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Bridge-like polymer synthesized by tandem metathesis cyclopolymerization and acyclic diene metathesis polymerization

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ABSTRACT: A facile synthesis of novel bridge-like polymer was accomplished by the combined procedure of metathesis cyclopolymerization (MCP) and acyclic diene metathesis (ADMET) polymerization. A telechelic double-stranded polyacetylene (PA) with two terminal alkenyl groups was firstly prepared through the third generation Grubbs catalyst-mediated chain terminating MCP of bis(1,6-heptadiyne) containing perylene bisimide (PBI) segment in the presence of 1,4-bis(10-undecenyloxy)-*cis*-2-butene, a symmetrical tri-olefinic ether acted as the functional terminating agent, and then utilized as the macromonomer in subsequent ADMET polymerization to yield the resultant bridge-like polymer, consisting of the nonconjugated polyolefin backbone and the separated pier-like double-stranded PA, with an increased molecular weight (25.2 - 122.4 kDa) as the reaction time prolonged and relatively broad polydispersity index (PDI = 1.41 - 1.75). The bridge-like polymer can assemble into an ordered ladder-like architecture and the fence-like ribbon morphology, and displayed excellent thermal stability with T_d of above 300 °C and high T_g between 175 and 189 °C, which is important for application in devices.

KEYWORDS: metathesis cyclopolymerization; acyclic diene metathesis polymerization; terminating agent; bridge-like polymer; ladder-like architecture.

Introduction

Since the discovery of metathesis cyclopolymerization (MCP) of 1,6-heptadiyne using Ziegle-Natta catalyst in 1961,[1] there has been enthusiasm studies on the MCP of nonconjugated 1,6-heptadiyne, giving the substituted polyacetylene (PA) with the unique structures of conjugated double bond backbone and cyclic recurring units, and the improved properties of solubility, stability, and processability.[2-10] Very recently, a breakthrough on MCP was disclosed by Choi et al.[6,11,12] who found that the third-generation Grubbs catalyst (**Ru-III**) underwent selective *α*-addition to produce PAs with only five-membered rings, and what is more important, MCP initiated by **Ru-III** can be performed in a living manner,[6] which may enable MCP to be terminated by the functional *α*,*ω*-alkenyl *cis*-olefinic ether or ester[13,14] to afford the mono-telechelic PA with one reactive end group. If MCP of bis(1,6-heptadiyne) derivative was utilized to construct the double-stranded polymer structure, like as the demonstration for synthesis of ladder polymers by ring-opening metathesis polymerization (ROMP),[15] the novel type of double-stranded PA with telechelic reactive end groups should be generated when MCP was terminated by the symmetrical *α*,*ω*-alkenyl *cis*-olefinic ether or ester.

It is noteworthy that ladder-like polymers have greater resistance to irradiation as well as thermal and chemical degradation with comparison to their counterparts.[16,17] Besides, the ladder-type arrays should have planar and rigid *π*-*π* structures that facilitate electron-delocalization and enhance conjugation.[17] A series of ladder polymers with various linkers including ferrocene moiety, azobenzene group, multilayer planar oligoaryl chromophores, hexa-*peri*-hexabenzocoronenes, cubane, cuneane, and cyclooctatetraene have been synthesized by ROMP of bis(norbornene) derivatives.[15] Perylene bisimide (PBI) is a rigid aryl chromophore and capable of electron transport as the *n*-type semiconductor on the basis of its optoelectronic property, high stability, low-lying lowest unoccupied molecular orbital (LUMO) energy level, and ease of synthesis.[18,19] Very impressively, the bay-linked doubly and triply PBI oligomers were synthesized via Ullmann and Still coupling reaction,[20] and the expansion of the conjugated aromatic system enlarged the delocalization of π-electron, which further lowered the LUMO energy to -4.36 eV and bandgap (E_g) to 1.85 eV. Thus, this kind of PBIs exhibited excellent air stability and sufficient utilization of solar energy. Nevertheless, the number of linked PBI segments can hardly increase to more than four, which probably limits its flexible application on large area. Additionally, because of the high sensitivity to ambient conditions and less optimal physicochemical properties, the development of pure *n*-type semiconductors with high air stability and high mobility is still lagged behind *p*-type semiconductor. Herein, we synthesized PBI-linked double-stranded PA with telechelic long chain alkenes by MCP of bis(1,6-heptadiyne) derivative and termination with the symmetrical α,ω-alkenyl *cis*-olefinic ether, which is a potential constructing unit and can be used as the macromonomer for subsequent acyclic diene metathesis (ADMET) polymerization[21] to build bridge-like polymer. To our knowledge, it is the first report that the fundamental preparation of bridge-like polymer containing PBI-linked double-stranded PA as the pier structure by tandem MCP and ADMET polymerization, and this type of polymer should be envisioned to have highly thermal and oxidative stability, excellent optoelectronic properties, and be attractive alternative to fullerene as the *n*-type of photovoltaic materials.

Experimental

Materials

The second generation Grubbs catalyst was purchased from Sigma-Aldrich. The third generation Grubbs catalyst (**Ru-III**),[22] 4-hydroxymethyl-1,6-heptadiyne,[23] and 11-bromo-1-undecene[24] were prepared according to the known synthetic procedures in literatures. 12-Amino dodecanoic acid, propionic acid, 4-dimethylaminopyridine (DMAP), and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI·HCl) were purchased from Alfa Aesar and used as received without purification. 1,6,7,12-Tetrachloroperylene-3,4:9,10-tetracarboxylic dianhydride (PTCDA) was purchased from commercial sources at analytical grade and used without further purification. Solvents were distilled over drying agents under nitrogen prior to use: dichloromethane (CH_2Cl_2), dimethylformamide (DMF), and chlorobenzene from calcium hydride; tetrahydrofuran (THF) from sodium/benzophenone. All reactions were carried out under dry nitrogen atmospheres using standard Schlenk-line techniques.

