Formation of Conjugated Polynaphthalene via Bergman Cyclization

CHANGCHENG MIAO, JIAN ZHI, SHIYUAN SUN, XI YANG, AIGUO HU

Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

Received 6 January 2010; accepted 23 February 2010
DOI: 10.1002/pola.23988
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of enediyne containing chiral phthalimides were synthesized through Sonogashira coupling reactions. These enediynes were then subjected to thermal Bergman cyclization under vacuum. Polynaphthalenes with pendant chiral groups were obtained and characterized using GPC, IR spectroscopy, NMR spectroscopy, UV–Vis spectroscopy, and photoluminescence analysis. Under properly optimized conditions, the chirality of chiral directing group was maintained according to CD spectra of final products. After removal of chiral directing groups, weak CD signals representative of main chain chirality were visible. Further modification of the structure of the enediyne compounds will facilitate the synthesis of chiral polynaphthalene through this rather simple way. Extension of the Bergman cyclization to polymer chemistry is promising in the construction of novel polymers with rigid polyarene backbones. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2187–2193, 2010

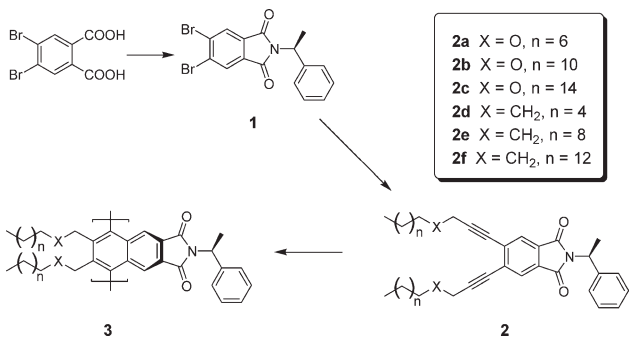
KEYWORDS: Bergman cyclization; chiral; conjugated polymers; differential scanning calorimetry (DSC); luminescence; oligomers; polynaphthalene

INTRODUCTION Conjugated polymers are a class of polymers with unique thermal, optical, and electrical properties.[1–7] Several family of conjugated polymers have been developed since the concept of conducting polymers was presented in the 1970s, including, poly(*para*-phenylene) (PPP), polyacetylene (PA), poly(phenylenevinylene) (PPV), poly(phenyleneethynylene) (PPE), polypyrrole (PPy), and polythiophene (PT). Because of the high rigidity and crystallinity of the backbone, unsubstituted conjugated polymers are typically insoluble, intractable, and infusible. Long alkyl pendant moieties were introduced in conjugated polymers to improve the solubility and modify the electrical and optical properties of these rodlike polymers. Conjugated polymers are typically synthesized via transition metal-catalyzed cross coupling reaction or coordination polymerization.[8–10] The residual metal complexes in the final polymers, however, seriously affect their electrical properties for wide applications in batteries, capacitors, light-emitting diodes, and transistors. Development of new synthetic strategies for metal-free conjugated polymers is challenging.

Polynaphthalenes (PNs) contain unique structural features compared with other conjugated polymers. Introduction of chiral binaphthyl moieties into the main chain offers a potential route to get circularly polarized emission. PNs with helical chirality showed great resistance to racemization due to the steric repulsion of 8- and 8′-hydrogens,[11] which could be useful for asymmetric catalysis and enantioselective separation.[12–16] PNs have been synthesized with different techniques including plasma polymerization of naphthalenes,[17] Suzuki coupling,[18] and oxidative coupling of 2,3-naphthadiol derivatives.[19,20] The structural viability, however, is limited due to the nature of these coupling reactions. Herein, we wish to report our work using Bergman cyclization polymerization to construct PNs.

Bergman cyclization of enediyne compounds was first studied by Bergman three decades ago.[21] The cytotoxicity of diradicals generated from Bergman cyclization has initiated a flurry of activities in pharmaceutical research and organic synthesis.[22–26] Bergman cyclization has also been used in synthesis of polyaryl compounds for precursors of glassy carbon,[27–29] surface functionalization of multilayer fullerenes,[30] initiating free radical polymerization of functionalized olefins,[31] and reaction probe for mechanical chemistry in a swelling polymeric network.[32] We noticed that PN could be synthesized from Bergman cyclization of dialkynylbenzene.[33] Because of the high rigidity and crystallinity of the backbone, most PN synthesized through this method are difficult to melt and insoluble in common solvents. A polymerizable surfactant type enediyne was developed recently to run Bergman cyclization inside mesoporous silica channels and ill-defined PN was obtained according to IR, UV–Vis, and photoluminescence (PL).[34] In this work, we introduced long alkyl substituents to overcome the solubility problem of final PNs prepared through Bergman cyclization, and a chiral directing

Correspondence to: A. Hu (E-mail: hagmhsn@ecust.edu.cn)
Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 2187–2193 (2010)



SCHEME 1 Synthetic route for polynaphthalenes.

group to drive the coupling of diradical asymmetrically to form soluble chiral PNs.

RESULTS AND DISCUSSION

Chiral imide (**1**) was synthesized through treatment of 4,5-dibromophthalic acid with a chiral amine, (R)-(+)-α-methylbenylamine, subsequent Sonogashira coupling with a variety of terminal alkynes gave enediyne containing chiral imides (**2**) in good to high yield (Scheme 1). The optical rotation and circular dichroism (CD) spectra of these imides are similar to each other as the alkyl functional groups are far away from chiral center (Fig. 1). IR spectra showed weak bands around 2220 cm^{-1} and ^{13}C NMR spectra showed two set of peaks around 85 ppm and 95 ppm as characteristic of alkynyl groups. Differential scanning calorimertry (Fig. 2) of **2a–c** showed one melting peak at low temperature and one exothermal peak starting at 190 °C, which corresponds to thermal Bergman cyclization of enediyne moiety. The onset temperatures of these enediynes are lower than their dialkynylbenzene analogous.[35,36] The electron withdrawing effect of two carbonyl groups is believed to be the key factor for lowering the energy barrier for Bergman cyclization. **2d–e** exhibited even lower onset temperature.

