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Synthesis of Novel "Rod−Coil" Brush Polymers with Conjugated Backbones through Bergman Cyclization

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ABSTRACT: This work reports synthesis of "rod−coil" brush polymers with rigid conjugated backbone. "Grafting through" strategy was employed via combination of ring-opening polymerization (ROP) and Bergman cyclization polymerization. Enediyne-containing macromonomers were first synthesized through ROP of caprolactone with dual-functional initiators conceiving free hydroxy groups and dialkynylbenzene moieties. After protection of terminal free hydroxy group of PCL chain and removal of trimethylsilyl protecting group of enediyne unit, the macromonomers were subjected to thermal Bergman cyclization under vacuum. The brush polymers obtained were characterized with GPC and NMR, IR, and UV−vis spectroscopy. The conjugated backbones were revealed as copolymers of naphthalene and indenylmethylene according to NMR analysis.

Introduction

Brush polymers as a special grafted polymer with a densely side chains distribution have draw much attention not only for their peculiar architectures related to properties but also for their potential applications.[1−5] As an important kind of nanoscopic macromolecule, brush polymers have been well investigated since the concept of hyperbranched polymers was first presented in theoretical work by Flory in 1953.[6] A variety of elegant synthetic methods have been developed in recent years; in general, there are three strategies for synthesis of brush polymers: "grafting from" (grafting side chains from the backbone), "grafting onto" (attachment of side chains to the backbone), and "grafting through" (homo- and copolymerization of macromonomers).[1,5,7] Extending synthetic organic chemistry, like "click chemistry"[8] and multiple hydrogen-bonding interactions[9,10] together with living polymerization, especially living radical polymerizations developed in past decade, into the molecular design in polymer chemistry has facilitated the synthesis of polymers with various architectures.[11]

Conjugated polymers are a class of polymers with unique thermal and electrical properties.[12−20] There are several families of conjugated polymers with respect to their backbones, including poly(*p*-phenylene) (PPP), polyacetylene (PA), poly(phenylenevinylene) (PPV), poly(phenyleneethynylene) (PPE), polypyrrole (PPy), and polythiophene (PT). Because of the high rigidity and crystallinity of backbone, pristine conjugated polymers are typically difficult to melt and insoluble in common solvents. Introducing a pendant moiety onto conjugated polymer to form brush polymer is a generic way to improve the solubility and modify the electrical property of these rodlike polymers. "Grafting through" is the method of choice in most cases for the synthesis of these brush polymers. After introduction of flexible groups (either polymer or long alkyl chain), macromonomers were subjected to transition-metal-catalyzed cross-coupling reaction or coordination polymerization to form brush polymers. The residual metal complexes in the final polymers, however, seriously affected 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. We noted that polyphenylene and polynaphthalene have been synthesized via an alternative way through thermal Bergman cyclization reported by Tour et al.[21,22] In many cases, polymers were obtained as insoluble tar.

Bergman cyclization is an intramolecular cyclization of enediyne compounds first studied by Bergman et al. three decades ago.[23] It was later found that some naturally occurred antibiotics like calicheamicin, dynemicin A, esperamicin A1, namenamicin, and shishijimicin A conceive a enediyne "warhead". Bergman cyclization of the enediyne moiety is initiated *in vivo* to generate a 1,4-phenylene diradical, which can cause DNA cleavage or cross-linking. The high cytotoxicity of these compounds is promising for anticancer applications. Following this line, a great deal of research work has been conducted on elucidation of the mechanism of Bergman cyclization, designing and total synthesis of bio-similar compounds with less complicated structures and lower toxicity.[24−32] Despite these activities, there were some discrete reports on applications of Bergman cyclization in polymer chemistry and material science. Diradicals from Bergman cyclization were used to initiate free radical polymerization of functionalized olefins.[33,34] Polynaphthalene from Bergman cyclization of bis(*o*-diynylarene) are good precursors for glassy carbon and surface functionality to solubilize carbon nano-onion in organic solvents.[35−37] Polystyrene with pendant enediyne group cured under high temperature showed high resistance to plasma etching.[38] Bergman cyclization could be triggered with a variety of stimuli, including heat, UV, acid, and organometallic catalysts. Together with structural variability of enediyne precursors, Bergman cyclization is prone to show wide applications in synthetic chemistry. However, exploration of Bergman cyclization in the polymer synthesis is still rare. Herein, we wish to report our work utilizing Bergman cyclization to synthesize "rod−coil" conjugated polymers with polycaprolactone as flexible side chains.

