Catalyst-Free Thiol−Yne Click Polymerization: A Powerful and Facile Tool for Preparation of Functional Poly(vinylene sulfide)s

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S *Supporting Information*

ABSTRACT: The "thio-click" polymerization is a well-expanded concept of click polymerization. Among the click polymerizations, the thiol−yne click polymerization is less developed and still in its infancy stage. In general, UV light, elevated temperature, amine, or transition metal complexes is needed to catalyze the thiol−yne click polymerization, which greatly complicates the experimental operation and limits its application. In this work, a facile and powerful thiol−yne click polymerization was developed, which could be carried out under very mild conditions without using external catalyst. Simply mixing the aromatic diynes (**1a−1e**) and dithiols (**2−4**) with equivalent molar ratio in THF at 30 °C will readily produce soluble and regioregular functional poly(vinylene sulfide)s (**PIa−PIe, PII, and PIII**) with high molecular weights (M_w up to 85 200) in excellent yields (up to 97%) after as short as 2 h. Furthermore, no double addition product of an ethynyl group was found. This catalyst-free thiol−yne click polymerization has remarkably simplified the reaction conditions and will facilitate the preparation of functional materials applied in diverse areas.
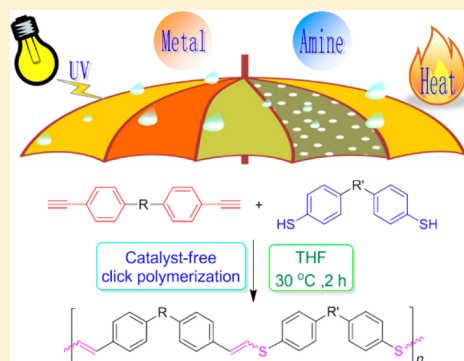
INTRODUCTION

The development of powerful and facile polymerization reactions is of vital importance to polymer science, through which materials with advanced properties could be facilely prepared. In general, most, if not all, polymerization processes are developed from known organic reactions of small molecules. However, it is not an easy task to develop an organic reaction into a successful polymerization technique because several important issues should be taken into account seriously, for example, the efficiency of catalyst system, the scope and availability of monomer, the tolerance of functional group, the optimization of the polymerization conditions, the control of molecular weights, and regio- and stereo-structures as well as the solubility and processability of the resultant polymers. Thus, an ideal organic reaction for this specific purpose must be highly efficient and could be carried out under mild conditions. Among the reported organic reactions, the click chemistry, proposed by Sharpless and co-workers in 2001,[1] was found to meet such requirements and thus considered to be a promising candidate to be developed into a powerful polymerization technique. Indeed, the Cu(I)-catalyzed azide−alkyne cycloaddition,[2] an archetypal click reaction, has been developed into an efficient click polymer-

ization.[3,4] Recently, great progress has also been made in the development of other type click polymerizations, for example, the metal-free azide−alkyne,[5] the Diels−Alder,[6] and thiol−ene click polymerizations.[7]

Although there are tremendous reports on the azide−alkyne click polymerizations, the research on the "thio-click" polymerizations, especially the thiol−yne click polymerization, is still in its infancy stage.[8,9] New type reactions, novel catalyst systems other than the dominated ones, i.e. photon, heat, organic base, and transition-metal complexes, as well as new functionalities of the resultant polymers are waiting for further development.

Our research groups have been working on the development of new polymerizations based on triple-bond building blocks for years.[10] As a natural extension of our research, we have expanded our efforts to develop the alkyne-based click reactions into powerful polymerization techniques. We have succeeded in establishing the Cu(I)-catalyzed and metal-free azide−alkyne click polymerizations and preparing functional polytriazoles with linear and hyperbranched structures.[11] Attracted by the

Scheme 1. Synthetic Route to Monomer 1a
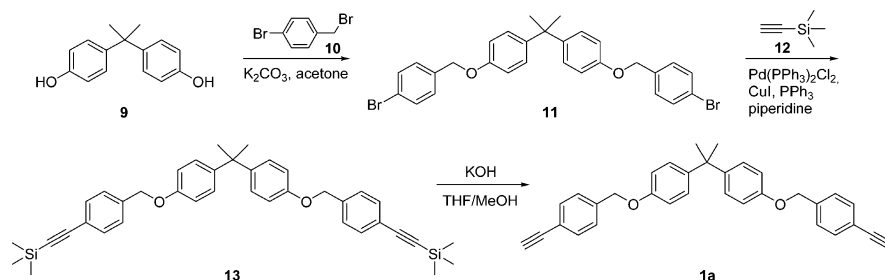
versatility and efficiency of the thiol−yne click reactions, we embarked on a project in this emerging area. The Rh-catalyzed thiol−yne and secondary amine-mediated thiol-activated alkyne click polymerizations have been developed, and functional poly(vinylene sulfide)s (PVSs) have been prepared in our group.[12] Inspired by these exciting results, we further explored other catalyst systems for the thiol−yne click polymerization.

Most recently, Zhang and co-workers reported an elegant copper-catalyzed thiol−yne reaction.[13] Interestingly, the stereoselectivity of this reaction could be fine-tuned by the CO_2 atmosphere. Since such reaction system is efficient and robust, we are interested in testing its possibility to be developed into a Cu(I)-catalyzed thiol−yne click polymerization. The preliminary results showed that the polymerization of diyne (1a) which was synthesized according to the routes shown in Scheme 1, and 4,4′-thiodibenzenethiol (2) in the presence of CuI at 60 °C for 10 h in N,N-dimethylformamide (DMF) or tetrahydrofuran (THF) furnished products with weight-averaged molecular weights (M_w) mostly less than 7000 and yields lower than 77%. When we changed the catalyst system from CuI to organosoluble Cu(PPh$_3$)$_3$Br, elevated the reaction temperature to 70 °C, replaced the solvents DMF or THF with toluene, and prolonged the reaction time to 12 h, the M_w values of the resulting products were slightly increased but still less than 10 000. Moreover, further lengthening the reaction time to 24 h in toluene could produce polymer with M_w of 16 900 in 85% yield.

