

Palladium-catalyzed Cycloaromatization Polymerization of Enediynes

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Electronic Supplementary Information

Abstract Bergman cyclization has shown great promise in constructing conjugated polymers. However, the application of this reaction in polymer science is still limited due to the harsh reaction condition and ill-defined structure of the achieved polymers. To this end, the cycloaromatization polymerization of enediynes catalyzed by a series of transition metal catalysts is investigated in this work, by taking advantage of the coordination chemistry of the enediyne with the transition metal complexes. According to the nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), ultraviolet-visible (UV-Vis) spectroscopies and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis, the cycloaromatization polymerization of enediynes proceeds under milder conditions and in a more controlled manner in the presence of palladium(II) complexes, giving structurally regulated conjugated polymers in high yields.

Keywords Transition metal catalysis; Enediyne; Polymerization; Cycloaromatization; Bergman cyclization

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INTRODUCTION

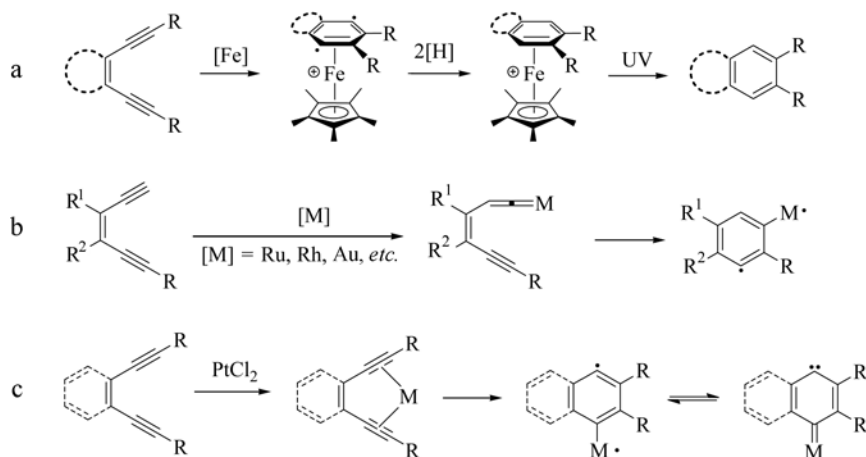
The Bergman cyclization of enediyne compounds has attracted increasing attentions as a promising tool in polymer and material science^[1–6]. This kind of cycloaromatization reactions has been investigated under the action of a variety of reagents, including radicals^[7–9], nucleophiles^[10–12], electrophiles^[13–15] and transition metal complexes^[16–20]. In the case of thermally-triggered Bergman cyclization that often requires elevated temperature, excess metal complexes are used to promote enediyne cycloaromatization under mild conditions^[20].

In the last decades, many metal-based triggering mechanisms of enediyne compounds have been reported, mostly including stoichiometric or excess amount of metal complexes. In 2005, O'Connor *et al.*^[21] firstly reported iron-catalyzed Bergman cycloaromatization of unbenzannelated enediynes at room temperature (Scheme 1a). The catalytic reactions exhibited a high yield and even available for *trans*-enediynes, but dissociation of the arene product from the Fe complex had to be induced by ultraviolet radiation, which might initiate photo-induced Bergman cyclization of the enediynes^[22] at the same time. Apart from this special mechanism including the iron complexes, most transition-metal-catalyzed cycloaromatizations pass through Myers-Saito-type mechanism (Scheme 1b)^[16, 19, 23–28], which involves rearrangement from an acyclic enediyne with a

terminal alkyne to a more reactive eneyne allene (vinylidene) complex. The rate of such a cyclization is found to be substantially faster than that of its precursor enediyne and is sensitive to the size of the metal fragment. Interestingly, Liu *et al.*^[17] reported that PtCl₂ (5 mol%) could efficiently catalyze cycloaromatization of enediynes to generate a platinum- π -alkyne intermediates, followed by aromatization and C–H bond insertion (Scheme 1c). This work offers a new example for generation of platinum-stabilized 1,4-benzene carbenoid intermediates *via* metal catalyzed activation.