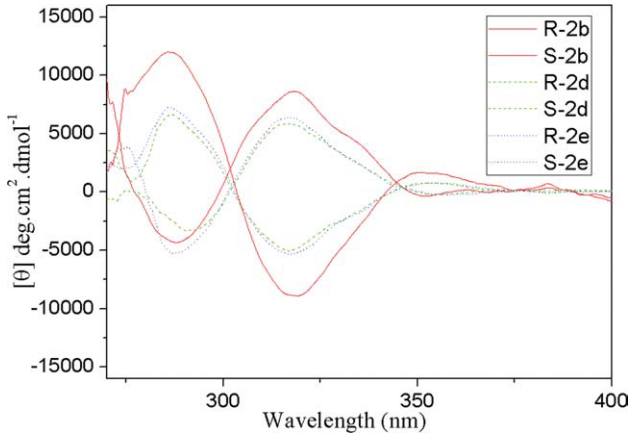


FIGURE 1 Representative CD spectra of enediyne compounds: **2b** (Red, solid), **2d** (green, dash), **2e** (blue, dot), 10^{-4} mol/L in CH_2Cl_2.

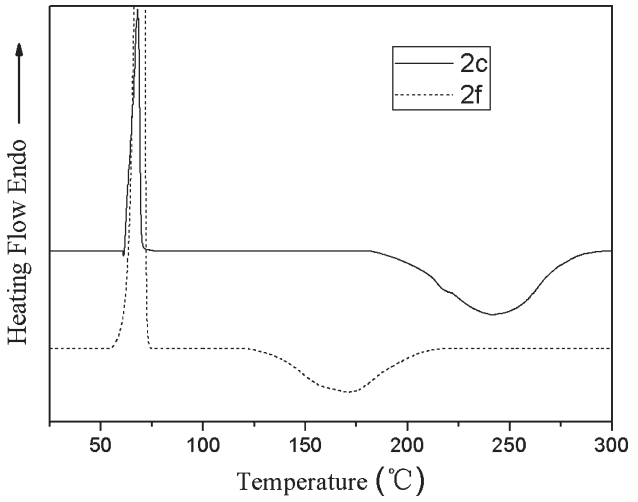


FIGURE 2 Representative DSC curves of enediyne compounds.

Thermal Bergman cyclization of these enediyne-containing imides was conducted in bulk under vaccum to eliminate any species that could quench radicals. After heating in a bath of boiling diphenyl ether (259 °C) for several hours, a brownish viscous oil was obtained in quantitative yield. Gel permeation chromatography (GPC) showed narrow molecular weights distributions. The number average molecular weight estimated through GPC using polystyrene standards were between 1500 and 5000, the corresponding degrees of polymerization (DP) were thus calculated to be between 4 and 10. It should be noted that these oligomers have more compact structures and smaller hydrodynamic volumes compared with polystyrene. Molecular weights and DPs should thus to be higher than the values obtained from GPC analysis. Steric hindrance of the alkyl groups at the 2,3-positions of the newly formed naphthalene moieties seems to suppress the DP. Nevertheless, these DPs are already very close to effective conjugation length of PNs[5] to be useful for luminencense applications (Table 1).

Occurrence of Bergman cyclization was confirmed with IR spectra analysis. Figure 3 shows a comparison of IR spectra of representative enediyne precursors and corresponding PN. The stretching band of C≡C at 2225 cm^{-1} in **2f** is absent in **3f** and is evidence for the reaction of the alkynyl groups after thermal Bergman cyclization. The disappearance of triple bonds could also be revealed via ^{13}C NMR analysis. After Bergman cyclization, both characteristic peaks of the alkynyl group at 83 ppm and 94 ppm were completely gone, whereas multiple peaks showed up to between 120 ppm and 150 ppm (Fig. 4) indicative of formation of the naphthalene moiety.

TABLE 1 GPC Analysis of Polyimides Measured in THF with a PS Calibration

	3a	3b	3c	3d	3e	3f
M_w	4849	4123	4226	1588	2079	2843
PDI	1.46	1.19	1.37	1.26	1.17	1.19

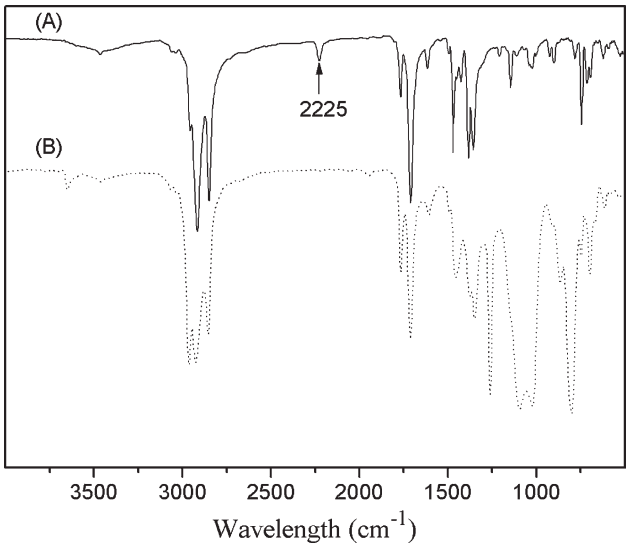


FIGURE 3 Comparison of FTIR spectra of (A) **2f** and (B) **3f**.

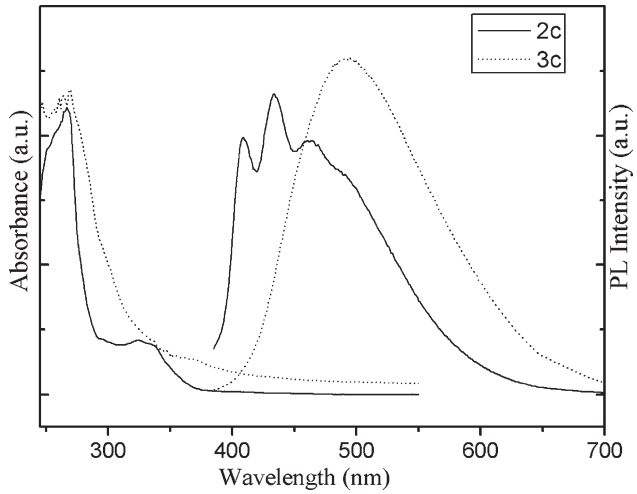


FIGURE 5 UV–Vis absorbance and photoluminescence spectra of enediyne precursors **2c** (solid line), PN **3c** (dot line), 10^{-4} mol/L in CH_2Cl_2.