Experimental Section

Materials. ε-Caprolactone (ε-CL; 99%, Acros Organics) was dried over calcium hydride (CaH_2), distilled under reduced

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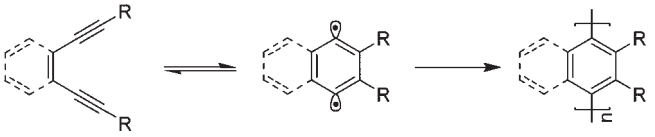
Scheme 1. Bergman Cyclization and Related Polymerization



pressure, and stored over activated 4 Å molecular sieves.[39,40] Tetrahydrofuran (THF), toluene, and triethylamine (Et_3N) were distilled over sodium or calcium hydride prior to use. Stannous(II) 2-ethylhexanoate ($SnOct_2$) (Sigma) and other reagents were commercial chemicals and used as received. All reactions were performed with dried Schlenk techniques under an atmosphere of nitrogen unless otherwise noted.

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). 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. Onset and peak temperature of the model compounds were studied with differential scanning calorimetry (DSC) using a Pyris Diamond thermal analysis workstation equipped with a model 822e DSC module under a constant nitrogen flow. Fourier transform infrared analysis (FTIR) was recorded from KBr pellets 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.

Synthesis. *3-(2-(2-(Trimethylsilyl)ethynyl)phenyl)prop-2-yn-1-ol* (***2a***). This compound was synthesized according to a literature procedure with minor modification.[41] To a triethylamine (15 mL) solution of 3-(2-bromophenyl)propargyl alcohol (3.17 g, 15 mmol) was added $Pd(PPh_3)_2Cl_2$ (0.53 g, 0.75 mmol), copper(I) iodide (0.09 g, 0.45 mmol), and trimethylsilylacetylene (2.21 g, 23 mmol). The mixture was then stirred at 90 °C for 20 h in seal tube. After cooled to room temperature, volatile components were removed *in vacuo*. The residue was dissolved in ethyl acetate, washed with saturated NH_4Cl and NaCl solution, and dried over anhydrous $MgSO_4$. LC separation on silica gel column (ethyl acetate/petroleum ether = 1:5, R_f = 0.5), giving pure product as a brown-red oil (1.23 g, 36%). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.47 (m, Ph−*H*, 1H), 7.43 (m, Ph−*H*, 1H), 7.28 (m, Ph−*H*, 1H), 7.24 (m, Ph−*H*, 1H), 4.54 (d, $-CH_2$OH−, 2H), 1.64 (m, −*OH*, 1H), 0.27 (s, Si−CH_3, 9H).

(2-(2-Bromophenyl)ethynyl)trimethylsilane. This compound was synthesized according to a literature procedure with minor modification.[42] To a mixture of 1-bromo-2-iodobenzene (1) (2.83 g, 10 mmol), $Pd(PPh_3)_2Cl_2$ (0.21 g, 0.3 mmol), and copper(I) iodide (0.06 g, 0.3 mmol) in dry Et_3N (15 mL), trimethylsilylacetylene (1.18 g, 12 mmol) was added under a nitrogen atmosphere. The reaction mixture was stirred overnight at room temperature. The mixture was concentrated *in vacuo*, then dissolved in ethyl acetate, and washed with saturated $NaHCO_3$ solution and saturated NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica gel column chromatography eluted with petroleum ether (R_f = 0.8) to give pure product as a yellow oil (2.52 g, 100%). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.37 (d, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 1.0 Hz, Ph−*H*, 1H), 7.29 (d, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.7 Hz, Ph−*H*, 1H), 7.04 (m, $^3J_{H-H}$ = 7.6 Hz, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.2 Hz, Ph−*H*, 1H), 6.96 (m, $^3J_{H-H}$ = 8.0 Hz, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.7 Hz, Ph−*H*, 1H), 0.09 (s, Si−CH_3, 9H).

