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Transition metal-free thiol–yne click polymerization toward *Z*-stereoregular poly(vinylene sulfide)s†

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Click polymerization has emerged as a versatile polymerization technique for the construction of functional polymers. In this work, a novel transition metal-free thiol–yne click polymerization with high regio- and stereoselectivities was successfully developed. The polymerizations were conducted in the presence of K_3PO_4, and sole anti-Markovnikov adducts of poly(vinylene sulfide)s (PVSs) with high molecular weights and high stereoregularity (*Z*-isomer contents up to 100%) were obtained in high yields after 24 h. The resultant PVSs are thermally stable and show high refractive indices owing to the high contents of aromatic rings and sulfur atoms in the structures. Moreover, PVSs with aggregation-induced emission (AIE) characteristics could also be produced by introducing AIE-active tetraphenylethene (TPE) moieties into the polymer chains. This K_3PO_4-mediated thiol–yne click polymerization with high efficiency and great robustness has great potential in the preparation of functional PVSs.

Introduction

Click polymerization has become a powerful and versatile polymerization technique for the construction of functional polymers with advanced structures owing to its fantastic click features, such as high efficiency, mild reaction conditions, atom economy, great functionality tolerance, and regio- and/or stereoselectivities.[1–11] In particular, click polymerization based on alkynes which can offer polymers with unique conjugated structures has drawn intense attention from polymer scientists.[12–14] Numerous alkyne-based click polymerizations, including azide–alkyne click polymerization, thiol–yne click polymerization, and Diels–Alder click polymerization, have been developed and applied to the preparation of novel polymer materials.[15–21] Recently, brand new amino–yne and hydroxyl–yne click polymerizations have also been established.[22–24]

As one of the famous click polymerizations, the thiol–yne click polymerization was extensively investigated by polymer chemists for the preparation of sulfur-containing functional polymers.[25–28] However, it still remains a challenge for scientists to well control the chemo-, regio- and stereoselectivities of this click polymerization. Theoretically, the hydrothiolation of alkynes can proceed through bis-addition and mono-addition routes to produce alkyl sulfides and vinyl sulfides, respectively. According to the works reported by Perrier *et al.* and Gao *et al.*, photo- and thermoinitiated thiol–yne click polymerizations usually occur *via* a bis-addition manner and have become useful tools for the preparation of hyperbranched polythioethers with high sulfur contents and a high degree of branching.[29–37] By controlling the ratio of thiols and alkynes, Voit *et al.* successfully obtained poly(vinyl sulfide)s through thermoinitiated thiol–yne click polymerization based on selective thiol radical mono-addition to diphenylacetylene derivatives.[38–43] Very recently, Di Giuseppe and Pérez-Torrente *et al.* reported that the thiol–yne click polymerization can proceed *via* a Markovnikov addition route to offer poly(vinylidene sulfide)s in the presence of a Rh(ɪ)-NHC catalyst.[44] Although both bis- and mono-adducts can be gained from the aforementioned thiol–yne click polymerizations, the mono-adducts are diversified, and thiol–yne click polymerizations through an anti-Markovnikov addition route remain to be developed for the preparation of stereoregular poly(vinylene sulfide)s (PVSs).

As research groups working on the exploitation of new and efficient polymerizations based on triple bond building blocks

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†Electronic supplementary information (ESI) available: Tables S1 and S2, FT-IR and NMR spectra of **P1a2b**, **P1a2c**, and **P1b2b**, and PL spectra of **P1b2b**. See DOI: 10.1039/c9py00161a
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for years, we are very interested in developing new alkyne-based click polymerizations with regio- and/or stereoselectivities.[45–48] Encouraged by the success in the establishment of azide–alkyne click polymerizations,[49–51] we embarked on our research in the area of thiol–yne click polymerization. In 2010, we first reported an organobase-mediated thiol–yne click polymerization.[52] With activated alkynes of propiolate derivatives as monomers and diphenylamine as a promoter, anti-Markovnikov adducts of PVSs with high Z-stereoregularites (Z contents up to 81.4%) were successfully furnished in high yields. In the next year, we developed a Rh(PPh₃)₃Cl-catalyzed thiol–yne click polymerization for the synthesis of E-stereoregular PVSs (E contents up to 100%).[53] Spontaneous thiol–yne click polymerization was also found to be very useful for the preparation of functional PVSs with linear and hyperbranched structures.[54,55] Inspired by these results, we kept on exploring efficient catalyst systems for the establishment of new thiol–yne click polymerizations with a wider scope and higher regio- and stereoselectivities. In 2013, Deng et al. reported that the regio- and stereoselectivities of the thiol–yne click reaction can be enhanced by an inorganic base of potassium phosphate (K₃PO₄) and that Z-vinyl sulfides can be selectively formed in high yields.[56] Therefore, we envisioned that regio- and stereoselective thiol–yne click polymerization could be developed for the preparation of Z-stereoregular PVSs with the promotion of K₃PO₄.

