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Regio- and stereoselective construction of stimuli-responsive macromolecules by a sequential coupling-hydroamination polymerization route†

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Herein we reported a new facile one-pot multicomponent sequential polymerization approach for the construction of conjugated nitrogen-substituted polymers. Catalyzed by Pd(PPh₃)₂Cl₂/CuI at room temperature, the coupling-hydroamination polymerizations of 1,2-bis(4-ethynylphenyl)-1,2-diphenylethene, terephthaloyl chloride and secondary aliphatic amines proceeded smoothly in a regioregular and stereoselective manner, furnishing poly(arylene enamino)s (PAEs) with high molecular weights (*M_w* up to 34 600) in satisfactory yields (up to 91%). A model compound was elaborately designed and synthesized to verify the chemical structures of the corresponding polymeric products. All the PAEs exhibited good solubility in common organic solvents and were thermally stable with degradation temperatures of up to 313 °C under nitrogen. They possessed good film-forming ability and their thin solid films showed high refractive indices (RI = 1.9318–1.6320) in a wide wavelength region of 400–1000 nm, whose value could be further modulated by UV irradiation. Although the model compound and the PAEs possessed a typical aggregation-induced emission luminogen of tetraphenylethene, they were weakly emissive either in solution or in the aggregated state, due to the photoinduced electron transfer (PET) effect. Their strong emission in the aggregated state could be readily recovered by the blockage of the PET effect through protonation of the amino groups. Thus, this work demonstrated a powerful polymerization tool to access conjugated polymeric materials with pH-responsive properties.

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Introduction

As a branch of tandem reactions,¹ sequential reactions incorporate two or more distinct transformations into one single sequence, and are one of the most powerful synthetic methodologies for the rapid buildup of molecular complexity and diversity.² Different from the conventional stepwise synthetic protocols, which suffer from complex reaction procedures,

harsh reaction conditions, painful isolations, severe side reactions, *etc.*,³ sequential reactions enjoy unique atom economy, high efficiency, simple reaction and isolation procedures.⁴ With these compelling advantages, sequential reactions have attracted much attention in promoting the elegance of synthesis and the development of green chemistry.⁵ Particularly, chemists have made great endeavor to introduce the sequential reactions into the polymer field in some reported frontier studies.⁶ Recently, catalytic sequential reactions involving hydroelement addition to alkyne have been widely investigated.¹ Among them, the palladium-catalyzed sequential reaction is one of the most efficient strategies for the construction of a variety of complicated molecular skeletons.⁷ However, to date only limited palladium-catalyzed sequential reactions involving hydroelement additions to alkyne have been explored for the construction of conjugated heteroatom-substituted polymers.⁸

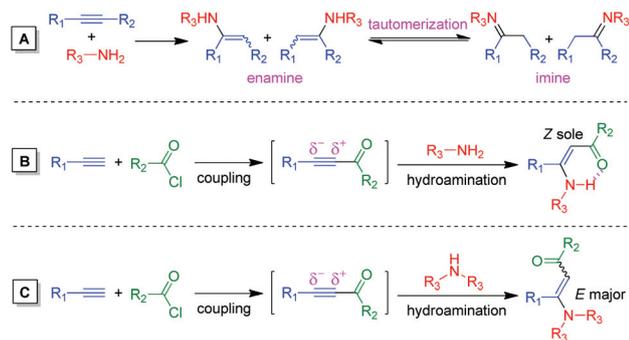
Recently, a three-component coupling-hydrothiolation-cyclocondensation reaction of alkyne, aryl chloride, and ethyl 2-mercaptoacetate was successfully developed into an efficient polymerization technique for preparing conjugated poly(arylene thiophenylene) by our group.⁹ To extend the reaction

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† Electronic supplementary information (ESI) available: Crystal data and structure refinement for model compound **4**; TGA thermogram of P1/2/3; emission spectra of **4** in THF/water mixtures; emission spectra of P1/2/3a in THF/water mixtures; emission spectra of P1/2/3a in THF/water mixtures acidified with 0.5 mM HCl solution. CCDC 1009269. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5py01424g



Scheme 1 (A) Alkyne hydroamination and enamine–imine tautomerization. (B, C) One-pot sequential coupling–hydroamination reactions of alkynes and carbonyl chlorides with (B) primary amines or (C) secondary amines.

scope, we intend to use amines to construct polymers *via* sequential coupling–hydroamination polymerization. However, polyhydroaminations with direct addition of amines to alkynes are rarely reported.¹⁰ Actually, it is a great challenge to synthesize such conjugated nitrogen-substituted polymers with well-defined structures by using polyhydroaminations. As shown in Scheme 1A, the reaction of an alkyne with a primary amine generally gives a mixture of enamine stereoisomers, whose tautomerization generates their regioisomeric imine counterparts. In 2003, Müller and coworkers reported that the one-pot three-component sequential coupling–addition reaction of alkynes, carbonyl chlorides and primary amines catalyzed by Pd(PPh₃)₂Cl₂/CuI could afford sole *Z*-enaminones with high efficiency and excellent regio- and stereoselectivity (Scheme 1B).¹¹ The carbonyl group in the intermediate ynone introduced polarization across the triple bond, which facilitated its regioselective hydroamination with primary amines. The six-membered ring formed by intramolecular hydrogen bond, on the other hand, helped to stabilize the *Z*-vinylene structure, avoiding tautomerization and *E/Z* isomerization and hence achieving high stereoselectivity. Therefore, addition of primary amines to ynone provides a perfect solution to solve the problems that occurred in polyhydroamination. What is the consequence when using secondary amine? As shown in Scheme 1C, tautomerization of products is avoided when using secondary amines as reactants.¹² Meanwhile, enamines with a predominant *E* configuration are obtained. Because of such promising results together with our rich experience in polymer science,¹³ such one-pot three-component coupling–hydroamination reaction is possible to be developed into an efficient and practical polymerization protocol towards novel conjugated nitrogen-substituted polymers.

