degree of polymerization [12c (olive solid circle), 12c' (olive open circle), 19 (red open triangle), and 21 (blue solid square)].

These results suggest that 15c, like 21 and 22, may adopt the same stereochemistry at the asymmetric carbons. It is worth mentioning that RCM for macrocyclic synthesis usually gives a mixture of cis and trans double bonds using ruthenium catalyst.²



Importance of Aromatic Pendants. The presence of aromatic pendants in the linker would be important to dictate the selectivity of the CMCP of 10 giving single-stranded polybisnorbornenes. Presumably, during the course of the polymerization, there would be possible interactions between the pending N-aryl group in the incoming monomer and the aryl pendant in ring-opened norbornene unit where the ruthenium catalyst is attached. In order to establish the importance of the aromatic pendants in the CMCP of bisnorbornenes, 24 was treated with 7 under the same conditions. The MALDI-TOF mass spectrum of the polymer(s) obtained from 24 indicates that the mixture may contain one, two, and three styrene end groups (Figure 6).³¹ Polymer with two styrene end groups (likely 26) was detected as the major product in addition to single-stranded RCM-ROMP polymer 25 and cross-linking polymer by the incorporation of three styrene end groups. Lack of $\pi - \pi$ interactions between the pendants in 24 may be responsible in poor selectivity in these metathesis reactions. Indeed, the related bisnorbornene 27 with oligomethylene linkage has been used as a cross-linking agent for the ROMP of norbornene derivatives.³²

STM Images. Single-³³ and double-stranded^{11–14,25,29} polynorbornenes are known to assemble nicely on highly oriented pyrolytic graphite (HOPG) to give highly ordered two-dimensional pattern, presumably due to π - π attractions between terminal groups (vinyl and styryl groups) along the longitudinal axis of the polymers and van der Waals interactions between polymeric backbones.^{11c} In a similar manner, **12c** shows to be a rodlike polymer assembled on the graphite surface to form a two-dimensional array as revealed by its STM image (Figure 7). It is worth noting that each of the monomeric units in **12c**



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Figure 6. MALDI-TOF mass spectrum of product from 24. The peaks marked with \square , O, and \blacktriangle represent polymers with one {H + [PhCH + (molecular mass of 24) × *n* + CH₂]}, two {H + [(PhCH) × 2 + (molecular mass of 24) × *n* + (CH₂) × 2]} and three {H + [(PhCH) × 3 + (molecular mass of 24) × *n* + (CH₂) × 3]} styrene end groups, respectively, where *n* is the number of repetitive units. The simulated values are in parentheses. Inset: expanded region from *m*/*z* 2500 to 2900.



could be identified, and the space separating these moieties was 0.5 nm, a typical span for a vinylcyclopentane moiety.^{17a} However, the spacing dividing adjacent two polymeric stripes may not be as regular as those in double-stranded ladderphanes reported previously.^{11–14,25,29} As shown in Figure 7, the distances between bright features of the adjacent strips range from 2.3 to 2.8 nm, which was shorter than those with the symmetrical ladderphanes^{11–14} (usually 3.4 nm). Accordingly, interactions



Figure 7. STM images of **12c** on HOPG. Panel a_2 was acquired by using an impedance smaller than that of panel a_1 to unveil the underlying HOPG. Panel a_3 is a zoomed-in image of panel a_1 . Imaging conditions of E_{bias} , $i_{\text{tunneling}}$, and image sizes: (a_1) 0.90 V, 50 pA, 13 × 13 nm; (a_2) 0.10 V, 600 pA, 4 × 4 nm; (a_3) 0.90 V, 50 pA, 4 × 4 nm.

between two adjacent polynorbornene backbones and between the polynorbornene strand of a polymer and the crown ether moieties of the adjacent polymer may not be the same. Such irregularity on the STM image is therefore not unexpected.

CONCLUSIONS

The chemistry described herein is the first example on the CMCP reaction of strained biscycloalkenes with flexible linkers. Single-stranded polybisnorbornenes are thus obtained. This approach offers an interesting synthesis of hammock-like crown ether moieties hanging on a hydrophobic polynorbornene scaffold. It seems likely that the monomeric bisnorbornene may be folded under the reaction conditions to give the corresponding syn conformer (like *syn-10*). Intramolecular $\pi - \pi$ interactions between the pending aryl groups may take place to direct the ring closure process (Scheme 2). Such $\pi - \pi$ interactions appear to be crucial for the success of the CMCP. The extension of this reaction for designing polymers of different structural variety using different kinds of monomeric biscycloalkenes is in progress.