In this work, after a systematic investigation of polymerization conditions, we developed a transition metal-free thiol–yne click polymerization which proceeds through an anti-Markovnikov addition in a Z-stereoselective manner. In the presence of K₃PO₄, aromatic diynes and aromatic dithiols could be facilely polymerized in N-methyl-2-pyrrolidinone (NMP) at 100 °C for 24 h, and PVSs with high molecular weights and high Z-stereoregularities (Z contents up 100%) could be produced in high yields (Scheme 1). The obtained PVSs are ther-
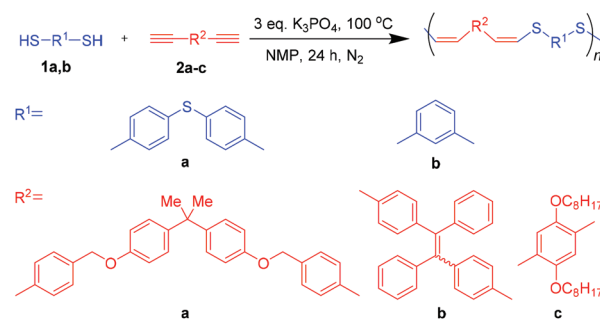
Scheme 1 Synthesis of Z-stereoregular poly(vinylene sulfide)s by K₃PO₄-mediated click polymerization of dithiols 1 and diynes 2.

mally stable and possess high refractive indices owing to the high contents of aromatic rings and sulfur atoms in their structures. Moreover, PVSs with aggregation-induced emission (AIE) features could also be prepared by introducing AIE-active tetraphenylethene (TPE) moieties into the polymer chains.

Results and discussion

Click polymerization

To establish the K₃PO₄-mediated thiol–yne click polymerization for the preparation of Z-stereoregular PVSs, aromatic diynes 2a–2c were synthesized according to the reported methods.[55] Dithiols 1a and 1b are commercially available. Using dithiol 1a and diyne 2a as model monomers, we systematically optimized the polymerization conditions. In our previous work, we found that stereorandom PVSs with high molecular weights can be obtained in 2 h by spontaneous thiol–yne click polymerization at 30 °C.[55] Thus, we firstly tried the K₃PO₄-mediated click polymerization of 1a and 2a in NMP at 30 °C (Table 1, entry 1). Unfortunately, no polymeric product was obtained. Raising the reaction temperature could gradually improve the polymerization results, and PVSs with moderate weight-average molecular weight (M_w) could be produced in good yields at 100 °C (Table 1, entries 2–4). As a result, further research on polymerization was executed at 100 °C.

In order to further enhance the M_w and yields of the obtained PVSs, we next studied the time course of the polymerization. As shown in Table 2, prolonging reaction time has a

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Anjun Qin

Table 1 Effect of temperature on the polymerization of 1a and 2a[a]

Entry	T (°C)	Yield (%)	M_w[b]	$Đ$[b]
1	30	Trace		
2	60	60	2500	1.04
3	80	70	5200	1.37
4	100	80	6900	1.18

[a] Carried out in the presence of K₃PO₄ in NMP under nitrogen for 2 h, [1a] = [2a] = 0.1 M, [K₃PO₄] = 3[1a] = 0.3 M. [b] Estimated by gel permeation chromatography (GPC) using THF as the eluent on the basis of a linear polystyrene calibration. M_w = weight-average molecular weight, M_n = number-average molecular weight, polydispersity index ($Đ$) = M_w/M_n.

Table 2 Time course of the polymerization of **1a** and **2a**[a]

Entry	t (h)	Yield (%)	M_w[b]	$Đ$[b]
1[c]	2	80	6900	1.18
2	8	82	10 400	1.37
3	12	80	12 400	1.45
4	16	85	16 500	1.69
5	24	95	18 500	1.61

[a] Carried out in the presence of K_3PO_4 in NMP under nitrogen at 100 °C, [**1a**] = [**2a**] = 0.1 M, [K_3PO_4] = 3[**1a**] = 0.3 M. [b] Estimated by GPC using THF as the eluent on the basis of a linear polystyrene calibration. M_w = weight-average molecular weight, M_n = number-average molecular weight, polydispersity index ($Đ$) = M_w/M_n. [c] Data taken from Table 1, entry 4.

positive influence on polymerization. A PVS with the highest M_w of 18 500 was produced in an excellent yield of 95% after 24 h. We thus used 24 h as the optimal reaction time.

