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Palladium-catalyzed alkyne polyannulation of diphenols and unactivated internal diynes: a new synthetic route to functional hetrocyclic polymers

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A new polymerization route for the preparation of functional hetrocyclic polymers was developed from diphenol derivatives and unactivated internal diynes. The alkyne polyannulations of 4,4'-sulfonyldiphenol and 4,4'-(α,ω-alkylenedioxy) bis(diphenylacetylene)s or 1,2-bis[4-(2-phenylethynyl)phenyl]-1,2-diphenylethene were catalyzed by $Pd_2(dba)_3$ in the presence of bathophenanthroline, silver acetate and copper(II) acetate monohydrate in 1,4-dioxane at 130 °C, affording polymers with benzofuran moieties in satisfactory yields and high molecular weights (M_w up to 34 000). All the polymers were thermally stable, losing merely 5% of their weight at high temperature of up to 376 °C. They showed good film-forming ability and their thin solid films showed high refractive indices (RI = 1.900–1.611) in a wide wavelength region of 400–1000 nm. Polymer carrying tetraphenylethene units in the backbone was photosensitive and could be utilized to generate fluorescent pattern by photolithography process.

Introduction

Developing new methodologies for the synthesis and preparation of novel polymeric materials is an important research topic in polymer science.[1-5] Among all plausible strategies, new polymerization reactions based on triple-bond building blocks have attracted much interest from our research group.[6-10] For many years, we have been working on the construction of functional macromolecules from alkynes by means of metathesis polymerization, polycoupling, polycyclotrimerization and click polymerization. Most of these polymerization tools were developed from organic reactions of small molecules. It is much more difficult to convert an organic reaction into a useful polymerization technique because several important issues have to be addressed, including the monomer availability, the catalytic efficiency, the interference between functional groups, the polymerization optimization, the structural selectivity, the control of molecular weights and the solubility and processability of the resulting polymers.

From the aspect of reaction mode, the polymerization reactions developed by our group can be roughly classified as direct-addition and ring formation. Polycyclotrimerization and alkyne-azide click polymerization are two outstanding examples among various ring formation strategies. Polycyclotrimerization was first employed for the construction of pure hydrocarbon polymers with stable benzene rings.[11-14] Afterwards, nitrogen-rich polytriazines were also obtained under simple and mild conditions by polycyclotrimerization of dinitriles to enrich the scope of this useful polymerization technique.[15] Meanwhile, the click polymerization derived from copper-catalyzed alkyne-azide cycloaddition reaction gave regio-regular polytriazoles and it was later developed to perform under metal-free conditions by using activated alkyne monomers.[16–19] However, another useful strategy to achieve ring formation which is less reported is the annulation process. Annulation refers to a chemical reaction in which a new (fused) ring was formed in an aromatic compound by its reaction with another molecule. Several pioneer projects have been reported by our group in recent years for the synthesis of new functional polymers by the so-called polyannulation. For example, we successfully developed rhodium-catalyzed oxidative polycoupling of arylboronic acids and internal diynes to polymers with highly substituted naphthalene rings.[20] Soon after, another rhodium-catalyzed atom-economical synthesis of poly(pyrazolyl-naphthalene)s from phenylpyrazole and internal diynes was also reported by the same researchers.[21] In these works, two triple bonds from two diyne monomers merged with the phenyl ring of arylboronic acid or phenylpyrazole to give a polymer with naphthelane skeleton so as to realize the same result as polycyclotrimerization through annulation polymerization.

Many different kinds of oxygen- or nitrogen-bearing heterocycles can be obtained by annulation, and when they are constructed from benzene rings, such a reaction is called benzannulation. Benzofuran is a privileged structure found in

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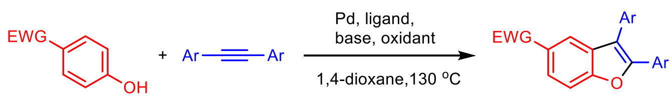
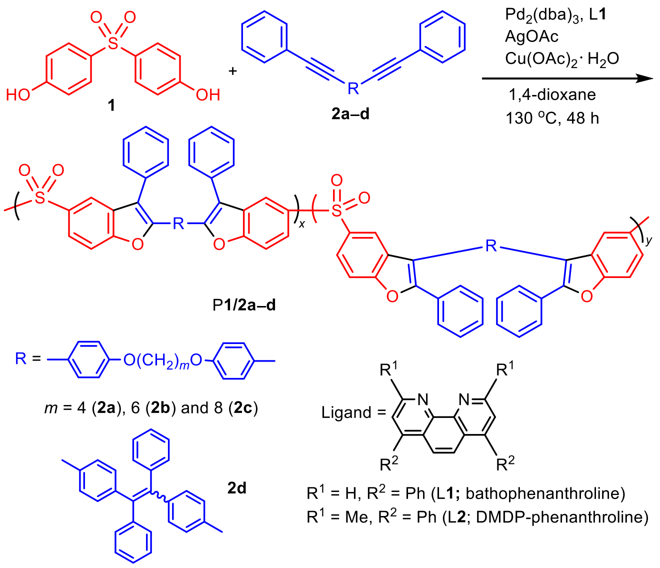
natural products and bio-active compounds, and methodology for its access thus has attracted much attention.[22–30] Transition metal-catalyzed oxidative annulation of phenols with alkynes offers a platform for the atom-economical formation of benzofuran in a straightforward way. Among them, the palladium-catalyzed annulation between phenol derivatives and unactivated internal alkynes brought by Sahoo and his co-workers. provided a promising pathway to highly substituted benzofuran (Scheme 1).[31] Starting from common phenol derivatives and simple internal alkyne without any activated functional groups, this reaction gave benzofuran motifs in high yield in the presence of palladium(0) catalyst and ligand with base and oxidant. Through a series of optimized experiments, tris(di-benzylideneacetone)dipalladium [$Pd_2(dba)_3$] and bathophen-anthroline were found to be effective catalyst and ligand, respectively, for this reaction. On the other hand, silver acetate (AgOAc) and copper(II) acetate monohydrate [$Cu(OAc)_2·H_2O$] were commonly used base and oxidant, respectively, to assist the catalytic cycle.

