

Synthesis of Chiral Polyphenylenes through Bergman Cyclization of Enediynes with Pendant Chiral Amino Ester Groups*

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Abstract Chiral enediynes with pendant chiral amino ester groups are synthesized through Sonogashira reactions and subjected to thermal triggered Bergman cyclization at elevated temperatures either in bulk or in solvents to produce chiral polyphenylenes. The disappearance of enediyne monomers are evidenced by FTIR and NMR spectroscopies. The formation of polyphenylenes is further confirmed by UV-Vis and MALDI-TOF mass spectroscopies (MS). Isotope pattern analysis of the MS spectra shows that the polymers prepared in solvents are terminated by the solvent molecules, whereas the chain ends of the polymers prepared in bulk consist of considerable amount of unmasked free radicals, which is further confirmed by EPR analysis. Circular dichroism (CD) spectra of the chiral polymers show blue shifts of the Cotton peaks, indicating the occurrence of the cycloaromatization reaction. A new set of peaks mirrored at the horizontal axis show up in the long wavelength range, which are assigned to main chain chirality of the polyphenylenes.

Keywords: Enediyne; Bergman cyclization; Chiral polyphenylene; MALDI-TOF/MS.

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INTRODUCTION

Optically active polymers like proteins and DNA play important roles in biological activities. These helical polymers show characteristic functionalities such as molecular recognition ability and catalytic activity, originating from the asymmetric induction in the polymer main chains or asymmetric perturbation of side chain chromophores^[1]. The interesting optical activity of these helical biological polymers has attracted much research attention lately. A large number of artificial helical polymers and oligomers with controlled helicity have been synthesized, not only to mimic biological helices, but also to develop chiral materials with functionalities^[1–13]. Optically active polymers are synthesized either by polymerizing monomers with optically active moieties or by introducing chirality into the polymer structure in an asymmetric environment^[14, 15].

Optical activity of polymers could be ascribed to a three-diisotactic structure that arises from helical structures and/or from the excess of chiral stereogenic centres (*S*) or (*R*). In other words, chiroptical properties of the polymers could originate from the contribution of chiral monomer residues or the repeat units. Depending on the difference of inversion barriers of the helical main chains, optically active polymers fall broadly into three

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categories^[2]. Foldmers represent a class of polymers that have strong tendency to form compact structure through inter/intramolecular interactions, the conformation preference of the foldmers might be random under certain conditions^[16]. Dynamic helical polymers are the polymers with interconvertable right- and left-handed helical conformations separated by rarely occurring helical reversals. These polymers, such as polyacetylenes^[17, 18], are readily used as stimuli-responsive smart biomimetic materials that are capable of chiral discrimination or enantiomeric recognition. Static helical polymers have the highest helical inversion barriers among all the optical active polymers, they show great resistance to racemization due to the steric repulsion between the main chain substituents and/or the giantpendant groups^[19]. The stable helical conformation of these polymers endows them significant chiral recognition ability for a wide variety of racemic compounds, affording a practically useful chiral stationary phase for high performance liquid chromatography and catalysts for asymmetric catalysis^[20–23].

Bergman cyclization of enediyne compounds was first studied by Bergman *et al.* at 1973^[24]. The enediyne compounds can be transformed into highly reactive biradical intermediates under various conditions. This process leads to double strand DNA cleavage and self-programmed cell death, possessing high antibiotic activities^[25]. Bergman cyclization also plays an important role in developing polymeric materials with valuable thermal and photo properties, and the synthesis of polycyclic compounds^[26–28]. The coupling reaction between the biradical intermediates leads to a simple but effective way to synthesize poly(*p*-phenylenes)^[29–31] and other carbon-rich materials^[32]. Recently, we found that Bergman cyclization of enediyne compounds with pendant chiral groups showed almost invisible CD signals^[33]. The loss of chirality was probably due to the extremely high reaction temperature that was necessary for triggering the Bergman cyclization. Herein, we report our work on the synthesis of chiral polymers through Bergman cyclization of maleimide-containing enediyne compounds. Interestingly, we found peaks mirrored at the horizontal axis in the long wavelength range, which were assigned to main-chain chirality of the poly(*p*-phenylenes).

EXPERIMENTAL

Materials

All the reagents used in the experiments were used as received without further purification except triethylamine (Et₃N), *N,N*-dimethylformamide (DMF) and toluene which were dried over calciumhydride (CaH₂) and then distilled. Maleic anhydride and *o*-xylene are commercial products. 3,4-Dibromofuran-2,5-dione (**1**)^[38] and 5,6-dibromoisobenzofuran-1,3-dione (**6**)^[33] were synthesized according to literature procedures with minor modifications. All the Sonogashira reactions and Suzuki reactions were performed with dry Schlenk techniques under an atmosphere of nitrogen.