Since the reaction solvent has a considerable effect on the stereoselectivity of the hydrothiolation of alkynes, the solvent influence on polymerization was also evaluated.[57] The polymerization carried out in NMP could produce PVSs with high M_w and excellent stereoregularity (Z-isomer content = 100%) (Table 3, entry 4). When the polymerizations were performed in polar solvents, such as N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO) or N,N-dimethylacetamide (DMAc), the yields of the obtained PVSs were good, while both M_w and Z-isomer contents obviously decreased (Table 3, entries 1–3). PVSs with even higher M_w could be produced upon polymerization conducted in chlorobenzene or toluene; however, their Z-stereoregularities were lost (Table 3, entries 5 and 6). In consideration of the yields, M_w, and Z-stereoregularity of the products, NMP was chosen as the optimal solvent for the polymerization.

The nucleophilicity of the sulfur atom could be increased under base conditions, and plays an important role in the nucleophilic addition of thiols to alkynes.[58,59] Hence, it is necessary to explore the base effect on the polymerization. As shown in Table 4, using K_2HPO_4 instead of K_3PO_4 as the base additive, the polymerization could also be promoted to furnish soluble PVS with slightly decreased M_w and stereoregularity (Z-isomer content = 90%) in good yield (Table 4, entries 1 and 2). In contrast, when KH_2PO_4 was adopted as the additive,

Table 3 Solvent effect on the polymerization of **1a** and **2a**[a]

Entry	Solvent	Yield (%)	M_w[b]	$Đ$[b]	Z/E[c]
1	DMSO	87	7500	1.60	58/42
2	DMF	85	6200	1.66	61/39
3	DMAc	83	11 800	1.98	78/22
4[d]	NMP	95	18 500	1.61	100/0
5	Chlorobenzene	86	17 000	2.04	60/40
6	Toluene	43	44 200	4.22	52/48

[a] Carried out in the presence of K_3PO_4 under nitrogen at 100 °C for 24 h, [**1a**] = [**2a**] = 0.1 M, [K_3PO_4] = 3[**1a**] = 0.3 M. [b] Estimated by GPC using THF as the eluent on the basis of a linear polystyrene calibration. M_w = weight-average molecular weight, M_n = number-average molecular weight, polydispersity index ($Đ$) = M_w/M_n. [c] Calculated from ^{1}H NMR spectra. [d] Data taken from Table 2, entry 5.

Table 4 Effect of base on the polymerization of **1a** and **2a**[a]

Entry	Base	Yield (%)	M_w[b]	$Đ$[b]	Z/E[c]
1[d]	K_3PO_4	95	18 500	1.61	100/0
2	K_2HPO_4	89	13 000	2.07	90/10
3	KH_2PO_4	92	5700	1.72	61/39
4	K_2CO_3	91	12 000	1.96	90/10
5	KOAc	90	11 000	1.96	87/13
6	$NaHCO_3$	90	15 000	2.15	94/6
7	NaOH	Insoluble			
8	KOH	Insoluble			

[a] Carried out in NMP under nitrogen at 100 °C for 24 h, [**1a**] = [**2a**] = 0.1 M, [base] = 3[**1a**] = 0.3 M. [b] Estimated by GPC using THF as the eluent on the basis of a linear polystyrene calibration, M_w = weight-average molecular weight, M_n = number-average molecular weight, polydispersity index ($Đ$) = M_w/M_n. [c] Calculated from ^{1}H NMR spectra. [d] Data taken from Table 2, entry 5.

both the M_w and the stereoregularity of the obtained PVS were significantly decreased (Table 4, entry 3). Under the promotion of K_2CO_3, KOAc or $NaHCO_3$, PVSs with an acceptable M_w and good stereoregularities (M_w > 11 000, Z-isomer contents ≥87%) could be produced in good yields (Table 4, entries 4–6). However, only insoluble products were generated in the presence of the strong base of NaOH or KOH, probably due to the formation of polymers with extremely high molecular weights (Table 4, entries 7 and 8). Thus, K_3PO_4 was considered as the most suitable base for the polymerization.

Subsequently, the effect of the base amount on polymerization was investigated. It was found that decreasing the amount of K_3PO_4 led to a decrease in the molecular weights of the resultant polymers, indicating that three equivalents of K_3PO_4 to thiol **1a** is indispensable for the polymerization to prepare PVSs with high M_w (Table S1†).

Finally, we also studied the monomer concentration impact on polymerization (Table S2†). The results showed that increasing the monomer concentration from 0.025 to 0.1 M could gradually improve the M_w and yields of the obtained PVSs probably owing to the enhanced intermolecular collision. However, when the monomer concentration was further increased to 0.2 M, the M_w of the product was slightly decreased. Therefore, the monomer concentration of 0.1 M was chosen as the optimal parameter.

Under these optimal polymerization conditions, the robustness of this polymerization was checked by polymerizing dithiols **1a** and **1b** with diynes **2a–2c**. As depicted in Table 5, all the polymerizations proceeded smoothly and PVSs with high M_w (up to 18 500) and excellent stereoregularities (Z-isomer content = 100%) were obtained in high yields (up to 95%), suggestive of the high efficiency and high regio- and stereoselectivities of this K_3PO_4-mediated thiol–yne click polymerization.