EXPERIMENTAL SECTION

Monomer 10a. To a solution of triethylene glycol (194 mg, 1 mmol) and Et₃N (300 mg, 3 mmol) in DCM (5 mL) at 0 °C was added a solution of the acid chloride 17 (570 mg, 2.1 mmol) in DCM (5 mL). The mixture was gradually warmed to rt and stirred for 10 h, poured into water (100 mL), and extracted with DCM (100 mL × 2). The organic layer was washed with brine (100 mL × 2), dried (MgSO₄), filtered, and evaporated in vacuo. The residue was chromatographed on silica gel (EtOAc/hexane = 1/1) to afford **10a** (425 mg, 68%); mp 120–123 °C. ¹H NMR (400 MHz, CDCl₃) δ : 1.51 (d, *J* = 8.0 Hz, 2 H), 1.61 (d, *J* = 8.0 Hz, 2 H), 2.91–2.96 (m, 8 H), 3.05–3.09 (m, 4 H), 3.23–3.28 (m, 4 H), 3.69 (s, 4 H), 3.79 (t, *J* = 4.8 Hz, 4 H), 4.38 (t, *J* = 4.8 Hz, 4 H), 6.13 (s, 4 H), 6.35 (d, *J* = 9.0 Hz, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ : 45.4, 46.6, 50.4, 52.1, 63.3, 69.5, 70.7, 110.7, 116.0, 131.2, 135.6, 150.2, 166.7. HRMS (FAB) calcd C₃₈H₄₅N₂O₆ [M + H]: 625.3278; found: 625.3268.

Monomer 10b. In a manner similar to that described above for **10a**, reaction of butane-1,4-diol (90 mg, 1 mmol) and **17** (570 mg, 2.1 mmol) yielded after chromatographic separation on silica gel (hexane/ DCM = 1/3) **10b** (350 mg, 62%); mp 218–219 °C. ¹H NMR (400 MHz, CDCl₃) δ : 1.51 (d, *J* = 8.1 Hz, 2 H), 1.61 (d, *J* = 8.1 Hz, 2 H), 1.88 (m, *J* = 2.8 Hz, 4 H), 2.92–3.00 (m, 8 H), 3.04–3.12 (m, 4 H), 3.22–3.32 (m, 4 H), 4.29 (m, 4 H), 6.14 (s, 4 H), 6.36 (d, *J* = 8.8 Hz, 4 H), 7.84 (d, *J* = 8.8 Hz, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ : 26.2, 45.6, 46.9, 50.6, 52.3, 63.8, 110.6, 116.2, 130.8, 135.3, 149.8, 166.4. HRMS (FAB) calcd for C₃₆H₄₀N₂O₄: 564.2988; found: 564.2994.

Monomer 10c. In a manner similar to that described above for **10a**, reaction of 4,13-diaza-18-crown-6 (260 mg, 1 mmol) and **17** (570 mg, 2.1 mmol) yielded after chromatographic separation on silica gel (DCM/MeOH = 95/5) **10c** (570 mg, 75%); mp 182–184 °C. ¹H NMR (400 MHz, CDCl₃) δ : 1.51 (d, J = 8.1 Hz, 2 H), 1.60 (d, J = 8.1 Hz, 2 H), 2.86–2.94 (m, 4 H), 2.96 (br, 4 H), 3.04–3.12 (m, 4 H), 3.18–3.28 (m, 4 H), 3.58 (br, 8 H), 3.69 (br, 16 H), 6.15 (s, 4 H), 6.35 (d, J = 8.3 Hz, 4 H), 7.25 (d, J = 8.3 Hz, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ : 45.5, 46.6, 50.5, 52.1, 70.1, 70.5, 110.9, 122.5, 128.4, 135.6, 148.1, 172.6. HRMS (FAB) calcd C₄₄H₅₇N₄O₆ [M + H]: 737.4278; found: 737.4284.

Polymer 12a. A solution of **10a** (22 mg, 0.04 mmol) and 7 (3.5 mg, 4×10^{-3} mmol) in DCM (23 mL) was stirred under Ar for 2 h at rt. Ethyl vinyl ether (2 mL) was then added, and the mixture was stirred for 10 min. The resulting solution was concentrated, and the polymer was precipitated in Et₂O (30 mL) as a white solid (20 mg, 92%). ¹H NMR (400 MHz, CDCl₃) δ : 1.42–1.52 (br, 2 H), 1.81–2.00 (br, 2 H), 2.82–3.23 (br, 16 H), 3.70–3.81 (br, 8 H), 4.12–4.68 (br, 4 H), 5.43–5.54 (br, 4 H), 6.10–6.80 (br, 4 H), 7.55–8.10 (br, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ : 35.9, 36.7, 37.7, 39.1, 45.1, 46.9, 47.0, 48.9, 49.3, 49.7, 50.0, 63.9, 64.5, 69.8, 70.8, 70.9, 111.1, 116.8, 125.9, 128.4, 131.3, 133.4, 150.5, 166.5. GPC (CHCl₃) M_n = 7800, PDI = 1.2.