4-(2-(2-(Trimethylsilyl)ethynyl)phenyl)but-3-yn-1-ol (***2b***). This compound was synthesized according to a literature procedure with minor modification.[43,44] To a triethylamine (15 mL) solution of the above-mentioned *o*-TMSA-substituted bromobenzene (2.92 g, 11.5 mmol) was added $Pd(PPh_3)_2Cl_2$ (0.24 g, 0.35 mmol), copper(I) iodide (0.07 g, 0.35 mmol), and but-3-yn-1-ol (0.97 g, 13.84 mmol). The mixture was then stirred at 80 °C for 20 h under a nitrogen atmosphere. After being cooled to room temperature, the solvent was removed *in vacuo*. The residue was dissolved in ethyl acetate, washed with saturated NH_4Cl and NaCl solution, and dried over anhydrous $MgSO_4$. LC separation on silica gel column (ethyl acetate/petroleum ether = 1:5, R_f = 0.5) gave pure product as a brown-red oil (1.51 g, 54%). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.46 (m, Ph−*H*, 1H), 7.39 (m, Ph−*H*, 1H), 7.23 (m, Ph−*H*, 2H), 3.82(m, $^3J_{H-H}$ = 6.2 Hz, $^3J_{H-H}$ = 6.3 Hz, $-CH_2$OH−, 2H), 2.73 (t, $^3J_{H-H}$ = 6.0 Hz, $-CH_2CH_2$OH, 2H), 2.14 (m, $^3J_{H-H}$ = 6.7 Hz, −*OH*, 1H), 0.27 (s, Si−CH_3, 9H).

Typical Procedure for the Synthesis of Polycaprolactone (*PCL,* ***3a***). All glassware and needles were dried overnight in an oven at 140 °C prior to use, and all reactions were performed under a dry nitrogen atmosphere. Compound **2a** (0.6 g, 2.5 mmol) was first dissolved in THF and dried over anhydrous $MgSO_4$ and then transferred to a Schlenk flask. After removal of THF *in vacuo*,[39] ε-caprolactone (1.42 g, 12.5 mmol), $Sn(Oct)_2$ (2 wt % CL), and toluene (3 mL) were added under nitrogen. The polymerizations were carried out in a 110 °C oil bath. After 24 h, the mixture was evaporated under reduced pressure and poured into cold methanol. The polymer was collected after filtration and dried at room temperature *in vacuo* for 4 h as a light-brown powder. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.43 (m, Ph−*H*, 1H), 7.38 (m, Ph−*H*, 1H), 7.22 (m, Ph−*H*, 2H), 4.28 (m, −C≡C−CH_2−*CH*$_2$, 2H), 4.06 (m, −*CH*$_2$−O−CO− in PCL), 2.80 (m, −C≡C−*CH*$_2$−, 2H), 2.30 (m, −O−CO−*CH*$_2$− in PCL), 1.64 (m, −*CH*$_2$−CH_2−O−CO− in PCL), 1.40 (m, −O−CO−CH_2−*CH*$_2$− in PCL), 1.29 (m, −O−CO−CH_2−CH_2−*CH*$_2$− in PCL), 0.27 (s, Si−CH_3, 9H).

Acetylated PCL. A mixture of polymer **3** and acetic anhydride was stirred at 80 °C for 6−8 h. The product was obtained after removal of the excess acetic anhydride *in vacuo*. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.45 (m, Ph−*H*, 1H), 7.39 (m, Ph−*H*, 1H), 7.23 (m, Ph−*H*, 2H), 4.29 (m, −C≡C−CH_2−*CH*$_2$, 2H), 4.07 (m, −*CH*$_2$−O−CO− in PCL), 2.82 (m, −C≡C−*CH*$_2$−, 2H), 2.31 (m, −O−CO−*CH*$_2$− in PCL), 2.05 (m, −O−CO−*CH*$_3$ in PCL, 3H), 1.67 (m, −*CH*$_2$−CH_2−O−CO− in PCL), 1.41 (m, −O−CO−CH_2−*CH*$_2$− in PCL), 1.37 (m, −O−CO−CH_2−CH_2−*CH*$_2$− in PCL), 0.28 (s, Si−CH_3, 9H).