Structural characterization

All the resultant PVSs were characterized by standard spectroscopic methods, and satisfactory results corresponding to their molecular structures were obtained (see the Experimental section for detailed analysis data). As the PVSs show similar

Table 5 Polymerizations of dithiols **1** and diynes **2**[a]

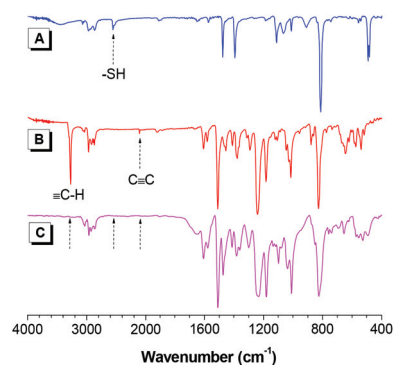| Entry	Monomers	Polymer	Yield (%)	M_w[b]	$Đ$[b]	Z/E[c]
1[d]	**1a** + **2a**	**P1a2a**	95	18 500	1.61	100/0
2	**1a** + **2b**	**P1a2b**	86	15 800	1.84	100/0
3	**1a** + **2c**	**P1a2c**	95	14 000	1.83	100/0
4	**1b** + **2b**	**P1b2b**	80	11 000	1.73	100/0

[a] Carried out in NMP in the presence of K_3PO_4 under nitrogen at 100 °C for 24 h, [**1**] = [**2**] = 0.1 M, [K_3PO_4] = 3[**1**] = 0.3 M. [b] Estimated by GPC using THF as the eluent on the basis of a linear polystyrene calibration, M_w = weight-average molecular weight, M_n = number-average molecular weight, polydispersity index ($Đ$) = M_w/M_n. [c] Calculated from ^{1}H NMR spectra. [d] Data taken from Table 2, entry 5.

spectral profiles, the structural illustration of **P1a2a** is given below as an example.

The FT-IR spectra of **P1a2a** and its corresponding monomers **1a** and **2a** are shown in Fig. 1. The stretching vibration of S–H was observed at 2557 cm^{-1} in the FT-IR spectrum of **1a** (Fig. 1A). Meanwhile, the absorption bands at 2107 and 3269 cm^{-1} in the FT-IR spectrum of **2a** were associated with the stretching vibration of C≡C and ≡C–H (Fig. 1B), respectively. These monomer characteristic peaks were absent in the spectrum of **P1a2a** (Fig. 1C), suggesting that the mercapto groups of **1a** and the ethynyl groups of **2a** have been consumed by polymerization.

To facilitate the structural characterization, E-stereoregular PVS of **P1a2a′** and stereorandom PVS of **P1a2a″** were also prepared by the previously reported $Rh(PPh_3)_3Cl$-catalyzed and spontaneous thiol–yne click polymerizations, respectively (Scheme 2). The ^{1}H NMR spectra of **P1a2a**, **P1a2a′** and **P1a2a″** and their monomers **1a** and **2a** in deuterated chloroform ($CDCl_3$) are given in Fig. 2 for comparison. Both the mercapto protons of **1a** resonated at $δ$ 3.46 and the ethynyl protons of **2a** resonated at $δ$ 3.09 almost disappeared in the spectra of their polymers **P1a2a**, **P1a2a′** and **P1a2a″**, which further substantiated the conversion of monomers.

Owing to the different chemical environments in different stereoisomers, the E- and Z-vinylene protons can be distinguished in the ^{1}H NMR spectrum, and their ratio can be
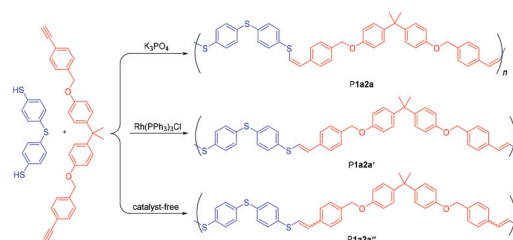
Scheme 2 Preparation of regioregular **P1a2a**, **P1a2a′** and **P1a2a″** with different stereostructures *via* thiol–yne click polymerizations of **1a** and **2a**.
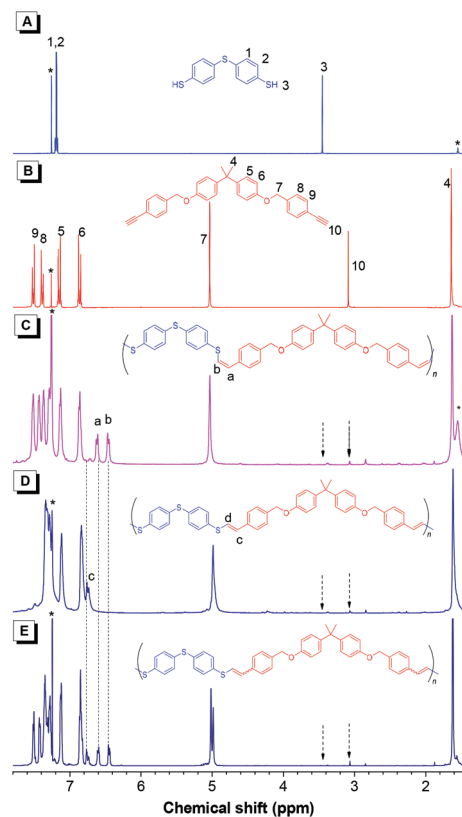
Fig. 2 ^{1}H NMR spectra of monomers (A) **1a**, (B) **2a** and their polymers (C) **P1a2a**, (D) **P1a2a′**, (E) **P1a2a″** in $CDCl_3$. The solvent peaks are marked with asterisks.