Direct coupling of the diradical intermediates generated by Bergman cyclization provides a straightforward way to synthesize conjugated polymers^[29]. The repeating units of the achieved polymers might be highly ordered^[5]. However, in many cases, they were composed of a mixture of 5- and 6-membered rings^[30, 31]. Under high temperature, intermolecular radical attack onto enediyne monomer competes with the intramolecular cycloaromatization of enediyne compounds. This mixed mechanism leads to uncontrolled polymerization and ill-defined polymer structure. To this end, metal catalyzed Bergman cyclization is considered as a detour as the onset temperature of Bergman cyclization of enediyne could be drastically lowered upon complexation with metal complexes^[32]. Meanwhile, transition-metal catalyst is able to direct the cycloaromatization to extraordinary 1,4-benzene intermediates^[17], showing great promise in constructing polymers with highly-ordered structure. Herein, we report the research on the cycloaromatization polymerization of enediynes catalyzed by a series of transition metal complexes to produce structurally regulated conjugated polymers.

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Scheme 1 Transition-metal-catalyzed cycloaromatizations of enediynes

EXPERIMENTAL

Materials

Tetrahydrofuran (THF), toluene, *o*-xylene and chlorobenzene were dried over calcium hydride (CaH_2) and distilled before use. All the other reagents were commercially available and used as received. 1,2-Diethynylbenzene (EDY 1) and 1,2-diethynyl-4,5-dimethylbenzene (EDY 2) were synthesized according to literature procedures with minor modifications^[33–35]. All the reactions were performed with dry Schlenk technique under an atmosphere of nitrogen.

Characterizations

^1H -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). Chemical shifts were reported in parts per million (ppm) downfield from the tetramethylsilane resonance which was used as the internal standard. Mass spectra of enediyne compounds were recorded on a Micromass LCTM mass spectrometer using the EI method. Fourier transform infrared analysis (FTIR) was performed using KBr pellets on a Nicolet Magna 5700 FTIR spectrometer. Absorption spectra were recorded on a Shimadzu UV-2550 UV-Vis spectrometer with ethyl acetate at room temperature. Fluorescence spectra were obtained on a Fluorolog-3-P UV-Vis-NIR fluorescence spectrophotometer (Jobin Yvon, France). The weight-averaged molecular weight (M_w) and the polydispersity index (PDI) of the polymers 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. MS (MALDI-TOF) of polymers was 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, and operating at an accelerating voltage of 20 kV in reflection 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 μL aliquot of a mixture of 2 mL of matrix (1,1,4,4-tetraphenyl-1,3-butadiene, 20 mg/mL in THF) and

1 mL of polymer (10 mg/mL in THF) on the target plate. The differential scanning calorimetry (DSC) was carried out on a SPA409PC Thermal Analyzer. The electron paramagnetic resonance (EPR) study was performed using an X-band EMX-8/2.7C EPR spectrometer (Bruker, Germany). The spectrometer settings were as follows: sweep width, 200 G; time constant, 163.84 ms; resolution, 1024 points; modulation amplitude, 1.00 G; conversion time, 40.96 ms; modulation frequency, 100.00 kHz; microwave power, 6.376 mW.

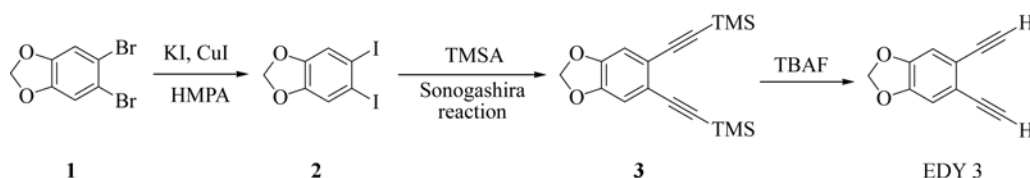
Synthesis of EDY 3 (Scheme 2)