In this work, we tried such possibility and herein showed that the polymerizations of tetraphenylethene (TPE)-containing diyne (**1**), terephthaloyl chloride (**2**) and secondary aliphatic amines (**3a** and **3b**) could proceed smoothly in THF under nitrogen in the presence of Pd(PPh₃)₂Cl₂, CuI and triethylamine (Et₃N) at room temperature, affording regio-

and stereoselective conjugated poly(arylene enaminone)s (P1/2/3) with high molecular weights in satisfactory yields. The resulting polymers displayed excellent solubility, good thermal stability, and high and tunable light refractivity. Although TPE is a well-known aggregation-induced emission (AIE) luminogen,¹⁴ all the polymers were weakly emissive in both solution and in the aggregated state due to the photoinduced electron transfer (PET) effect. Their intense aggregated-state emission could be readily recovered by protonation. Such a change in the emission behavior in response to the variation in pH makes them potential environmentally sensitive macromolecules that can be crafted into new smart functional materials.¹⁵

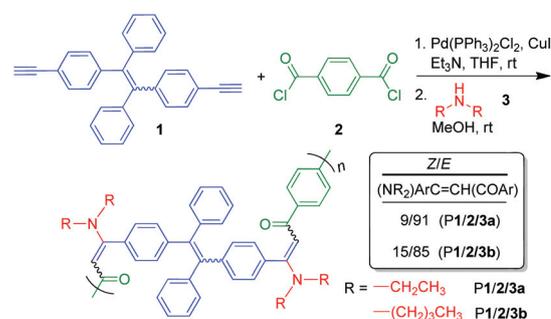
Results and discussion

Polymerization

To exploit the organic reaction in Scheme 1C as a powerful tool for the buildup of functional conjugated polymers, we prepared diyne **1** according to our previous published work.¹⁶ Monomer **2** and secondary amines (**3a** and **3b**), on the other hand, were commercially available. Diyne **1** was first reacted with **2** for 1 h at room temperature in THF under nitrogen in the presence of Pd(PPh₃)₂Cl₂, CuI and Et₃N. Afterwards, the secondary amine **3a** or **3b** and methanol were injected into the reaction system to undergo the subsequent hydroamination reaction, producing nitrogen-containing conjugated poly(arylene enaminone)s (P1/2/3) (Scheme 2).

To search the best conditions for such polymerization, the effect of reaction time was first investigated using **1**, **2**, and **3a** as monomers (Table 1). Although the isolated yield slightly increased when prolonging the reaction time, the molecular weight of the polymeric product was significantly enhanced. The highest value (*M_w* = 34 600) was obtained at 30 h, which was 2.36-fold higher than that achieved at 12 h. This suggests the positive factor of the polymerization time to the polymerization process. Thus, we fixed 30 h as the optimized reaction time for the later investigation.

We then studied the effect of monomer concentration on the polymerization while keeping the monomer feed ratio constant. As shown in Table 2, when the polymerization was



Scheme 2 Synthetic route to P1/2/3 by three-component sequential polymerizations of diyne, diacyl chloride and secondary amines.

Table 1 Time course on the polymerization^a

Entry	Yield (%)	Time (h)	M_w^b	M_n^b	M_w/M_n^b
1	80	12	10 300	6100	1.7
2	82	18	16 100	7300	2.2
3	85	24	22 900	11 500	2.0
4	86	30	34 600	12 400	2.8

^a Carried out in THF under nitrogen at room temperature in the presence of Pd(PPh₃)₂Cl₂, CuI and Et₃N. [Pd] = 4 mol%, [Cu] = 8 mol%, [Et₃N] = 0.10 M, [1] = 0.05 M, [2] = 0.05 M, [3a] = 0.15 M. Monomer 1 reacted with 2 for 1 h prior to the addition of 3a. ^b Estimated by gel permeation chromatography (GPC) in THF on the basis of a linear polystyrene calibration.

Table 2 Effect of monomer concentration on the polymerization^a

Entry	[1] (M)	Yield (%)	M_w^b	M_n^b	M_w/M_n^b
1	0.10	Gel			
2 ^c	0.05	86	34 600	12 400	2.8
3	0.03	73	29 400	14 700	2.0
4	0.02	63	22 800	14 300	1.6

^a Carried out in THF under nitrogen at room temperature for 30 h in the presence of Pd(PPh₃)₂Cl₂, CuI and Et₃N. [Pd] = 4 mol%, [Cu] = 8 mol%, [Et₃N] = 2[1], [2] = [1], [3a] = 3[1]. Monomer 1 reacted with 2 for 1 h prior to the addition of 3a. ^b Estimated by GPC in THF on the basis of a linear polystyrene calibration. ^c Data taken from Table 1, entry 4.

carried out at a relatively high monomer concentration of 0.10 M, an insoluble gel was formed quantitatively before the addition of monomer 3a. The obtained gel was also not soluble in other common organic solvents. Diluting the monomer concentration to 0.05 M helped to suppress the gel formation and a soluble polymeric product with a high M_w of 34 600 was, delightfully, isolated in 86% yield. When the concentration of monomer 1 was further decreased to 0.03 M or 0.02 M, soluble polymers with satisfactory molecular weights were also produced, albeit in reduced isolated yields.