obtained from their integrals. As shown in Fig. 2E, three new resonance peaks were observed in the spectrum of **P1a2a″**. According to a previous work, the resonance peaks at $δ$ 6.46 and 6.62 originated from the Z-vinylene protons, while the resonance peak at $δ$ 6.76 was assigned to one of the E-vinylene protons (another was seriously overlapped with the aryl protons).[55] The E/Z ratio of **P1a2a″** was then calculated to be 47/53 from the ^{1}H NMR spectrum, further confirming the stereorandom nature of **P1a2a″**. In contrast, only a new peak at $δ$ 6.76 was found in the ^{1}H NMR spectrum of **P1a2a′** (Fig. 2D), implying the successful preparation of a stereoregular PVS with 100% E-isomer units. By comparing the ^{1}H NMR spectrum of **P1a2a** with those of **P1a2a′** and **P1a2a″**, we found that a pair of

Fig. 1 FT-IR spectra of monomers (A) **1a**, (B) **2a**, and their polymer (C) **P1a2a**.

peaks assigned to Z-vinylene protons was observed at δ 6.46 and 6.62 and the resonance peak related to E-vinylene protons was missing at δ 6.76, suggesting that the K_3PO_4-mediated thiol–yne click polymerization can successfully furnish the stereoregular PVS with a Z-isomer content of 100%.

In the ^{13}C NMR spectrum of **P1a2a**, the absence of resonance peaks at δ 83.7 and 77.7 assigned to the ethynyl carbon atoms of the monomer **2a** further verified the occurrence of the polymerization, which is well consistent with the conclusions drawn from the FT-IR and ^1H NMR analysis (Fig. 3).

Thermal stability

The thermal properties of the resultant PVSs were studied by thermogravimetric analysis (TGA) under nitrogen. The results showed that the PVSs enjoy high thermal resistance with decomposition temperature at 5% weight loss higher than 312 °C (Fig. 4). Additionally, owing to the conjugated aromatic structures, the char yields of **P1a2b** and **P1b2b** are higher than 60%, which might enable them to be applicable in catalytic and nanomaterial fields.

Light refractivity

Polymeric materials with high refractive indices (n) have received significant attention and found widespread applications in the areas of camera lenses, eyeglasses, telecommunication systems, antireflective coatings, *etc*.[60,61] As a rule of thumb, the introduction of aromatic rings and heteroatoms into the polymer chain is conducive to enhancing the n values of the polymers. Thus, the prepared PVSs containing high contents of aromatic rings and sulfur atoms are expected to possess high n values. Indeed, as the results of wavelength-dependent refractive measurements shown in Fig. 5, the thin
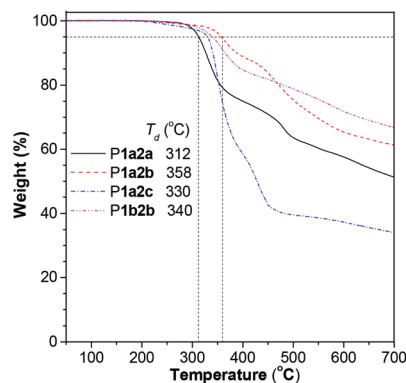

Fig. 4 TGA thermograms of the obtained PVSs under nitrogen. T_d represents the temperature of 5% weight loss.
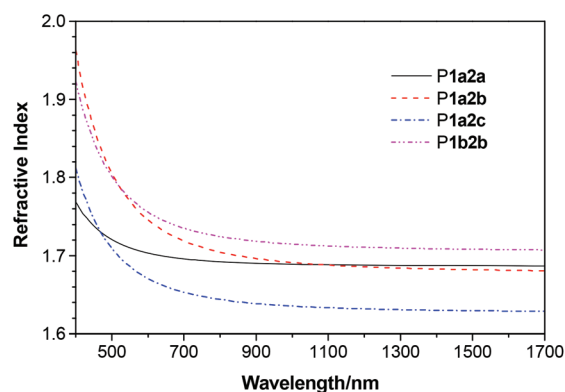

Fig. 5 Wavelength-dependent refraction indices of the thin solid films of **P1a2a**, **P1a2b**, **P1a2c**, and **P1b2b**.

films of the PVSs show n values higher than 1.628 in the wavelength region of 400–1700 nm. Notably, these n values are much higher than those of commercially important optical plastics. For example, the $n_{632.8}$ (n values at 632.8 nm) of polystyrene, polycarbonate, and poly(methyl methacrylate) are 1.588, 1.580, and 1.489,[62] whereas, those of **P1a2a**, **P1a2b**, **P1a2c**, and **P1b2b** are 1.700, 1.735, 1.664, and 1.748, respectively. These high n PVSs might found application in the organic photonic field.