Characterization

^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded using tetramethylsilane as an internal standard on a Bruker DPX spectrometer. The HR-MS was measured by a Bruker QTOF micromass spectrometer. IR spectra were recorded by Perkin Elmer Spectrum One FTIR spectrophotometer. UV-vis absorption spectra were measured on a UV-1800 spectrometer. Gel permeation chromatography (GPC) was used to calculate relative molecular weight (M_n) and molecular weight distribution (M_w/M_n) equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (7.8 × 300 mm, 5 mm bead size; 10^3, 10^4, and 10^5 Å pore size). GPC measurements were carried out at 150 ^oC using 1,2,3-trichlorobenzene as the eluent with a flow rate of 1.0 mL/min. The system was calibrated with polystyrene standard. Thermal gravimetric analysis (TGA) was performed using a SDTA851e/SF/1100 TGA Instrument under nitrogen flow at a heating rate of 10 ^{o}C/min from 50 to 800 ^{o}C. Differential scanning calorimeter (DSC) was performed on a Netzsch 204F1 in nitrogen atmosphere. An indium standard was used for temperature and enthalpy calibrations. The sample was first heated from 25 to 300 °C and held at this temperature for 3 min to eliminate the thermal history, and then cooled to room temperature and heated again from 25 to 300 °C at a heating or cooling rate of 10 °C/min. Samples for transmission electron microscopy (TEM) measurement were prepared by depositing a drop of CH_2Cl_2 solution (1 mg/mL) on the copper grids coated with carbon, followed by air-drying. Additionally, the samples were not stained before measurement. TEM images were recorded on the JEOL2100F microscopes operating at 120 kV. Atom force microscopy (AFM) observations were performed on SPM AJ–III atomic force microscope at a measure rate of 1.0005 Hz in the tapping mode, and the AFM images were obtained at room temperature in air. Samples were prepared by drop coating of a 0.01 - 0.0025 mg/mL of CH_2Cl_2 solution on a freshly cleaved mica surface, which were then air-dried at room temperature. The sample was examined at least twice under the same conditions, and the images were found to be very reproducible.

Synthesis of 1,4-bis(10-undecenyloxy)-*cis*-2-butene

A solution of *cis*-1,4-butenediol (2.69 g, 30.0 mmol) in THF (30 mL) was added to a suspension of sodium hydride (6.1 g, 150.0 mmol) in THF (30 mL) at 0 ºC, the reaction mixture was warmed to room temperature and subsequently stirred for 6 h under nitrogen allowing for the formation of sodium alkoxide. An excess of 11-bromo-1-undecene (17.1 g, 72.0 mmol) in THF (30 mL) was then added dropwise to the above mixture. After 2 days, the resulting solution was filtered off and the filtrate was washed three times with deionized water (3 × 80 mL), and the organic layer was dried over anhydrous $MgSO_4$. Solvent was then evaporated and the crude product was purified by column chromatography on silica gel using CH_2Cl_2 as the eluent to give the product as a colorless liquid (3.90 g, 53.4 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.94 - 5.60 (m, 4H, $CH_2C\mathit{H}CH_2$ + $C\mathit{H}{=}C\mathit{H}$), 5.07 - 4.83 (m, 4H, $C\mathit{H}_2CH_2CH_2$), 4.17 - 3.90 (s, 4H, $OC\mathit{H}_2CH$), 3.51 - 3.30 (t, 4H, J = 5.80 Hz, $OC\mathit{H}_2CH_2$), 2.15 - 1.90 (d, 4H, J = 6.18 Hz, $CH_2CHC\mathit{H}_2$), 1.46 - 0.92 (m, 28H, $CH_2C\mathit{H}_2CH_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.73, 129.68, 113.76, 70.66, 66.33, 33.75, 29.76, 29.53, 29.43, 29.08, 28.90. HR-MS: Calcd. For $C_{26}H_{48}O_2Na$ $[M+Na]^+$: 415.3547, Found: 415.3564.

Synthesis of carboxyl-contained perylene bisimide (PBI-COOH)

A mixture of PTCDA (2.65 g, 5 mmol) and 12-amino dodecanoic acid (2.58 g, 12 mmol) in propionic acid (40 mL) was heated to reflux at 140 ^{o}C for 36 h under a nitrogen atmosphere. The resulting mixture was cooled and poured into water, filtrated, and washed with water until the filtrate reached neutrality. The crude solid was dried at 70 ^{o}C under vacuum. After being purified by column chromatography on silica gel using a mixture of HAc/CH_2Cl_2 1/150 to 1/125 as eluent, the product of carboxyl-contained perylene bisimide (PBI-COOH) was obtained as an orange-red powder (4.02 g, 4.3 mmol, 87 %); ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.69 (s, 4H, pery), 4.32 - 4.18 (m, 4H, $NC\mathit{H}_2CH_2$), 2.45 - 2.31 (m, 4H, $CH_2C\mathit{H}_2COOH$), 1.82 - 1.71 (m, 4H, $NCH_2C\mathit{H}_2$), 1.70 - 1.62 (m, 4H, $C\mathit{H}_2CH_2COOH$), 1.55 - 1.18 (m, 28H, $CH_2C\mathit{H}_2CH_2$). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 178.78, 161.94, 134.75, 132.61, 130.81, 128.67, 123.29, 40.43, 33.42, 29.04, 28.68, 27.58, 26.48, 24.10; HR-MS: Calcd. For $C_{48}H_{50}Cl_4N_2O_8Na$ $[M+Na]^+$: 945.2321, Found: 945.2313.