We then studied the concentration effect of 3a on the polymerization. As verified by the results shown in Table 3, the yield and the molecular weight of the obtained polymer

Table 3 Effect of amine concentration on the polymerization^a

Entry	[3a] (M)	Yield (%)	M_w^b	M_n^b	M_w/M_n^b
1 ^c	0.15	86	34 600	12 400	2.8
2	0.20	81	27 100	12 900	2.1
3	0.25	81	17 900	9900	1.8
4	0.30	64	15 500	8600	1.8

^a Carried out in THF under nitrogen at room temperature for 30 h in the presence of Pd(PPh₃)₂Cl₂, CuI and Et₃N. [Pd] = 4 mol%, [Cu] = 8 mol%, [Et₃N] = 0.1 M, [1] = 0.05 M, [2] = 0.05 M. Monomer 1 reacted with 2 for 1 h prior to the addition of 3a. ^b Estimated by GPC in THF on the basis of a linear polystyrene calibration. ^c Data taken from Table 1, entry 4.

Table 4 Polymerization of 1, 2 and 3^a

Entry	Monomer	Yield (%)	Z/E	M_w^b	M_n^b	M_w/M_n^b
1 ^c	1 + 2 + 3a	86	9/91	34 600	12 400	2.8
2	1 + 2 + 3b	91	15/85	32 100	14 000	2.3

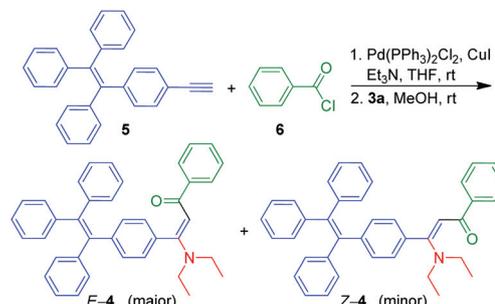
^a Carried out in THF under nitrogen at room temperature for 30 h in the presence of Pd(PPh₃)₂Cl₂, CuI and Et₃N. [Pd] = 4 mol%, [Cu] = 8 mol%, [Et₃N] = 0.1 M, [1] = 0.05 M, [2] = 0.05 M, [3] = 0.15 M. Monomer 1 reacted with 2 for 1 h prior to the addition of 3. ^b Estimated by GPC in THF on the basis of a linear polystyrene calibration. ^c Data taken from Table 1, entry 4.

decreased when a higher concentration of 3a was used for the polymerization. The addition of more amine molecules to the intermediate poly(arylene ynonylene) chain furnishes more steric bulky poly(arylene enamino)s, which hampers its further growth by a coupling reaction with 1 and 2.

With these optimized reaction parameters in hand, we investigated the monomer scope for the polymerization. Similar to 3a, polymerization employing dibutylamine (3b) also proceeded under mild conditions, affording soluble conjugated polymer P1/2/3b with a high molecular weight (M_w = 32 100) in 91% yield (Table 4, entry 2). We also used diphenylamine or dibenzylamine for the polymerization but obtained no desired polymers, which demonstrated the important role of the steric bulkiness of the amine in the polymerization.

Structural characterization

To confirm the occurrence of the sequential coupling-hydroamination polymerization and assist the characterization of the polymer structure, a model reaction was performed (Scheme 3). Under the similar conditions for preparing the polymers, the coupling reaction of monoyne 5¹⁶ and commercially available benzoyl chloride 6 followed by hydroamination of the intermediate with 3a generated an isomeric mixture of model compound 4 (Scheme 3). Single crystals were obtained from their dichloromethane/hexane solution and three crystals were randomly chosen for single-crystal X-ray diffraction. All of them showed the same crystal structure (Fig. 1). Detailed crystal data were summarized and are given in Table S1.† Through such analysis, it was recognized that the major product generated during the one-pot sequential reaction was

**Scheme 3** Synthetic route to model compound 4.

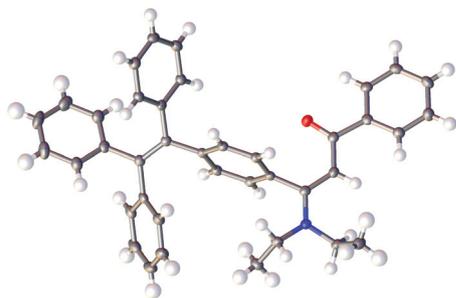


Fig. 1 ORTEP drawing of crystal structure of **4** (CCDC 1009269).