5,6-Diiodobenzo[*d*][1,3]dioxole (2)

An oven-dried flask was charged with **1** (5 g, 17.86 mmol), and 50 mL of hexamethylphosphoramide (HMPA). Then the mixture was stirred intensely and KI (29.6 g, 178.6 mmol), CuI (17 g, 89.3 mmol) were added successively under nitrogen atmosphere. After raising the reaction temperature up to 120 °C and keeping in dark place for 15 h, the dark brown mixture was washed with dilute HCl and saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and extracted with ethyl acetate. Then the organic layer was dried over anhydrous MgSO_4 and the crude product was purified through column chromatography (silica, petroleum ether) to yield white crystalline product (5.87 g, 88%). ^1H -NMR (CDCl_3 , 400 MHz, δ , ppm): 7.30 (s, 2H, Ph-H), 5.98 (s, 2H, $-\text{CH}_2-$).

5,6-Bis(trimethylsilyl)ethynylbenzo[*d*][1,3]dioxole (3)

An oven-dried flask was charged with **2** (1 g, 2.68 mmol), CuI (30 mg, 0.16 mmol), and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (56 mg, 0.08 mmol). Then degassed THF (15 mL), *n*-butylamine (2 mL) and trimethylsilylacetylene (TMSA, 1.05 g, 10.7 mmol) were added successively under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 18 h. The resulting dark brown solution was partitioned with saturated aqueous NH_4Cl and ethyl acetate, and the organic layer was dried over anhydrous MgSO_4 . After removal of the solvent, the crude product was purified through column chromatography (silica, petroleum ether) to yield white crystalline product (0.65 g, 77%). ^1H -NMR (CDCl_3 , 400 MHz, δ , ppm): 6.87 (s, 2H, Ph-H), 5.97 (s, 2H, $-\text{CH}_2-$), 0.25 (s, 18H, CH_3). ^{13}C -NMR (CDCl_3 , 100 MHz, δ , ppm): 147.6, 120.3, 111.7, 103.1, 101.7, 97.0, 0.0. HRMS (EI): m/z Calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_2\text{Si}_2$ 314.1158; Found: 314.1159.



Scheme 2 Synthesis of EDY 3

5,6-Diethynylbenzo[d][1,3]dioxole (EDY 3)

Tetrabutylammonium fluoride hydrate (TBAF·3H₂O, 1.3 g, 4.13 mmol) and *p*-toluenesulfonic acid (392 mg, 2.06 mmol) were rapidly added to a solution of **3** (648 mg, 2.06 mmol) in THF (20 mL). The obtained mixture was stirred at room temperature for 30 min and then subjected to rotating evaporation under reduced pressure to remove the solvent. The residual was purified through column chromatography (silica, petroleum ether) to yield white crystalline product (345 mg, 98%). ¹H-NMR (CDCl₃, 400 MHz, δ , ppm): 6.91 (s, 2H, Ph-H), 6.00 (s, 2H, -CH₂-), 3.25 (s, 2H, C≡CH). ¹³C-NMR (CDCl₃, 100 MHz, ppm): 147.9, 119.4, 112.0, 101.9, 81.8, 79.9. HRMS (EI): *m/z* Calcd. for C₁₁H₆O₂ 170.0368; Found: 170.0370.

Polymerization

All the enediyne compounds were treated with transition metal catalyst (for metal-free Bergman reaction, no catalyst was added) in redistilled solvent under a dry nitrogen atmosphere. The mixture was stirred at reasonable temperature in a sealed tube until the disappearance of all the enediyne compounds. After removal of the solvent, the crude products were precipitated into a large amount of methanol, collected by centrifugation, and dried under vacuum to afford dark brown polymers.