Deprotection of the Acetylated PCL (***4***). To a solution of acetylated PCL (0.3 g) in THF (3 mL) was added tetrabutylammonium fluoride (0.44 g, 10 equiv to TMS group).[45] After stirring for 1.5 h at room temperature, the solution was passed through a short silica gel column and eluted with THF to get the product. Note: this reaction was run in a dark environment. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.25−7.47 (m, Ph−*H*, 4H), 4.28 (m, −C≡C−CH_2−*CH*$_2$, 2H), 4.06 (m, −*CH*$_2$−O−CO− in PCL), 3.27 (s, Ph−C≡C−H, 1H), 2.82 (m, −C≡C−*CH*$_2$−, 2H), 2.31 (m, −O−CO−*CH*$_2$− in PCL), 2.05 (m, −O−CO−*CH*$_3$ in PCL, 3H), 1.67 (m, −*CH*$_2$−CH_2−O−CO− in PCL), 1.41 (m, −O−CO−CH_2−*CH*$_2$− in PCL), 1.37(m, −O−CO−CH_2−CH_2−*CH*$_2$− in PCL).

"Bottle-Brush" Polymer ***5*** *through Bergman Cyclization*. Polymer **4** was transferred into a tube and sealed under vacuum. The tube was then embedded in a refluxing diphenyl ether (or diethyl succinate) bath. After 6 h of heating, a brownish oil was obtained inside the tube, which was proven to be brush polymer with high polydispersity. The high molecular weight fraction was obtained either by repeat precipitation in a mixture solvent of THF and methanol or dialysis in THF with dialysis membranes (MWCO: 50 000).

Results and Discussion

Synthesis of PCL Macromomomer (4). Compound **2** was chosen for this study due to its structural feature and facial preparation. Hydroxy group can be easily modified with a variety of reactions to introduce functional groups onto this

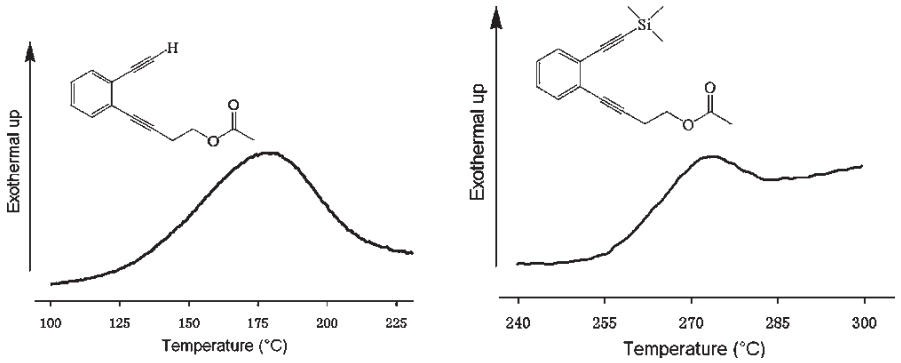


Figure 1. DSC curves of model compounds.

molecule. In this study, we used the hydroxy group to initiate ring-opening polymerization of cyclic lactone to introduce a flexible PCL chain onto enediyne compound. Trimethylsilyacetylene group is a synthetic equivalent of ethyne, and the steric effect of trimethylsilyl (TMS) group also inhibits unwanted Bergman cyclization or oxidative coupling of terminal alkyne during preparation and storage. DSC studies for model compounds revealed that with TMS group thermal Bergman cyclization could not take place until it was heated up to 260 °C; however, after removal of TMS group, Bergman cyclization took place at much lower temperature (Figure 1).