Encouraged by these preliminary results, we further optimized the catalyst system. For the purpose of comparison, we carried out a control polymerization of 1a and 2 under the same reaction conditions but without addition of the Cu(I) catalyst. To our surprise, this polymerization furnished product with M_w of 17 300 in moderate yield (55%). We thus changed our strategy to conduct a systematically investigation on this special thiol−yne polymerization.

In this paper, we report the first example of a new type of thiol−yne click polymerization. This polymerization could be carried out under mild reaction conditions without addition of any catalysts. Mixing the dithiols and diynes in THF at 30 °C will produce PVSs with high molecular weights (M_w up to 85 200) in excellent yields (up to 97%) after as short as 2 h.

■ **RESULTS AND DISCUSSION**

Catalyst-Free Thiol−Yne Click Polymerization. We first studied the effect of temperature on the polymerization using 1a and 2 as monomers (Scheme 2). The M_w and polydispersity (PDI) values of the products decreased with gradually lowering the reaction temperatures from 70 to 25 °C while the yields remained almost unchanged (>92%). Delightfully, the polymers with M_w of 27 500 and PDI of 1.54 could be obtained in 92% yields even when the reactions were conducted at room

Scheme 2. Syntheses of Poly(vinylene sulfide)s by Catalyst-Free Thiol−Yne Click Polymerizations of Diynes 1 and Dithiols 2 or 3
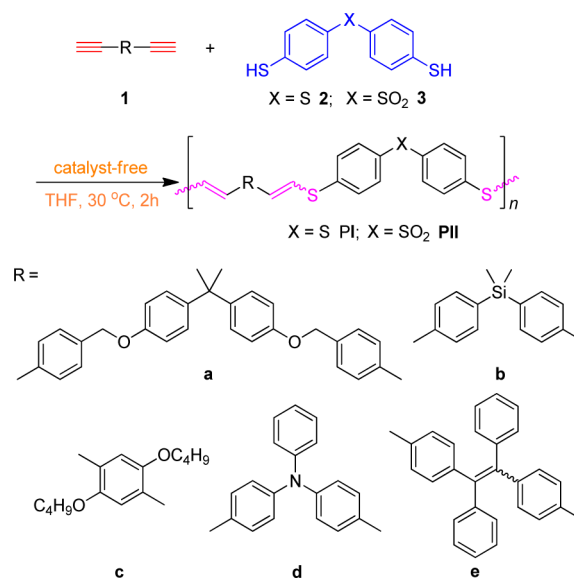
temperature (Table 1). While the M_w of the polymer produced at 30 °C was almost doubled (52 600) but the PDI increased

Table 1. Effect of Temperature on the Thiol−Yne Polymerization of 1a and 2[a]

entry	T (°C)	yield (%)	S[b]	M_w[c]	M_w/M_n[c]
1	25	92	√	27 500	1.54
2	30	93	√	52 600	1.77
3	50	98	√	90 600	2.22
4	70	93	Δ	85 700	2.16

[a]Carried out in THF under nitrogen for 4 h; [M]$_0$ = 50 mM. [b]Solubility (S) tested in common used organic solvents such as THF and chloroform; √ = completely soluble, Δ = partially soluble. [c]Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; M_w = weight-average molecular weight; M_w/M_n = polydispersity index (PDI); M_n = number-average molecular weight.

slightly to 1.77 compared to those at 25 °C, we thus chose 30 °C as the preferable polymerization temperature.

Next, we carried out the polymerizations in toluene, 1,4-dioxane, chloroform, THF, and DMF to optimize the reaction solvent. Partially soluble products were obtained in toluene and DMF after 1 and 4 h, respectively, and the M_w values of soluble parts were moderate (<10 300) (Table 2). It is worth noting that the polymer with quite low M_w was yielded in chloroform,

Table 2. Effect of Solvent on the Thiol−Yne Polymerization of 1a and 2[a]

entry	solvent	t (h)	yield (%)	S[b]	M_w[c]	M_w/M_n[c]
1	toluene	1	56	Δ	5 400	2.08
2	dioxane	4	91	√	58 300	1.83
3	chloroform	4	80	√	9 300	2.10
4	THF	4	93	√	52 600	1.77
5	DMF	4	73	Δ	10 300	2.02

[a]Carried out at 30 °C under nitrogen; $[M]_0$ = 50 mM. [b]Solubility (S) tested in common organic solvents such as THF and chloroform; √ = completely soluble, Δ = partially soluble. [c]Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; M_w = weight-average molecular weight; M_w/M_n = polydispersity index (PDI); M_n = number-average molecular weight.

implying the radical mechanism of such reaction. The results of the polymerizations carried out in 1,4-dioxane and THF are similar; we thus assigned the THF as the optimal solvent because it is a popular solvent used in the laboratory.