RESULTS AND DISCUSSION

Starting with EDY 1–3 as monomers, we examined the feasibility of transition-metal-catalyzed reactions under different conditions (Table 1). Directly heating EDY 1 in chlorobenzene at 130 °C for 3 days (entry 1) gives dark brown polymer in nearly quantitative yield, which follows typically thermal-triggered Bergman cyclization polymerization,

producing polymers with ill-defined structure as demonstrated by Matzger *et al.*^[31] When 1% of Pd(PET₃)₂Cl₂ is added, the conversion of EDY 1 is greatly accelerated, and completed in 1 day at 100 °C (entry 2), giving polymer with comparable yield and molecular weight as that from thermal Bergman cyclization. It should be noted that the formed polymers from enediynes are structurally more compact in comparison with general polystyrene standards, so the molecular weights could be severely underestimated when determined by gel permeation chromatography (GPC). When the polymerization was conducted in toluene, higher molecular weight polymer was obtained (entry 3). However, when the polymerization was conducted in *o*-xylene, a great amount of precipitate was formed, which was insoluble in organic solvents such as ethyl acetate, dichloromethane, DMF, DMSO, toluene. Surprisingly, the yield of the precipitate is over 1100% of the weight of the enediyne monomer, indicating that *o*-xylene must have participated in the polymerization. The incorporation of solvent molecule in the polymer chain severely messes up the polymerization mechanism and limits the control over the polymer structure. Therefore, inert solvent, such as chlorobenzene should be used for this reaction. Other Pd complexes also mediate the polymerization of enediynes under mild condition (entries 5–9), but PdCl₂ and Pd/C give polymers with very broad molecular weight distributions (entries 10 and 11). The complexes of transition metal in the same group as Pd, like Ni and Pt, were also screened for this reaction. Unfortunately, no acceleration of the conversion of enediyne monomers was observed. Overall, Pd(PET₃)₂Cl₂ is considered as the best catalyst for this reaction. Under the optimized condition, the catalytic polymerization of EDY 2 and EDY 3 proceeded smoothly to give the desired product in short time. The on-set

Table 1 Catalytic polymerization of enediyne compounds

Entry	Enediyne	Catalyst	Reaction condition ^a	Solvent	<i>M_w</i> (kDa)	PDI
1	EDY 1	–	130 °C, 3 days	Chlorobenzene	3.8	3.35
2	EDY 1	Pd(PET ₃) ₂ Cl ₂	100 °C, 1 day	Chlorobenzene	2.5	2.16
3	EDY 1	Pd(PET ₃) ₂ Cl ₂	100 °C, 1 day	Toluene	6.3	– ^d
4	EDY 1	Pd(PET ₃) ₂ Cl ₂	100 °C, 1 day	<i>o</i> -Xylene	Insoluble	– ^d
5	EDY 1	Pd(PET ₃) ₂ Br ₂	100 °C, 1 day	Chlorobenzene	1.2	2.26
6	EDY 1	Pd(PET ₃) ₂ I ₂	100 °C, 1 day	Chlorobenzene	1.3	2.21
7	EDY 1	Pd(PPh ₃) ₂ Cl ₂	100 °C, 1 day	Chlorobenzene	3.0	2.99
8	EDY 1	Pd(dppf)Cl ₂ ^b	110 °C, 1 day	Chlorobenzene	5.0	6.20
9	EDY 1	Pd(NHC)PyCl ₂ ^c	110 °C, 1 day	Chlorobenzene	2.3	2.51
10	EDY 1	PdCl ₂	100 °C, 1 day	Chlorobenzene	1.9	– ^d
11	EDY 1	Pd/C	110 °C, 5 days	Chlorobenzene	2.2	– ^d
12	EDY 2	Pd(PET ₃) ₂ Cl ₂	100 °C, 8 h	Chlorobenzene	4.2	3.82
13	EDY 3	Pd(PET ₃) ₂ Cl ₂	100 °C, 1 day	Chlorobenzene	2.2	2.33

^a The reaction time indicates the complete conversion of monomer; ^b dppf: 1,1'-diphenylphosphinoferrocene; ^c NHC: *N*-heterocyclic carbene; Py: 3-chloropyridine; ^d The GPC curve is too broad to give a reasonable PDI value.

temperatures of these three enediynes for thermal Bergman cyclization are all over 130 °C according to the differential scanning calorimetry (DSC) analysis (Fig. S1, in electronic supplementary information, ESI). Clearly, the presence of the Pd complexes greatly facilitates the polymerization of the enediyne compounds.