Poly(ε-caprolactone) **3** was synthesized through ring-opening polymerization at 110 °C with the feed molar ratio of caprolactone to initiator from 5:1 to 15:1. The PCL chain was readily obtained as a powder by precipitation from methanol to remove the residual monomer and initiator. GPC showed monomodal trace and low molecular weight distribution, which revealed living polymerization nature. The molecular weights calibrated with polystyrene standard were further corrected with a known equation for PCL system,[20] which were consistent with NMR terminal group analysis. In the ^{1}H NMR spectra of the obtained polymers, the major signals around 2.3 and 4.1 ppm were assigned to the methylene protons adjacent to the ester group of the PCL main chain, and the remaining high signals in the range from 1.3 to 1.7 ppm were assigned to the inner methylene protons of the polymer backbone. Four multiplet signals between 7.2 and 7.5 ppm were assigned to the aryl protons in the initiator, two triplets around 2.8 and 4.3 ppm were assigned to methylene protons next to triple bond of enediyne moiety (in the case of **3b**, a singlet around 5.0 ppm was assigned to methylene protons adjacent to triple bond), and one singlet around 0.3 ppm was assigned to TMS group. The initiating efficiencies for enediyne-containing alcohol calculated from molecular weight analysis are between 35% and 50%. The steric effect of neighboring TMS group could be the reason for low efficiency.

The free terminal hydroxy groups of **3** were masked with acetyl group as we found that hydroxy groups could quench the free radicals generated by Bergman cyclization and terminate the related polymerization. The protection of the hydroxy group was achieved via treatment with excess of acetic anhydride. NMR analysis showed complete protection of terminal hydroxy group. The polymer was then subjected to deprotetion of TMS group in a tetrabutylammonium fluoride THF solution. The removal of TMS group was completed in 1.5 h as evidenced by NMR analysis (Figure 2).

Synthesis of Brush Polymer (5). Thermal Bergman cyclization of macromonomer **4** was conducted in bulk. To exclude

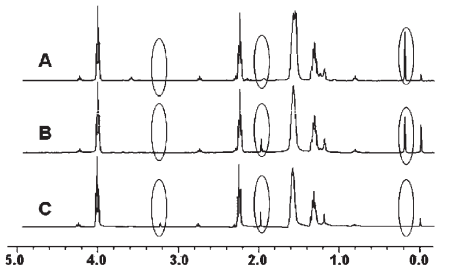


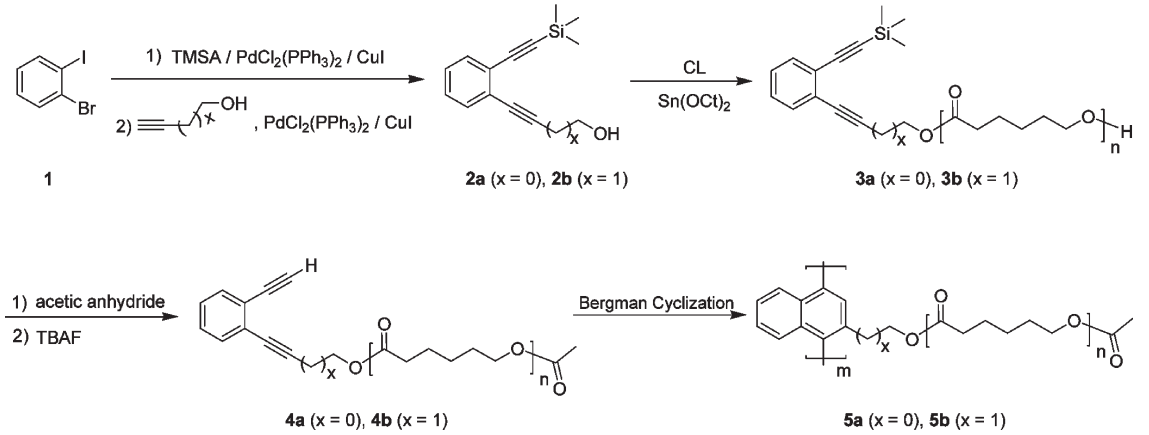
Figure 2. ^{1}H NMR spectra ($CDCl_3$) of (A) as-synthesized PCL, (B) acetylated PCL, and (C) after removal of trimethylsilyl group.

species that could be quencher to radicals, these reactions were done under vacuum. According to the DSC results of model compound of **4**, Bergman cyclization of **4** could be triggered at 160 °C. The formation of brush polymer can be even faster at higher temperature. GPC analysis for brush polymers revealed broad molecular weight dispersion, which was due to the step-growth nature of coupling reaction of diradicals generated via Bergman cyclization.[21] The apparent molecular weight of brush polymer varied under different reaction conditions. There was, however, no clear relationship between reaction temperature and molecular weight of brush polymers. The high molecular fraction could be readily obtained via dialysis or repeat precipitation (Figure 3). DSC analysis revealed much higher T_g (20.4 °C for **5a** and 22.5 °C for **5b**) than free PCL (−61 °C), indicative of restriction of motion of PCL segments after formation of brush polymers.