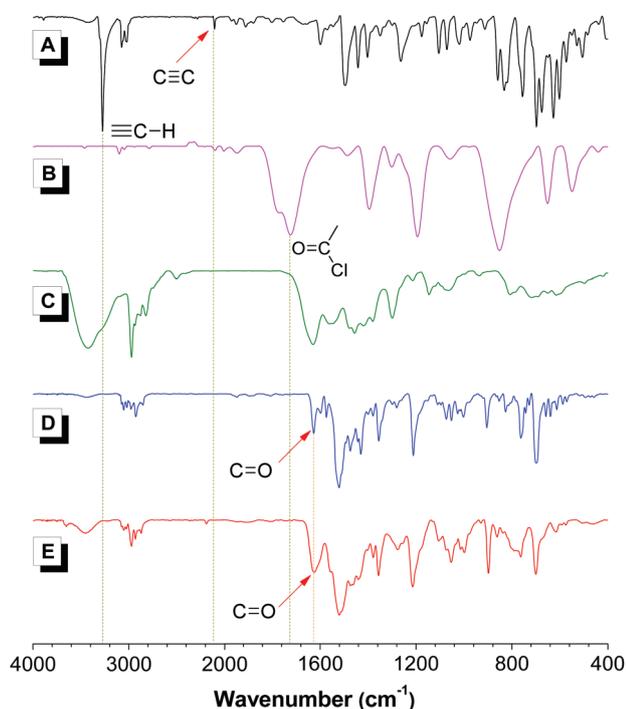


Fig. 2 IR spectra of (A) **1**, (B) **2**, (C) **3a**, (D) **4** and (E) P1/2/3a.

the *E*-isomer. Together with the data from NMR analysis, the sequential coupling-hydroamination reaction was proved to proceed regioselectively and stereoselectively, giving an exclusive addition product with a high *E*-content of up to 93%.

The chemical structures of model compound **4** and the corresponding polymers (P1/2/3) are fully characterized by standard spectroscopy techniques with satisfactory results. The IR and NMR spectra of P1/2/3a, its monomers (**1**, **2** and **3a**) and model compound **4** are shown as examples. The two absorption bands observed at 2106 and 3275 cm⁻¹ in monomer **1** were associated with its C=C and ≡C-H stretching vibrations, respectively (Fig. 2). All these bands disappeared in the spectra of **4** and P1/2/3a, demonstrating the complete consumption of the C=C functionality by model reaction and polymerization. Meanwhile, the carbonyl stretch-

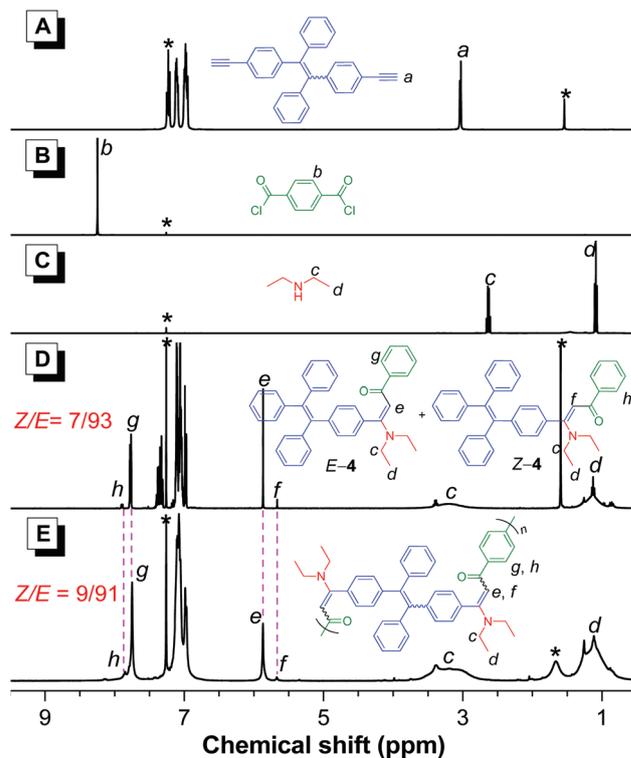


Fig. 3 ¹H NMR spectra of (A) **1**, (B) **2**, (C) **3a**, (D) **4** and (E) P1/2/3a in CDCl₃.

ing vibration of **2** absorbed at 1726 cm⁻¹ shifted to 1626 cm⁻¹ after the sequential reaction.

The ¹H and ¹³C NMR spectra provide detailed information on the structures of the model compound and the polymers. As shown in Fig. 3, the resonance of the ethynyl protons of monomer **1** peaked at δ 3.03, which entirely disappeared in the spectra of **4** and P1/2/3a. After hydroamination, the resonance of the CH₂ protons next to the nitrogen atom of **3a** at δ 2.63 shifted to a low field at δ ~3.37. In contrast, the absorption of the aromatic protons of **2** at δ 8.25 moved to a high field. On the other hand, new peaks assigned to resonances of the newly formed C=CH functionality emerged in the spectra of **4** and P1/2/3a. Due to different chemical environments, the *E*- and *Z*-olefin protons could be readily distinguished in the spectra of **4** and P1/2/3a. While the *E*-olefin proton absorbed at δ 5.87, its *Z*-counterpart resonated at δ 5.67. Meanwhile, the *Z*- and *E*-isomers could be also differentiated from the absorptions of the aromatic protons adjacent to the carbonyl group at δ 7.97 (*Z*-**4**) and 7.84 (*E*-**4**). From the peak integrals at δ 5.87 and 5.67, the *E*/*Z*-olefin ratios of **4**, P1/2/3a and P1/2/3b were calculated to be 93/7, 91/9 and 85/15, respectively, indicating high stereoselectivity of the hydroamination reaction.