Formation of a conjugated polymer was also confirmed via UV–Vis and PL spectroscopies. As shown in Figures 5 and 6, enediyne precursors **2** showed maximum absorbance at around 260 nm, and a shoulder peak at 320 nm, whereas after Bergman cyclization, a broad featureless peak showed up. In PL spectra, enediynes **2a–c** showed PL in violet-blue region with three peaks at 405, 430, and 455 nm (**2d–f** showed broad peaks centraled at 450 nm). After Bergman cyclization, all the PL red-shifted to blue-green region with a broad peak tailing up to 650 nm. The bathochromic effect has been used to relate the formation of conjugated polymer and adsorbance.[37]

The chiral α-methylbenzylamine was initially installed in enediyne to direct the coupling of diradicals generated through Bergman cyclization. However, after thermal Bergman cyclization at 259 °C, only featureless CD spectra were obtained for all the PNs, indicative of a racemic mixture. The thermal racemization of binaphthyl is reported to be relatively fast at high temperature (220 °C, $t_{1/2} \sim 40$ min).[38] The loss of asymmetric control during coupling of diradicals could thus be rationalized to be due to the harsh reaction condition, under which the chiral center of α-methylbenzylamine could also be unstable.

It is difficult to conduct Bergman cyclization of **2a–c** under milder conditions, as we found that thermal coupling of these compound were sluggish below 200 °C. Nonetheless, changing the alkyloxypropargyl to simple long alkynyl chains, e.g., **2d–f** resulted in dramatic drop of the onset temperature of Bergman cyclization for an unclear reason. Thermal Bergman cyclizations of **2d–f** were conducted in a bath of boiling *N,N*-dimethylacetamide (166 °C), viscous oils were obtained after several hours heating, which were revealed as PNs similar to those obtained under high temperature according to GPC analysis. As shown in Figure 7, almost mirror-image CD spectral patterns were observed between the polymers obtained from ***R*-2f** and ***S*-2f**. To differentiate the

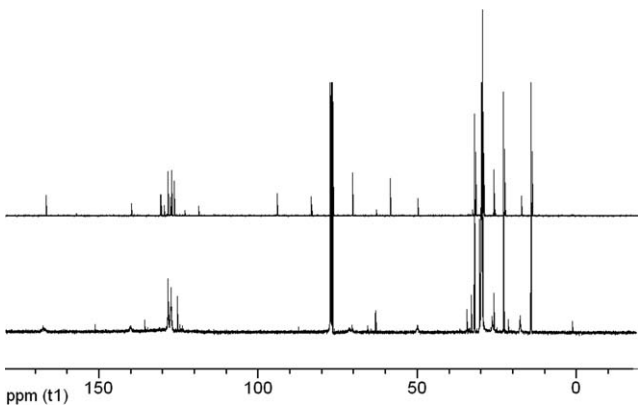


FIGURE 4 Comparison of ^{13}C NMR spectra of (top) **2c** and (bottom) **3c**.

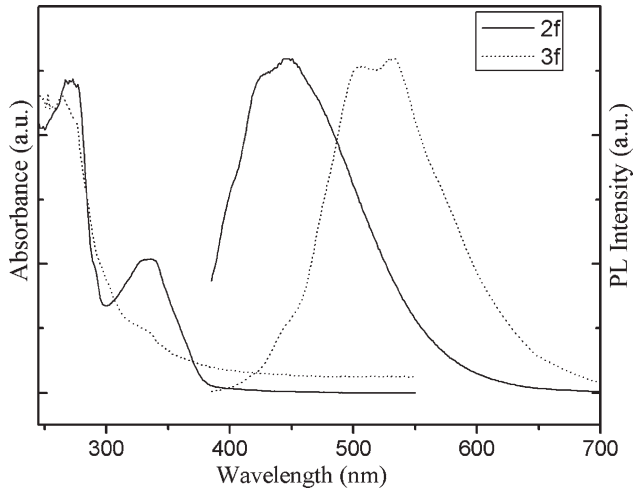


FIGURE 6 UV–Vis absorbance and photoluminescence spectra of enediyne precursors **2f** (solid line), PN **3f** (dot line), 10^{-4} mol/L in CH_2Cl_2.

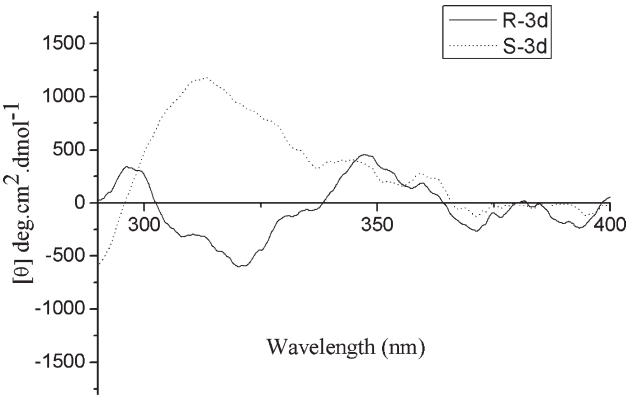


FIGURE 7 CD spectra of **3d** obtained from **R-2d** (solid line) **3d** obtained from **S-2d** (dot line), 10^{-4} mol/L in THF.

contribution of side chain chirality, polymers were treated with hydrazine in a refluxing ethanol/THF solution for several hours and purified via silica gel chromatography. According to NMR analysis, the chiral directing group α-methylbenylamine was completely removed from PN main chain, and phthalimide moieties were successfully converted to dihydrophthalazinedione as evidenced by the disappearance of methine proton at 5.53 ppm and appearance of azinedione protons at 8.32 ppm. In CD spectra, the peak corresponding to chiral imide unit was completely gone, whereas a weak peak at 270 nm were still visible, which could be rationalized as main chain chirality[20] of PNs.