The occurrence of Bergman cyclization was confirmed through IR analysis. Two adsorption peaks in model compounds were clear seen around 2180 and 2230 cm^{-1}, which were assigned to internal and terminal triple bonds. Both of these peaks were absent after Bergman cyclization as shown in Figure 4, indicative of disappearance of both triple bonds in enediyne moiety after thermal Bergman cyclization.[46] The reaction at triple bond moieties was further supported by ^{13}C NMR analysis. Four characteristic peaks between 80 and 105 ppm in macromonomers are completely gone in brush polymers.

The UV−vis spectra of macromonomers and brush polymers are shown in Figure 5. The adsorption spectra of macromonomers showed three well-defined peaks at 237, 263, and 278 nm without notable difference between two types of macromonomers (**3a** and **3b**) and corresponding model compounds. After Bergman cyclization, all above-mentioned features in UV−vis spectra disappeared, while an intensive, broad peak showed up. All these polymers showed strong adsorption tailing up to 450 nm, which indicated the formation of longer conjugated system after Bergman cyclization.

Scheme 2. Synthetic Route for Brush Polymers



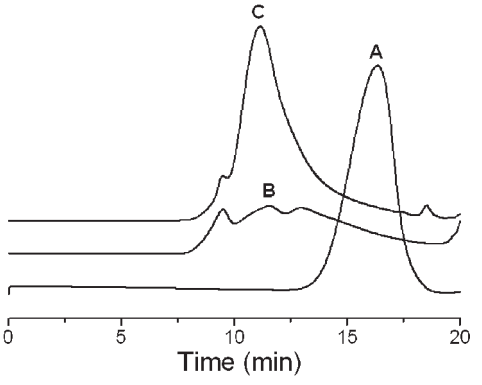


Figure 3. GPC traces of (A) PCL, (B) brush polymer, and (C) brush polymer after dialysis.

Table 1. Enediyne-Containing Macromonomers and Brush Polymers

			PCL macromonomer			brush polymer		
entry	enediyne	[CL]:[**2**]	$M_{w,GPC}$[a]	PDI[a]	$M_{w,GPC}$[a]	PDI[a]	$M_{w,GPC}$[a,b]	PDI[a,b]
1	**2a**[c]	17:1	13.8	1.43	554.0	13.78	1027.3	7.74
2	**2a**[d]	30:1	19.5	1.57	112.9	8.90	138.0	4.97
3	**2b**[d]	8:1	7.8	1.21	294.2	7.17	184.2	2.45
4	**2b**[c]	8:1	7.8	1.21	62.7	8.08	72.3	1.72
5	**2b**[d]	5:1	6.0	1.28	110.9	7.42	194.6	4.09
6	**2b**[d]	5:1	5.2	1.22	516.2	32.00	661.5	1.28

[a] Measured by GPC analysis in THF with a PS calibration, molecular weight in kilodaltons. [b] After fractionation. [c] Reaction run at 217 °C. [d] Reaction run at 259 °C.

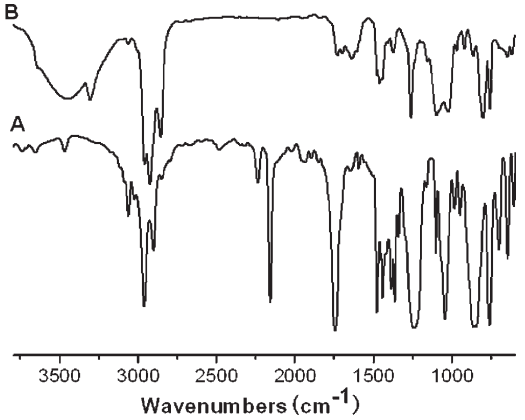


Figure 4. FT-IR spectra of model compound before (A) and after Bergman cyclization (B).