Afterward, we followed the time course of the polymerization. Unexpectedly, the polymerization of **1a** and **2** is so efficient that a polymer with M_w of 38 300 was yielded even after as short as 1 h (Table 3), which is also more efficient than

Table 3. Time Course on the Thiol−Yne Polymerization of 1a and 2[a]

entry	t (h)	yield (%)	S[b]	M_w[c]	M_w/M_n[c]
1	1	93	√	38 300	1.65
2	2	93	√	60 100	1.85
3	3	87	√	60 300	1.84
4	4	93	√	52 600	1.77
5	6	100	√	59 500	1.87
6	12	95	√	60 000	1.93

[a]Carried out in THF at 30 °C under nitrogen; $[M]_0$ = 50 mM. [b]Solubility (S) tested in common organic solvents such as THF and chloroform; √ = completely soluble. [c]Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; M_w = weight-average molecular weight; M_w/M_n = polydispersity index (PDI); M_n = number-average molecular weight.

those with other catalyzed systems. Since the M_w, PDI, and yield of the resultant polymer reacted for more than 2 h remain almost unchanged, we prefer 2 h as the reaction time.

Finally, we investigated the effect of monomer concentration on the polymerizations, and the experiments showed that the best results (M_w: 60 100; yield: 93%) were recorded with the monomer concentration of 50 mM (Table 4), which was, thus, adopted for further polymerizations.

With the optimized reaction conditions in hand, we performed the polymerizations using other aromatic diynes **1b−1e** with the dithiol **2** (Scheme 2). All the polymerization reactions propagated smoothly, and the polymers of **PIb−PIe** with high M_w (up to 53 900) in excellent yields (up to 97%) were produced, manifesting the universality of this powerful and efficient polymerization (Table 5).

As far as we know, the predominant thiol−yne polymerizations are initiated or catalyzed by the UV light, thermal, organic base, or transition metal complexes, but no catalyst-free system has ever been reported. It is no doubt that such a polymerization reaction will remarkably simplify the reaction conditions and facilitate the preparation of functional materials

Table 4. Effect of Monomer Concentration on the Thiol−Yne Click Polymerization of 1a and 2[a]

entry	$[M]_0$ (mM)	yield (%)	S[b]	M_w[c]	M_w/M_n[c]
1	25	88	√	33 400	1.51
2	50	93	√	60 100	1.85
3	100	95	√	59 600	1.95

[a]Carried out in THF at 30 °C under nitrogen for 2 h. [b]Solubility (S) tested in common organic solvents such as THF and chloroform; √ = completely soluble. [c]Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; M_w = weight-average molecular weight; M_w/M_n = polydispersity index (PDI); M_n = number-average molecular weight.

Table 5. Click Polymerizations of Diynes 1 with Dithiols 2−4[a]

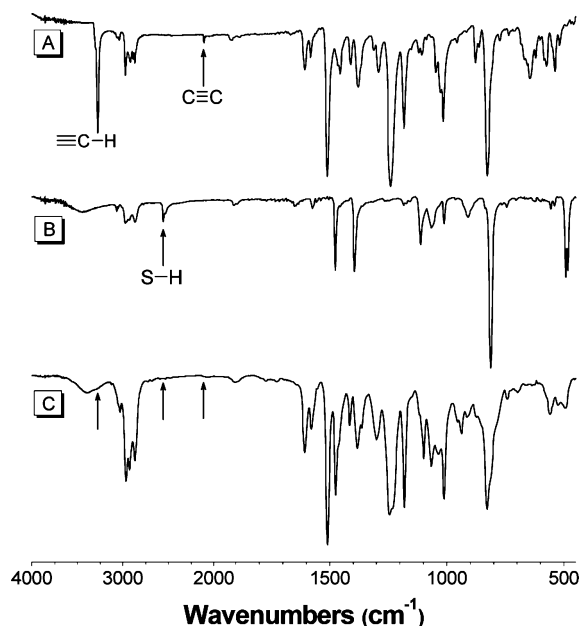| entry	monomers	polymer	yield (%)	M_w[b]	M_w/M_n[b]
1	1a + 2	PIa	93	60 100	1.85
2[c]	1a + 2	PIa	91	84 800	2.05
3[d]	1a + 2	PIa	96	85 200	2.15
4	1b + 2	PIb	92	17 600	2.74
5	1c + 2	PIc	78	29 900	3.11
6	1d + 2	PId	90	53 900	2.40
7	1e + 2	PIe	97	9 100	2.48
8	1a + 3	PII	95	21 300	1.49
9	1a + 4[e]	PIII	75	6 200	1.65

[a]Carried out in THF at 30 °C under nitrogen for 2 h; $[M]_0$ = 50 mM. [b]Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; M_w = weight-average molecular weight; M_w/M_n = polydispersity index (PDI); M_n = number-average molecular weight. [c]Reacted in darkness. [d]Reacted with UV irradiation. [e]4 = 1,5-pentanedithiol.

which could be widely applied in diverse areas. Interestingly, the polymerization also propagated smoothly in darkness, and no obvious difference was observed as compared to those in daylight (entry 2, Table 5). In addition, the UV light also exerts negligible impact on the polymerization results (entry 3, Table 5). More importantly, the polymerization could also be performed between **1a** and electron-withdrawing sulfone-containing aromatic dithiol of **3** and aliphatic 1,5-pentanedithiol (**4**), and polymers with high M_w (21 300 and 6200, respectively) could be successfully obtained in satisfactory yields (95 and 75%, respectively), further proving the universality of such polymerization.