Characterizations

¹H-NMR (400 MHz) and ¹³C-NMR (100 MHz) spectra were recorded in chloroform-*d* (CDCl₃) on an Ultra Shield 400 spectrometer (BRUKER BIOSPIN AG, Magnet System 400 MHz/54 mm). Chemical shifts (δ) were reported in parts per million downfield from the Me₄Si resonance which was used as the internal standard. Fourier transform infrared spectra (FTIR) were recorded from KBr pallets on a Nicolet Magna 5700 FTIR spectrometer. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on a SPA409PC Thermal Analyzer. The samples were heated at a constant rate of 10 K/min from room temperature to 240 °C under N₂ flow. GPC analysis was performed with three Waters Styragel columns (pore size 10, 10², and 10³ nm), equipped with detectors: a DAWN HELEOS (14°–154°) Wyatt multiangle laser light scattering detector (He-Ne 658.0 nm), and OptilabrEX (Wyatt). THF was used as the eluent at a flow rate of 1.0 mL/min at 35 °C. Mass spectra (MS) were recorded on a Micromass LCTTM mass spectrometer using ESI method. MALDI-TOF MS measurements were performed on a Mass spectrometer 4800 plus MALDI-TOF/TOF MS Analyzer (AB Sciex, USA) equipped with a Nd:YAG laser emitting at 355 nm, operating at an accelerating voltage of 20 kV in reflection mode and linear mode. 4000 series Explorer and DATA Explorer (AB Sciex, USA) were used for data acquisition and processing. The extraction delay time used was 450 ns. All mass

spectra were collected by averaging the signals of 500 individual laser shots. Dried-droplet samples were prepared by spotting 1 μ L of a mixture of 5 μ L of CHCA as matrix (10 mg/mL in THF) and 1 μ L of polymer (10 mg/mL in THF) on the target plate. All of the mass differences discussed above were calculated by comparing the mass values of two base peaks of the most abundant isotopomers. Electron paramagnetic resonance (EPR) spectroscopy was measured with Bruker EMX-8/2.7. The spectrometer settings were: sweep width, 50 G; time constant, 163.84 ms; conversion time, 40.96 ms; scan time, 41.94 s; 1024 points; modulation amplitude, 1.00 G; and microwave power, 6.36 mW. Absorption spectra and circular dichroism spectra were measured using a Chirascan spectropolarimeter (Applied Photophysics Ltd, UK) at 25 °C in CH_2Cl_2 (cell path length of 2 mm, scanning rate of 200 nm/min, bandwidth of 2 nm, and time perpoint of 0.5 s). The steady-state fluorescence experiments were performed on a Varian Cary Eclipses fluorescence spectrometer.

Synthesis of Small Molecules

(S)-2-(3,4-dibromo-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)-4-methylpentanoic acid (**2a**)^[39]

To a solution of (*L*)-leucine (2.62 g, 20 mmol) in acetic acid (30 mL), a solution of compound 1 (5.12 g, 20 mmol) in acetic acid (30 mL) was added. The mixture was then stirred at 40 °C for 24 h. After removal of the solvent under vacuum, the residue was washed with deionized water for several times and recrystallized in water to give the title product (**2a**) as a white solid (3.8 g, 49%). ¹H-NMR (DMSO-*d*₆, δ): 13.37 (s, $-\text{COOH}$, 1H), 4.70–4.66 (m, $-\text{CH}-\text{COOH}$, 1H), 2.07–1.71 (m, $-\text{CH}_2-\text{CH}-(\text{CH}_3)_2$, 2H), 1.58–1.51 (m, $-\text{CH}_2-\text{CH}-(\text{CH}_3)_2$, 1H), 0.87–0.83 (d, $-\text{CH}-(\text{CH}_3)_2$, 6H). ¹³C-NMR (DMSO-*d*₆, δ): 170.3, 163.9, 129.5, 51.6, 24.0, 22.9, 20.6. HRMS (ESI): *m/z* calcd. for $\text{C}_{10}\text{H}_{16}\text{Br}_2\text{NO}_4$ (M-H)[−]: 365.8977; found: 365.8969. The (*R*)-enantiomer was synthesized in a similar manner with (*D*)-leucine as the starting material.

(S)-cyclohexyl 2-(3,4-dibromo-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)-4-methylpentanoate (**3a**)

Compound 2 (1.8 g, 4.9 mmol), cyclohexanol (0.98 g, 9.8 mmol), and *p*-toluenesulfonic acid (1.07 g, 6.24 mmol) were suspended into toluene (10 mL) and refluxed for 12 h. After the reaction, all volatile components were removed under vacuum to give a brown viscous liquid. The crude product was then purified through silica column chromatography (petroleum ether:ethyl acetate = 35:1) to yield a light yellow viscous liquid (1.17 g, 53%). ¹H-NMR (CDCl_3 , δ): 4.80–4.73 (m, $-\text{C}(\text{O})-\text{CH}-$ and $-\text{O}-\text{CH}-$, 2H), 2.25–2.19 (m, $-\text{CH}_2-\text{CH}-(\text{CH}_3)_2$, 1H), 1.90–1.25 (m, $-\text{CH}_2-$, 12H), 0.94–0.91 (d, $-\text{CH}-(\text{CH}_3)_2$, 6H). ¹³C-NMR (CDCl_3 , δ): 168.3, 163.6, 129.6, 74.6, 52.8, 37.1, 31.2, 25.2, 25.1, 23.3, 23.1, 20.8. HRMS (ESI): *m/z* calcd. for $\text{C}_{16}\text{H}_{21}\text{Br}_2\text{NO}_4\text{Na}$ (M+Na)⁺: 471.9740; found: 471.9735. The (*R*)-enantiomer was synthesized in a similar manner.