Herein, for the extension of our research and the purpose of exploring new polymerization methods, we tried to develop the abovementioned reaction into a novel polymerization. In this work, we presented the polymerizations of diphenol derivative **1** and unactivated internal diynes **2a**–**d** and the properties of the resulting polymers P**1**/**2a**–**d**. The monomers are either commercially available or easily synthesized.



Scheme 1 Formation of benzofuran through palladium-catalyzed oxidative annulation of phenol and unactivated internal alkyne.



Scheme 2 Palladium-catalyzed oxidative polyannulation of 4,4'-sulfonyldiphenol **1** and internal diynes **2a**–**d**.

Table 1 Effect of ligand on the polymerization[a]

no.	ligand	yield (%)	M_w[b]	M_w/M_n[b]
1	**L1**	65	34 000	3.9
2	**L2**	7	3 300	1.4

[a] Carried out in 1,4-dioxane under nitrogen in the presence of $Pd_2(dba)_3$, ligand, AgOAc, $Cu(OAc)_2·H_2O$ at 130 °C for 48 h. [**1**] = [**2b**] = 0.10 M, [$Pd_2(dba)_3$] = 10% [**2b**], [ligand] = 2[$Pd_2(dba)_3$], [Ag] = [Cu] = 4[**2b**]. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration.

Table 2 Effect of catalyst loading on the polymerization[a]

no.	[Pd] (% equiv.)[b]	yield (%)	M_w[b]	M_w/M_n[b]
1	20	82	18 100	2.6
2	15	53	27 400	2.6
3[c]	10	65	34 000	3.9
4	5	45	5 900	2.2

[a] Carried out in 1,4-dioxane under nitrogen in the presence of different concentrations of $Pd_2(dba)_3$, **L1**, AgOAc, $Cu(OAc)_2·H_2O$ at 130 °C for 48 h. [**1**] = [**2b**] = 0.10 M, [**L1**] = 2[$Pd_2(dba)_3$], [Ag] = [Cu] = 4[**2b**]. [b] Equivalent to [**2b**]. [c] Determined by GPC in THF on the basis of a linear polystyrene calibration. [c] Data taken from Table 1, no. 1.

Results and Discussion

Monomer synthesis

To examine whether the annulation reaction is a useful tool for synthesizing polymers, we prepared a series of diynes with different molecular structures, and examined whether they can be polymerized. While 4,4'-sulfonyldiphenol (monomer **1**) was commercially available, the diyne monomers **2a**–**2c** with different numbers of methylene spacer (4, 6 and 8 for **2a**, **2b** and **2c**, respectively) were obtained according to the literature methods.[20] On the other hand, the tetraphenylethene (TPE)-containing monomer (**2d**) was prepared by a two-step synthetic route which consisted of Sonogashira coupling reaction of phenylacetylene and 4-bromobenzophenone followed by the McMurry homo-coupling of the obtained product. All the monomers were characterized by standard spectroscopic methods and gave satisfactory analysis data corresponding to their structures.

Polymerization

Several parameters such as catalyst, solvent, monomer concentration and reaction time need to be taken into consideration for optimizing a polymerization system. Thus, we first studied the effect of ligand on the polymerization using **1** and **2b** as monomers.

According to the annulation mechanism, we fixed the concentration of the ligand to that of $Pd_2(dba)_3$ as 2:1. The catalytic effect of two phenanthroline-based ligands with a subtle difference in the R^1 group (H for **L1** and Me for **L2**) was examined. Interestingly, complete different results were obtained. In the presence of **L1**, a polymer was obtained in a moderate yield of 65 % with an M_w value of 34 000 (Table 1 no. 1). However, only a trace amount of oligomer was obtained when changing the ligand to **L2**. Such a contrasted result suggested that the steric bulkiness of the ligand was a key factor to determine its coordination ability and hence its catalytic capability.

Transition metals were usually required to initiate the annulation reactions, especially those involving unactivated internal alkynes due to their comparative low reactivity. In this work, $Pd_2(dba)_3$ was employed as catalyst. Because the Pd(0) metal centre was stabilized by the dba ligand, the presence of bathophenanthroline was needed to generate the real catalytic species. Generally speaking, increasing the catalyst concentration results in a higher isolated yield but leads to a lower molecular weight. Our trials on investigating the effect of $Pd_2(dba)_3$ concentration on the polymerization were basically in agreement with this statement. Compared the results obtained at different Pd concentrations (20, 15, 10 and 5% of [**2b**]), it was found that the polymerization conducted at 20% catalyst concentration generated a polymer with a satisfactory molecular weight in a high yield. Although higher molecular weight polymers were furnished at lower catalyst concentrations (15% and 10%), the isolated yield became lower. Poorer results were obtained when the catalyst concentration was further decreased to 5%. Considering the balance between the yield and molecular weight, we fixed the concentration of $[Pd_2(dba)_3]$ to 10 % for latter investigation.

Solvent is an external parameter which exerts a great influence on the polymerization. Many intrinsic characters of the solvents influence the reaction process. In a polymerization reaction, good dissolving ability to the monomers and the corresponding polymers is one of the vital parameters to consider for the selection of solvent. In this case, it may be difficult to find a suitable solvent for diphenol monomer **1** because of its relatively high polarity, while the lesser polar monomer **2b** with a quite long alkyl chain can be readily dissolved in many solvents. We selected several solvents of different natures with high boiling temperature for our investigation. Among all the tested organic solvents, 1,4-dioxane seemed to be the most suitable one for the polymerization. Such results was consistent with that for the small molecule reaction (Table 3 no. 1). Polymers with higher molecular weight were produced in *o*-xylene but the obtained amount was low (Table 3 no. 2). This might be attributed to the poor solubility of monomer **1** in the solvent. However, the incorporation of benzofuran moiety and alkyl chain in the polymer structure promoted the solubility and thus facilitated the further growth of the polymer chain and hence its molecular weight. In contrast, no polymer was generated in toluene, which might be imputed to the reaction temperature despite the solubility issue. Other non-protic polar solvents, like *N*,*N*-dimethylformamide (DMF), and protic solvents, like 1-pentanol were not suitable for this polymerization and polymers with low molecular weights were produced in poor yields in these solvents.