Photophysical properties

Since **P1a2b** and **P1b2b** contain the typical AIE-active TPE moieties in their backbones, we anticipated that these PVSs preserve the AIE features. The AIE, conceptually termed in 2001 by our group, refers to a unique photophysical phenomenon that some propeller-shaped luminogens show very weak or no emission in their dilute solutions but intensely fluoresce in aggregate states.[63–68] To confirm this anticipation, we systematically investigated the emission behaviours of **P1a2b** and **P1b2b** in THF/water mixtures with different water fractions (f_w). As exhibited in Fig. 6A, **P1a2b** is almost non-emissive in the good solvent of THF, giving almost a flat line parallel to the abscissa in the photoluminescence (PL) spectrum.
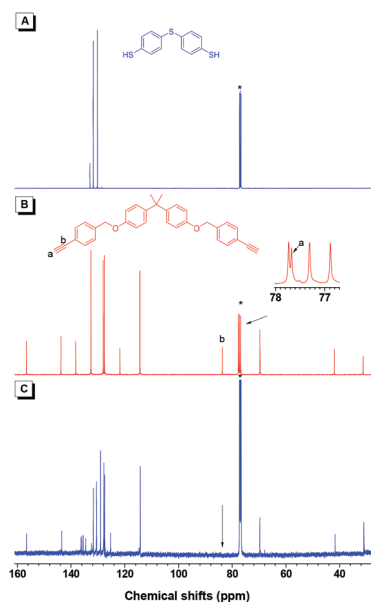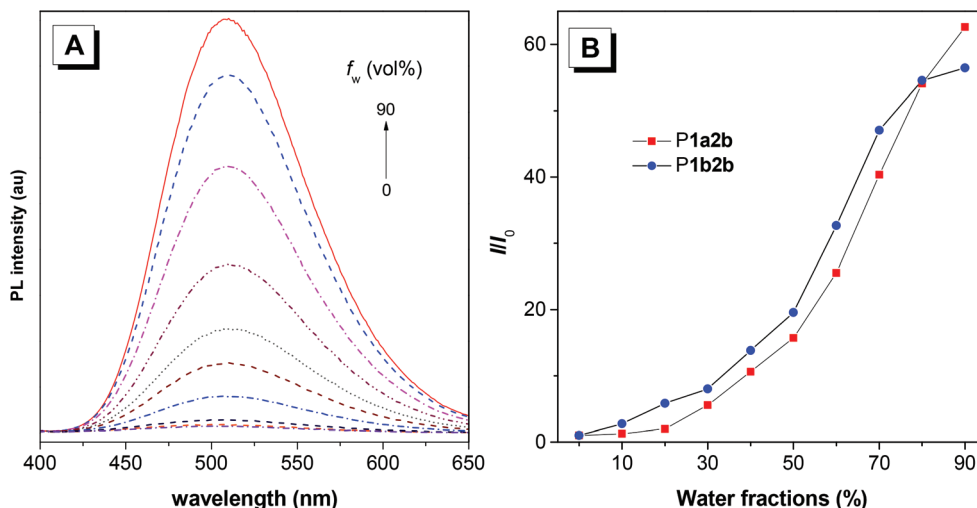

Fig. 3 ^{13}C NMR spectra of monomers (A) **1a**, (B) **2a** and their polymer (C) **P1a2a** in CDCl$_3$. The solvent peaks are marked with asterisks.

Fig. 6 (A) PL spectra of **P1a2b** in THF/water mixtures with different water fractions (f_w). (B) Plots of I/I_0 of **P1a2b** and **P1b2b** *versus* water fractions, where I = peak intensity and I_0 = peak intensity at f_w = 0. Polymer concentration: 10^{-5} M. Excitation wavelength: 352 nm.

However, with the addition of the poor solvent of water, the emission gradually enhanced and the highest fluorescence intensity was recorded in a THF/water mixture with f_w of 90% (I_{90}), which was 62-fold higher than that in THF (I_0) (Fig. 6B). This emission behaviour indicates the AIE feature of **P1a2b**.[69,70] A similar AIE behaviour of **P1b2b** was also recorded (Fig. S12†). These results demonstrated that this robust K_3PO_4-mediated thiol–yne click polymerization is a useful tool for the preparation of AIE-active polymers.