(S)-cyclohexyl 2-(2,5-dioxo-3,4-bis(phenylethynyl)-2,5-dihydro-1H-pyrrol-1-yl)-4-methylpentanoate (**4a**)

CuI (64.8 mg, 20 mmol, 10%), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (178.9 mg, 0.26 mmol, 7.5%) were mixed in a 50 mL Schlenk flask. Then a solution of compound 3 (1.53 g, 3.4 mmol) in degassed DMF (5 mL) and Et_3N (1 mL) were added successively under a nitrogen atmosphere. Phenylacetylene (0.88 mL, 8 mmol) was added after the flask was subjected to three freeze-pump-thaw cycles. The reaction mixture was stirred at 50 °C for 1 h. The resulting dark brown solution was partitioned with saturated brine solution and ethyl acetate, and the organic layer was dried over anhydrous MgSO_4 . After removal of the solvent under vacuum, the crude product was purified through silica column chromatography (petroleum ether:ethyl acetate = 45:1) to yield a yellow solid product (0.93 g, 55.4%). ¹H-NMR (CDCl_3 , δ): 7.65–7.63 (d, Ph-H, 4H), 7.45–7.40 (m, Ph-H, 6H), 4.83–4.80 (m, $-\text{C}(\text{O})-\text{CH}-$ and $-\text{O}-\text{CH}-$, 2H), 2.32–2.24 (m, $-\text{CH}_2-\text{CH}-(\text{CH}_3)_2$, 1H), 1.94–1.87 (m, $-\text{CH}_2-\text{CH}-(\text{CH}_3)_2$, 1H), 1.81–1.26 (m, $-\text{CH}_2-\text{CH}-(\text{CH}_3)_2$ and $-\text{CH}_2-$, 11H), 0.96–0.95 (d, $-\text{CH}-(\text{CH}_3)_2$, 6H). ¹³C-NMR (CDCl_3 , δ): 168.7, 166.6, 132.5, 130.4, 128.6, 127.7, 121.4, 110.1, 80.4, 74.3, 51.8, 37.0, 31.3, 31.2, 25.2, 25.0, 23.4, 23.4, 23.2, 20.9. MALDI-TOF (MS): *m/z* calcd. for $\text{C}_{32}\text{H}_{32}\text{NO}_4$ (M + H)⁺: 494.2326; found: 494.2740. The (*R*)-enantiomer was synthesized in a similar manner.

(S)-2-(5,6-dibromo-1,3-dioxoisindolin-2-yl)-4-methylpentanoic acid (**7**)

A solution of compound 6 (3.19 g, 10.4 mmol) in acetic acid (30 mL) was added to a solution of (*L*)-leucine

(1.37 g, 10.4 mmol) in acetic acid (30 mL), and the mixture was stirred at 60 °C for 24 h. The solvent was removed under vacuum after the reaction, and the precipitate was filtered, washed with deionized water, and dried, giving the title product (**7**) as white solid (2.1 g, 48.2%). ¹H-NMR (DMSO-d₆, δ): 8.29 (s, Ph-H, 2H), 4.77–4.73 (m, -CH-COOH, 1H), 2.16–2.09 (m, -CH₂-CH-(CH₃)₂, 1H), 1.86–1.79 (m, -CH₂-CH-(CH₃)₂, 1H), 1.50–1.40 (m, -CH₂-CH-(CH₃)₂, 1H), 0.90–0.84 (m, -CH-(CH₃)₂, 6H). ¹³C-NMR (DMSO-d₆, δ): 170.4, 165.7, 131.2, 131.0, 128.4, 50.6, 36.6, 24.4, 23.0, 20.7, HRMS (ESI): *m/z* calcd. for C₁₄H₁₂Br₂NO₄ (M-H)⁻: 415.9133; found: 415.9130.

(S)-cyclohexyl 2-(5,6-dibromo-1,3-dioxoisindolin-2-yl)-4-methylpentanoate (8)

Compound **7** (0.43 g, 1.03 mmol), cyclohexanol (0.3 g, 3 mmol), and *p*-toluenesulfonic acid (0.23 g, 1.31 mmol) were suspended into toluene (10 mL) and refluxed for 12 h. After the reaction, all the volatile components were removed under vacuum to give a brown viscous liquid. The crude product was then purified through silica column chromatography (petroleum ether:ethyl acetate = 45:1) to yield a white solid (0.31 g, 59%). ¹H-NMR (CDCl₃, δ): 8.09 (s, Ph-H, 2H), 4.90–4.85 (m, -C(O)-CH-, 1H), 4.84–4.78 (m, -O-CH-, 1H), 2.31–1.90 (m, -CH₂-CH-(CH₃)₂, 2H), 1.82–1.24 (m, CH₂-CH-(CH₃)₂ and -CH₂-, 11H), 0.93–0.90 (t, -CH-(CH₃)₂, 6H). ¹³C-NMR (CDCl₃, δ): 168.6, 165.8, 131.6, 131.5, 128.5, 74.3, 51.4, 37.1, 31.3, 31.2, 29.6, 25.2, 23.4, 23.1, 21.0. HRMS (ESI): *m/z* calcd. for C₂₀H₂₃Br₂NO₄Na (M+Na)⁺: 521.9892; found: 521.9890.