EXPERIMENTAL

Materials

Triethylamine (TEA) was distilled over calcium hydride (CaH_2) and *N,N*-dimethylformamide was distilled over calcium hydride (CaH_2) under reduced pressure before use. Other reagents were commercial chemicals and used as received. All the Sonogashira reactions were performed with dry Schlenk techniques under an atmosphere of nitrogen unless otherwise noted. All the Bergman cyclization (BC) reactions were performed under vacuum in a sealed glass tube with refluxing fluid outside as heating medium. 4,5-Dibromo-*o*-xylene[39] and 4,5-dibromo-*o*-phthalic acid[40] are known compounds. 2-Benzyl-5,6-dibromoisoindoline-1,3-dione[41] and long chain alkynes were synthesized according to literature procedures[42,43] with minor modifications.

Characterization

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in chloroform-*d* ($CDCl_3$) on an Ultra Shield 400 spectrometer (BRUKER BIOSPIN AG, Magnet System 400 MHz/54 mm). Differential scanning calorimetry (DSC) was measured with a Pyris Diamond thermal analysis work station equipped with a model 822e DSC module under a constant nitrogen flow. The apparent M_n, M_w, and PDI were determined by gel permeation chromatography (GPC) on a WATERS 1515 equipped with a series of PS gel columns, using THF as an eluent at 40 °C with a PS calibration. Fourier transform infrared analysis (FTIR) was recorded from KBr pallets on a Nicolet Magna 5700 FTIR spectrometer. UV analyses were performed on a UNICO UV-21-2 PCS spectrometer from CH_2Cl_2 solutions at room temperature. Fluorescence spectra were obtained by Fluorolog-3-p (Jobin Yvon Inc. Corp. France) in CH_2Cl_2. Mass spectra were obtained with a Micromass LCTTM mass spectrometer using ESI method. All circular dichroism spectra were obtained with J-810 (JASCO Corp.) using CH_2Cl_2 or THF as solvent. Optical rotations were measured on Autopol III Automatic polarimeter/double wavelengths (Rodulph research analytical) using CH_2Cl_2 as solvent. Element analysis data were obtained with Vario EL III (Elementar Analysensysteme Gmbh. German).

Synthesis

2-Benzyl-5,6-dibromoisoindoline-1,3-dione

A solution of 4,5-dibromo-*o*-phthalic acid (1.29 g, 4 mmol) and acetic anhydride (10 mL) was heated to flux for 4 h.[38] The solvent was removed under high vacuum to afford corresponding anhydride as a colorless powder. The intermediate was mixed with benzylamine (0.43 g, 4 mmol) in acetic acid (10 mL) and heated to reflux for 12 h. The crude compound was recrystallized from acetic acid (1.11 g, 70%). ^{1}H NMR ($CDCl_3$, ppm): 8.07 (s, Ph-*H*, 2H), 7.41–7.27 (m, Ph-*H*, 5H), 4.82 (s, —CH_2—, 2H).

5,6-Dibromo-2-((R)-1-phenylethyl)isoindoline-1,3-dione (R-1)

This compound was synthesized similar to the aforementioned compound, 98%. ^{1}H NMR ($CDCl_3$, ppm): 8.03 (s, Ph-*H*, 2H), 7.47–7.28 (m, Ph-*H*, 5H), 5.53 (m, CH_3—C*H*—, 1H), 1.91 (d, CH_3—CH—, 2H). ^{13}C NMR ($CDCl_3$, ppm): 166.1, 139.7, 131.6, 131.2, 128.5, 128.3, 127.9, 127.4, 50.2, 17.4. MS: *m/z* calcd. for $C_{16}H_{11}Br_2NO_2$: 408.9136; found: 408.9118. Elem. Anal.: calcd. for $C_{16}H_{11}Br_2NO_2$: C, 46.98; H, 2.71; N, 3.42. Found: C, 47.05; H, 2.78; N, 3.12. ***S*-1** was synthesized in the same manner.

General Procedure for Reaction of Propargyl Alcohol with Alkylbromide

1-(Prop-2-ynyloxy)hexadecane[39]

60 wt % of NaH (1.37 g, 68.7 mmol) was added to a solution of propargyl alcohol (1.0 mL, 17.2 mmol) and hexadecyl bromide (3.5 g, 11.5 mmol) in DMF at 0 °C. After stirring for 3 h, saturated NH_4Cl (17 mL) was added to the reaction mixture. The resulting mixture was poured into water and extracted with diethyl ether. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and filtered. The filtrate was evaporated in *vacuo* to give the crude product, which was purified by silica gel column chromatography. Elution with petroleum ether (PE) to afford the title compound (2.6 g, 81%) as a colorless oil. ^{1}H NMR ($CDCl_3$, ppm): 4.12 (s, —C≡C—CH_2—O—, 2H), 3.50 (t, —CH_2—CH_2—O—, 2H), 2.40 (s, *H*—C≡C—CH_2—, 1H), 1.59 (t, —CH_2—CH_2—O—, 2H), 1.33 (m, CH3—CH_2—, 2H), 1.25 (m, —CH_2—CH_2—CH_2—, 24H), 0.88 (t, CH_3—CH_2—, 3H).

1-(Prop-2-ynyloxy)dodecane

Colorless oil, 78%. ^{1}H NMR ($CDCl_3$, ppm): 4.11 (s, —C≡C—CH_2—O—, 2H), 3.50 (t, —CH_2—CH_2—O—, 2H), 2.39 (s, *H*—C≡C—CH_2—, 1H), 1.58 (t, —CH_2—CH_2—O—, 2H), 1.33 (m, CH3—CH_2—, 2H), 1.25 (m, —CH_2—CH_2—CH_2—, 16H), 0.87 (t, CH_3—CH_2—, 3H).

1-(Prop-2-ynyloxy)octane

Colorless oil, 61%. ^{1}H NMR ($CDCl_3$, ppm): 4.10 (s, —C≡C—CH_2—O—, 2H), 3.49 (t, —CH_2—CH_2—O—, 2H), 2.38 (s, *H*—C≡C—CH_2—, 1H), 1.57 (t, —CH_2—CH_2—O—, 2H), 1.33 (m, CH3—CH_2—, 2H), 1.26 (m, —CH_2—CH_2—CH_2—, 8H), 0.86 (t, CH_3—CH_2—, 3H).