Synthesis of monomer (1)

Compound PBI-COOH (2.5 g, 2.7 mmol) was firstly dissolved in 20 mL of anhydrous DMF and 25 mL of CH_2Cl_2. To this solution, 4-hydroxymethyl-1,6-heptadiyne (1.32 g, 10.8 mmol), EDCI·HCl (1.24 g, 5.4 mmol) and DMAP (0.30 g, 0.54 mmol) were added under a nitrogen atmosphere in ice-water bath for 2 h, then the reaction progress proceeded at room temperature and was monitored by TLC. After 3 days, the mixture was evaporated to remove CH_2Cl_2 and then poured to 200 mL of water to precipitate dark red solid. The solid was filtered and purified by column chromatography on silica gel using CH_2Cl_2 as the eluent. The monomer **1**, PBI-contained bis(1,6-heptadiyne), was obtained as a red powder (2.01 g, 66 %); ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.69 (s, 4H, pery), 4.26 - 4.18 (m, 4H, NCH_2CH_2), 4.17 - 4.12 (d, 4H, J = 6.10 Hz, OCH_2CH), 2.45 - 2.36 (dd, 4H, J = 2.64, 6.40 Hz, CH_2COOCH_2), 2.36 - 2.27 (t, 8H, J = 7.48 Hz, $CHCH_2CCH$), 2.22 - 2.09 (m, 2H, CH_2CHCH_2), 2.02 (t, 4H, J = 2.55 Hz, CH_2CCH), 1.82 - 1.69 (m, 4H, NCH_2CH_2), 1.68 - 1.52 (m, 4H, CH_2CH_2COOH), 1.51 - 1.19 (m, 28H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 174.13, 162.11, 135.70, 131.83, 129.11, 123.28, 80.98, 70.51, 65.08, 41.03, 36.36, 34.44, 29.59, 28.08, 27.06， 25.00, 19.86. HR-MS: Calcd. For $C_{64}H_{66}Cl_4N_2O_8Na$ $[M+Na]^+$: 1153.3508, Found: 1153.3465.

Metathesis cyclopolymerization of monomer

A 150 mL Schlenk flask was charged with monomer **1** (500 mg, 0.44 mmol) dissolved in 100 mL of THF. In another 25 mL flask, catalyst **Ru-III** (38 mg, 0.043 mmol) was dissolved in 2 mL of THF. After degassed with three freeze-vacuum-thaw cycles, the catalyst solution of **Ru-III** was then injected into the preheated monomer solution via a syringe under vigorous stirring at 30 ^{o}C. After confirming the monomer conversion by TLC (5 min), an excess of **TA** (182 mg, 0.44 mmol) was added to the mixture and stirring for another 10 h, and the THF solution was concentrated and precipitated into acetone. After filtration, the solid was then dissolved in a minimal amount of $CHCl_3$ and precipitated into 50 mL of acetone with vigorous stirring to yield 502 mg of double-stranded poly(**1**) in nearly quantitative yield. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.55 (s, pery), 6.58 (s, C*H*=C*H* on backbone), 5.79 - 5.50 (d, C*H*=CH_2), 5.48 - 5.01 (m, CH=CH_2), 4.35 - 3.60 (m, OCH_2 + CH_2N), 3.06 - 1.98 (m, CH_2COO + CH_2C*H*CH_2), 1.83 - 0.92 (m, NCH_2(CH_2)$_9$CH_2COO); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.94, 162.13, 138.68, 135.14, 132.78, 131.29, 128.35, 122.80, 119.21, 67.76, 40.63, 36.99, 34.09, 29.16, 28.92, 28.07, 27.73, 27.11, 26.37, 24.85; The values of M_n and M_w/M_n of poly(**1**) were 11.2 kDa and 1.12, respectively.