We then investigated the influence of monomer concentration on the polymerization. Generally, increasing the monomer concentration will lead to more efficient intermolecular collision between reacting monomers, thus giving a better polymerization result. While keeping the molar ratio of **1**/**2b** at 1/1 unchanged, the molecular weight of the obtained polymer was gradually enhanced from 10 300 to 39 200 when the monomer concentration was increased from 0.05 M to 0.20 M (Table 4). The isolated yield, however, decreased gradually, possibly due to the increase in the viscosity of reaction mixture upon thickening the monomer concentration. Furthermore, gelation occurred at a monomer concentration of 0.50 M. The formation of gel may provide an explanation for the decrease in polymer yield as mentioned above. Thus, from both the economical point of view and satisfactory reaction results, we chose 0.10 M as the suitable monomer concentration for this polymerization.

We then monitored the time course on the polymerization by calculating the isolated yield and GPC analysis. As shown in Table 5, prolonging the reaction time from 6 h to 48 h significantly enhanced the M_w value by nearly 4-fold from 7 900 to 34 000. The effect of reaction time on the isolated yield was not obvious. However, further extension of the reaction time from 48 h to 60 h even caused a slight decrease in both the molecular weight and isolated yield. Therefore, the polymerization was generally terminated after 48 h.

Table 3 Solvent effect on the polymerization[a]

no.	solvent	yield (%)	M_w[b]	M_w/M_n[b]
1[c]	1,4-dioxane	65	34 000	3.9
2	o-xylene	33	19 600	3.4
3	DMF	39	4 900	1.8
4	1-pentanol	10	2 100	1.2
5[d]	toluene	trace		

[a] Carried out in different solvents under nitrogen in the presence of $Pd_2(dba)_3$, L**1**, AgOAc, $Cu(OAc)_2 \cdot H_2O$ at 130 °C for 48 h. [**1**] = [**2b**] = 0.10 M, $[Pd_2(dba)_3]$ = 10% [**2b**], [L**1**] = $2[Pd_2(dba)_3]$, [Ag] = [Cu] = 4[**2b**]. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration. [c] Data taken from Table 1, no. 1. [d] Reaction conducted with a condenser.

Table 4 Effect of monomer concentration on the polymerization[a]

no.	[**1**] (M)	[**2b**] (M)	yield (%)	M_w[b]	M_w/M_n[b]
1	0.50	0.50	gel		
2	0.20	0.20	59	39 200	4.4
3[c]	0.10	0.10	65	34 000	3.9
4	0.05	0.05	71	10 300	3.4

[a] Carried out in 1,4-dioxane under nitrogen in the presence of $Pd_2(dba)_3$, L**1**, AgOAc, $Cu(OAc)_2 \cdot H_2O$ at 130 °C for 48 h. $[Pd_2(dba)_3]$ = 10% [**2b**], [L**1**] = $2[Pd_2(dba)_3]$, [Ag] = [Cu] = 4[**2b**]. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration. [c] Data taken from Table 1, no. 1.

Table 5 Time course on the polymerization[a]

no.	time (h)	yield (%)	M_w[b]	M_w/M_n[b]
1	6	34	7 900	1.6
2	12	41	15 400	2.2
3	24	46	17 900	3.0
4[c]	48	65	34 000	3.9
5	60	58	31 000	2.9

[a] Carried out in 1,4-dioxane under nitrogen in the presence of $Pd_2(dba)_3$, L**1**, AgOAc, $Cu(OAc)_2 \cdot H_2O$ at 130 °C. [**1**] = [**2b**] = 0.10 M, $[Pd_2(dba)_3]$ = 10% [**2b**], [L**1**] = $2[Pd_2(dba)_3]$, [Ag] = [Cu] = 4[**2b**]. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration. [c] Data taken from Table 1, no. 1.

Table 6 Polymerization of **1** with different diyne monomers **2a**–**d** under optimized conditions[a]

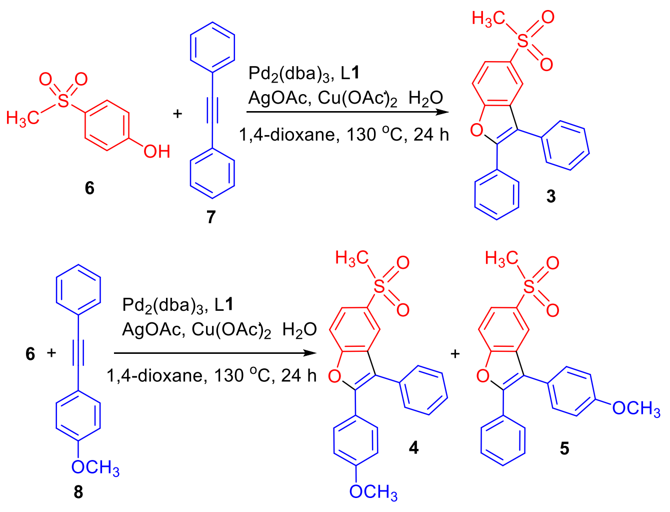
no.	polymer	yield (%)	M_w[b]	M_w/M_n[b]	S[d]
1	P**1**/**2a**	82	19 200	3.6	Δ
2[c]	P**1**/**2b**	65	34 000	3.9	√
3	P**1**/**2c**	62	23 100	3.2	√
4	P**1**/**2d**	34	13 000	1.8	√

[a] Carried out in 1,4-dioxane under nitrogen in the presence of $Pd_2(dba)_3$, L**1**, AgOAc, $Cu(OAc)_2{\cdot}H_2O$ at 130 °C for 48 h. [**1**] = [**2b**] = 0.10 M, [$Pd_2(dba)_3$] = 10% [**2b**], [L**1**] = 2[$Pd_2(dba)_3$], [Ag] = [Cu] = 4[**2b**]. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration. [c] Data taken from Table 1, no. 1. [d] Solubility (S) tested in common used organic solvents such as THF and chloroform; √ = completely soluble, Δ = partially soluble.