Structural Characterization. The obtained **PIa-PIe**, **PII**, and **PIII** are soluble in commonly used organic solvents such as THF and chloroform. Thanks to their excellent solubility, the polymer structures of **PIa-PIe**, **PII**, and **PIII** could be characterized spectroscopically by "wet" methods. As the spectral profiles of **PIa−PIe** and **PII** are similar (Figure 1 and Figures S1−S5), the FTIR spectra of **PIa** and its monomers **1a** and **2** were discussed here as an example (Figure 1). The stretching vibrations of ≡C−H and S−H in **1a** and **2** were observed at 3275 and 2557 cm^{-1}, respectively. These characteristic peaks, however, disappeared in the spectrum of **PIa**, indicating that the triple bonds of **1a** and the mercapto groups of **2** have been reacted by the polymerization reaction.

The ^{1}H NMR spectroscopy could offer more detailed information about the polymer structures. To facilitate the structure characterization of **PIa−PIe** and **PII**, model reaction of aromatic monoyne of phenylacetylene (**5**) and monothiol of
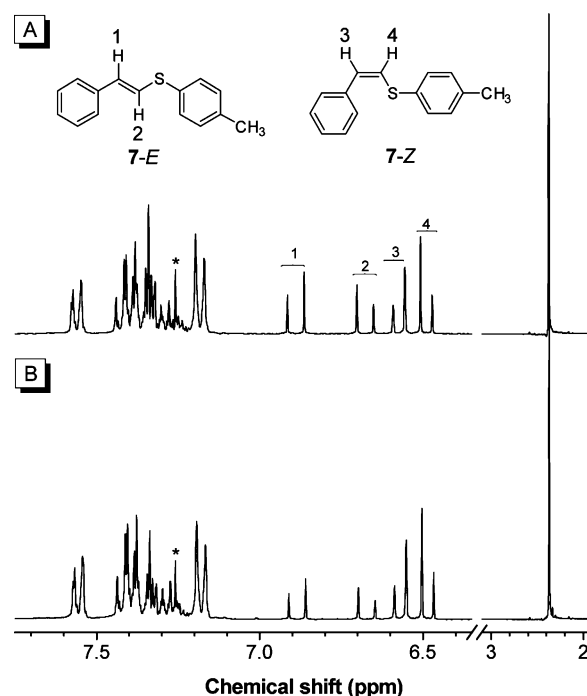
Figure 1. FTIR spectra of monomers (A) **1a** and (B) **2** and (C) polymer **PIa**.

Figure 2. ^{1}H NMR spectra of (A) compound **7** and (B) crude product of model reaction with equimolar of **5** and **6** in CDCl$_3$. The solvent peaks are marked with asterisks.

p-thiocresol (**6**) was performed under the same reaction conditions as the polymerization ones (Scheme 3).

Theoretically, the reaction of alkyne and thiols could proceed through Markovnikov and anti-Markovnikov addition routes to yield regioisomers with branched and linear structures, respectively.[14] Figure 2 shows the ^{1}H NMR spectra of the crude product which was obtained by merely evaporating THF after reaction and the purified compound. After carefully analyzing these spectra, we found that solely anti-Markovnikov product of **7**, in which the vinyl protons presented as two singlet peaks below δ 6.0, was obtained.[12] The GC-MS measurement of the crude product also excluded the formation of **8** and other theoretically possible disulfide derivatives (Figure S6). These results suggest the catalyst-free thiol—yne reaction could furnish regioregular product and thus could be regarded as a kind of click reaction. Furthermore, as can be seen from the ^{1}H NMR spectrum of **7** that there are no resonances of double addition products existed probably due to the aromatic conjugation effect of formed vinyl sulfides.[12b]

On the basis of the above results, we characterized our PVSs by NMR techniques. Figure 3 shows the ^{1}H NMR spectra of **PIa** and its monomers **1a** and **2** in chloroform-*d* as an example. The ethynyl and mercapto protons of **1a** and **2** resonate at δ 3.09 and 3.46, respectively, which almost disappear in the spectrum of **PIa**, further substantiating the conclusion drawn from the IR analysis. As suggested by the ^{1}H NMR spectrum of **7**, we could readily assign the resonances at δ 6.45, 6.58, and 6.76 to the linear vinyl sulfide units. Furthermore, two isomeric

units of vinyl sulfides could be observed and be readily assigned due to the difference in their coupling constants. The resonances at δ 6.45 and 6.58 are assigned to the *Z*-isomeric units, whereas the peak at δ 6.76 is the resonance of one of the *E*-vinylene protons (another is seriously overlapped with the aryl protons). The *E*/*Z* ratio of **PIa** thus could be calculated from their integrals, which is 44/56. Similar results were also observed in the ^{1}H NMR spectra of other PVSs (Figures S7—S12).

The ^{13}C NMR spectrum of polymer **PIa** shows no resonance peaks of the ethynyl carbon atoms of monomer **1a** at δ 83.7 and 77.7 (Figure 4). Furthermore, new peaks corresponding to the resonances of the olefinic carbons were observed at downfield. These results again indicate the conversion of the C≡C triple bonds of **1a** into the C═C double bonds in **PIa**. Similar results were observed for **PIb-PIe**, **PII**, and **PIII** as well (Figures S13—S18).