ADMET polymerization of macromonomer

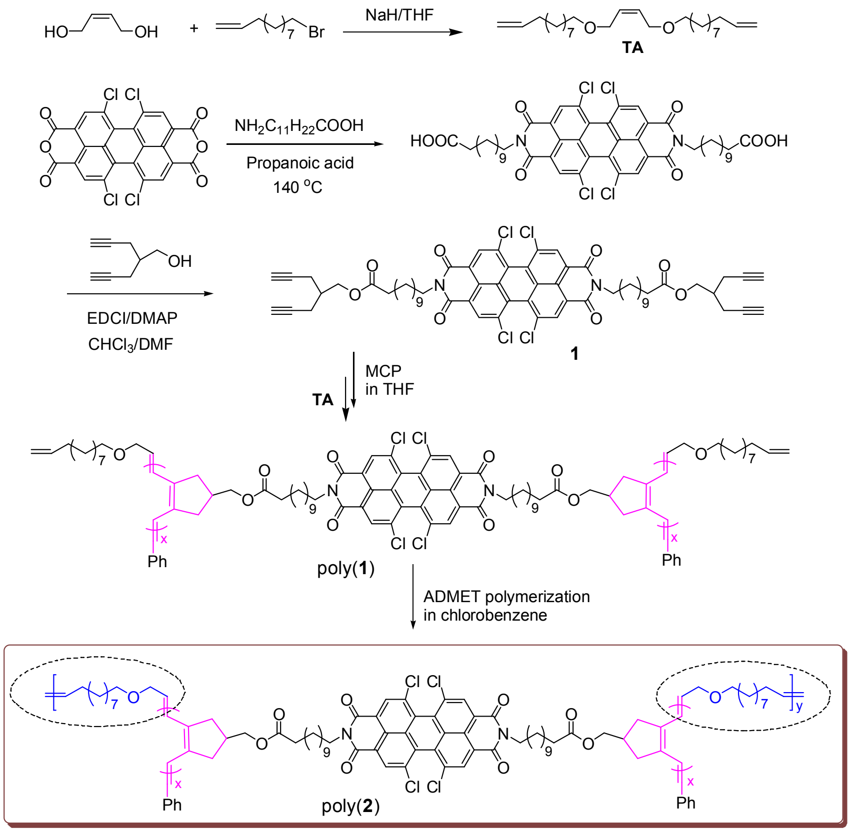
In a nitrogen-filled Schlenk tube, a solution of **Ru-III** (0.5 mg, 0.4 μmol) in 0.5 mL of degassed chlorobenzene with three freeze-vacuum-thaw cycles was added to the solution of poly(**1**) (240 mg, 0.02 mmol) in 1 mL of chlorobenzene degassed with the same procedure. The reaction mixture was then held stirring at 50 ºC for 1 - 3 days with simultaneous purging with an inert atmosphere, and a fresh batch of 0.5 % mol equiv of the catalyst is then added to the reaction vessel at about 24 h intervals. The polymerization was quenched by adding ethyl vinyl ether with stirring for 30 min and then precipitated into an excess of methanol. The precipitate was isolated by filtration, dried under vacuum to give the polymer as a dark red solid. The resultant poly(**2**) can be easily soluble in various halogenated solvents, such as CH_2Cl_2, $CHCl_3$, and chlorobenzene. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.55 (s, pery), 6.58 (s, conjugated C*H*=C*H* on backbone), 5.67 (s, *trans* non-conjugated C*H*=C*H*), 5.37 (s, *cis* non-conjugated C*H*=C*H*), 4.35 - 3.60 (m, OCH_2 + CH_2N), 3.06 - 1.98 (m, CH_2COO + CH_2C*H*CH_2 + CH_2CH_2CH_2CH), 1.83 - 0.92 (m, NCH_2(CH_2)$_9$CH_2COO + CH_2C$H_2$$CH_2$CH); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.74, 162.22, 138.66, 135.34, 132.97, 131.37, 128.46, 123.17, 67.97, 40.73, 37.04, 34.27, 29.08, 28.10, 27.82, 27.11, 24.85; GPC data: M_n = 25.2 kDa, M_w/M_n = 1. 41 for 1 day; M_n = 51.6

kDa, $M_w/M_n = 1.75$ for 2 days; $M_n = 122.4$ kDa, $M_w/M_n = 1.54$ for 3 days.

Results and discussion

Preparation of functional terminating agent (TA) and monomer

The novel tri-olefinic ether, 1,4-bis(10-undecenyloxy)-*cis*-2-butene, used as the terminating agent (**TA**) for MCP, was readily prepared by the conventional Williamson coupling reaction of *cis*-2-butene-1,4-diol with 11-bromo-1-undecene in moderate yield (Scheme 1).[25] The structure and purity of **TA** were fully tested by HR-MS, ^{1}H NMR, and ^{13}C NMR spectroscopy (Fig. S1 and S2, ESI†).



Scheme 1 Syntheses of polymers by MCP and ADMET polymerization.

The functional monomer **1**, bis(1,6-heptadiyne) derivative bearing two polymerizable diyne groups and one rigid PBI segment, was synthesized starting from the imidization reaction of PTCDA with 12-amino dodecanoic acid to firstly achieve two carboxyl groups-contained PBI, PBI-COOH, which was then easily transformed into PBI-spaced bis(1,6-heptadiyne) by the esterification reaction with 4-hydroxymethyl-1,6-heptadiyne in CH_2Cl_2/DMF solution at room temperature. The crude product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent to give monomer **1** as a red powder. The HR-MS, NMR, and IR spectroscopy were employed to confirm the chemical composition and structure of the compound.

The ^{1}H NMR spectrum (Fig. 1a) of **1** indicated the presence of aromatic protons on PBI moiety at 8.69 ppm and acetylenic protons at 2.02 ppm. Moreover, the integration ratio for these two types of protons was exactly 1 : 1, which was agreed well with the theoretical value of 4 : 4. In ^{13}C NMR spectrum (Fig. S5, ESI†), the resonances of perylene core appeared at 135.70 - 123.28 ppm, and the signals at 80.98 and 70.51 ppm were contributed to the carbons of C_i and C_j on 1,6-heptadiyne moiety. The signals of carbonyl carbons on imide and ester are presented at 162.11 and 174.13 ppm, respectively. Additionally, in the IR spectrum (Fig. S6, ESI†) of monomer **1**, the absorption bands at 3320 and 2120 cm^{-1} were attributed to the stretching vibration of unsaturated C≡C–H and C≡C, respectively. All of these points confirmed that monomer **1** has been successfully synthesized with the expected chemical structure.

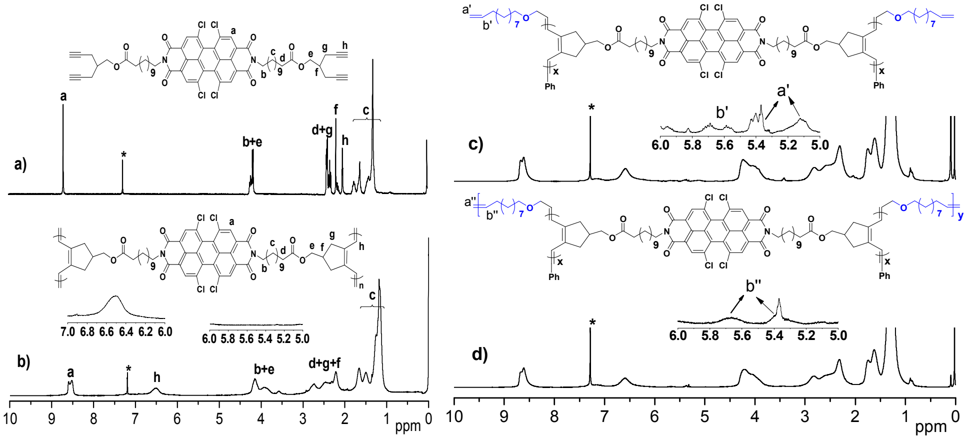


Fig. 1 ^{1}H NMR spectra of (a) **1**, (b) poly(**1**)*, (c) poly(**1**), and (d) poly(**2**) in $CDCl_3$.