After systematic study on the polymerization conditions, we applied the optimized conditions to polymerize other unactivated internal diyne monomers, i.e. **2a**, **2c** and **2d**. All the polymerization reactions proceeded smoothly to give polymers in satisfactory to high yields and high molecular weights (M_w from 13 000 to 34 000). All the polymers possessed good solubility in common organic solvents like dichloromethane, tetrahydrofuran (THF) and chloroform except P**1**/**2a**, possibly due to its short alkyl chain length which made it to have a low solvating ability. Such problem can be readily solved by incorporation of long alkyl chains or twisted moieties into the polymer structure such as in P**1**/**2c** and P**1**/**2d**.

Model reaction

The annulation reaction of 4-methylsulfonylphenol (**6**) and a symmetric unactivated internal alkyne **7** was intensively studied to serve as the model reaction (Scheme 3). In the presence of $Pd_2(dba)_3$, L**1**, AgOAc and $Cu(OAc)_2{\cdot}H_2O$ in 1,4-dioxane at 130 °C for 24 h under nitrogen, a model compound **3** was obtained at a yield of 51%. Moreover, in order to check the regio-selectivity of this annulation reaction, we further examined the model reaction of **6** with an unsymmetric unactivated internal alkyne **8** with the purpose of simulating the chemical environment of monomers **2a**–**c** (Scheme 3).



Scheme 3 Synthetic routes to model compound **3** and a mixture of **4** and **5**.

Structure characterization

Model compounds. The chemical structure of **3** was confirmed by NMR, IR and high resolution mass spectroscopies with satisfactory results. For example, the phenyl protons ortho to the sulfonyl group of **6** resonated at δ 7.65, which shifted to δ 8.12 and δ 7.93 after the annulation (Fig. 1C). Similarly, the resonance of the phenyl carbons para to the sulfonyl group of **6** shifted from δ 161.1 to δ 156.3 after the reaction due to the formation of benzofuran ring in **3** (Fig. 2C). After column purification, single crystals of **3** were obtained from its dichloromethane/hexane solution and their structure was characterized crystallographically (Fig. 3A). Interestingly, neither the pale yellow powder of **3** showed solid-state emission nor its nano aggregates in THF/H_2O mixture exhibited the aggregation-induced-emission effect. However, its micro crystallites emitted blue light, demonstrating a phenomenon of crystallization-induced-emission (Fig. 3C).

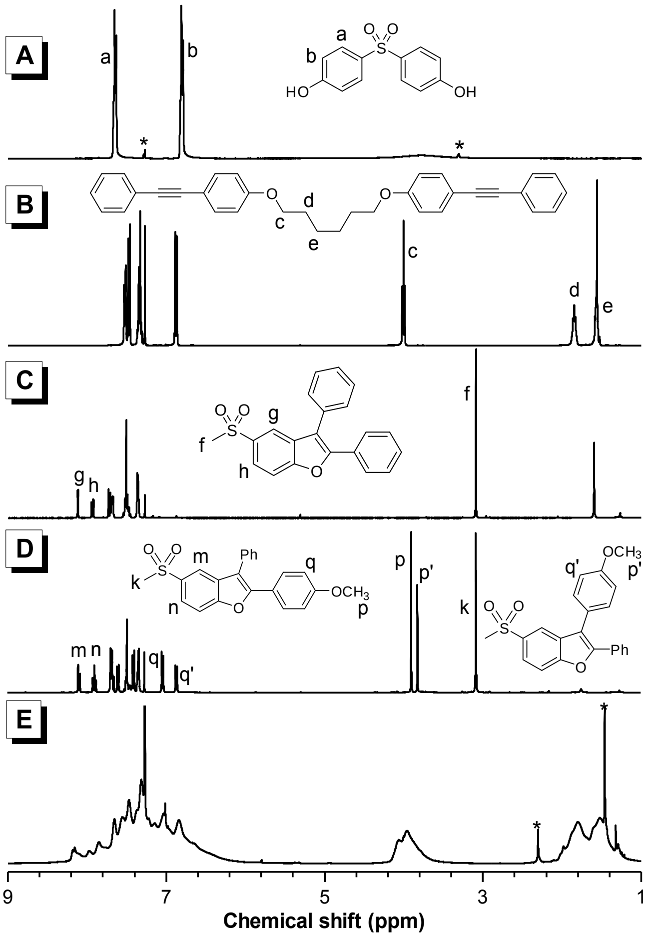


Fig. 1 ^1H NMR spectra of (A) **1**, (B) **2b**, (C) **3**, (D) a mixture of **4** and **5** and (E) P**1**/**2b** in chloroform-*d*. The solvent peaks were marked with asterisks. A few drops of methanol-d_3 were added in (A) to assist the dissolution of **1**.