General Procedure for Reaction of Trimethylsilylacetylene with Alkylbromide

***Trimethyl(octadec-1-ynyl)silane*[40]**

To a stirred solution of (trimethylsilyl)acetylene (5 mL, 35.2 mmol) in dry THF (35 mL), *n*-BuLi (2.5*M*, 29.3 mmol) in dry hexane (11.7 mL) was added dropwise while keeping the temperature approximately at −78 °C. After 45 min, HMPA (11.7 mL) and hexadecyl bromide (3.58 g, 11.7 mmol) were added dropwise to the reaction mixture while maintaining the temperature approximately at −78 °C. After 24 h at room temperature, the reaction mixture was worked up by pouring into a large volume of water and extracting with diethyl ether. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The mixture was filtered, evaporated, and purified by silica gel column chromatography. Elution with petroleum ether afforded the title compound (3.20 g, 84%) as a colorless oil. ^{1}H NMR ($CDCl_3$, ppm): 2.21 (t, —C≡C—CH_2—CH_2—, 2H), 1.52 (m, —C≡C—CH_2—CH_2—, 2H), 1.36 (m, CH_3—CH_2—, 2H), 1.25 (m, —CH_2—CH_2—CH_2—, 24H), 0.88 (t, CH_3—CH_2—, 3H), 0.14 (s, Si—CH_3, 9H).

Trimethyl(tetradec-1-ynyl)silane

Colorless oil, 84%. ^{1}H NMR ($CDCl_3$, ppm): 2.20 (t, —C≡C—CH_2—CH_2—, 2H), 1.52 (m, —C≡C—CH_2—CH_2—, 2H), 1.36 (m, CH_3—CH_2—, 2H), 1.26 (m, —CH_2—CH_2—CH_2—, 16H), 0.88 (t, CH_3—CH_2—, 3H), 0.14 (s, Si—CH_3, 9H).

(Dec-1-ynyl)trimethylsilane

Colorless oil, 83%. ^{1}H NMR ($CDCl_3$, ppm): 2.20 (t, —C≡C—CH_2—CH_2—, 2H), 1.51 (m, —C≡C—CH_2—CH_2—, 2H), 1.37 (m, CH_3—CH_2—, 2H), 1.28 (m, —CH_2—CH_2—CH_2—, 8H), 0.88 (t, CH_3—CH_2—, 3H), 0.14 (s, Si—CH_3, 9H).

General Procedure for Removal of Trimethylsilyl Group

Octadec-1-yne

A mixture of trimethyl(octadec-1-ynyl)silane (2.00 g, 6.2 mmol) in 20 mL of dry THF was stirred at 0 °C, and then tetrabutylammonium fluoride (3.24 g) in THF (12 mL) was added dropwise to the stirred solution. After 2 h, the reaction mixture was quenched with a 1 M HCl solution and extracted with diethyl ether. The organic extracts were dried over anhydrous $MgSO_4$ and concentrated in *vacuo* to afford the title compound as a colorless oil (1.56 g, 100%). ^{1}H NMR ($CDCl_3$, ppm): 2.18 (m, —C≡C—CH_2—CH_2—, 2H), 1.93 (t, *H*—C≡C—CH_2—, 1H), 1.53 (m, —C≡C—CH_2—CH_2—, 2H), 1.38 (m, CH_3—CH_2—, 2H), 1.26 (m, —CH_2—CH_2—CH_2— 24H), 0.88 (t, CH_3—CH_2—, 3H).

Tetradec-1-yne

Colorless oil, 86%. ^{1}H NMR ($CDCl_3$, ppm): 2.18 (m, —C≡C—CH_2—CH_2—, 2H), 1.93 (t, *H*—C≡C—CH_2—, 1H), 1.52 (m, —C≡C—CH_2—CH_2—, 2H), 1.38 (m, CH_3—CH_2—, 2H), 1.26 (m, —CH_2—CH_2—CH_2—, 16H), 0.88 (t, CH_3—CH_2—, 3H).

Dec-1-yne

Colorless oil, 63%. ^{1}H NMR ($CDCl_3$, ppm): 2.18 (m, —C≡C—CH_2—CH_2—, 2H), 1.93 (t, *H*—C≡C—CH_2—, 1H), 1.52 (m, —C≡C—CH_2—CH_2—, 2H), 1.38 (m, CH_3—CH_2—, 2H), 1.28 (m, —CH_2—CH_2—CH_2—, 8H), 0.88 (t, CH_3—CH_2—, 3H).

General Procedure for Synthesis of Enediyne

2-Benzyl-5,6-bis(3-(hexadecyloxy)prop-1-ynyl) isoindoline-1,3-dione

2-Benzyl-5,6-dibromoisoindoline-1,3-dione (0.55 g, 1.39 mmol), CuI (7.9 mg, 0.0417 mmol), 1-(prop-2-ynyloxy)hexadecane (1.01 g, 3.61 mmol), and $Pd(PPh_3)_2Cl_2$ (29.3 mg, 0.0417 mmol) were mixed in a 25 mL Schlenk flask, then added 2 mL degassed TEA, 3 mL degassed DMF under a nitrogen atmosphere. After stirred for 16 h at 80 °C, the resulting solution was partitioned with saturated aqueous NaCl, 1 M HCl, and dichloromethane, the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under vacuum, the residual was purified by silica chromatography with PE/EtOAc (40/1) as eluent to yield yellow solid product, 75%. ^{1}H NMR ($CDCl_3$, ppm): 7.87 (s, Ph—*H*, 2H), 7.42–7.28 (m, Ph—*H*, 5H), 4.83 (s, Ph—CH_2—, 2H), 4.42 (s, C≡C—CH_2—O—CH_2—CH_2—, 4H), 3.59 (t, C≡C—CH_2—O—CH_2—CH_2—, 4H), 1.62 (t, C≡C—CH_2—O—CH_2—CH_2—, 4H), 1.35 (m, CH_3—CH_2—, 4H), 1.25 (m, —CH_2—CH_2—CH_2—, 48H), 0.88 (t, CH_3—CH_2—, 6H). ^{13}C NMR ($CDCl_3$, ppm): 166.7, 136.0, 131.0, 130.8, 128.7, 128.6, 127.9, 126.7, 94.3, 83.4, 70.5, 58.6, 41.9, 31.9, 29.7, 29.6, 29.3, 26.2, 22.7, 14.1. MS: *m/z* calcd. for $C_{53}H_{79}NO_4$: 793.6009; found: 793.6011. Elem. Anal.: calcd. for $C_{53}H_{79}NO_4$. 2hexane. H_2O: C, 79.29; H, 11.16; N, 1.42. Found: C, 79.63; H, 11.96; N, 1.41.