Polymer 12b. In a manner similar to that described above for 12a, reaction of 10b (22 mg, 0.04 mmol) with 7 (3.5 mg, 0.004 mmol) yielded 12b as a white solid (21 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ : 1.30–1.65 (br, 2 H), 1.65–2.10 (br, 6 H), 2.48–3.70 (br, 16 H), 4.00–4.56 (br, 4 H), 4.80–5.90 (br, 4 H), 6.00–6.80 (br, 4 H), 7.50–8.20 (br, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ : 25.8, 26.1, 36.7, 38.0, 45.1, 45.4, 46.1, 46.6, 49.9, 63.7, 111.3, 117.2, 125.9, 128.4, 131.1, 131.3, 150.5, 166.6. GPC (CHCl₃) $M_{\rm p}$ = 5300, PDI = 1.3.

Polymer 12c. In a manner similar to that described above for **12a**, reaction of **10c** (30 mg, 0.04 mmol) with 7 (3.5 mg, 0.004 mmol) yielded **12c** as a white solid (27 mg, 90%). ¹H NMR (500 MHz, CDCl₃) δ : 1.30–1.55 (br, 2 H), 1.60–2.05 (br, 2 H), 2.50–3.05 (br, 8 H), 3.05–3.40 (br, 8 H), 3.40–3.65 (br, 12 H), 3.65–4.20 (br, 12 H), 5.20–5.80 (br, 4 H), 6.20–6.80 (br, 4 H), 7.10–7.60 (br, 4 H). ¹³C NMR (125 MHz, CDCl₃) δ : 36.2, 45.0, 46.3, 49.9, 70.0, 70.5, 112.1, 123.8, 126.0, 128.5, 131.4, 148.9, 172.6. GPC (CHCl₃) M_n = 6500, PDI = 1.3.

Polymer 12c'. In a manner similar to that described above for **12a**, reaction of **10c** (30 mg, 0.04 mmol) and 7 (7.0 mg, 8×10^{-3} mmol) yielded **12c'** as a white solid (20 mg, 84%). ¹H NMR (400 MHz, CDCl₃) δ : 1.11–1.71 (br, 2 H), 1.73–2.08 (br, 2 H), 2.50–3.02 (br, 8 H), 3.04–3.35 (br, 8 H), 3.38–4.03 (br, 24 H), 5.17–5.76 (br, 4 H), 6.34–6.75 (br, 4 H), 7.01–7.54 (br, 4 H). ¹³C NMR (125 MHz, CDCl₃) δ : 35.8, 45.2, 46.2, 49.9, 70.1, 70.6, 111.9, 123.7, 125.9, 128.4, 130.5, 131.5, 135.6, 148.9, 172.5. GPC (CHCl₃) $M_{\rm n}$ = 3700, PDI = 1.2.

General Procedure for the Hydrolysis–Esterification of 12. Under a N_2 atmosphere, to a solution or suspension of 12 (0.07 mmol of ester group) in THF (anhydrous, 20 mL) was added at rt water (18 mg, 1 mmol) and KO^tBu (1.2 g, 10 mmol). After stirring at rt for 48 h, the mixture was poured into water (30 mL) and extracted with ethyl ether (50 mL). The aqueous layer was separated and neutralized with HCl (1 M) at 0 °C to afford a white precipitate, which was directly used for the next reaction without further purification. A mixture of the above precipitate, CsF (40 mg, 0.3 mmol) and EtI (82 mg, 0.5 mmol) in DMF (2 mL), was stirred at rt for 24 h. The mixture was poured into water (20 mL), and 15 was precipitated as yellowish solid. ¹H NMR (400 MHz, CDCl₃) δ: 1.10–1.50 (br, 4 H), 1.70–2.00 (br, 1 H), 2.60-2.80 (br, 2 H), 2.80-3.10 (br, 2 H), 3.10-3.60 (br, 4 H), 4.10-4.50 (br, 2H), 5.20-5.60 (br, 2 H), 6.25-6.70 (br, 2 H), 7.60-8.10 (br, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ: 14.5, 35.7, 36.2, 37.5, 39.9, 44.5, 44.8, 46.4, 46.8, 49.4, 49.5, 60.1, 111.4, 117.4, 125.9, 128.4, 131.2, 131.7, 131.8, 150.8, 166.9. 15a (85%): GPC (CHCl₃) $M_{\rm n} = 6700$, PDI = 1.2; **15b** (85%): $M_{\rm n} = 4600$, PDI = 1.2; **15c** (75%): $M_{\rm n} = 5000, \, {\rm PDI} = 1.2.$