Similarly, the spectra of **4** and P1/2/3a showed no resonances of the acetylene carbons of **1** at δ 77.7 and δ 83.9 (Fig. 4). Instead, a new peak associated with the resonance of the newly formed olefin carbon (=C_{Ar}(NR₂)) was observed at δ 163.3. This demonstrates that the acetylene group of **1** was

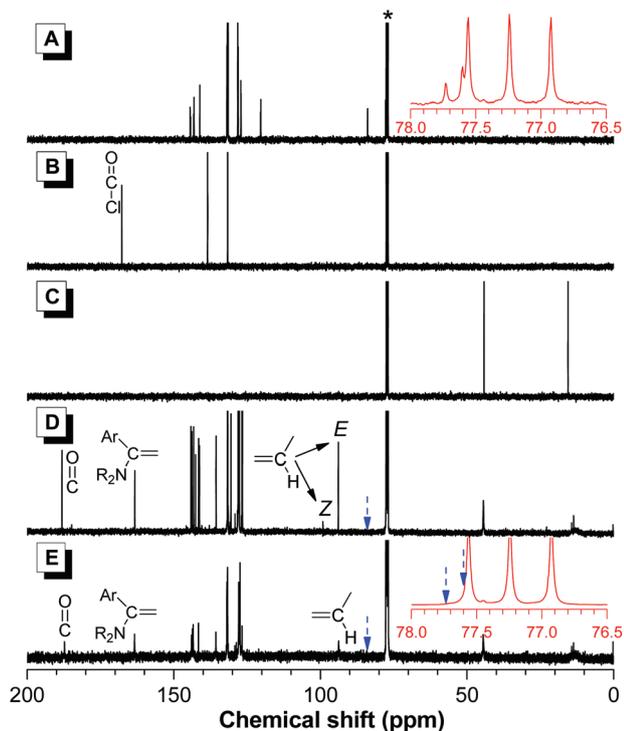


Fig. 4 ^{13}C NMR spectra of (A) 1, (B) 2, (C) 3a, (D) 4 and (E) P1/2/3a in CDCl_3 .

completely transformed into the olefin unit. On the other hand, the carbonyl carbon resonance of 2 was observed at δ 167.7, which downfield shifted to δ 187.2 after the polymerization. In addition, two peaks, owing to the absorptions of *E*- and *Z*-olefin carbons in $=\text{CH}(\text{COAr})$ fractions, emerged at δ 93.8 and 99.2 in the spectrum of 4. All the obtained results were well consistent with those from the ^1H NMR analysis, proving the occurrence of the sequential coupling-hydroamination reaction. P1/2/3a shared similar NMR spectral patterns with 4, confirming the desired molecular structure as shown in Scheme 2.

Solubility and thermal stability

The resulting conjugated polymers are readily soluble in common organic solvents, such as dichloromethane, chloroform, THF, DMF, *etc.*, though they are comprised of many aromatic rings. It is largely attributed to the twisted TPE units in the polymer backbone. Furthermore, they possess good film-forming abilities and uniform tough solid films can be readily obtained by spin-coating their solutions. The thermal stability of the polymers was then evaluated by thermogravimetric analysis (TGA). As shown in Fig. S1,† P1/2/3 lose 5% of their weights at 297–313 °C under nitrogen, revealing their reasonably high resistance to thermolysis at high temperatures.

Light refractivity and chromatic dispersion

Processable macromolecules with high refractive indices (n or RI) are promising materials with a variety of practical appli-

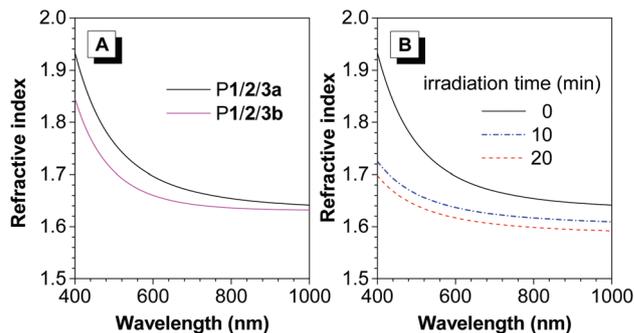


Fig. 5 (A) Wavelength dependence of refractive indices of thin films of P1/2/3. (B) Change in refractive index of a thin film of P1/2/3a by UV irradiation.

cations, such as in advanced optoelectronic fabrication of lenses, prisms, memories, substrates for advanced display devices, *etc.*¹⁷ Conventional organic polymeric materials, including polycarbonate, poly(methyl methacrylate) and polystyrene, exhibit low refractive indices in the range of 1.49–1.58,¹⁸ which limits their photonic applications. Conjugated polymers P1/2/3 are comprised of abundant polarizable aromatic rings, TPE moieties, carbonyl groups, heteroatoms and a conjugated polymer backbone. Thus they are expected to exhibit high n values. This is proved to be the case. As shown in Fig. 5A, thin films of P1/2/3a and P1/2/3b exhibited high n values of 1.9318–1.6413 and 1.8445–1.6320 in a wide wavelength region of 400–1000 nm, respectively.

It is also of great importance to develop polymeric materials with tunable refractive indices,¹⁹ as the modulation of the refractive index is a critical technological issue in optical communication and optical data storage devices.²⁰ Since the carbonyl groups and the vinyl units in P1/2/3 are photosensitive,²¹ their structures and hence their n values may be readily changed by light irradiation. Indeed, when a thin film of P1/2/3a was exposed to UV light for 20 min, its n values dropped rapidly to 1.6977–1.5918 in the wavelength range of 400–1000 nm. This indicates the efficient RI tunability of the polymer.