5,6-Bis(3-(octyloxy)prop-1-ynyl)-2-((R)-1-phenylethyl)isoindoline-1,3-dione (R-2a)

Yellow viscous liquid. ^{1}H NMR ($CDCl_3$, ppm): 7.83 (s, Ph—*H*, 2H), 7.49-7.24 (m, Ph—*H*, 5H), 5.54 (m, CH_3—C*H*—, 1H), 4.41 (s, C≡C—CH_2—O—CH_2—CH_2—, 4H), 3.59 (t, C≡C—CH_2—O—CH_2—CH_2—, 4H), 1.91 (d, CH_3—CH—, 3H), 1.62 (t, C≡C—CH_2—O—CH_2—CH_2—, 4H), 1.37 (m, CH_3—CH_2—, 4H), 1.27 (m, —CH_2—CH_2—CH_2—, 16H), 0.87 (t, CH_3—CH_2—, 6H). ^{13}C NMR ($CDCl_3$, ppm): 166.8, 140.0, 130.9, 130.7, 129.6, 128.5, 127.7, 127.4, 126.5, 94.2, 83.4, 70.5, 58.6, 49.9, 32.8, 31.8, 29.6, 29.4, 29.2, 26.1, 22.6, 17.4, 14.0. MS: *m/z* calcd. for $C_{38}H_{49}NO_4$: 583.3; found: 583.4. Elem. Anal.: calcd. for $C_{39}H_{64}NO_4$: C, 76.67; H, 10.56; N, 2.29. Found: C, 76.50; H, 10.69; N, 2.36. $[\alpha]_D = +25.4°$ (c 1.24, CH_2Cl_2). ***S*-2a** was synthesized in the same manner.

5,6-Bis(3-(dodecyloxy)prop-1-ynyl)-2-((R)-1-phenylethyl)isoindoline-1,3-dione (R-2b)

Yellow solid. ^{1}H NMR ($CDCl_3$, ppm): 7.83 (s, Ph—*H*, 2H), 7.49–7.27 (m, Ph—*H*, 5H), 5.54 (m, CH_3—C*H*—, 1H), 4.41 (s, C≡C—CH_2—O—CH_2—CH_2—, 4H), 3.59 (t, C≡C—CH_2—O—CH_2—CH_2—, 4H), 1.91 (d, CH_3—CH—, 3H), 1.62 (t, C≡C—CH_2—O—CH_2—CH_2—, 4H), 1.36 (m, CH_3—CH_2—, 4H), 1.25 (m, —CH_2—CH_2—CH_2—, 32H), 0.88 (t, CH_3—CH_2—, 6H). ^{13}C NMR ($CDCl_3$, ppm): 166.8, 140.0, 130.9, 130.7, 128.5,

127.7, 127.4, 126.5, 94.2, 83.4, 70.5, 58.6, 50.0, 31.9, 29.6, 29.3, 26.1, 22.6, 17.4, 14.0. MS: *m/z* calcd. for $C_{46}H_{65}NO_4$: 695.4914; found: 695.4925. Elem. Anal.: calcd. for $C_{46}H_{65}NO_4$. 5hexane. $3.5H_2O$: C, 77.17; H, 12.33; N, 1.10. Found: C, 77.10; H, 12.14; N, 1.18. $[\alpha]_D = +25.0^\circ$ (c 0.81, CH_2Cl_2). ***S*-2b** was synthesized in the same manner.

5,6-Bis(3-(hexadecyloxy)prop-1-ynyl)-2-((R)-1-phenylethyl)isoindoline-1,3-dione (R-2c)

Yellow solid, 74%. ^{1}H NMR ($CDCl_3$, ppm): 7.83 (s, Ph—*H*, 2H), 7.49–7.24 (m, Ph—*H*, 5H), 5.55 (m, CH_3—C*H*—, 1H), 4.41 (s, C≡C—CH_2—O—CH_2—CH_2—, 4H), 3.59 (t, C≡C—CH_2—O—CH_2—CH_2—, 4H), 1.91 (d, CH_3—CH—, 3H), 1.62 (t, C≡C—CH_2—O—CH_2—CH_2—, 4H), 1.35 (m, CH_3—CH_2—, 4H), 1.25 (m, —CH_2—CH_2—CH_2—, 48H), 0.88 (t, CH_3—CH_2—, 6H). ^{13}C NMR ($CDCl_3$, ppm): 166.8, 140.0, 130.9, 130.7, 129.6, 128.5, 127.7, 127.4, 126.5, 94.2, 83.4, 70.5, 58.6, 49.9, 31.9, 29.7, 29.6, 29.5, 29.3, 26.2, 22.7, 17.4, 14.1. MS: *m/z* calcd. for $C_{54}H_{81}NO_4$: 807.6166; found: 807.6169. Elem. Anal.: calcd. for $C_{54}H_{81}NO_4$. 5.5hexane. H_2O: C, 80.37; H, 12.40; N, 1.08. Found: C, 80.44; H, 13.08; N, 1.12. $[\alpha]_D = +10.9^\circ$ (c 1.03, CH_2Cl_2).