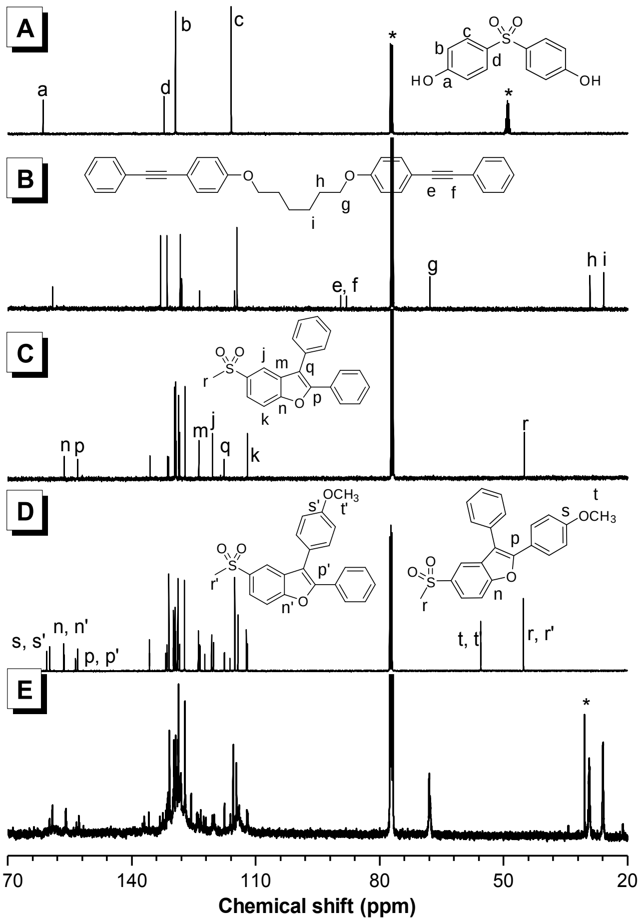


Fig. 2 ^{13}C NMR spectra of (A) **1**, (B) **2b**, (C) **3**, (D) a mixture of **4** and **5** and (E) P**1**/**2b** in chloroform-*d*. The solvent peaks were marked with asterisks. A few drops of methanol-d_3 were added in (A) to assist the dissolution of **1**.

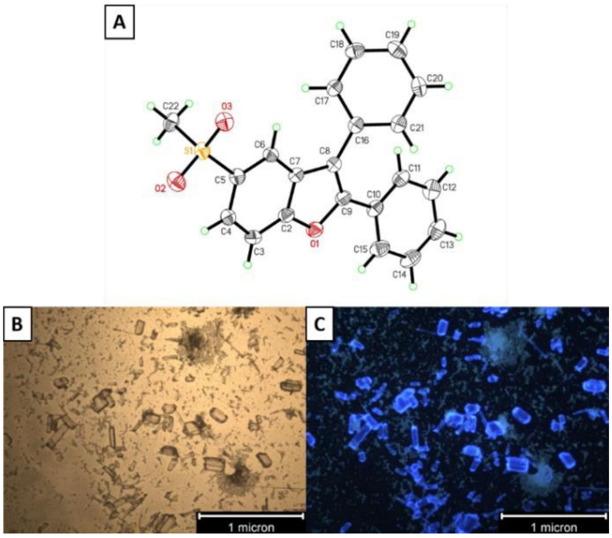


Fig. 3 (A) Crystal structure of model compound **3**, (B) Bright-field and (C) fluoroscent microscopic images of micro-crystallites of **3**.

Under the same conditions used for preparing **3**, a mixture of **4** and **5** was generated from **6** and **8**. Due to their similar physical properties, it was difficult to separate them by using column chromatography. The attempt to grow single crystals from this mixture also failed probably due to their poor molecular packing stemmed from their more irregular structures. However, different methoxy proton resonances (labeled as p and p′ for **4** and **5** in Fig. 1D, respectively) and absorptions of the phenyl protons (labeled as q and q′ for **4** and **5**, respectively) adjacent to the methoxy group were observed in their ^1H NMR spectrum. From the integral of the peaks (p and p′), the ratio of **4**/**5** was calculated to be ~3:2, suggesting a poor regio-selectivity of this reaction and also a random alternative sequence of repeating units in the polymers. The characteristic peaks associated with the resonances of the protons of the benzofuran ring were also found with a complicated splitting pattern due to the asymmetric nature of the starting material.

Polymer. All the polymers gave satisfactory spectroscopic data corresponding to their molecular structures. The IR and NMR spectra of P**1**/**2b** are given below as examples.

Fig. 1 shows the ^1H NMR spectra of P**1**/**2b** and its corresponding monomers **1** and **2b** as well as model compound **3** and a mixture of **4** and **5**. As we discussed previously, the two phenyl protons adjacent to the sulfonyl group of **3** resonated at δ 8.12 and 7.93. These peaks were also observed in the spectrum of the polymer but appeared broader, possibly due to the existence of polymer chains with various lengths or molecular weights. Other characteristic peaks of the model compounds were all reserved and could be readily identified. For example, the methylene protons next to the oxygen atom absorbed at δ 4.00 in **2b**, which was observed in the spectrum of P**1**/**2b** at the same position as that in the monomer. The peaks for the alkyl chain absorption were also observed at high field.

The ^{13}C NMR analysis also provides persuasive information on the polymer structure. The characteristic carbon resonances of the benzofuran ring were clearly observed at δ 159.9, 159.1 and 155.9 in the ^{13}C NMR spectrum of P**1**/**2b**. Moreover, the internal acetylene carbons (C≡C) of **2b** resonated at δ 89.4 and 88.0 (Fig. 4B), which were not observed in the ^{13}C NMR spectra of both model compounds and P**1**/**2b**. The disappearance of these two peaks indicated the complete consumption of diyne functional groups and thus the accomplishment of the polymerization. The absorption peaks for the alkyl chain carbons in **2b** (δ 68.0, 29.3 and 26.0) were preserved at high field in the polymer spectrum.

The IR spectrum of P**1**/**2b** is shown in Fig. 4 and the spectra of its monomers and model compounds are also given in the same figure for comparison. The large absorption band with two sharps at 3411 and 3372 cm^{-1} was stemmed from the OH stretching vibration of monomer **1** (Fig. 4A). On the other hand, the C≡C stretching vibration of **2b** emerged as a small sharp band at 2218 cm^{-1}. Both these bands disappeared in the spectrum of P**1**/**2b**. Meanwhile, an absorption band associated with the benzofuran skeleton arose at 1760 cm^{-1}. This band was also observed in the spectra of the model compounds although with a much lower intensity. Other typical absorption bands in the monomers, like those at 2940, 2864 and 1600 cm^{-1}, were all reserved in the spectrum of the polymer.