The Abbé number (ν_D) of a material describes the variation or dispersion in its n values with wavelength. Normally a small ν_D value may lead to an undesired effect on the images' resolution. Polymers with high ν_D values or low chromatic dispersions D ($D = 1/\nu_D$) are promising candidates in a wide range of applications. The equation for calculating ν_D is: $\nu_D = (n_D - 1)/(n_F - n_C)$, where n_D , n_F and n_C are the n values at wavelengths of 589.3, 486.1 and 656.3 nm, respectively. As shown in Table 5, P1/2/3a and P1/2/3b possessed similar ν_D and D values. On the other hand, the ν_D values of P1/2/3a after UV treatment fall in the range of 7.2259–16.9783, corresponding to D values of 0.1384–0.0589. Hence, the RI tunability and low optical dispersion of the present polymers allow them to be promising coating materials in the advanced optical display systems.²²

Table 5 Refractive indices and chromatic dispersions of P1/2/3 before and after UV irradiation^a

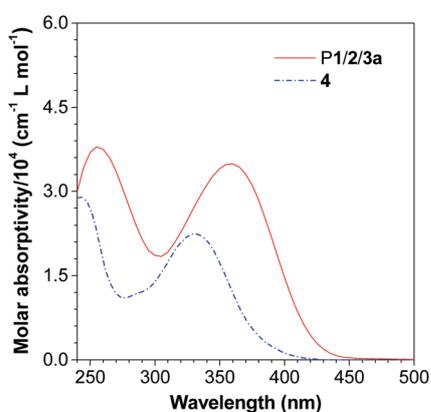
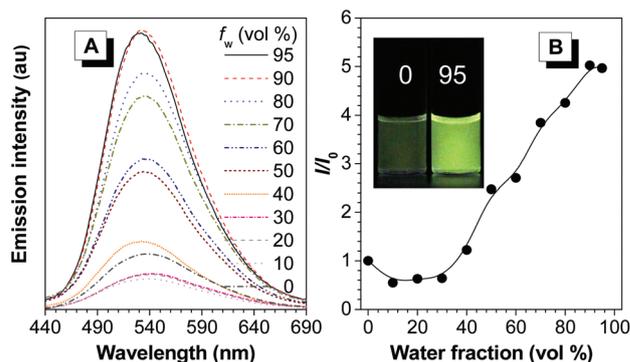
No.	Polymer	Time (min)	$n_{632.8}$	ν_D	D
1	P1/2/3a	0	1.6847	7.2259	0.1384
2	P1/2/3a	10	1.6316	16.9677	0.0589
3	P1/2/3a	20	1.6122	16.9783	0.0589
4	P1/2/3b	0	1.6526	9.7128	0.1030

^a Abbreviations: n = refractive index, ν_D = Abbé number = $(n_D - 1)/(n_F - n_C)$, where n_D , n_F and n_C are the n values at wavelengths of 589.2, 486.1 and 656.3 nm, respectively, D = chromatic dispersion = $1/\nu_D$.

Photophysical properties

Fig. 6 shows the UV spectra of **4** and P1/2/3a in diluted THF solutions (10 μ M). The absorption maximum of **4** peaked at 330 nm, whilst, that of P1/2/3a was located at 360 nm, indicating a better conjugation in the polymer. On the other hand, TPE and its derivatives are well-known fluorophores with AIE characteristics.²³ The restriction of intramolecular rotation (RIR) process was proposed as the main cause for their AIE effect.²⁴ In solution, the phenyl rings rotate *via* the single-bond axes, serving as a relaxation channel for the decay of excited states and hence rendering the molecules nonemissive. In the aggregated state, such rotation is physically restricted, which blocks the nonradiative decay pathway and thus allows the molecules to emit intensely. As expected, **4** and P1/2/3a were non-emissive in THF (Fig. S2 and S3[†]). Surprisingly, no signals were recorded even when they were aggregated upon the addition of a large amount of a poor solvent (water) into their THF solutions.

What is the cause for this phenomenon? Careful investigation of their molecular structures reveals that the PET process from the amine moiety to the excited fluorophore unit should be responsible for such behavior. If the amine group is protonated, the PET process may be forbidden and the emission of the polymer may be recovered. To prove this, we studied the emission properties of P1/2/3a again in THF/water

**Fig. 6** Absorption spectra of **4** and P1/2/3a in pure THF solutions. Solution concentration: 10 μ M.**Fig. 7** (A) Emission spectra of P1/2/3a in THF/water mixtures with different water fractions (f_w) acidified with 1 mM of hydrochloric acid. (B) Plot of relative emission intensity (I/I_0) versus the composition of the acidified aqueous solution of P1/2/3a. Inset: Fluorescence photographs of P1/2/3a in THF/water mixtures with f_w of 0% and 95% taken under UV light irradiation. Solution concentration: 10 μ M; excitation wavelength: 360 nm.

mixtures acidified with 1 mM of hydrochloric acid (Fig. 7). In pure THF solution, a weak emission band with a maximum at 536 nm was detected. The emission decreased slightly when a small amount of water (≤ 30 vol%) was added to the THF solution, presumably due to the enhancement of the intramolecular charge transfer effect from the electron-donating amine unit to the electron-accepting carbonyl group. Afterwards, the intensity increased gradually without a noticeable emission peak shift due to the activation of the RIR process by aggregate formation. The highest emission intensity was achieved in the THF/water mixture at 90% water fraction, which was about 4.0-fold higher than that in pure THF solution. The fluorescence photographs of P1/2/3a in THF and 95% aqueous solution taken under UV irradiation are shown in the inset of Fig. 7B. Compared to the weak emission in THF solution, the aggregates of P1/2/3a formed in the THF/water mixture were more emissive. Clearly, aggregate formation has enhanced the emission of P1/2/3a. A similar phenomenon was also observed when a lower concentration of hydrochloric acid (0.5 mM) was used (Fig. S4[†]).