Proposed Mechanism. In general, the UV light or elevated temperature initiated free-radical, amine-mediated nucleophilic addition, and transition-metal involved migratory insertion are the mostly studied mechanisms for the thiol—yne reactions.[12,14a,15] As aforementioned, the polymerization results of **1a** and **2** in chloroform which is a chain transfer reactant in a radical polymerization have suggested a free-radical mechanism

**Scheme 3. Model Reaction of Phenylacetylene (5) and *p*-Thiocresol (6)**
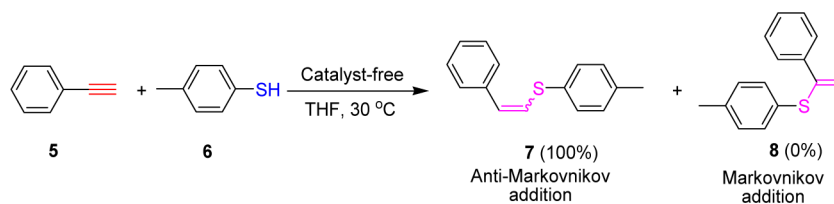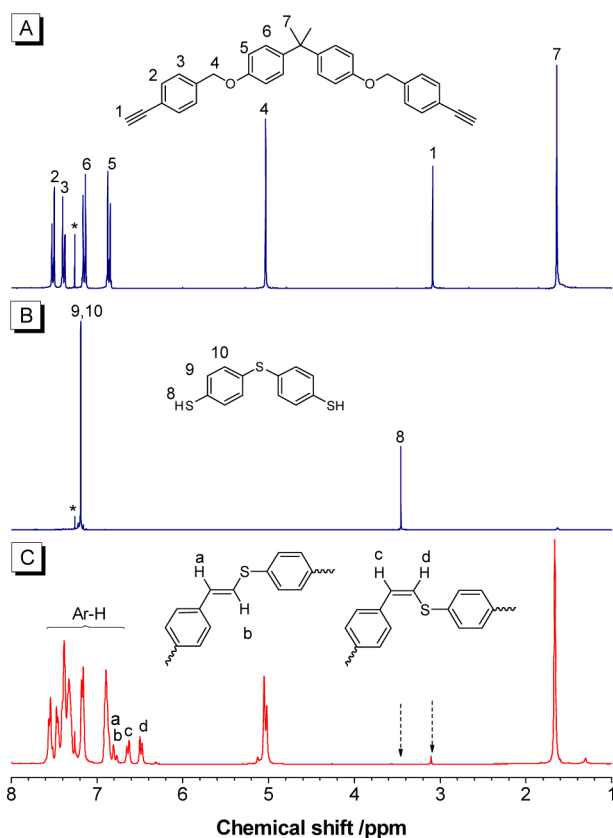
Figure 3. ^{1}H NMR spectra of monomers (A) **1a** and (B) **2** and (C) polymer **PIa** in CDCl$_3$. The solvent peaks are marked with asterisks.

for this click polymerization.[14a,c,16] To confirm it, we carried out a series of controlled experiments.

It is well-known that γ-terpinene (1-isopropyl-4-methylcyclohexa-1,4-diene) could serve as a radical trapper. We thus added this compound to the polymerization system of **1a** and **2** before the reaction. As expected, the M_w of yielded polymers greatly decreased from 60 900 to 1000 (Table 6). We thus could draw a conclusion that the dominant mechanism of our reported catalyst-free thiol−yne click polymerizations are free-radical processes but no catalyst, light source, or heating is needed, showing the advantage of spontaneity.

Thermal Stability. The thermal properties of the PVSs of **PIa−PIe** and **PII** were evaluated by thermogravimetric analysis (TGA) under nitrogen. The 5% weight losses of these polymers are at temperatures higher than 303 °C (Figure 5). It is worth noting that the char yields of **PId** and **PIe** are as high as 60% probably due to the conjugated aromatic structures, whereas the relatively low char yields of **PIa−PIc** are likely ascribed to their containing alkyl chains.

Light Refractivity. With a detailed survey on the polymer structures, we can find that PVSs of **PIa−PIe** and **PIIa** are rich in aromatic rings and sulfur atoms, making them possible to possess high refractive index (RI) and find broad applications in the areas of lenses, prisms, optical waveguides, memories, and holographic image recording systems, etc.[8c,17] Indeed, all the PVSs exhibit high RI values (n). Wavelength-dependent refractivity measurement reveals that the RI values of these PVSs are higher than 1.63 in the wavelength region of 400−1600 nm (Figure 6). It is worth noting that these RI values are much higher than those of commercially important optical plastics, such as polycarbonate (n = 1.581 at 632.8 nm) and
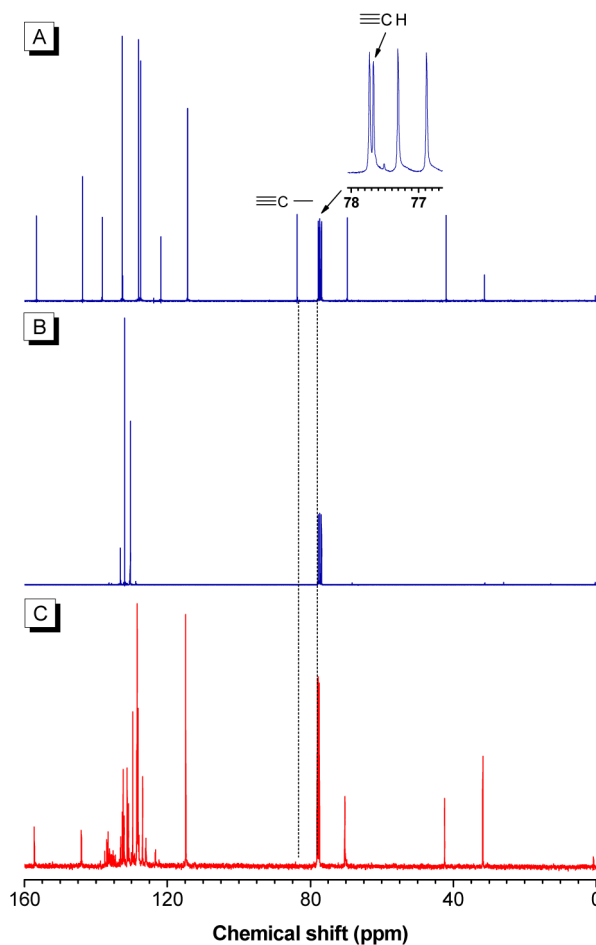
**Figure 4.** ^{13}C NMR spectra of monomers (A) **1a** and (B) **2** and (C) polymer **PIa** in CDCl$_3$.