5,6-Di(dec-1-ynyl)-2-((R)-1-phenylethyl)isoindoline-1,3-dione (R-2 d)

Yellow viscous liquid. ^{1}H NMR ($CDCl_3$, ppm): 7.75 (s, Ph—*H*, 2H), 7.49-7.23 (m, Ph—*H*, 5H), 5.53 (m, CH_3—C*H*—, 1H), 2.48 (t, C≡C—CH_2—CH_2—, 4H), 1.90 (d, CH_3—CH—, 3H), 1.63 (t, C≡C—CH_2— CH_2—, 4H), 1.47 (m, CH_3—CH_2—, 4H), 1.30 (m, —CH_2—CH_2—CH_2—, 16H), 0.88 (t, CH_3—CH_2—, 6H). ^{13}C NMR ($CDCl_3$, ppm): 167.1, 140.1, 132.0, 129.7, 128.3, 127.5, 127.3, 126.2, 99.2, 78.9, 49.7, 31.8, 30.2, 29.6, 29.1, 28.9, 28.5, 22.6, 19.7, 17.3, 14.0. MS: *m/z* calcd. for $C_{36}H_{45}NO_2$: 523.3450; found: 523.3452. Elem. Anal.: calcd. for $C_{36}H_{57}NO_2$: C, 80.69; H, 10.72; N, 2.61. Found: C, 80.34; H, 10.54; N, 2.92. $[\alpha]_D = +28.9^\circ$ (c 0.46, CH_2Cl_2). ***S*-2d** was synthesized in the same manner.

5,6-Di(tetradec-1-ynyl)-2-((R)-1-phenylethyl) isoindoline (R-2e)

Yellow solid. ^{1}H NMR ($CDCl_3$, ppm): 7.75 (s, Ph—*H*, 2H), 7.49–7.25 (m, Ph—*H*, 5H), 5.53 (m, CH_3—C*H*—, 1H), 2.48 (t, C≡C—CH_2—CH_2—, 4H), 1.90 (d, CH_3—CH—, 3H), 1.63 (t, C≡C—CH_2— CH_2—, 4H), 1.47 (m, CH_3—CH_2—, 4H), 1.26 (m, —CH_2—CH_2—CH_2—, 32H), 0.88 (t, CH_3—CH_2—, 6H). ^{13}C NMR ($CDCl_3$, ppm): 167.1, 140.1, 132.0, 129.7, 128.3, 127.5, 127.3, 126.2, 99.2, 79.0, 49.7, 31.8, 29.6, 29.5, 29.3, 29.2, 28.9, 28.5, 22.6, 19.7, 17.3, 14.0. MS: *m/z* calcd. for $C_{44}H_{61}NO_2$: 635.4702; found: 635.4701. Elem. Anal.: calcd. for $C_{44}H_{61}NO_2$. 2.5hexane. $2H_2O$: C, 79.85; H, 11.36; N, 1.58. Found: C, 79.68; H, 11.53; N, 1.57. $[\alpha]_D = +24.9^\circ$ (c 0.55, CH_2Cl_2). ***S*-2e** was synthesized in the same manner.

5,6-Di(octadec-1-ynyl)-2-((R)-1-phenylethyl) isoindoline-1,3-dione (R-2f)

Yellow solid. ^{1}H NMR ($CDCl_3$, ppm): 7.75 (s, Ph—*H*, 2H), 7.49–7.30 (m, Ph—*H*, 5H), 5.53 (m, CH_3—C*H*—, 1H), 2.48 (t, C≡C—CH_2—CH_2—, 4H), 1.90 (d, CH_3—CH—, 3H), 1.63 (t, C≡C—CH_2— CH_2—, 4H), 1.46 (m, CH_3—CH_2—, 4H), 1.25 (m, —CH_2—CH_2—CH_2—, 48H), 0.88 (t, CH_3—CH_2—, 6H). ^{13}C NMR ($CDCl_3$, ppm): 167.2, 140.2, 132.1, 129.8, 128.4, 127.6, 127.4, 126.3, 99.3, 79.0, 49.8, 31.9, 29.7, 29.4, 29.2, 28.9, 28.5, 22.7, 19.8, 17.4, 14.1. MS: *m/z* calcd. for $C_{52}H_{77}NO_2$: 747.5954; found: 747.5957. Elem. Anal.: calcd. for $C_{58}H_{100}NO_2$: C, 82.59; H, 11.95; N, 1.66. Found: C, 82.88; H, 12.06; N, 1.67. $[\alpha]_D = +10.3^\circ$ (c 1.05, CH_2Cl_2). ***S*-2f** was synthesized in the same manner.

General Procedure for Synthesis of Polynaphthalene

Enediyne **2** was transferred into a tube and sealed under vacuum. The tube was then embedded in a refluxing diphenyl ether (or *N,N*-dimethylacetamide) bath. After 6 h of heating, a brownish oil was obtained inside the tube, which was proven to be soluble polynaphthalene.

General Procedure for Hydrazinolysis

Hydrazine hydrate (0.41 mL, 0.83 mmol) was added to **2c** (0.11 g, 0.14 mmol) in refluxing ethanol (3 mL) (for polymer, THF was added as cosolvent) and stirred for 10 min, then cooled down to 50 °C. Excess amount of concentrated HCl was added to the reaction mixture, the temperature was maintained for 10 min. After filtration, the filtrate was concentrated under vacuum to obtained product (0.10 g, 91%). For polymers, silica gel chromatography was used to remove the chiral amine.

CONCLUSIONS

In summary, we have successfully synthesized soluble conjugated PNs via a catalyst-free Bergman cyclization of dialkynyl phthalimide precusors. IR and NMR spectra showed disappearance of acetylene units after Bergman cyclization, the formation of long conjugated backbones was further confirmed with UV–Vis and PL spectroscopy. Under milder reaction condition, PNs with main chain chirality could be obtained by installation of chiral directing groups in enediyne precursors. All PNs obtained in this work are readily soluble in common organic solvents. By utilizing thermal Bergman cyclization, conjugated polymers could be obtained in metal-free manner. Further optimization enediyne structures for low temperature Bergman cyclization and exploration of optoelectronic properties of these polymers are underway in our lab.

The authors thank National Natural Science Foundation of China (No. 20874026; No. 20704013), Shanghai Pujiang Program (07PJ14024), Shuguang Project (07SG33), New Century Excellent Talents in University, and Shanghai Leading Academic Discipline Project (B502) for financial support.