(S)-cyclohexyl 2-(1,3-dioxo-5,6-diphenylisindolin-2-yl)-4-methylpentanoate (9)

Compound **8** (500 mg, 1 mmol), phenylboronic acid (304 mg, 2.5 mmol), Pd(PPh₃)₂Cl₂ (70 mg, 0.1 mmol) were added into a 250 mL three-necked flask. Then a mixed solvent (100 mL, toluene:ethanol:water = 2:2:1) and aqueous Na₂CO₃ (626 mg, 6 mmol, degassed with N₂ for 20 min) were added successively under a nitrogen atmosphere. The reaction mixture was stirred at 30 °C for 1 h. The resulting brown solution was partitioned with saturated brine solution and ethyl acetate, and the organic layer was dried over anhydrous MgSO₄. After removal of the solvent under vacuum, the crude product was purified through silica column chromatography (petroleum ether:ethyl acetate = 35:1) to yield a light purple oil (0.93 g, 55%). ¹H-NMR (CDCl₃, δ): 7.93 (s, Ph-H, 2H), 7.29–7.24 (m, Ph-H, 6H), 7.17–7.14 (m, Ph-H, 4H), 5.00–4.95 (m, -C(O)-CH-, 1H), 4.90–4.84 (m, -O-CH-, 1H), 2.41–1.96 (m, -CH₂-CH-(CH₃)₂, 2H), 1.85–1.12 (m, -CH₂-CH-(CH₃)₂ and -CH₂-, 11H), 1.01–0.96 (d, -CH-(CH₃)₂, 6H). ¹³C-NMR (CDCl₃, δ): 169.13, 167.7, 146.8, 139.7, 130.7, 129.6, 128.2, 127.7, 125.6, 74.2, 51.1, 37.3, 31.3, 31.2, 25.2, 25.1, 23.5, 23.4, 23.2, 21.1. HRMS (ESI): *m/z* calcd. for C₃₂H₃₄NO₄ (M + H)⁺: 496.2488; found: 496.2488.

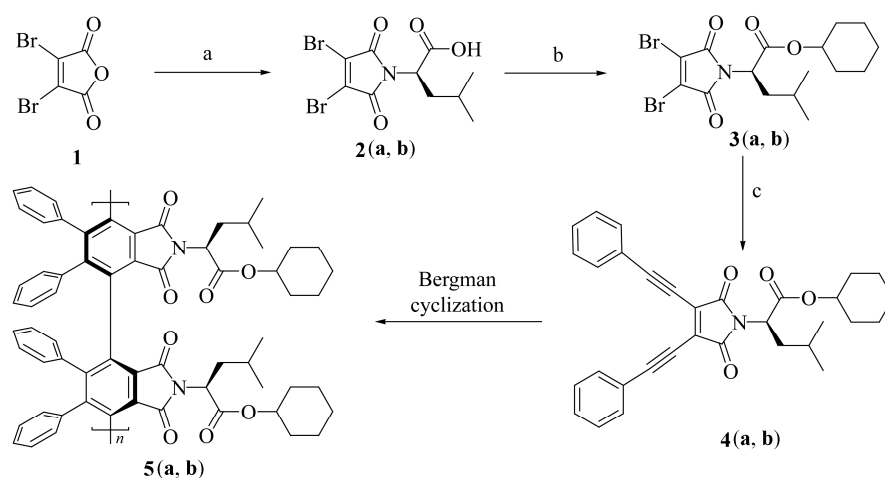
Polymerizations of Chiral Eneidyne

The Bergman cyclization polymerizations in bulk: chiral enediyne **4a** (50 mg, 1.01 mmol) was put into a 10 mL sealed tube, and then subjected to three freeze-pump-thaw cycles. The sample was later on heated at 165 °C for 8 h under vacuum to give the polymeric product in a quantitative yield. The Bergman cyclization polymerizations in solvent: **4a** (50 mg, 1.01 mmol) and anhydrous solvent (5 mL) were put into a 10 mL sealed tube. The solution was subjected to three freeze-pump-thaw cycles and then stirred at 165 °C for 8 h. The solvent was removed under vacuum to give the polymeric product in a quantitative yield.

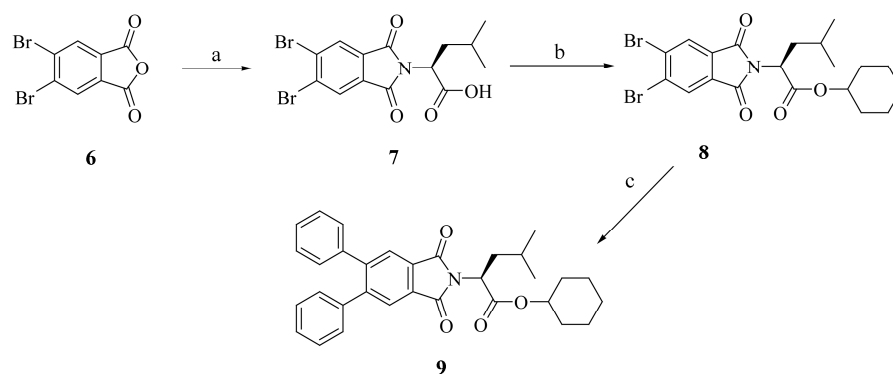
RESULTS AND DISCUSSION

Scheme 1 shows the synthetic procedure of the chiral enediyne monomers and the resulting chiral polyphenylenes. Treating 3,4-dibromomaleic anhydride (**1**) with equal amount of (*L*-)/(*D*-) leucine in acetic acid produced an imide intermediate (**2**). Subsequently esterification with cyclohexanol afforded compound **3** in high yield. Sonogashira coupling reaction between compound **3** and phenylacetylene in the presence of palladium catalyst gave the enediyne monomers **4a/4b**. A model compound (*S*-) **9** features the repeating unit of the corresponding polymers (**5a**) was also synthesized (Scheme 2). The dibromo-substituted phthalic anhydride (**6**) was synthesized from *o*-xylene in three steps according to a known procedure^[33]. Following a similar procedure as the synthesis of enediyne compound, (*L*-) leucine was firstly incorporated^[34] followed by esterification with cyclohexanol. The final product was synthesized through Suzuki coupling reaction between compound **8** and