Table 6. Polymerization of 1a with 2 in the Presence of γ-Terpinene^a

| entry	[add]^b (mM)	yield (%)	S^c	$M_w{}^d$	$M_w/M_n{}^d$
1	0	97	√	60900	1.98
2	50	63	√	1400	1.50
3	100	53	√	1000	1.36

^{a}Carried out in THF at 30 °C under nitrogen for 2 h; [M]$_0$ = 50 mM. ^{b}add = γ-terpinene. ^{c}Solubility (S) tested in common organic solvents such as THF and chloroform; √ = completely soluble. ^{d}Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; M_w = weight-average molecular weight; M_w/M_n = polydispersity index (PDI); M_n = number-average molecular weight.

polystyrene (n = 1.587 at 632.8 nm).[18] Among these PVSs, **PId** shows the best light refractivity (n = 1.771 at 632.8 nm and 1.702 at 1550 nm) probably due to the higher conjugation and stronger polarizability as well as higher content of hetero atoms. In addition, no or little birefringence for PVSs was detected, indicative of the amorphous nature of their thin solid films.

Aggregation-Induced Emission. **PIe** contains the moiety of tetraphenylethene (TPE), an archetypical luminogen featured the unique aggregation-induced emission (AIE) characteristics: it is virtually nonluminescent when molecularly dissolved in its good solvents but emits intensely when aggregated in its poor solvents or fabricated into thin solid films.[19] Does **PIe** behave in a similar way? To answer this
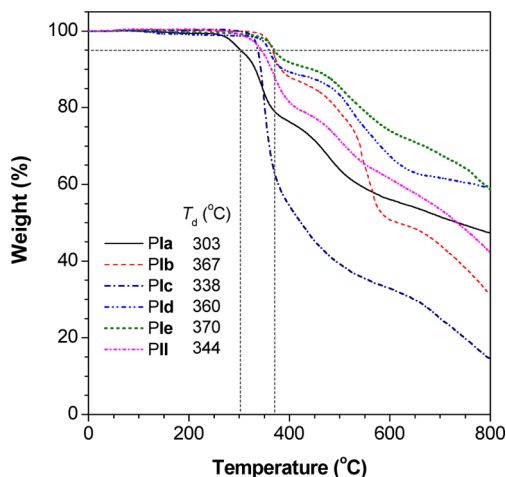
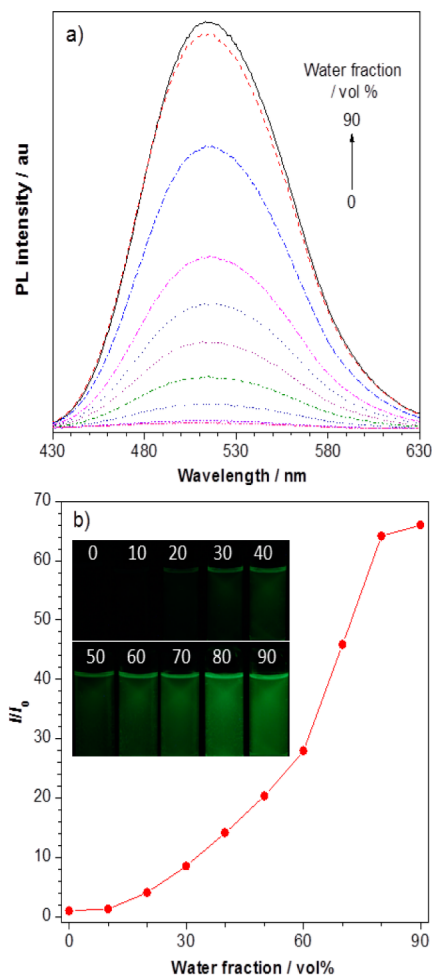**Figure 5.** TGA thermograms of polymers **PIa–PIe** and **PII**. T_d represents the temperature of 5% weight loss.
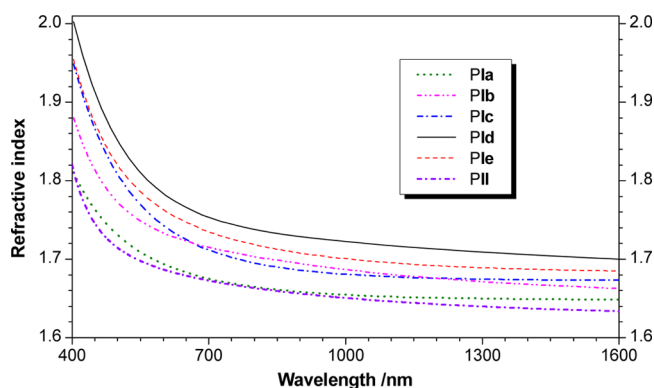
Figure 6. Light refraction spectra of thin solid films of polymers **PIa–PIe** and **PII**.

Figure 7. (a) PL spectra of **PIe** in THF and THF/water mixtures. Polymer concentration: 10 μM. Excitation wavelength: 330 nm. (b) Plot of relative PL intensity versus water fraction in THF/water mixtures, where I = peak intensity and I_0 = peak intensity in pure THF. Inset: fluorescent images of **PIe** in THF and THF/water fractions taken under a hand-held UV lamp.

question, we studied its photoluminescence (PL) behaviors in the solution and aggregated states.