Metathesis cyclopolymerization of monomer and ADMET polymerization of macromonomer

Preparation and characterization of telechelic double-stranded polyacetylene

It has been known that living MCP of 1,6-heptadiyne derivative can be realized with the utilization of catalyst **Ru-III** in THF.[6] In this case, to get the telechelic poly(**1**) with relatively low molecular weight, MCP of monomer **1** was initiated by **Ru-III** (Scheme S1, ESI†) with the monomer to catalyst ratio of 10/1. Upon addition of **Ru-III**, the color of reaction solution immediately changed from yellow to red. After fully consumption of monomer monitored by TLC (within 5 min), excess **TA** was added and further stirred for another 10 h to ensure the fully replacement of the ruthenium-alkylidene end group on the growing polymer chain by the olefinic group of **TA**, giving the telechelic double-stranded poly(**1**) bearing two long chain alkenyl groups in quantitative yield. The result of GPC analysis suggested that the polymer, having low molecular weight (M_n =11.2 kDa) and narrow polydispersity index (PDI = 1.12), has a degree of polymerization (DP) of 10, which is in accordance with the feed ratio of 10.

For comparison, the ^{1}H NMR spectrum (Fig. 1b) of double-stranded poly(**1**)* obtained by MCP without terminating reaction showed a broad peak at 6.53 ppm due to the protons on the conjugated double bonds of poly(**1**)*. As expectation, after MCP of monomer **1** fully proceeded and terminated by **TA**, the acetylenic proton peaks of monomer **1** originally at 2.02 ppm disappeared, the peaks of protons on the conjugated double bonds of double-stranded poly(**1**) appeared at 6.58 ppm, and the resonances of telechelic alkenyl protons of poly(**1**) at 5.01 - 5.48 ppm (a’) and 5.51 - 5.79 ppm (b’) were observed from the ^{1}H NMR spectrum (Fig. 1c), which is deemed as the evidence for the formation of double-stranded structure and the newly incorporated long alkenyl end groups from **TA** at two living chain ends of poly(**1**) precursor. Additionally, from the integration ratio (13.28 : 0.60) of four protons (a) on each perylene core at 8.69 ppm to two protons (b') on terminal group at 5.51 - 5.79 ppm, the DP of telechelic poly(**1**) was calculated to be 11, and the corresponding molecular weight ($M_{n,NMR}$) was 12.7 kDa, which was close to that of 11.2 kDa from GPC curve. It is noteworthy that a symmetric single broad peak at 6.58 ppm was observed for the olefinic protons of poly(**1**), confirming that the conjugated double bonds on double-stranded backbone are all based on *cis*-conformation.[12] Besides, the peaks of acetylenic carbons on 1,6-heptadiyne moiety, which should appear at 70 and 81 ppm (Fig. S5, ESI†), were not seen in the ^{13}C NMR spectrum of poly(**1**) (Fig.S6b, ESI†). Instead, the peak of the methylene carbon on CH_2O group, which is adjacent to the ring, appears at 67.1 ppm. On the basis of the symmetrical single peak at 6.58 ppm in ^{1}H NMR spectrum and the single peak of CH_2O at 67.1 ppm in ^{13}C NMR spectrum, it is suggested that MCP triggered by initiator **Ru-III** produced poly(**1**) with exclusively (> 95%) five-membered ring units, i.e., 1,2-(cyclopent-1-enylene)-vinylenes.[8b] After fully replacement of the ruthenium-alkylidene end group on the growing polymer chain by the olefinic group of **TA**, the telechelic double-stranded poly(**1**) showed one peak of newly formed terminal alkenes at 119 ppm (Fig.S6b, ESI†), while the other peak at nearly 140 ppm was not observed, which is likely overlapped with the perylene core.

The IR spectrum of poly(**1**) (Fig. S7, ESI†) showed neither the acetylenic hydrogen stretching nor the carbon-carbon triple-bond stretching which are expected to be present at 3320 and 2120 cm^{-1} for **1**, respectively. Besides, the absorption at 684 cm^{-1} was the characteristic band of the *cis* double bonds, which is consistent with the ^{1}H NMR result. These observations confirmed that the double-stranded poly(**1**) with telechelic alkenyl groups has successfully been synthesized by MCP accompanied with terminating reaction, which should be of the candidate for macromonomer in subsequent ADMET polymerization. MCP of **1** catalyzed by **Ru-III** gave double-stranded poly(**1**) with all double bonds in *cis* configuration and thus induced all PBI segments aligned coherently toward the same direction. Probably, π-π interactions between these PBI segments might take place during the course of MCP and would be responsible for the stereo-selectivity,[26] which finally guarantees the formation of expected double-stranded structure and ladder-like morphology.