phenylboronic acid in high yield. The structures of all these compounds were confirmed with NMR and HR-MS spectroscopies (see experimental section and SI).



Scheme 1 Synthesis of chiral enediyne compounds and Bergman cyclization: (a) (*L*)-leucine, acetic acid, 40 °C, 24 h; (b) cyclohexanol, *p*-toluenesulfonic acid, toluene, reflux, 12 h and (c) phenylacetylene, CuI, Pd(PPh₃)₂Cl₂, DMF, Et₃N, 50 °C, 1 h



Scheme 2 Synthesis of the chiral model compound: (a) (*L*)-leucine, acetic acid, 60 °C, 24 h; (b) cyclohexanol, *p*-toluenesulfonic acid, toluene, reflux, 12 h and (c) phenylboronic acid, Pd(PPh₃)₂Cl₂, toluene/ethanol/water, Na₂CO₃, 30 °C, 1 h

As proven in our previous work^[30], the embedding of the maleimide moiety in enediyne compounds significantly decreases the activation barrier of thermal Bergman cyclization. Differential scanning calorimetry (DSC) curve of enediyne compound **4** is shown in Fig. S1. A sharp endothermic peak at 123 °C and a broad exothermic peak starting at 135 °C are clearly seen, which are corresponding to the melting of the crystals and the occurrence of thermal Bergman cyclization of enediyne moiety, respectively. The peak temperature (167 °C) of the enediyne determined with DSC is comparable to that of other maleimide-based enediynes, indicating that the introduction of chiral amino ester group does not affect the activation energy of thermal Bergman cyclization. Thermal gravity analysis (TGA) curve of **4a** (Fig. S1) showed that the chiral enediyne compound is thermally stable, less than 3% weight loss was found at 250 °C under nitrogen, revealing its strong resistance to thermolysis at elevated temperatures.

Thermal triggered Bergman cyclization polymerization of these chiral enediynes was conducted under vacuum (in bulk) or under nitrogen atmosphere (in solvents). The chiral enediyne compounds were heated in a heating bath setting at 167 °C for 8 h. After worked up, brownish viscous oily polymers were obtained. Gel permeation chromatography (GPC) with multiangle laser light scattering detector showed high molecular

weights for all the resultant polymers (Table 1). For the polymers prepared in solvents, the apparent molecular weights are much lower than those made in bulk. The Bergman cyclization polymerizations might be terminated by the solvent molecules because of their hydrogen-donor abilities for the highly reactive biradicals generated through Bergman cyclization, leading to the termination of the propagating chains.

Table 1. GPC analysis of the chiral polyphenylenes prepared in different mediums ^a

Reaction medium	$M_n (\times 10^3 \text{ Da})$	$M_w (\times 10^3 \text{ Da})$	PDI
bulk	248	283	1.14
Toluene	15	34	2.20
<i>o</i> -Xylene	21	32	1.52
DMF	84	124	1.47
DMAC	106	164	1.54
<i>o</i> -dichlorobenzene	51	80	1.57
DMSO	43	92	2.16

^a Molecular weights and PDI were measured in THF by GPC with multiangle laser light scattering detector

The occurrence of Bergman cyclization was confirmed by FTIR spectroscopy analysis. Figure 1 shows a comparison of FTIR spectra of enediyne precursor (**4a**) and corresponding polymer (**5a**) prepared in bulk. The stretching band of the triple bond at 2198 cm^{-1} in **4a** is almost disappeared in **5a**, which is the direct evidence for the reaction of the alkynyl groups during heating. NMR spectroscopy was also used to confirm the formation of the conjugated polymers through Bergman cyclization polymerization. Figure 2 shows the ^1H - and ^{13}C -NMR spectra of a representative enediyne compound **4a** and the corresponding polymer. The peaks associated with the aromatic protons at $\delta = 7.40\text{--}7.65$, the protons on the tertiary carbon at $\delta = 4.80\text{--}4.83$, the methylene protons at $\delta = 1.26\text{--}1.94$ and the methyl protons at $\delta = 0.95\text{--}0.96$ are all broadened after the polymerization, which directly evidence the formation of a rigid polymer backbone. The disappearance of triple bonds was also verified *via* ^{13}C -NMR analysis. After Bergman cyclization, both characteristic peaks of the alkynyl group at $\delta = 80.4$ and 110.1 were completely gone, whereas a broad peak around $\delta = 130$ showed up, indicative of the formation of the polyphenylene backbone. Meanwhile, peaks at $\delta = 18\text{--}32$ corresponding to the methylene carbons are also broadened. The signal broadening in the NMR spectra might also be caused by the presence of paramagnetic residues. As demonstrated by Smith's work^[35] and our early results^[30], unmasked free radicals were found in the Bergman cyclization of different kinds of enediyne compounds. The existence of free radicals in the polymer is directly evidenced by electron paramagnetic resonance (EPR) spectroscopy. As shown in Fig. 3, an intense peak at around 3518 gauss was detected for polymer **5a**. The calculated g-value for this peak is 2.0024, which indicates the presence of carbon-centered radicals in the sample^[36].