Figure 1 shows the ^1H - and ^{13}C -NMR spectra of EDY 1 and the corresponding polymer P1 (entry 2, catalyzed by 1% $\text{Pd}(\text{PET}_3)_2\text{Cl}_2$ in chlorobenzene). The single peak associated with the terminal alkynyl protons at 3.34 ppm completely disappears after the polymerization, so do the ^{13}C -NMR signals of acetylenic carbons at about 81.1 and 81.8 ppm. Meanwhile the peaks attributed to the phenyl protons at about 7.3–7.5 ppm (Fig. 1a) and the phenyl carbon at about 125.0, 128.5 and 132.6 ppm (Fig. 1b) are all broadened after the polymerization, which is a direct evidence of the formation of a rigid polymer backbone.

FTIR spectroscopy analysis was also employed to confirm the occurrence of cycloaromatization polymerization. As shown in Fig. 2, the stretching band of carbon-carbon triple bond at 2115 cm^{-1} and characteristic band of terminal alkyne at 3290 cm^{-1} of EDY 1 all disappear after the reactions through Bergman cyclization (Table 1, entry 1) or catalytic polymerization in the presence of $\text{Pd}(\text{PET}_3)_2\text{Cl}_2$ (Table 1, entry 2), corroborating that both reactions take place at the enediyne moiety.

Formation of the conjugated backbones was further confirmed via UV-Vis and fluorescence spectroscopy. The enediyne compounds typically show $\pi\text{-}\pi^*$ transition below 300 nm. After the catalytic polymerization (Table 1, entries 2, 12 and 13), strong absorption tailing up to 500 nm (Fig. 3a) is

observed, indicating the formation of long conjugated system. The fluorescence spectroscopy shown in Fig. 3(b) demonstrates that the maximum emission wavelengths (λ_{max}) of EDY 1–3 are 318, 304 and 323 nm, respectively, while the λ_{max} of the corresponding polymers shifts to 495, 506 and 468 nm, respectively. The clear red-shift of the fluorescence emission indicates a higher π -conjugated degree of the polymers, directly relating to the formation of conjugated polynaphthalene backbone.

Matrix assisted laser deionization/time of flight (MALDI-TOF) mass spectrometry is one of the most informative tools to study the structure of species with high molecular weight. Figure 4 shows the MALDI-TOF mass spectra of polymers prepared under different conditions. The peaks featured with an equal interval consistent with the calculated m/z value of a monomer unit (126.0470) are observed in all the spectra. According to end-group analysis, the peak series marked with blue boxes (Fig. 4) correspond to the mass of the proposed polynaphthalene (capped by external hydrogen donors), while the series marked in pink and orange boxes are consistent with the calculated m/z value of a monomer unit plus 92 and 106 (the molecular weight of toluene and *o*-xylene), respectively, indicating that the polymer chains were capped by toluene or *o*-xylene molecule. This result shows that the propagating chains might be terminated by trapping solvent molecules. Interestingly, in the MALDI-TOF mass spectrum of the polymer prepared in chlorobenzene (Fig. 4a), no peak corresponding to the addition of solvent molecule is determined, showing the very low hydrogen donor ability of chlorobenzene, which is very important for preparing high