Conclusions

In summary, a transition metal-free thiol–yne click polymerization with high regio- and stereoselectivities was successfully developed. The polymerizations of dithiols **1a** and **1b** with diynes **2a–2c** were carried out in NMP in the presence of K_3PO_4 at 100 °C for 24 h. Sole anti-Markovnikov adducts of PVSs with high molecular weights and high stereoregularities (*Z*-isomer contents up to 100%) were obtained in high yields. The resultant PVSs enjoy good thermal stability with $T_d \geq 312$ °C. The high contents of sulfur atoms and aromatic rings endow the PVSs with high n values ($n > 1.628$ in the wavelength region of 400–1700 nm). Moreover, TPE moieties could be introduced to the polymer chains by this polymerization to offer the resultant **P1a2b** and **P1b2b** with AIE features. Thanks to its high efficiency and great robustness, this K_3PO_4-mediated thiol–yne click polymerization has great potential in the preparation of functional PVSs.

Experimental section

Materials

NMP (TCI), DMSO (Aldrich), and DMF (Aldrich) were dried over 4 Å molecular sieves and stored under nitrogen prior to use. THF and toluene were distilled under nitrogen from

sodium benzophenone ketyl immediately prior to use. 4,4′-Thiodibenzenethiol (**1a**), 1,3-benzenedithiol (**1b**), bases like K_3PO_4, Rh(PPh$_3$)$_3$Cl and other chemicals were purchased from Aldrich or TCI and used directly without further purification. 4,4′-(Isopropylidenediphenyl)-bis(4-ethynylbenzyl) ether (**2a**), 1,2-bis(4-ethynylphenyl)-1,2-diphenylethene (**2b**), and 1,4-diethynyl-2,5-bis(octyloxy)benzene (**2c**) were prepared according to our previously published procedures.[55]

Instruments

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance 500 or 600 MHz NMR spectrometer using tetramethylsilane (TMS, $\delta = 0$) as the internal reference and CDCl$_3$ as the solvent. FT-IR spectra were measured on a Bruker Vector 22 spectrometer. The weight-average molecular weights (M_w), number-average molecular weights (M_n) and polydispersity indices (PDI = M_w/M_n) of the polymers were estimated using a Waters advanced polymer chromatography (APC) system equipped with a photo-diode array (PDA) detector, using a suite of monodisperse polystyrenes as standards for the molecular weight calibration. THF was used as the eluent at a flow rate of 0.5 mL min^{-1}. Thermogravimetric analysis (TGA) measurements were taken on a Shimadzu TGA-50 analyzer under dry nitrogen at a heating rate of 10 °C min^{-1}. UV-vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. PL spectra were recorded on a Horiba Fluoromax-4 spectrophotometer. UV and PL spectra were measured immediately after the 1 × 10^{-5} M solutions of **P1a2b** and **P1b2b** with different water fractions (0–90 vol%) were prepared.

Refractive indices of the polymers were measured on J. A. Woollam V-VASE variable angle ellipsometry system with a region from 400 to 1700 nm. The polymer films were prepared by spin coating using 1,2-dichloroethane (DCE) as the solvent on crystalline silicon. The Cauchy dispersion law was applied to analyse the polymer layer from the visible to the IR spectroscopic region.

Polymerization

All the thiol–yne click polymerization reactions were conducted under N_2 using a standard Schlenk technique. The procedures of the polymerization of **1a** and **2a** for preparing **P1a2a**, **P1a2a′** and **P1a2a″** are given below as examples.

K₃PO₄-mediated thiol–yne click polymerization. Into a 20 mL Schlenk tube were placed a magnetic stick, **1a** (50.1 mg, 0.2 mmol), **2a** (91.2 mg, 0.2 mmol) and K_3PO_4 (127.4 mg, 0.6 mmol). After being evacuated and refilled with nitrogen three times, dry NMP (2.0 mL) was injected into the tube and the mixture was stirred at 100 °C for 24 h. Afterward, the mixture was cooled to room temperature, then diluted with THF (10 mL) and added dropwise to 300 mL of hexane through a cotton filter under stirring. The precipitate was allowed to stand overnight, then collected by filtration and dried to a constant weight in a vacuum oven at 40 °C.

Rh(PPh₃)₃Cl-catalyzed thiol–yne click polymerization. Into a 20 mL Schlenk tube were placed a magnetic stick and 4 mg (0.004 mmol) of Rh(PPh₃)₃Cl under N_2 in a glove box. Then, 2.0 mL of DCE was injected into the tube using a hypodermic syringe. After the catalyst was dissolved, **1a** (50.1 mg, 0.2 mmol) and **2a** (91.2 mg, 0.2 mmol) dissolved in 2.0 mL of DCE were injected. The resultant mixture was stirred at room temperature under N_2 for 24 h. Then, the mixture was added dropwise to 300 mL of hexane *via* a cotton filter under stirring after the resultant solution was diluted with 10 mL DCE. The precipitates were allowed to stand overnight and then collected by filtration. The polymer was washed with hexane and dried under vacuum at room temperature to a constant weight.