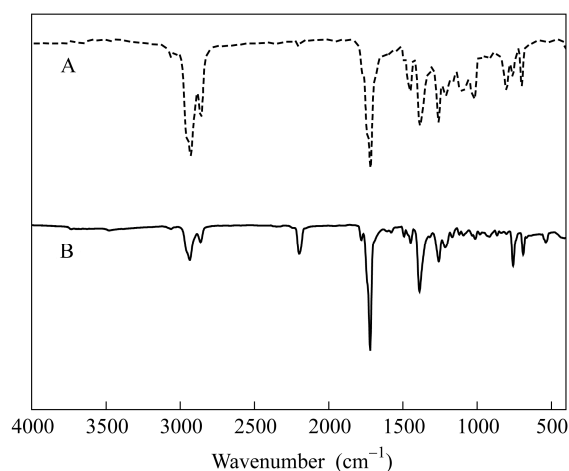


Fig. 1 FTIR spectra of **4a** (B) and **5a** (A)

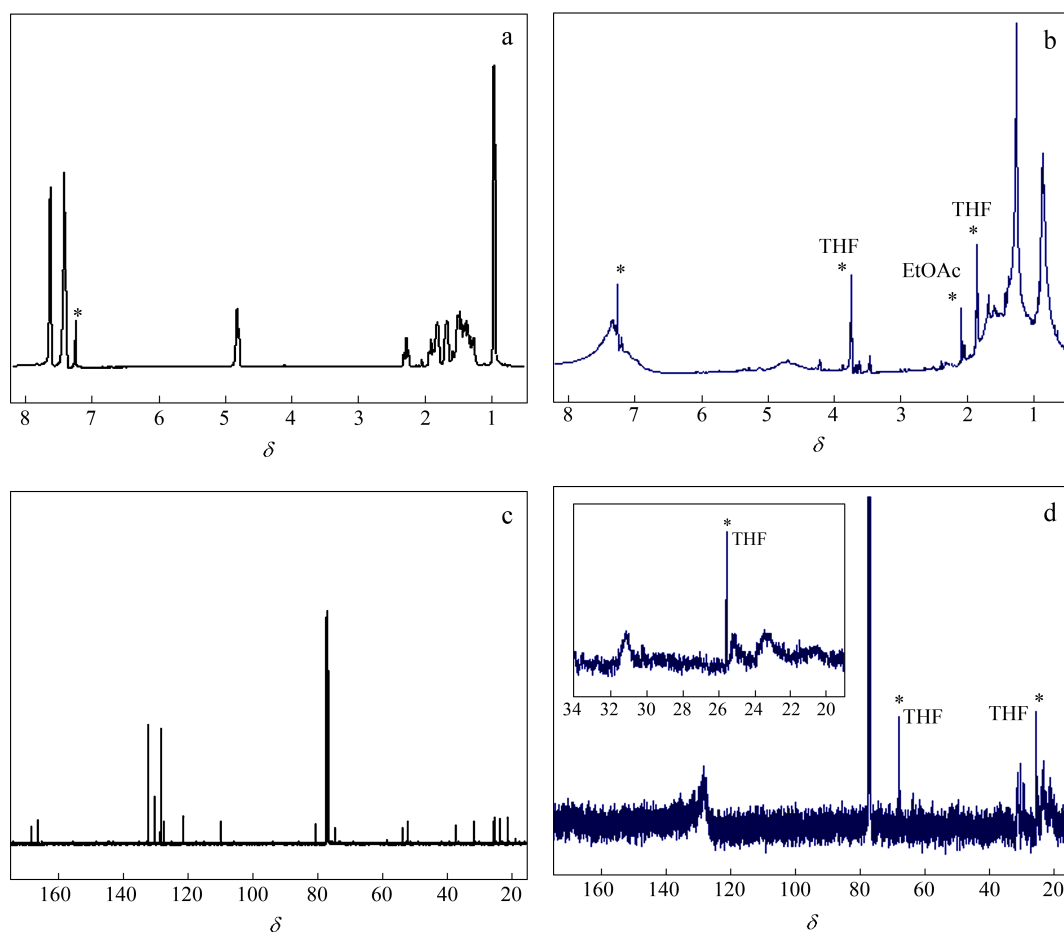


Fig. 2 ^1H - and ^{13}C -NMR spectra of **4a** (a, c) and **5a** (b, d)

Asterisks indicate the solvent peaks. The inset shows the partial amplification of a selected region of the spectrum.