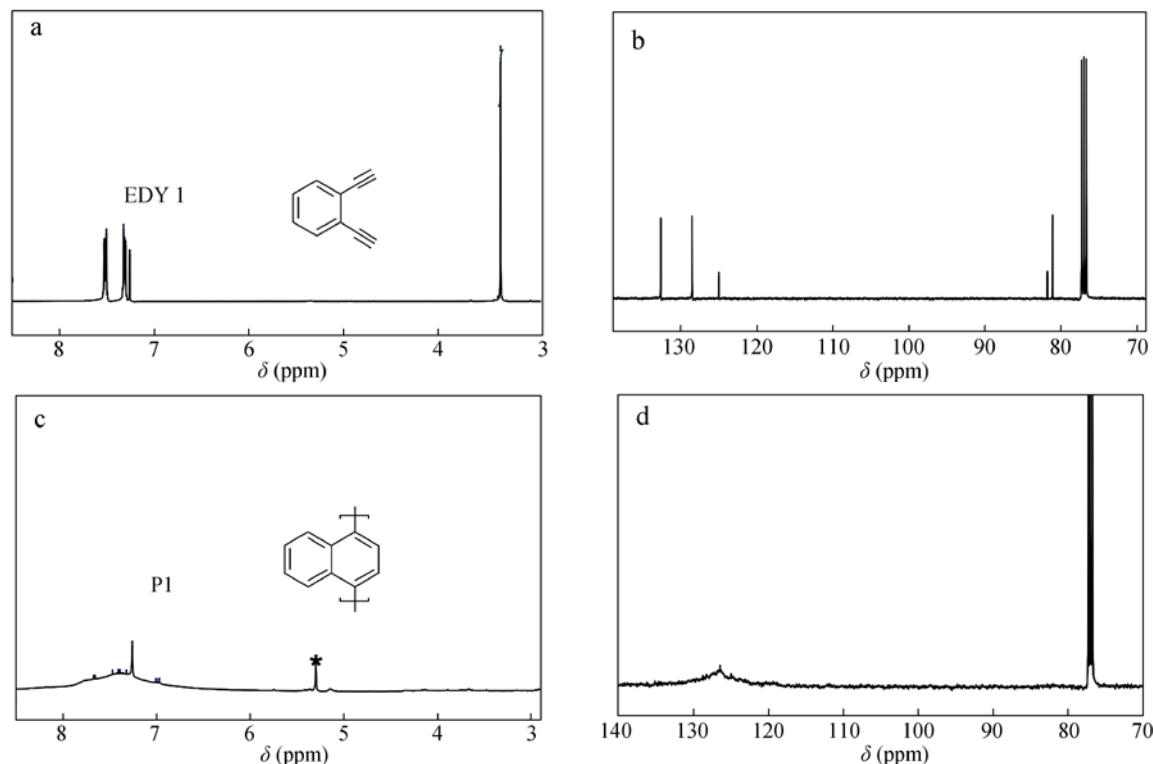


Fig. 1 The ^1H - (a, c) and ^{13}C - (b, d) NMR spectra of EDY 1 (a, b) and P1 (c, d)

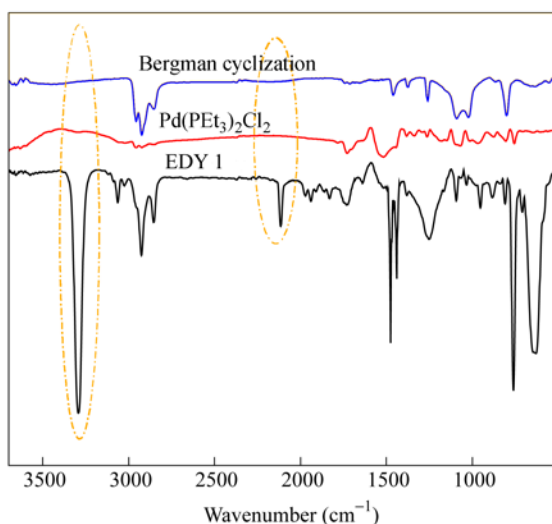


Fig. 2 IR spectra of EDY 1 and the corresponding polymer catalyzed by $\text{Pd}(\text{PEt}_3)_2\text{Cl}_2$ (entry 2) and through Bergman cyclization (entry 1)