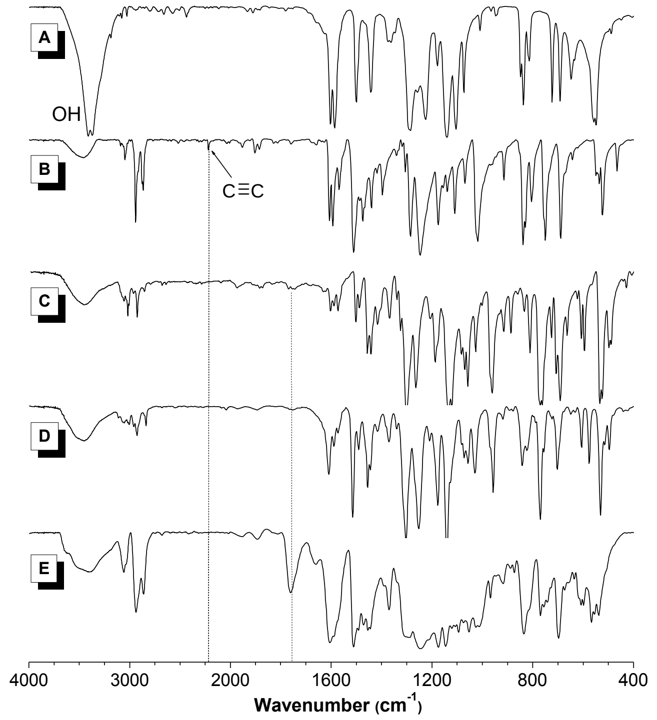


Fig. 4 FT-IR spectra of (A) **1**, (B) **2b**, (C) model compound **3**, (D) a mixture of **4** and **5** and (E) P**1**/**2b**.

Thermal stability

The thermal stabilities of all the polymers were evaluated by thermogravimetric analysis (TGA). Among the polymers generated from diyne monomers with different alkyl chain lengths, P**1**/**2b** showed better thermal stability, losing merely 5% of its weight at temperature (degradation temperature, T_d) above 300 °C under nitrogen (Fig. 5). The T_d value of other two polymers (P**1**/**2a** and P**1**/**2c**) with shorter or longer alkyl chain, were lower than P**1**/**2b** but were still above 200 °C. The thermal stability of TPE-containing P**1**/**2d** was outstanding, showing a high T_d at 376 °C. More importantly, P**1**/**2d** retained more than 50% of its original weight when heated to 800 °C. Such property made it promising as a ceramic material.

Light refraction

All the polymers showed good film-forming ability. Transparent thin films could be easily prepared by spin-coating their dicholoromethane solutions on silica substrates. As shown in Fig. 6, the thin films of all the polymers showed high refractive indices (RI or n) in a wide wavelength region (400–1000 nm). As summarized in Table 7, the RI values of all the polymers at 632.8 nm were ≥1.64, which were much higher than those of many commercial optical plastics. Among them, the RI value of P**1**/**2d** with TPE moieties impressively reached 1.72 due to its relatively high aromatic content. Similar to the result obtained from the TGA analysis, the RI value of P**1**/**2b** was 1.67 which was the highest among all the polymers with alkyl chains.

Chromatic Dispersion

The chromatic dispersion (D) describes the wavelength dependence of the refractive index of a material. Polymers with small D value exhibit good chromatic dispersion and are promising for applications as optical materials because large D value leads to unfavorable effect such as degradation of images resolution. The Abbé number (ν_D) of a material serves as a measure of the variation or dispersion in its RI value with wavelength which is defined as $(n_D-1)/(n_F-n_C)$, where n_D, n_F and n_C are the RI values at wavelengths of Fraunhofer D, F and C spectral lines of 589.2, 486.1 and 656.3 nm, respectively.[20] The ν_D values of all the tested polymers fell in the scale of 9.7–21.5 and the corresponding D values (the reciprocal of ν_D) were around 0.046–0.103. The optical data of refractive indices and the Abbé numbers indicated that most of our polymers had low optical dispersions and hence demonstrated their potential applications as optical materials.

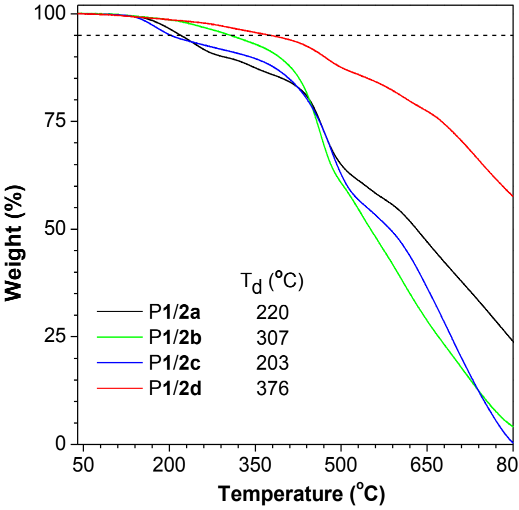


Fig. 5 TGA thermograms of P**1**/**2** recorded under nitrogen at a heating rate of 10 °C/min.

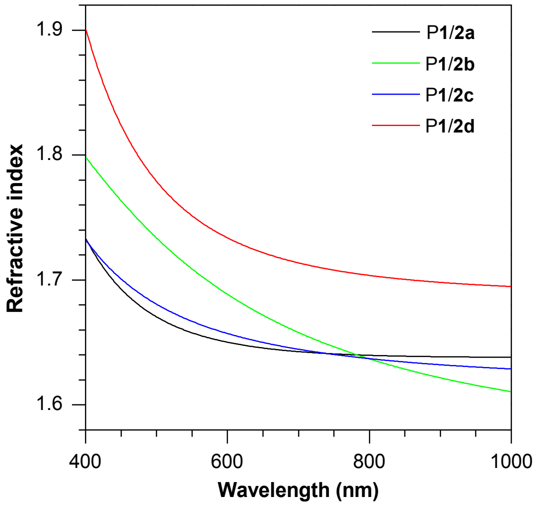


Fig. 6 Wavelength dependence of refractive indices of thin films of P**1**/**2**.