Spontaneous thiol–yne click polymerization. Into a 20 mL Schlenk tube were placed a magnetic stick, **1a** (50.1 mg, 0.2 mmol) and **2a** (91.2 mg, 0.2 mmol). After being evacuated and refilled with nitrogen for three times, 2 mL THF was injected into the tube to dissolve the monomers. The mixture was then stirred at room temperature for 2 h. Then, the resultant solution was diluted with 10 mL THF and added dropwise to 300 mL of hexane through a cotton filter under stirring. The precipitate was allowed to stand overnight, then collected by filtration and dried under vacuum to a constant weight.

Characterization data for polymer P1a2a. White powder; yield: 95%. M_w 18 500; M_w/M_n 1.61. FT-IR (thin film), ν (cm^{-1}): 2964, 1606, 1508, 1471, 1237, 1178, 1009, 825. ^{1}H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 7.66–7.00 (m, Ar–H), 6.89–6.79 (m, Ar–H), 6.62 (d, J = 10.0 Hz, =C–H proton from the Z-vinylene unit), 6.46 (d, J = 10.0 Hz, =C–H proton from the Z-vinylene unit), 5.03 (s, CH₂), 1.63 (s, CH₃). ^{13}C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 156.95, 143.77, 136.65, 136.26, 135.79, 134.90, 132.00, 130.90, 129.32, 128.12, 127.80, 125.62, 114.53, 70.05, 42.07, 31.39.

Characterization data for polymer P1a2a′. White powder; yield: 76%. M_w 7000; M_w/M_n 1.38. ^{1}H NMR (600 MHz, CDCl₃), δ (TMS, ppm): 7.46–7.05 (m, Ar–H), 6.79–6.89 (m, Ar–H and =C–H proton from the E-vinylene unit), 6.76 (d, J = 15.0 Hz, =C–H proton from the E-vinylene unit), 5.00 (s, CH₂), 1.63 (s, CH₃).

Characterization data for polymer P1a2a″. White powder; yield: 92%. M_w 27 500; M_w/M_n 1.55. ^{1}H NMR (600 MHz, CDCl₃), δ (TMS, ppm): 7.58–7.20 (m, Ar–H), 7.13 (d, Ar–H), 6.89–6.80 (m, Ar–H and =C–H proton from the E-vinylene unit), 6.75 (d, J = 15.2 Hz, =C–H proton from the E-vinylene unit), 6.60 (d, J = 10.7 Hz, =C–H proton from the Z-vinylene unit), 6.45 (d, =C–H proton from the Z-vinylene unit), 4.95–5.05 (m, CH₂), 1.62 (s, CH₃).

Characterization data for polymer P1a2b. Yellow powder; yield: 86%. M_w 15 800; M_w/M_n 1.84. FT-IR (thin film), ν (cm^{-1}): 3000, 1595, 1572, 1498, 1473, 1441, 1390, 1355, 1095, 1012, 811, 766, 698. ^{1}H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 7.40–6.80 (m, Ar–H), 6.57–6.25 (=C–H proton from the Z-vinylene unit). ^{13}C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 143.61, 142.73, 140.81, 135.59, 134.41, 131.96, 131.31, 130.46, 128.31, 127.86, 124.64.

Characterization data for polymer P1a2c. Brown solid; yield: 95%. M_w 14 000; M_w/M_n 1.83. FT-IR (thin film), ν (cm^{-1}): 2921, 2842, 1576, 1469, 1417, 1216, 1188, 1092, 1002, 814. ^{1}H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 7.40–7.29 (m, Ar–H), 6.97–6.95 (m, Ar–H), 6.47–6.45 (m, =C–H proton from the Z-vinylene unit), 4.04–4.01(m, OCH₂), 1.82–1.27 (m, CH₂), 0.87–0.85 (m, CH₃). ^{13}C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 150.12, 135.83, 134.60, 132.11, 132.03, 131.73, 131.39, 131.31, 130.71, 130.05, 129.95, 125.40, 124.74, 123.08, 113.11, 69.47, 31.99, 29.56, 29.54, 29.43, 26.35, 22.81, 14.27.

Characterization data for polymer P1b2b. Yellow powder; yield: 80%. M_w 11 000; M_w/M_n 1.73. FT-IR (thin film), ν (cm^{-1}): 3022, 1597, 1562, 1498, 1458, 1436, 1400, 1352, 1073, 843, 760, 694. ^{1}H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 7.54–6.80 (m, Ar–H), 6.59–6.18 (m, J = 53.8 Hz, =C–H proton from the Z-vinylene unit). ^{13}C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 143.60, 142.74, 140.80, 137.57, 134.37, 131.42, 130.29, 129.66, 128.25, 127.92, 127.76, 126.58, 124.44.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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