To illustrate the PET process, the frontier orbital theory is presented in Fig. 8A.²⁵ Generally, a typical PET system comprises an aliphatic amine, a fluorophore and a short methylene chain as the linker. When excited by an appropriate light, the electron in the highest occupied molecular orbital (HOMO) of the fluorophore was promoted to the lowest unoccupied molecular orbital (LUMO). As the HOMO of an aliphatic amine was located between the LUMO and HOMO of the fluorophore, the amine electron could easily transfer to the HOMO of the fluorophore. This hinders the return of electron in the LUMO to the HOMO, thus leading to the emission quenching. When the amine groups were protonated, its HOMO was then located at a lower energy than the HOMO of the fluorophore (Fig. 8B). This makes the PET process difficult to occur. Now, the electron in the LUMO of the fluorophore could undergo radiative decay, which recovered the emission of the polymer.

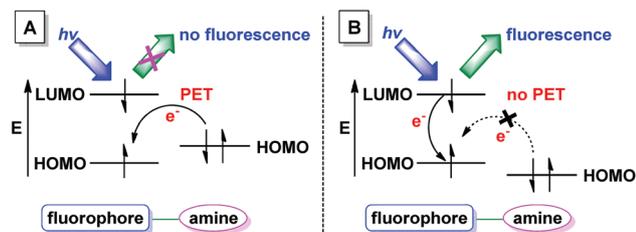


Fig. 8 Frontier molecular orbital theory of the PET process.

Conclusions

In this work, we have developed an efficient one-pot multi-component sequential polymerization approach to access functional polymers. The coupling-hydroamination polymerization of diyne, diaroyl chloride and secondary amines was catalyzed by $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and CuI in regio- and stereoselective manners, affording conjugated heteroatom-substituted polymers with high molecular weights in satisfactory yields. All the polymers were soluble, showing a good film-forming ability and reasonably high thermal stability. They exhibited high tunable refractive indices in a wide wavelength region. They were weakly emissive in both solution and aggregated states due to the PET effect, although they possessed the TPE chromophoric unit. Their strong aggregated-state emission, however, could be readily recovered by protonation. Thus, the present work paves a way to facile synthesis of heteroatom-containing polymers with stimuli-responsive properties.

Experimental

Materials

THF was distilled from sodium benzophenone ketyl under nitrogen and then used immediately. Terephthaloyl dichloride and Et_3N were purchased from Sigma-Aldrich. $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI and methanol were ordered from Zhejiang Metallurgical Research Institute Co., Ltd, International Laboratory USA, and Merck, respectively. Other chemicals and reagents were all purchased from J&K or Aldrich. All of the chemicals and solvents were used as received without further purification. Diyne **1** and monoyne **5** were synthesized according to procedures reported in the literature.¹⁶

Instrument

The ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 NMR spectrometer using CDCl_3 as the solvent and tetramethylsilane (TMS; $\delta = 0$ ppm) as the internal standard. High resolution mass spectra (HRMS) and IR spectra were recorded on a GCT Premier CAB 048 mass spectrometer operated in MALDI-TOF mode and a PerkinElmer 16 PC FT-IR spectrophotometer, respectively. Single crystal X-ray diffraction was carried out at 100 K on a Bruker-Nonius Smart Apex CCD diffractometer with graphite monochromated $\text{Mo-K}\alpha$ radiation.

Analysis of the data was performed through the SAINT and SADABS programs, meanwhile, the structure and refinement were obtained from the SHELTL suite of X-ray programs (Version 6.10). The weight-average molecular weights (M_w) and number-average molecular weights (M_n) as well as the polydispersity indices (M_w/M_n) of the polymers were evaluated through a GPC system (Waters) equipped with UV, RI and fluorescence detectors. THF (HPLC grade) was used as the eluent at a flow rate of 1.0 mL min^{-1} . A series of standard linear polystyrenes covering the molecular weight range of 10^3 – 10^7 were employed for the molecular weight calibration. The polymeric products were dissolved in THF ($\sim 2 \text{ mg mL}^{-1}$), filtered through $0.45 \mu\text{m}$ PTFE syringe-type filters and injected into the GPC system for measurements afterwards.

A PerkinElmer TGA 7 analyzer was employed to estimate TGA thermograms under nitrogen at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. The UV-vis absorption spectra, emission spectra and n values were obtained on a Milton Roy Spectronic 3000 Array spectrophotometer, a PerkinElmer LS 55 spectrofluorometer and a J. A. Woollam M-2000 V Multiwavelength Ellipsometer, respectively. The polymer films were prepared by spin-coating the polymer solutions (10 mg in 1 mL of 1,2-dichloroethane) at 1000 rpm for 1 min on silicon wafers and then dried in a vacuum oven at room temperature overnight. Modulation of the RI values of the polymer films was achieved by UV irradiation using a Spectroline ENF-280C/FUV lamp with an intensity of *ca.* 18.5 mW cm^{-2} at a distance of 3 cm.