Monomer 24. To a solution of 2-aza-1,2-dihydro-*endo*-dicyclopentadiene (284 mg, 2.1 mmol) and Et_3N (300 mg, 3 mmol) in DCM (5 mL) at 0 °C was added a solution of the succinic acid dichloride, prepared from succinic acid (118 mg, 1 mmol) and oxalyl chloride (265 mg, 2.1 mmol), in DCM (5 mL). The mixture was gradually warmed to rt and stirred for 10 h, poured into water (100 mL), and extracted with DCM (100 mL × 2). The organic layer was washed with brine (100 mL × 2), dried (MgSO₄), filtered, and evaporated in vacuo. The residue was chromatographed on silica gel (DCM/MeOH = 95/5) to afford 24 (264 mg, 75%); mp 122–124 °C. ¹H NMR (400 MHz, CDCl₃) δ : 1.43 (d, *J* = 8.4 Hz, 2 H), 1.55 (d, *J* = 8.4 Hz, 2 H), 2.32 –2.53 (m, 4 H), 2.86–2.95 (m, 8 H), 3.09–3.10 (m, 2 H), 3.18–3.21 (m, 2 H), 3.26–3.29 (m, 2 H), 3.42–3.44 (m, 2 H), 6.14–6.16 (m, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ : 29.75, 29.78, 44.22, 46.00, 46.03, 46.81, 46.84, 48.15, 49.18, 51.96, 134.34, 134.40, 135.44, 135.47, 169.06. HRMS (FAB) calcd C₂₂H₂₈N₂O₂: 352.2151; found: 352.2147.

CMCP of 24. To a solution of 24 (14 mg, 0.04 mmol) in DCM (20 mL) stirred under Ar was added 7 (3.5 mg, 4×10^{-3} mmol) in DCM (2 mL). After stirring for 2 h at rt, ethyl vinyl ether (2 mL) was added, and the mixture was stirred for 10 min. The resulting solution was concentrated, and the polymer was precipitated in Et₂O (30 mL) as a white solid (13 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ : 1.40–1.72 (br, 4 H), 1.78–4.00 (br, 16 H), 5.00–5.82 (br, 4 H).

MALDI-TOF Experiments. The MALDI/TOF mass spectrometer was equipped with a nitrogen pulsed laser with lasing wavelength at 337 nm. The laser energy per pulse was calibrated with a laser power meter (PEM 101, Laser Technik, Berlin, Germany) so that the laser fluence could be precisely measured. The typical laser fluence applied was 160 mJ/cm², and 50 laser shots were accumulated to obtain the final spectrum. The laser beam diameter was ca. 100 μ m on the sample target. The accelerating voltage on the sample plate was set at 20 kV. The grid voltage was set up as 95% of the accelerating voltage, and the guide wire voltage was 0.2% of the accelerating voltage. The delay extraction time could be adjusted from 10 to 500 ns. The vacuum inside the flight tube was kept between 10^{-7} and 10^{-6} Torr. The spectra was acquired by a Voyager DETE-PRO (Applied Biosystems, Foster City, CA). A sample in THF (ca. 1 μ mol, 1 mL) was mixed with an equal volume of the matrix solution prepared from dithranol (0.1 M in THF), TFA (0.1 M in THF), and silver trifluoroacetate (5 g/L in THF) in v/v ratio as 1000:10:1. The sample solution $(1 \ \mu L)$ was mixed with the matrix solution (1 μ L), and the mixture was air-dried before introduced for the MALDI-TOF experiment.

Dynamic Light Scattering (DLS) Measurements. The sample was dissolved in $CHCl_3$ (0.1 mM), and 3 mL of the aliquot was used for DLS measurements on a Zetasizer Nano S90 instrument; the results are shown in Figures S2 and S3.

Intrinsic Viscosity Measurements. Polymers were dissolved in CHCl₃ and measured by the Ubbelohde viscometer to get the specific viscosity (η_{sp}). A plot of η_{sp} divided by the corresponding concentration against the concentration gave a straight line. The intrinsic viscosity [η] was obtained from the intercept at zero concentration.³⁴ The details are shown in Figures S4 and S5.

STM Imaging. The STM imaging was performed with a PicoScan controller (4500, Agilent Technologies) at rt, and commercially available Pt/Ir tips (PT, Nanotips, Veeco Metrology Group/Digital Instruments) were used as the STM probes. Typical bias voltage and tunneling current ranged from 0.5 to 0.9 V and from 30 to 100 pA, respectively. The sample for imaging was prepared by placing a 10 μ L aliquot consisting of **12** in 1-phenyloctane on HOPG with a micropipet. In order to acquire stable images, samples were subjected to a shear flow which allows molecules being packed into a 2D motif.^{13c}

ASSOCIATED CONTENT

S Supporting Information

¹H and ¹³C NMR spectra of all new compounds, DLS data, GPC profiles, and details of data treatment. 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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