Table 7 Refractive indices and chromatic dispersions of P**1**/**2**[a]

polymer	$n_{632.8}$	v_D	D
P**1**/**2a**	1.6469	21.5	0.046
P**1**/**2b**	1.6770	9.7	0.103
P**1**/**2c**	1.6522	18.3	0.055
P**1**/**2d**	1.7253	10.8	0.093

[a] Abbreviation: n = refractive index, v_D = Abbé number = $(n_D\text{-}1)/(n_F\text{-}n_C)$, where n_D, n_F and n_C are the RI values at wavelengths of 589.2, 486.1 and 656.3 nm, respectively, D = chromatic dispersion = $1/v_D$.

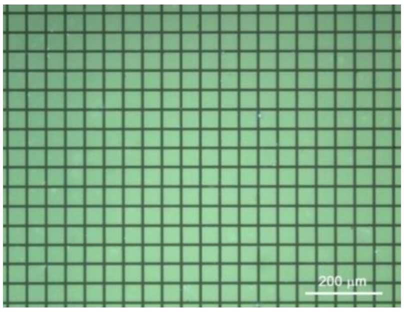


Fig. 7 Two-dimensional fluorescent photopattern generated by UV-induced oxidation of a thin film of P**1**/**2d** in air. The photograph was taken under UV light illumination (330–385 nm).

Photopatterning

Since the TPE-containing P**1**/**2d** possessed good film-forming ability and was light-emissive in the solid state as verified by emission spectrum show in Fig. S1, we thus utilized such properties for the fabrication of luminescent pattern by the photolithography process. After the polymer solution in 1,2-dichloroethane was spin-coated on a silicon wafer, the obtained thin film was irradiated by UV light in air for 20 min through a copper photomask. The irradiated parts (dark lines) underwent UV-induced oxidation in air and their emission was thus quenched. On the other hand, the emission of the covered parts (green squares) remained unaffected. Consequently, a two-dimensional fluorescent pattern with sharp edges was fabricated without going through the development process.

Conclusions

In this work, a new polymerization route for the preparation of heterocyclic polymers was developed. The alkyne polyannulation of diphenols and internal diynes catalyzed by $Pd_2(dba)_3$ in the presence of bathophenanthroline, AgOAc and $Cu(OAc)_2{\cdot}H_2O$ proceeded smoothly in 1,4-dioxane at 130 °C for 48 h, generating polymers with benzofuran rings in satisfactory yields with high molecular weight, good solubility and high thermal stability. High refractive indices were acquired from the thin solid films of the polymers in a wide wavelength region of 400–1000 nm. The TPE-containing polymer could be utilized for the fabrication of fluorescent pattern.

Experimental section

General information

$Pd_2(dba)_3$ was purchased from Alfa Aesar. Chemicals such as monomer **1**, L**1**, $Cu(OAc)_2{\cdot}H_2O$, AgOAc and other reagents concerned with monomer synthesis were all purchased from Aldrich and used as received without further purification. THF was distilled under nitrogen from sodium benzophenone ketyl immediately prior to use. Other solvents including 1,4-dioxane, *o*-xylene, DMF, 1-pentanol and toluene were commercially available from Aldrich.

Weight- (M_w) and number-average (M_n) molecular weights and polydispersities (M_w/M_n) of the polymers were estimated by a Waters Gel Permeation Chromatography (GPC) system equipped with a Waters 515 HPLC pump, a set of Styragel columns (HT3, HT4 and HT6; molecular weight range: 10^2 to 10^7), a column temperature controller, a Waters 486 wavelength-tunable UV-vis detector and a Waters 2414 differential refractometer. The polymers were dissolved in THF (~1 $mg{\cdot}mL^{-1}$) and filtered through 0.45 μm PTFE syringe-type filters before being injected into the GPC system. THF was used as an eluent at a flow rate of 1.0 $mL{\cdot}min^{-1}$. The column temperature was maintained at 40 °C and the working wavelength of the UV-vis detector was set at 254 nm. A set of monodispersed polystyrene standards (from Waters) covering the molecular weight range of 10^3 to 10^7 were used for the molecular weight calibration. IR spectra were recorded on a Perkin-Elmer 16 PC FTIR spectrophotometer. ^1H and ^{13}C NMR spectra were measured on a Bruker ARX 400 NMR spectrometer using chloroform-*d* as the solvent. High resolution mass spectra (HRMS) were recorded on a GCT Premier CAB 048 mass spectrometer operated in a MALDI-TOF model. Single crystal X-ray diffraction intensity data was recorded at 100 K on a Bruker-Nonices Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation. Processing of the intensity data was carried out through the SAINT and SADABS routines and the structure and refinement were obtained employing the SHELTL suite of X-ray programs (version 6.10). UV–vis absorption spectra was recorded on a Milton Roy Spectronic 3000 array spectrophotometer. Thermogravimetric analyses (TGA) were conducted under nitrogen on a Perkin-Elmer TGA 7 analyzer at a heating rate of 10 $^oC{\cdot}min^{-1}$. Refractive indices (RI or *n*) were determined on a J A Woollam Variable Angle Ellipsometry System with a wavelength tunability from 400 to 1000 nm. Photopatterning of the polymer film was conducted on a Spectroline ENF-280C/F UV lamp at a distance of 3 cm as light source. The incident light intensity was ~18.5 mW cm^{-2}. The films for RI measurement and photopattern were prepared by spin-coating the polymer solution (10 mg of P**1**/**2d** in 1 mL of 1,2-dichloroethane) at 1000 rpm for 1 min on a silicon wafer. The polymer film was dried in a vacuum oven at room temperature overnight. The pattern was generated by UV irradiation of the polymer film through copper photomask for 20 min in air without going through the development process. The photo was taken on an optical microscope (Olympus BX 41) under a UV light source.

Monomer synthesis

All the diyne monomers, named 4,4'-(α,ω-alkylenedioxy) bis(diphenylacetylene)s (**2a**–**2c**) and 1,2-bis[4-(2-phenylethynyl)phenyl]-1,2-diphenyl-ethene (**2d**) were synthesized according to the literature methods. All the characterization data were consistent with those reported in literature.