Figure 7 shows the PL spectra of **PIe** in THF and THF/water mixtures with different water fractions. When excited at 330 nm, the PL spectrum of the diluted solution of polymer gives almost a flat line parallel to the abscissa, manifesting that **PIe** is weakly emissive when molecularly dissolved. As shown in the inset of Figure 7b, a faint green emission was observed in the THF/water mixture with 20% water fraction under UV light. Afterward, the emission gradually intensified and the strongest emission was recorded in THF/water mixture with 90% water fraction, which is 66-fold higher than that in pure THF. It is worthy to note that the maximum emission peaks at ~520 nm remain unchanged with addition of water, which is similar to the behaviors of TPE but with ~50 nm red-shift as a result of the extended conjugation in **PIe**.

■ EXPERIMENTAL SECTION

Materials. 4,4′-Thiobisbenzenethiol (**2**) was purified before use by standard method. 1,5-Pentanedithiol (**4**), phenylacetylene (**5**), *p*-thiocresol (**6**), and other chemicals and reagents were purchased from Sigma-Aldrich or Alfa and used as received without further purification. Tetrahydrofuran (THF), toluene, and dioxane were distilled under nitrogen at normal pressure from sodium benzophenone ketyl immediately prior to use. Triethylamine (Et₃N) was distilled and dried over potassium hydroxide. DMF was extra-dry grade.

Instruments. FT-IR spectra were recorded on a Bruker Vector 22 spectrometer as thin films on KBr pellets. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 500, Bruker AV 400 or Varian NMR 300 spectrometer in chloroform-*d* using tetramethylsilane (TMS; δ = 0) as internal reference. Elemental analysis was performed on a ThermoFinnigan Flash EA 1112. High-resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operated in MALDI-TOF mode. Gas chromatography–mass spectrometry (GC-MS) was performed on an Agilent GC-6890/MS-5973. Relative molecular weights (M_w and M_n) and polydispersity indices (PDI, M_w/M_n) of the polymers were estimated by a Waters PL-GPC-50 gel permeation chromatography (GPC) system equipped with refractive index (RI) detector, using a set of monodisperse polystyrenes as calibration standards and THF as the eluent at a flow rate of 1.0 mL/min. Thermal stabilities were evaluated by measuring thermogravimetric analysis (TGA) thermograms on a PerkinElmer TGA 7 under dry nitrogen at a heating rate of 10 °C/min. Refractive index (RI) values were determined on a Metricon Models 2010 and 2010/M prism coupler thin film thickness/refractive index measurement system. UV–vis spectra were measured on a Varian VARY 100 Bio UV–vis spectrophotometer. Photoluminescence (PL) spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer.

For the AIE measurement, a stock solution of **PIe** in THF (1 × 10^{-4} M) was first prepared. Aliquots of this stock solution were transferred

into volumetric flasks (10 mL), into which appropriate volumes of THF and water were added dropwise under vigorous stirring to furnish 1×10^{-5} M solutions with different water contents (0−90 vol %). UV and PL spectra were measured immediately after the solutions were prepared.

Monomer Preparation. The synthetic route of model monomer **1a** is shown in Scheme 1. The other monomers were prepared according to previously published procedures, and the detailed synthetic routes are given in the Supporting Information. Detailed experimental procedures for the synthesis of **1a** are given below as an example.

4,4′-(Isopropylidenediphenyl)-bis(4-bromobenzyl) ether (11). To a solution of bisphenol A (1.694 g, 7.4 mmol) and 1-bromo-4-(bromomethyl)benzene (4.081 g, 16.3 mmol) in acetone (60 mL) was added 2.557 g of potassium carbonate (18.5 mmol). The resulted suspension was heated with refluxing overnight and then cooled to room temperature. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using petroleum ether (PE) as eluent. A white needle-like product **11** was obtained in 99% yield (4.128 g). ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.50 (d, 4H, Ar−H), 7.30 (d, 4H, Ar−H), 7.14 (d, 4H, Ar−H), 6.85 (d, 4H, Ar−H), 4.99 (s, 4H, CH$_2$), 1.64 (s, 6H, CH$_3$CCH$_3$).

4,4′-(Isopropylidenediphenyl)-bis{[4-(2,2-trimethylsilyl)ethynyl]-benzyl} ether (13). Into a 250 mL round-bottom flask were added PdCl$_2$(PPh$_3$)$_2$ (197 mg, 0.28 mmol), CuI (107 mg, 0.56 mmol), PPh$_3$ (220 mg, 0.84 mmol), **11** (3.964 g, 7 mmol), and a mixture of THF/TEA/piperidine (60:30:10 v/v/v) (100 mL) under nitrogen. After the catalysts were completely dissolved, trimethylsilylacetylene (**12**, 3.0 mL, 21 mmol) was injected. The solution was stirred at 50 °C for 2 days, and then the formed precipitates were removed by filtration and washed with diethyl ether. The filtrate was concentrated by a rotary evaporator under reduced pressure, and the crude product was purified by a silica gel column chromatography using PE/dichloromethane (DCM) (10:1 v/v) as eluent. White powder of **13** was obtained in 95% yield (3.980 g). ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.47 (d, 4H, Ar−H), 7.35 (d, 4H, Ar−H), 7.13 (d, 4H, Ar−H), 6.84 (d, 4H, Ar−H), 5.02 (s, 4H, CH$_2$), 1.63 [s, 6H, C(CH$_3$)$_2$], 0.26 [s, 18H, Si(CH$_3$)$_3$].