The typical fluorescence change as shown in Fig. 2 is indicative of the transformation from monomer to polymer. The dilute $CHCl_3$ solutions of **1** are highly emissive under UV illumination at 365 nm and 254 nm (Fig. 2a) or excited at 520 nm (Fig. 2b); after MCP, the fluorescence of poly(**1**) is quenched. This behavior is in good consistent with the previous results reported in literature, because the conjugated PA backbone possibly works as a quenching site for light emission, which absorbs the light emitted from the PBIs.[27]

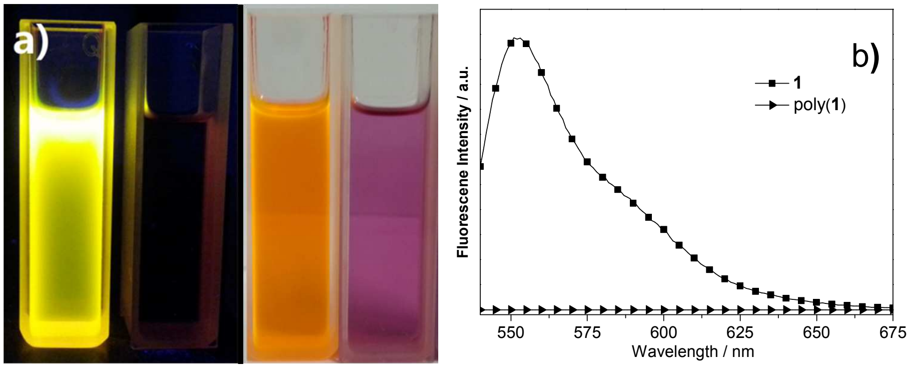


Fig. 2 (a) Photographs of **1** and poly(**1**) in $CHCl_3$ solution upon 365 nm (left) and 254 nm (right) illumination, respectively, and (b) fluorescence spectra of **1** and poly(**1**) measured in $CHCl_3$ excited at 520 nm.

Preparation and characterization of bridge-like polymer

After obtaining the telechelic double-stranded poly(**1**) with two reactive alkenyl groups, which can be used as macromonomer, ADMET polymerization was performed in high-boiling solvent of chlorobenzene,[28] with continuously purging with an inert atmosphere.[29] The reaction proceeded homogeneously, and the effect of reaction time on molecular weight of the resultant polymer, poly(**2**), was subsequently investigated. Because the length of the catalyst's lifetime in the reaction solution limits the effectiveness of prolonging the polymerization time past 72 h, a fresh batch of 0.5 % equiv. of catalyst is then added to the reaction vessel at about 24 h intervals. After ADMET polymerization, the ^{1}H NMR spectrum (Fig. 1d) of poly(**2**) with the polymerization time of 72 h showed negligible or undetectable signals of the terminal olefins (a''), and the peaks at 5.37 and 5.67 ppm arose from the protons (b'') of internal double bonds on the backbone. The obtained polymer, poly(**2**), has both *cis* and *trans* double bonds as there are two peaks at 5.37 and 5.67 ppm, and the *cis*/*trans* ratio is nearly 1 : 2. In ^{13}C NMR spectrum (Fig. S6c) of poly(**2**), it was found that the peak assigned to the terminal alkenes (*a*') at 119 ppm in poly(**1**) disappeared after ADMET polymerization, while the *cis*/*trans* double bonds can not be distinguished from the ^{13}C NMR spectrum. The GPC traces of poly(**2**) obtained from different polymerization time were shown in Fig. 3. With the progress of polymerization, the elution curves are gradually shifted to higher molecular weight region (25.2, 51.6, and 122.4 kDa) and PDI also became broad (1.41, 1.75, and 1.54) as compared to those of macromonomer poly(**1**) (M_n = 11.2 kDa, PDI = 1.12), indicating the obvious increase of polymer chain length. What is more important, these results gave an indirect evidence to the correctness of double-stranded structure of poly(**1**) with telechelic two end groups, otherwise, any other possible structures such as poly(**1**)* without or with single end group should impede or terminate the progress of ADMET polymerization.

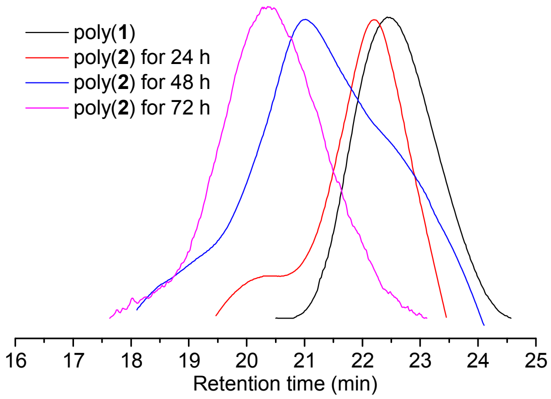
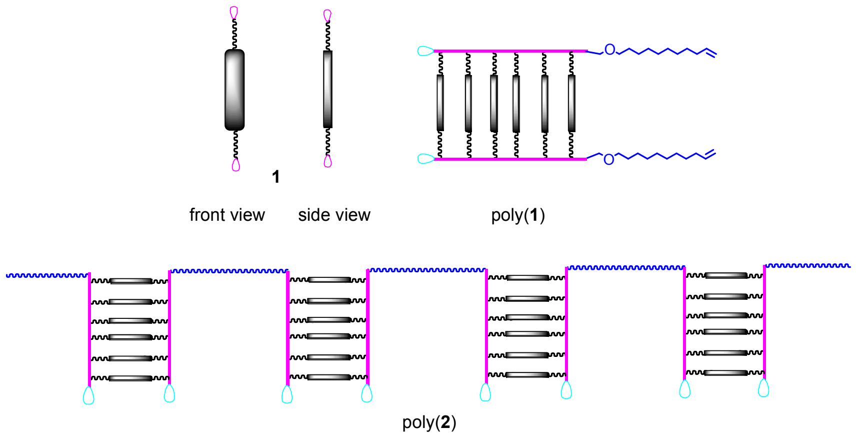


Fig. 3 GPC curves of macromonomer and corresponding polymers.