Synthesis of model compounds

Synthesis of model compound 3. To a 50 mL Schlenk tube were added 4-methylsulfonylphenol (**6**, 172 mg, 1 mmol), diphenylacetylene (**7**, 89 mg, 0.5 mmol), $Pd_2(dba)_3$ (23 mg, 0.025 mmol), bathophenanthroline (L**1**, 18 mg, 0.05 mmol), AgOAc (167 mg, 1 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (199 mg, 1 mmol). After purged with nitrogen for 3 times, 4 mL of degassed 1,4-dioxane was injected into the tube by using a hypodermic syringe. The resulting mixture was stirred at 130 ^{o}C for 24 h under nitrogen atmosphere in a sealed Schlenk tube. The reaction mixture was then cooled to room temperature, diluted with dichloromethane, and filtered through cotton. After solvent evaporation under the reduced pressure, the crude product was purified by using silica-gel column chromatography using hexane/ethyl acetate mixture as the eluent to give model compound **3** as a yellow solid (88 mg, 51%). IR (KBr), ν (cm^{-1}): 3059, 3019, 2923, 1768, 1602. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.12 (d, J = 1.7 Hz, 1H), 7.93 (dd, J = 8.6, 1.9 Hz, 1H), 7.72 (d, 1H), 7.68 (m, 2H), 7.50 (m, 5H), 7.36 (t, J = 3.3 Hz, 3H), 3.09 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 156.3, 153.1, 135.6, 131.3, 131.1, 129.6, 129.5, 129.3, 129.2, 128.6, 128.3, 127.1, 123.8, 120.5, 117.7, 112.0, 103.7, 45.0. HRMS (MALDI-TOF): *m/z* 348.0820 (M$^+$, calcd 348.0820).

Synthesis of model compounds 4 and 5. A mixture of compounds **4** and **5** were prepared from **6** (172 mg, 1 mmol), 1-methoxy-4-(phenylethynyl)benzene (**8**, 104 mg, 0.5 mmol), $Pd_2(dba)_3$ (23 mg, 0.025 mmol), L**1** (18 mg, 0.05 mmol), AgOAc (167 mg, 1 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (199 mg, 1 mmol) using the same procedure for preparing compound **3** as described above. Yellow solid, yield 62% (117 mg). IR (KBr), ν (cm^{-1}): 3064, 2925, 2839, 1755, 1607. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.09 (d, J = 7.7 Hz, 1H), 7.91 (t, J = 7.5 Hz, 1H), 7.69 (t, J = 7.2 Hz, 2H), 7.62 (d, J = 7.7 Hz, 1H), 7.50 (m, 2H), 7.42 (d, 1H), 7.35 (m, 2H), 7.05 (d, J = 7.5 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 3.91 and 3.84 (s, 3H), 3.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 160.3, 159.5, 156.1, 156.0, 153.3, 152.7, 135.4, 135.4, 131.45, 131.2, 131.2, 130.7, 129.6, 129.6, 129.2, 129.0, 128.6, 128.5, 128.1, 126.9, 123.6, 123.3, 123.2, 122.0, 120.4, 119.9, 117.3, 116.0, 114.7, 114.0, 111.9, 111.8, 55.3, 55.2, 44.9. HRMS (MALDI-TOF): *m/z* 378.0926 (M$^+$, calcd 378.0926).

Polymerization

All the polymerization reactions were carried out under nitrogen atmosphere in a sealed Schlenk tube except for Table 3, no.5 as toluene was used as solvent. A typical procedure for the polymerization of **1** and **2b** is given below as an example.

In a 25 mL Schlenk tube with a three-way stopcock on the sidearm were added **1** (50 mg, 0.2 mmol), **2b** (92 mg, 0.2 mmol), $Pd_2(dba)_3$ (18.3 mg, 0.02 mmol), L**1** (13.3 mg, mmol), AgOAc (133.5 mg, 0.8 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (159.7 mg, 0.8 mmol) under nitrogen. After purged with nitrogen for 3 times, 2 mL of degassed 1,4-dioxane was injected into the tube by using a hypodermic syringe. The resulting mixture was stirred at 130 ^{o}C for 48 h under nitrogen atmosphere. The solution was added dropwise into 100 mL of hexane/chloroform mixture via a cotton filter under stirring. The precipitate was collected by centrifugation and dried under vacuum at room temperature to a constant weight. A brown powder of polymer P**1**/**2b** was obtained in 65% yield. M_w 34 000; M_w/M_n 3.9 (Table 6 no. 2). IR (KBr), ν (cm^{-1}): 3060, 2937, 2861, 1761, 1603. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.14–6.83 (aromatic protons), 3.95 (OCH_2 protons), 1.81–1.53 (alkyl chain). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 159.9, 159.1, 155.9, 153.4, 152.7, 137.1–112.0, 68.0, 29.3, 26.0.

P**1**/**2a**: brownish powder; yield 82%. M_w 19 200; M_w/M_n 3.6 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3058, 2922, 2872, 1754, 1605. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.13–6.83 (aromatic protons), 4.04 (OCH_2 protons), 1.96 (alkyl chain). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 159.1, 155.9, 152.8, 133.4–114.9, 67.6, 26.1.

P**1**/**2c**: brownish powder; yield 62%. M_w 23 100; M_w/M_n 3.2 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3058, 2924, 2853, 1761, 1605. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.16–6.83 (aromatic protons), 4.04–3.93 (OCH_2 protons), 1.76–1.44 (alkyl chain). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 160.0, 159.2, 156.0, 153.4, 152.7, 137.0–112.1, 68.1, 29.4, 26.1.

P**1**/**2d**: yellow powder; yield 34%. M_w 13 000; M_w/M_n 1.8 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3054, 3025, 2959, 2857, 1764, 1591. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.16–7.11 (aromatic protons). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 155.9, 152.9, 143.4–112.11, 89.7.

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Table of Contents Entry

Palladium-catalyzed alkyne polyannulation of diphenols and unactivated internal diynes: a new synthetic route to functional hetrocyclic polymers