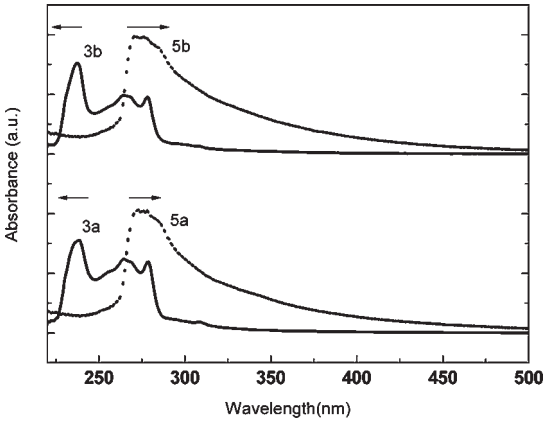


Figure 5. UV−vis spectra of **3a** (solid line), **3b** (solid line), **5a** (dotted line), and **5b** (dotted line) in CH_2Cl_2.

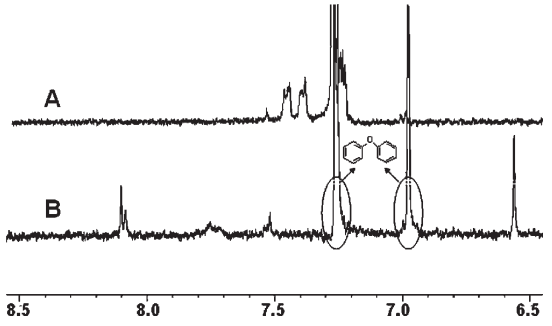


Figure 6. Aromatic region of ^{1}H NMR spectra ($CDCl_3$) of the (A) PCL **4** and (B) brush polymer **5**.

The structure of "polynaphthalene" synthesized via Bergman cyclization was questioned recently.[47] It was found that polynaphthalenes from Kumada coupling of 1,4-dibromonaphthalene and Bergman cyclization of *o*-diethynylbenzene were very different according to TGA, pyrolysis GC-MS, and (CP-MAS) NMR analysis. Detailed structural analysis showed that polynaphthalene from Bergman cyclization consisted of not only naphthalene but also indene subunits. A radical chain growth mechanism besides step-growth mechanism was proposed for the formation of indene moiety. In this mechanism, enediyne is first attacked by a radical (formed from Bergman cyclization) at the 1- or 2-position of the alkynyl group to form a vinyl radical intermediate (intermediate A or B), the subsequent 5-exo-dig cyclization of A, and the 5-endo-dig cyclization of B give radicals with an indene moiety, while 6-endo-dig cyclization of A gives

radical with a naphthalene moiety. A direct evidence for the formation of indenyl intermediate, however, is difficult to find out in this system due to the insolubility of the "polynaphthalene". Thanks to the flexibility of PCL side chain, a solution NMR spectrum can be obtained for brushed "polynaphthalene". After Bergman cyclization, two new set of peaks appeared around 8.1 and 6.6 ppm (Figure 6), which were assigned to naphthalene subunits and indene subunits,[48,49] respectively. The main chain of these brush polymers can thus be rationalized as random conjugated copolymers of naphthalene and indenylenemethylene.

Conclusion

We have successfully synthesized brush polymers with conjugated backbone via a catalyst-free Bergman cyclization of enediyne-containing macromonomers. The size distributions of brush polymers were wide in all cases; higher molecular weight fractions could be obtained through repeat centrifugation or dialysis. IR and NMR spectra showed disappearance of acetylene units after Bergman cyclization; the formation of long conjugated backbones was further confirmed with UV−vis spectroscopy. The structure of backbone of brush polymers were rationalized as a copolymer of naphthalene and indenylenemethylene. All the brush polymers obtained are readily soluble in common organic solvents. By utilizing thermal Bergman cyclization, conjugated polymers could be obtained in metal-free manner. Further exploration of thermal and optoelectronic properties of these polymers are underway in our lab.

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