Finely observation for the structure and morphology of poly(**1**) and poly(**2**) was carried out through the HR-TEM analysis. As can be seen from the HR-TEM image (Fig.4a), obviously, poly(**1**) forms parallel stripes (like as ladder) in the same direction, suggesting the flat aromatic PBI core chose edge-on orientation with respect to substrate surface as shown in Scheme 2, and there is a strong interaction between molecules.[15e,15f,15i,30,31] Presumably, π-π stacking among PBI segments in the longitudinal direction and van der Waal interactions between the polymeric backbones in the horizontal dimension may account for this highly oriented ladder morphology.[15e] We could clearly identify the ladder length of 4.1 nm and each ladder consists of 12 monomeric units (Fig. S8), which is almost consistent with the DP value of poly(**1**) by GPC analysis. The average spacing between stripes being 0.37 nm is exactly coincide with π-π stacking distance. Moreover, SAED (inset in Fig. 4a) acquired during the TEM analysis also confirmed the ordered architecture of polymer. The HR-TEM image (Fig. 4b) revealed that poly(**2**) also assembled into an ordered ladder-like structure, which is mainly attributed to the double-stranded poly(**1**).



Scheme 2 Schematic illustrations of monomer **1**, double-stranded poly(**1**) with 6 repeat units, and bridge-like poly(**2**) with 4 repeat macro-units.

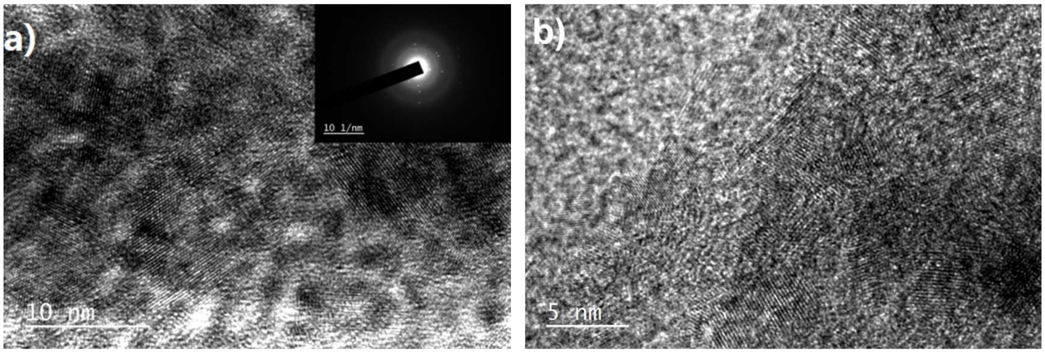


Fig. 4 HR-TEM images of (a) poly(**1**) (inset is the corresponding SAED pattern) and (b) poly(**2**).

Atomic force microscopy (AFM) was also employed to characterize the morphology, and the images (Fig.5) of poly(**2**) with different concentrations were recorded at the same location within 10 min. Interestingly, poly(**2**) with concentration of 0.0025 mg/mL assembled into a continuous fence-like ribbon with 4 μm in length and 4.6 nm (area 1) or 11.0 nm (area 2) in height, and the fence grown nicely in directions perpendicular to the mica surface. The length of the fence reached up to a scale of several microns, which is much longer than the size of a polymer molecule. This result indicates that the ladder-like poly(**1**) was successfully connected in series via ADMET technique, and the assembly of poly(**2**) may take place on mica due to π-π attractions between ladders (conjugated double bonds and PBI segments) along longitudinal axis and van der Waals interactions between the neighboring polymeric backbones.[15f] Most importantly, the height of marked area 1 being 4.6 nm coincides well with the length of the ladder-like poly(**1**) (4.1 nm obtained from TEM analysis), while the height of bright area 2 is twice more higher than that of area 1. In addition, poly(**2**) with higher concentration of 0.01 mg/mL assembled into a rugged hill-like band with height in 4.2 nm arraying along the same direction. Thus, the chain of poly(**2**) in very diluted CH_2Cl_2 solution possibly has folding or overlapped structure, resulting in the height increased more than double size to 11 nm, while this folding behavior could be depressed and inhibited when poly(**2**) was at high concentration.

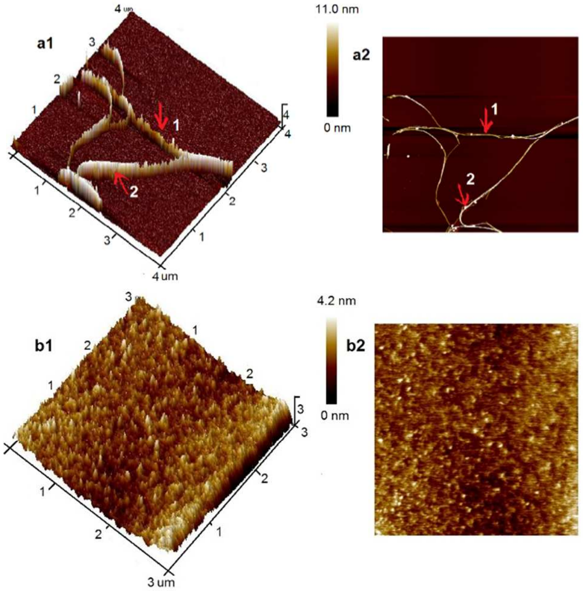


Fig. 5 AFM images of poly(**2**) (a) at 0.0025 mg/mL (4 μm × 4 μm), and (b) at 0.01 mg/mL (3 μm × 3 μm). The left column is 3D images and the right column is 2D images.