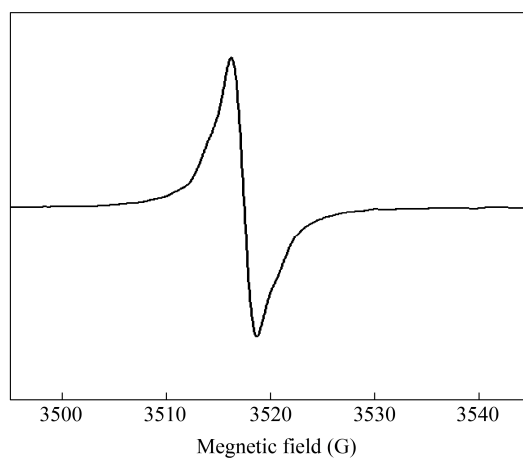


Fig. 3 EPR spectrum of **5a** in chloroform

MALDI-TOF mass spectrometry has been proven to be one of the most informative tools to confirm the structure of the proposed polymers. As shown in Fig. 4, several sets of peaks are observed for oligomer part of

the polymer **5a**, and regular differences between the intense peak series of **5a** are clearly seen. These peaks feature an interval of 493.25, which is consistent with the calculated m/z value of a monomer unit (493.23). The observed peaks at $m/z = 1502.71$, 1995.96, 2490.19, 2983.43 represent the mass of $(3M + Na)^+$, $(4M + Na)^+$, $(5M + Na)^+$, and $(6M + Na)^+$, respectively. In linear mode MALDI-TOF spectrum (inset of Fig. 4), peaks corresponding to the polymer with degree of polymerization up to 13 are observed. The isotope patterns of the m/z peaks play an important role in end-group analysis. Figure 5 shows the enlarged isotope pattern of the oligomer $(3M + Na)^+$. Interestingly, the biradicals are not completely capped by external hydrogen donors, 81% polymers are present in the form of stable biradicals in **5a** according to the fitting value of isotope patterns. This result is consistent with the EPR result and the line broadening in NMR. The MALDI-TOF mass spectra of polymers generated from different solvents are listed in Fig. S2. End-group analysis for all the polymers prepared in solvents shows that the terminals of the polymer chains have been capped by the hydrogen donor solvents. Two series of peaks are observed for **5a** prepared both in toluene and *o*-xylene (Fig. S2 A and B), both sets of peaks feature an interval of 493.26 (m/z), which matches the calculated m/z value of a monomer unit (493.23). Regular differences of 90.03 and 104.04 between every two intense peak series of **5a** are also observed, which correspond to the addition of a toluene molecule and an *o*-xylene molecule to the chain end, respectively. This result unambiguously showed that the propagating chains were terminated by trapping solvent molecules. The chain terminations by solvent molecules were also observed in DMF, DMAC and DMSO. The peaks corresponding to the addition of solvent fragments to the polymers chains were observed in their MALDI-TOF mass spectra (Fig. S2 C, D and F). In the mass spectra of the polymer prepared in *o*-dichlorobenzene (Fig. S2 E), no peak corresponding to the addition of solvent molecule was determined, showing the low hydrogen donor ability of *o*-dichlorobenzene.

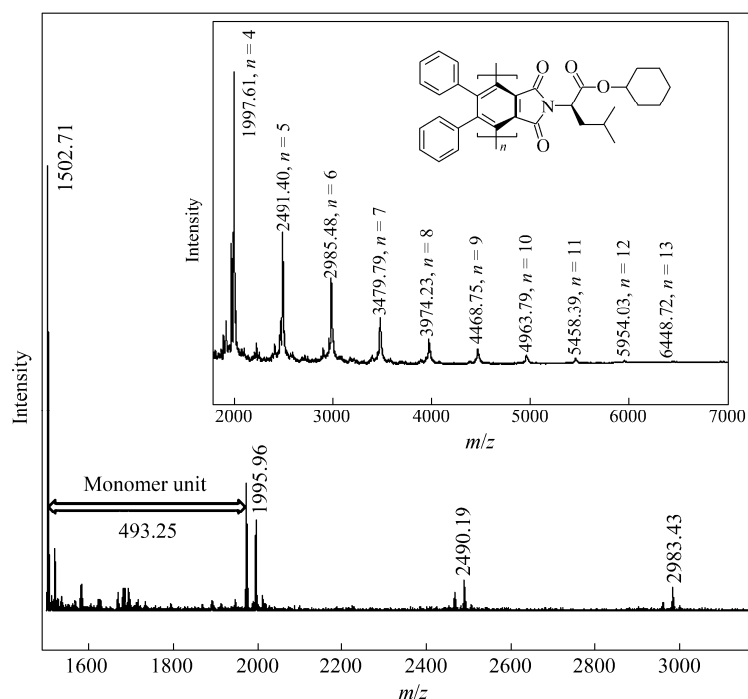


Fig. 4 MALDI-TOF mass spectrum (reflector mode) of polymer **5a** prepared in bulk. The inset shows the linear mode MALDI-TOF mass spectrum of the same sample.