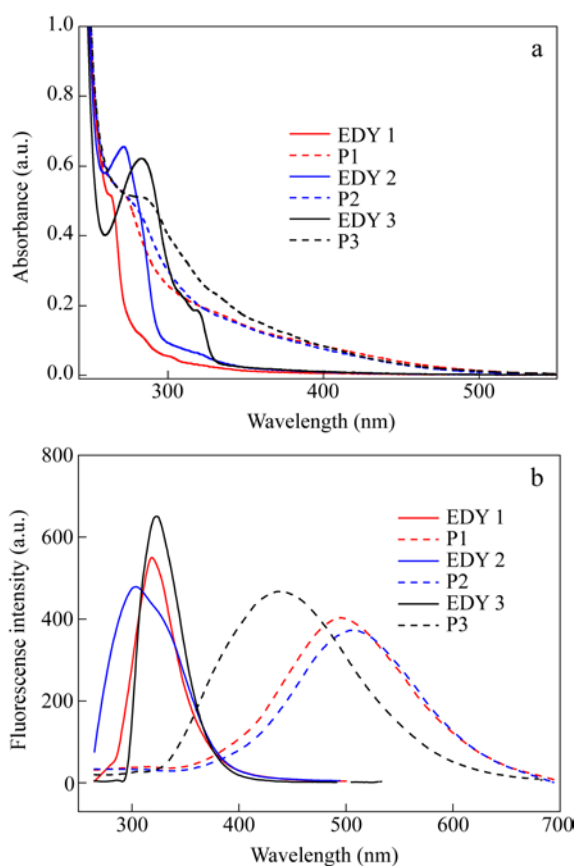


Fig. 3 UV-Vis (a) and fluorescence emission (b) spectra of enediynes and the corresponding polymers in THF ($c = 10^{-3}$ mg/mL; Excitation wavelengths of EDY 1–3 are 263, 272 and 283 nm, respectively. The online version is colorful.)

molecular weight polymers through this method. On the other hand, the MALDI-TOF mass spectrum (Fig. 4d) of the polymer prepared through Bergman polymerization (Table 1, entry 1) is quite complicated, demonstrating the ill-defined structure of this reaction as previously shown by

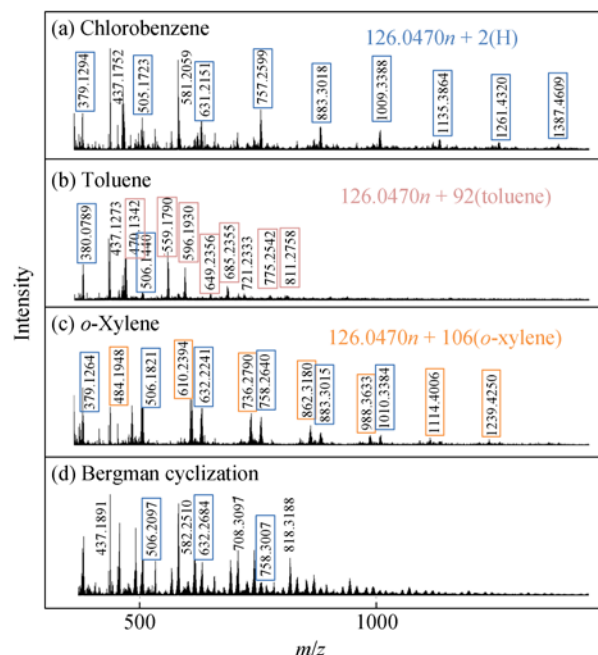
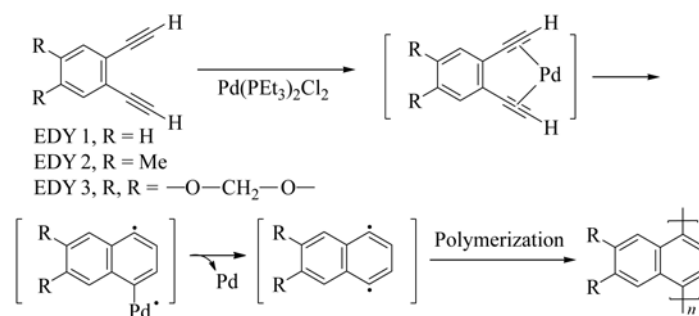