Polymer synthesis

All the polymerization reactions were carried out under nitrogen using the standard Schlenk technique. A typical polymerization procedure of **1**, **2** and **3** is given below as an example.

Into a 25 mL Schlenk tube equipped with a magnetic stirrer were charged diyne **1** (0.2 mmol, 76.1 mg) and terephthaloyl chloride **2** (0.2 mmol, 40.6 mg). Then, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.008 mmol, 6.0 mg), CuI (0.016 mmol, 3.0 mg), 4.0 mL of THF and 0.06 mL of Et_3N were subsequently added under nitrogen. After reacting for 1 h at room temperature, diethylamine **3a** (0.6 mmol, 0.06 mL) and 0.5 mL of methanol ($V_{\text{methanol}} : V_{\text{THF}} = 1 : 8$) were injected into the reaction system. The mixture was further reacted for 30 h at the same temperature under nitrogen. Afterwards, the solution was added dropwise through a cotton filter into 300 mL of methanol under stirring. The formed precipitates were collected by filtration, washed with methanol and further dried under vacuum at room temperature to a constant weight.

P1/2/3a (Table 4, entry 1): yellow powder; yield 86%. $M_w = 34\,600$; $M_w/M_n = 2.8$. IR (KBr), ν (cm^{-1}): 3061, 3028, 2923, 2884, 2832, 2807, 1662, 1603, 1494, 1453, 1281, 1219. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.85, 7.75, 7.11, 7.10, 7.08, 7.06, 6.99, 6.97, 5.87, 5.67, 3.38, 1.26. ^{13}C NMR (100 MHz, CDCl_3), δ (CDCl_3 , ppm): 187.23, 163.35, 143.93, 143.63, 143.27, 141.59, 135.62, 131.84, 131.67, 127.82, 127.54, 127.40, 126.69, 93.75, 44.48, 13.62.

P1/2/3b (Table 4, entry 2): yellow powder; yield 91%. $M_w = 32\,100$; $M_w/M_n = 2.3$. IR (KBr), ν (cm^{-1}): 3061, 3025, 2953, 2830,

2805, 1664, 1594, 1494, 1453, 1280, 1218. ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.84, 7.73, 7.26, 7.09, 7.00, 6.96, 5.81, 5.66, 3.30, 2.88, 1.30, 0.95, 0.87, 0.79. ^{13}C NMR (100 MHz, CDCl_3), δ (CDCl_3 , ppm): 187.23, 163.35, 143.93, 143.63, 143.27, 141.59, 135.62, 131.84, 131.67, 127.82, 127.54, 127.40, 126.69, 93.75, 44.48, 32.70, 20.11, 13.62.

Model reaction

The model compound 3-(diethylamino)-1-phenyl-3-(4-(1,2,2-triphenylvinyl)phenyl)prop-2-en-1-one (**4**) was synthesized according to a similar procedure for preparing P1/2/3a with some modifications.

Into a 25 mL Schlenk tube were placed monoyne **5** (0.5 mmol, 178.2 mg) and benzoyl chloride **6** (0.5 mmol, 0.06 mL). $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.01 mmol, 8.0 mg), CuI (0.02 mmol, 4.0 mg), 5.0 mL of freshly distilled THF and 0.06 mL of Et_3N were then added into the reaction system under nitrogen. After stirring at room temperature for 1 h, 1.0 mL of methanol and diethylamine **3a** (0.68 mmol, 0.07 mL) were injected. The mixture was allowed to react at room temperature for 18 h. The mixture was then extracted with 40 mL of water and 60 mL of dichloromethane three times. The organic layer was combined and dried over MgSO_4 . The crude product was condensed and purified by silica-gel column chromatography using the hexane/dichloromethane mixture (v/v = 5/1) as the eluent. A white solid was obtained in 63% yield. IR (KBr), ν (cm^{-1}): 3061, 3025, 2972, 2916, 2845, 1626, 1524, 1477, 1427, 1352, 1207. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.90 (d, 0.14 H), 7.77 (d, 1.86 H), 7.36 (m, 3 H), 7.13 (m, 17 H), 6.98 (d, 2 H), 5.87 (s, 0.93 H), 5.67 (s, 0.07 H), 3.39 (q, 4 H), 1.13 (t, 6 H). ^{13}C NMR (100 MHz, CDCl_3), δ (CDCl_3 , ppm): 188.11, 184.81, 163.26, 144.10, 143.81, 143.72, 143.17, 142.56, 141.49, 141.21, 135.55, 131.69, 131.67, 131.59, 131.55, 130.47, 128.05, 127.92, 127.86, 127.79, 127.68, 127.60, 126.70, 126.67, 126.58, 99.13, 93.88, 44.40, 13.66. HRMS (MALDI-TOF): m/z 534.2813 ($[\text{M} + \text{H}]^+$, calcd 534.2791).

Preparation of aggregates

Stock THF solutions of **4** and P1/2/3a with a concentration of 1.0 mM were firstly prepared, respectively. Quantitative hydrochloric acid was added into the stock THF solution of P1/2/3a to afford an acidified one. Then 0.1 mL of stock THF solution of **4**, THF solution of P1/2/3a and acidified THF solution of P1/2/3a were transferred into 10.0 mL volumetric flasks, respectively. After addition of appropriate amounts of THF, water was added dropwise under vigorous stirring to furnish 1×10^{-5} M solutions with a specific f_w of 0–95%. The absorption and emission spectra of the resulting solutions were then recorded.

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