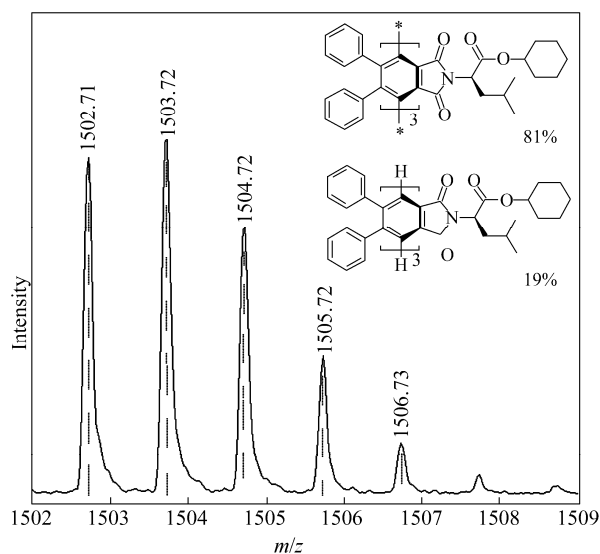


Fig. 5 Selected isotope patterns in the MALDI-TOF mass spectra (enlarged view of the data shown in Fig. 4) for **5a** (Solid line: experimental data; Dot line: calculated data)

Figure 6 shows the UV-Vis absorption and CD spectra of the monomers **4a**, **4b**, polymers **5a**, **5b** prepared in bulk and the model compound (*S*-) **9** in CH_2Cl_2 solution. For the (*S*-) monomer **4a**, the UV-Vis absorption shows two well-defined peaks at 265 nm and 420 nm, corresponding to $\pi\text{-}\pi^*$ transition of aromatic rings and $\pi\text{-}\pi^*$ transition in the enediyne moiety. CD spectrum of **4a** shows a weak negative Cotton effect at 375 nm and a strong positive one at 315 nm, mainly attributed to the twisting of the conjugated system due to the presence of chiral pendant group and the $n\text{-}\pi^*$ transition of the carbonyl group in the N-substituent. The CD spectrum of **4b** mirrored that of **4a** at the horizontal axis as they are enantiomers. After Bergman cyclization polymerization, the features in UV-Vis spectra of enediyne compound disappeared, and a broad peak tailing up to 500 nm showed up, indicating the formation of conjugated systems after Bergman cyclization polymerization^[31], which was also evidenced with the bathochromic effect of the polymers in the photoluminescence (PL) spectrum (Fig. S15)^[37]. The CD spectra of **5a** and **5b** showed blue shift of the peaks that appear in the spectra of **4a** and **4b**. Meanwhile, weak but broad Cotton peaks mirrored at the horizontal axis show up in the longer wavelength range. By comparison with the CD spectrum of the model compound (**9**), we speculated that the blue shift of Cotton peaks after polymerization was due to the narrowing of the π -conjugation system after the diphenylacetynyl-substituted maleimide was transformed into diphenyl-substituted phthalimide. The two phenyl groups were forced to twist against each other due to the steric repulsive effect, weakening their π -conjugation with the main polymer chain. The absorption band around 372 nm of the polymer is due to the $\pi\text{-}\pi^*$ transition of conjugated main-chain axis. Hence, the CD couplet zero crossing at 372 nm was mainly due to the exciton coupling of neighboring phthalimide chromophores. The positive CD couplet at 372 nm observed in **5a** suggested the formation of a right-handed chiral organization. This Cotton effect appeared in polymer was thus assigned to main chain chirality of the polyphenylene backbone. In comparison, the polymers prepared in solvents showed no Cotton effects at long wavelength region (Fig. S16), indicating that the chiral induction from the pendant leucine group was disturbed probably by the solvent molecules.

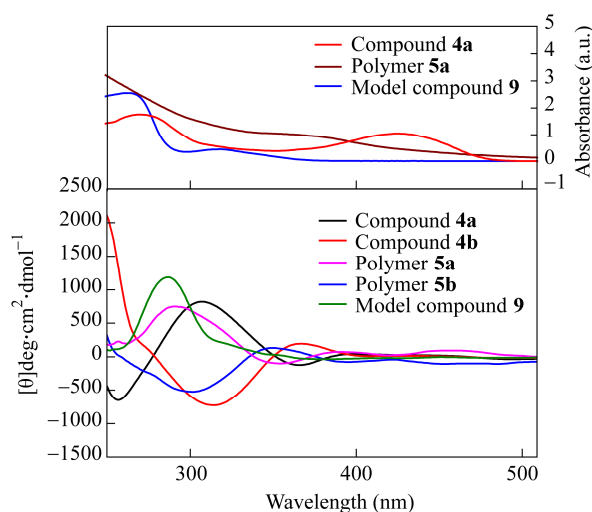


Fig. 6 UV-Vis and CD spectra of enediyne compounds, polymers and model compound (10^{-3} mol/L in CH_2Cl_2)

CONCLUSIONS

Chiral enediynes with relatively high reactivity were synthesized, which permitted us to prepare chiral conjugated polyphenylenes *via* Bergman cyclization in bulk and in several kinds of solvents under moderate temperatures. IR and NMR spectra showed disappearance of acetylene units after Bergman cyclization. The structure of the polymer was confirmed by MALDI-TOF spectroscopy. End-group analysis showed that more than 80% of radicals are persisted after the polymerization in bulk, which was also confirmed by EPR spectroscopy analysis. While the polymers prepared in solvents were mainly terminated by the solvent molecules. UV-Vis spectroscopy confirmed the formation of conjugated backbones, CD spectra showed blue shift of two Cotton peaks due to the narrowing of π -conjugated system after the cycloaromatization. Interestingly, a new set of peaks mirrored at the horizontal axis showed up in the long wavelength range. After comparison with the CD spectrum of a model compound that features the structure of the repeating units in the polymers, the newly appeared Cotton peaks are assigned to the main-chain chirality. By utilizing thermal Bergman cyclization, static helical polymers can be obtained in a simple way, which can be further used in chiral separation and asymmetric catalysis.

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