Fig. 4 The MALDI-TOF mass spectra of polymers produced in (a) chlorobenzene, (b) toluene, (c) *o*-xylene using $\text{Pt}(\text{PEt}_3)_2\text{Cl}_2$ as the catalyst, and (d) through Bergman cyclization polymerization

Matzger *et al.*^[31] The superiority of $\text{Pd}(\text{PEt}_3)_2\text{Cl}_2$ over other Pd species as catalyst for this reaction is also demonstrated by MALDI-TOF analysis. As shown in Fig. S2(a) (in ESI), the polymer obtained in the presence of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ presents two series of signals corresponding to a monomer unit plus 137 and 213 (the molecular weight of PPh_2 and PPh_3), indicating that the propagating chains were terminated by trapping the ligand “ PPh_3 ”. When heating EDY 1 with PdCl_2 , Pd/C as catalysts, the reactions are rather sluggish (Table 1, entries 10 and 11). The MALDI-TOF mass spectra of the obtained polymers are messy and complicated, similar to that obtained from neat thermal Bergman cyclization polymerization. The mass spectra of the polymers obtained with other Pd complexes, shown in Fig. S3 (in ESI), are more complicated than that of the polymer obtained with $\text{Pd}(\text{PEt}_3)_2\text{Cl}_2$ as catalyst, implying that $\text{Pd}(\text{PEt}_3)_2\text{Cl}_2$ is the optimal catalyst in this polymerization.

The radical nature of this Pd catalyst polymerization is confirmed through radical trapping experiment. The reactive carbon radicals generated by (catalyzed) Bergman cyclization either couple with each other to form polymer or (at the same time) attack radical trapping agent to form stable radicals that can be easily seen through electron paramagnetic resonance (EPR) analysis. To this end, excess of phenyl *tert*-butyl nitron (PBN) was added to the $\text{Pd}(\text{PEt}_3)_2\text{Cl}_2$ catalyzed polymerization system of EDY 1. After reaction at 100 °C for 1 day, the obtained polymeric product was subjected to EPR analysis. The EPR spectrum (Fig. S4, in ESI) of the polymer clearly evidences the presence of N—O free radicals. The multiplex in EPR is probably due the complex microenvironment in the polymer chain.

Based on all the information above, a polymerization mechanism is proposed as shown in Scheme 3. In the first step, the two alkynyl groups are coordinated to Pd catalyst to



Scheme 3 Proposed mechanism of [Pd]-catalyzed cycloaromatization polymerization of enediynes

generate a metal- π -alkyne intermediate, resulting in a shorter “cd distance” (the distance between C1–C6)^[36]. Therefore, the cycloaromatization would take place at lower temperature. Meanwhile, the coordination of Pd metal directs the reaction to exclusively go through the 6-endo pathway^[17], generating aromatic diradicals with a pendant Pd complex. The weakly coordinating Pd complex quickly dissociates from the intermediate and runs into another catalysis cycle. When there is free radical donor like solvent molecules (toluene, *o*-xylene) present in the reaction system, the radicals might attack these species to generate premature low molecular weight polymer chain with complicated structure. When all the species that can quench free radical intermediates are excluded, the free diradical intermediate prefers to couple with each other to form conjugated polynaphthalene.

CONCLUSIONS

In summary, we have studied the transition-metal-catalyzed cycloaromatization polymerization of enediynes to produce a series of conjugated polymers. The formation of the rigid main chain was confirmed with a variety of techniques including NMR, FTIR, UV-Vis and MALDI-TOF mass spectroscopy. The transition metal catalysts, especially the palladium(II) complexes, mediate the cycloaromatization polymerization of enediynes at relatively low temperature and in a controlled way to produce structurally regulated polynaphthalene in high yield.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2088-9>.

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