REFERENCES AND NOTES

1 Rudick, J. G.; Percec, V. New J Chem 2007, 31, 1083–1096.

2 Cheng, Y. J.; Yang, S. H.; Hsu, C. S. Chem Rev 2009, 109, 5868–5923.

3 Wang, H. B.; Jost, R.; Wudl, F. J Polym Sci Polym Chem 2007, 45, 800–808.

4 Amrutha, S. R.; Jayakannan, M. Macromolecules 2007, 40, 2380–2391.

5 Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. Chem Rev 2009, 109, 897–1091.

6 Percec, V.; Rudick, J. G.; Peterca, M.; Heiney, P. A. J Am Chem Soc 2008, 130, 7503–7508.

7 Liu, J. Z.; Lam, J. W. Y.; Tang, B. Z. Chem Rev 2009, 109, 5799–5867.

8 Nehls, B. S.; Galbrecht, F.; Brauer, D. J.; Lehmann, C. W.; Scherf, U.; Farrell, T. J Polym Sci Polym Chem 2006, 44, 5533–5545.

9 Zeng, Q.; Lam, J. W. Y.; Jim, C. K. W.; Qin, A. J.; Qin, J. G.; Li, Z.; Tang, B. Z. J Polym Sci Polym Chem 2008, 46, 8070–8080.

10 Chen, L.; Chen, Y. W.; Yao, K.; Zhou, W. H.; Li, F.; Chen, L. P.; Hu, R. R.; Tang, B. Z. J Polym Sci Polym Chem 2009, 47, 4723–4735.

11 Kranz, M.; Clark, T.; Schleyer, P. v. R. J Org Chem 1993, 58, 3317–3325.

12 Takeshi, M.; Takeshi, T.; Yoshio, F.; Toshikazu, T. J Polym Sci Polym Chem 2004, 42, 4693–4703.

13 Morgan, B. J.; Xie, X.; Phuan, P.-W.; Kozlowski, M. C. J Org Chem 2007, 72, 6171–6182.

14 Okamoto, Y. J Polym Sci Polym Chem 2009, 47, 1731–1739.

15 Yashima, E.; Maeda, K.; Furusho, Y. Acc Chem Res 2008, 41, 1166–1180.

16 Nakano, T.; Okamoto, Y. Chem Rev 2001, 101, 4013–4038.

17 Sun, R.; Peng, J.; Kobayashi, T.; Ma, Y.; Zhang, H.; Liu, S. Jpn J Appl Phys Part 2 1996, 35, L1506–L1508.

18 Mori, T.; Kijima, M. J Polym Sci Polym Chem 2008, 46, 4258–4263.

19 Habaue, S.; Ajiro, H.; Yoshii, Y.; Hirasa, T. J Polym Sci Polym Chem 2004, 42, 4528–4534.

20 Habaue, S.; Seko, T.; Okamoto, Y. Macromolecules 2003, 36, 2604–2608.

21 Bergman, R. G. Acc Chem Res 1973, 6, 25–31.

22 Kar, M.; Basak, A. Chem Rev 2007, 107, 2861–2890.

23 Biggins, J. B.; Onwueme, K. C.; Thorson, J. S. Science 2003, 301, 1537–1541.

24 Basak, A.; Mitra, D.; Kar, M.; Biradha, K. Chem Commun 2008, 3067–3069.

25 Kovalenko, S. V.; Alabugin, I. V. Chem Commun 2005, 1444–1446.

26 Yoshimura, F.; Lear, M. J.; Ohashi, I.; Koyama, Y.; Hirama, M. Chem Commun 2007, 3057–3059.

27 Smith, D. W.; Shah, H. V.; Perera, K. P. U.; Perpall, M. W.; Babb, D. A.; Martin, S. J. Adv Funct Mater 2007, 17, 1237–1246.

28 Zengin, H.; Smith, D. W. J Mater Sci 2007, 42, 4344–4349.

29 Perpall, M. W.; Perera, K. P. U.; DiMaio, J.; Ballato, J.; Foulger, S. H.; Smith, D. W. Langmuir 2003, 19, 7153–7156.

30 Rettenbacher, A. S.; Perpall, M. W.; Echegoyen, L.; Hudson, J.; Smith, D. W. Chem Mater 2007, 19, 1411–1417.

31 Rule, J. D.; Wilson, S. R.; Moore, J. S. J Am Chem Soc 2003, 125, 12992–12993.

32 Hickenboth, C. R.; Rule, J. D.; Moore, J. S. Tetrahedron 2008, 64, 8435–8448.

33 John, J. A.; Tour, J. M. J Am Chem Soc 1994, 116, 5011–5012.

34 Bhongale, C. J.; Yang, C.-H.; Hsu, C.-S. Chem Commun 2006, 2274–2276.

35 Shah, H. V.; Babb, D. A.; Smith, D. W. Polymer 2000, 41, 4415–4422.

36 Chen, X. H.; Tolbert, L. M.; Hess, D. W.; Henderson, C. Macromolecules 2001, 34, 4104–4108.

37 McCaughey, B.; Costello, C.; Wang, D. H.; Hampsey, J. E.; Yang, Z. Z.; Li, C. J.; Brinker, C. J.; Lu, Y. F. Adv Mater 2003, 15, 1266–1269.

38 Meca, L.; Reha, D.; Havlas, Z. J Org Chem 2003, 68, 5677–5680.

39 Ashton, P. R.; Girreser, U.; Giuffrida, D.; Kohnke, F. H.; Mathias, J. P.; Raymo, F. M.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. J Am Chem Soc 1993, 115, 5422–5429.

40 Wang, X.; Zhang, Y.; Sun, X.; Bian, Y.; Ma, C.; Jiang, J. Inorg Chem 2007, 46, 7136–7141.

41 El-Sharief, A. M. S.; Hammad, N. E. Ind J Chem B 1981, 20, 1039–1042.

42 Nakamura, T.; Yonesu, K.; Mizuno, Y.; Suzuki, C.; Sakata, Y.; Takuwa, Y.; Nara, F.; Satoh, S. Bioorg Med Chem 2007, 15, 3548–3564.

43 Carballeira, N. M.; Sanabria, D.; Oyola, D. ARKIVOC 2007, 49–57.