UV-vis spectra (Fig. 6) of monomer **1** exhibited three characteristic absorptions of PBI moiety at 427, 488, and 520 nm. However, poly(**1**) and poly(**2**) showed an additional shoulder absorption near 590 nm (0 - 0 transition), which was attributed to the conjugated PA with the energy bandgap of 1.96 eV, and this value is analogous to those for other MCP-generated PAs,[11,32,33] suggesting the regioregular PA consisted exclusively five-membered ring structure. For the polymers with different molecular weights obtained by the reaction time from 24 to 72 h, UV-vis spectra of poly(**2**) remained unchange. It could be concluded from these observations that longer non-conjugated chain length derived from ADMET polymerization has no effect on the optical properties.

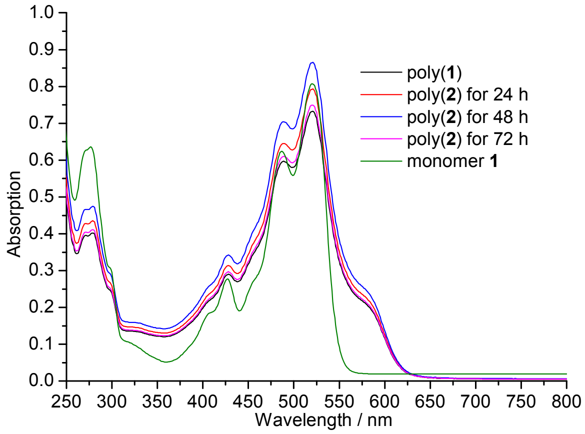


Fig. 6 UV-vis spectra of monomer and polymers measured in $CHCl_3$ at 10^{-3} mg/mL.

Thermal properties of poly(**1**) and poly(**2**) with different molecular weights were systematically investigated with TGA and DSC techniques. The decomposition temperature (T_d) for 5 % weight loss of poly(**1**) is 353 °C (Fig. 7a), which is higher than those of the previously reported PAs with a single-stranded backbone (about 200 °C),[7] suggesting the ladder-like conformation plays an important role on increasing the thermal stability of polymer. Although it suffered from the severe thermal decomposition, the residue was up to 54 %. After ADMET polymerization, the three poly(**2**) samples exhibited two stage decomposition attributed to the pyrolysis of nonconjugated main-chain and conjugated ladder-like PA block, respectively. In fact, the T_d values of poly(**2**) with different polymerization time are lower than that of poly(**1**) and changed as the following order: 300 °C (24 h) < 336 °C (48 h) < 350 °C (72 h), and the residue remained about 48 %. DSC analysis (Fig. 7b) proved that all polymers have high glass transition temperature over 175 °C, i.e. from 175 to 189 °C as the molecular weight increased, while no melting transition up to 250 °C.

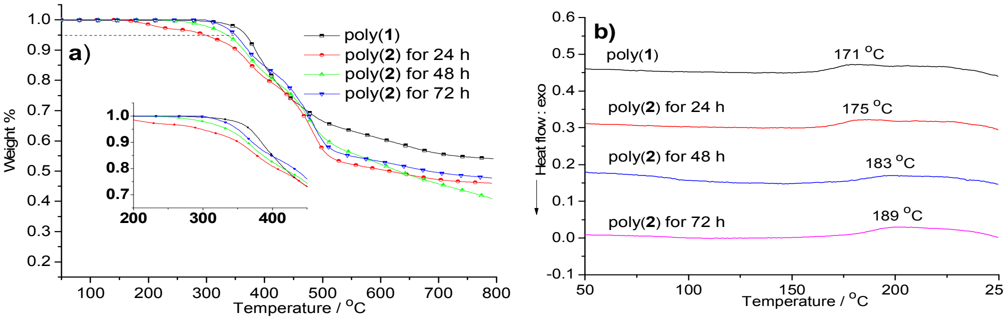


Fig. 7 TGA (a) and DSC (b) curves of polymers.

Conclusions

In this work, a new strategy was developed for the synthesis of bridge-like polymer with the nonconjugated polyolefin backbone and the pier-like unit of conjugated double-stranded PA through tandem MCP and ADMET polymerization. It was confirmed that the double-stranded poly(**1**) with telechelic alkenyl end groups, obtained from MCP of bis(4-PBI substituted-1,6-heptadiyne)-based monomer **1** by using the catalyst **Ru-III** and trifunctional *cis*-olefinic **TA**, was a useful constructing unit and can be used as a macromonomer in subsequent ADMET polymerization, yielding the resultant bridge-like poly(**2**). GPC analysis showed that the double-stranded poly(**1**) has low molecular weight of 11.2 kDa with a narrow PDI of 1.12, and bridge-like poly(**2**) has relatively high molecular weights of 25.2 - 122.4 kDa and reasonable PDI values of 1.41 - 1.75. TGA and DSC measurements for both poly(**1**) and poly(**2**) demonstrated the good thermal stabilities with T_d of above 300 °C and high T_g between 171 and 189 °C, which is important for further application in devices. The double-stranded poly(**1**) and bridge-like poly(**2**) can assemble into highly ordered ladder-like structure, and even exhibited the fence-like ribbon morphology with nearly 4 μm length for poly(**2**). In brief, this strategy would lead to the possibility of including new functionalities in polymers directly in order to fully combine the unique properties of polyolefin and PA reasonably with a view to a future modification to their properties and architectures in a straightforward approach via tandem MCP and ADMET chemistry.

Acknowledgments

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†Electronic Supplementary Information (ESI) available: Schemes, IR and NMR spectra, and TEM images. See DOI: 10.1039/c000000x/

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For the Table of contents entry

Bridge-like polymer synthesized by tandem metathesis cyclopolymerization and acyclic diene metathesis polymerization

Wei Song, Huijing Han, Jianhua Wu and Meiran Xie*

A novel bridge-like polymer with excellent thermal stability, ordered ladder-like structure, and fence-like ribbon morphology was synthesized by tandem metathesis cyclopolymerization and acyclic diene metathesis polymerization.