4,4′-(Isopropylidenediphenyl)-bis(4-ethynylbenzyl) ether (1a). Into a 250 mL round-bottom flask was added **13** (3.305 g, 5.5 mmol) and THF (60 mL). Then KOH (2.468 g, 44 mmol) dissolved in methanol (80 mL) was added. The mixture was stirred at room temperature overnight. After most of the solvent was evaporated, 1 M HCl solution (50 mL) was added. The aqueous solution was extracted with DCM for three times. The organic phases were combined and washed with water and brine and then dried over MgSO$_4$ for an hour. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using PE/DCM (10:1 v/v) as eluent. White powdery product of **1a** was obtained in 91% yield (2.275 g). IR (thin film), ν (cm^{-1}): 3275 (≡C−H stretching), 2108 (weak C≡C stretching). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.50 (m, 4H, Ar−H), 7.38 (m, 4H, Ar−H), 7.14 (m, 4H, Ar−H), 6.85 (m, 4H, Ar−H), 5.03 (s, 4H, CH$_2$), 3.09 (s, 2H, ≡CH), 1.64 [s, 6H, C(CH$_3$)$_2$]. ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 156.6, 143.8, 138.2, 132.6, 128.0, 127.5, 121.8, 114.4, 83.7, 77.7, 69.7, 42.0, 31.3. Anal. Calcd for C$_{33}$H$_{28}$O$_2$: C, 86.81; H, 6.18. Found: C, 86.88; H, 5.83.

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

Thiol−Yne Click Polymerization. Into a 10 mL Schlenk tube were placed **1a** (22.8 mg, 0.05 mmol) and **2** (12.5 mg, 0.05 mmol). After being evacuated and refilled with nitrogen for three times, THF (1.0 mL) was injected into the tube to dissolve the monomers. The mixture was stirred at 30 °C for 2 h. Then, the resultant solution was diluted with THF (2.0 mL) and added dropwise into 300 mL of hexane through a cotton filter under stirring. The precipitate was 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.

The control polymerizations for mechanism study were performed with similar procedures except that the γ-terpinene was injected into the reaction system using a syringe before the addition of solvent.

Preparation of Model Compound. The synthetic route to model compound 7 is shown in Scheme 3. Into a 10 mL Schlenk tube were placed phenylacetylene (**5**, 102 mg, 1.0 mmol) and *p*-thiocresol (**6**, 124 mg, 1.0 mmol). After being evacuated and refilled with nitrogen for three times, THF (1.0 mL) was injected into the tube using a hypodermic syringe. The mixture was stirred at 30 °C for 4 h. After solvent evaporation, the crude product was purified by a silica gel column chromatography using PE as eluent. Light yellow oily product of **7** was obtained in 89% yield (202 mg). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.57−7.17 (Ar−H), 6.91 (d, J = 15.3 Hz, =C−H from the *E*-vinylene unit), 6.70 (d, J = 15.3 Hz, =C−H from the *E*-vinylene unit), 6.55 (d, J = 10.8 Hz, =C−H from the *Z*-vinylene unit), 6.50 (d, J = 10.8 Hz, =C−H from the *Z*-vinylene unit), 2.38 (s, CH$_3$).

Characterization Data of PIa. White powder; yield: 93%. M_w 60 100; M_w/M_n 1.85. IR (thin film), ν (cm^{-1}): 2960, 1606, 1510, 1475, 1383, 1302, 1242, 1182, 1099, 1065, 1010, 939, 827, 559, 495. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.58−7.17 (Ar−H), 6.90 (Ar-H and =C−H from the *E*-vinylene unit), 6.82 (d, J = 14.8 Hz, =C−H from the *E*-vinylene unit), 6.64 (d, J = 10.4 Hz, =C−H from the *Z*-vinylene unit), 6.51 (d, J = 10.4 Hz, =C−H from the *Z*-vinylene unit), 5.06 (CH$_2$), 3.10 (≡C−H), 1.66 (CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 157.2, 144.0, 136.6−123.4, 114.8, 70.3, 42.4, 31.7.

Characterization Data of PIb. White powder; yield: 92%. M_w 17 600; M_w/M_n 2.74. IR (thin film), ν (cm^{-1}): 2956, 1593, 1473, 1390, 1250, 1105, 1068, 1010, 939, 810, 775, 683, 528, 492. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.57−7.32 (Ar−H), 6.89 (d, J = 15.2 Hz, =C−H from the *E*-vinylene unit), 6.80 (d, J = 15.2 Hz, =C−H from the *E*-vinylene unit), 6.62 (d, J = 10.0 Hz, =C−H from the *Z*-vinylene unit), 6.51 (d, J = 10.0 Hz, =C−H from the *Z*-vinylene unit), 0.58 (CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 137.2, 134.8, 134.5, 132.9, 131.9, 130.4, 128.3, 125.7, 123.3, −2.1.

Characterization Data of PIc. Yellow powder; yield: 78%. M_w 29 900; M_w/M_n 3.11. IR (thin film), ν (cm^{-1}): 2954, 1575, 1493, 1475, 1419, 1388, 1205, 1099, 1070, 1030, 1010, 953, 814, 746, 490. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.41−7.28 (Ar−H), 7.05−6.94 (Ar−H and =C−H), 6.87 (=C−H), 6.49 (d, J = 10.4 Hz, =C−H from the *Z*-vinylene unit), 4.06 (CH$_2$), 1.80 (CH$_2$), 1.52 (CH$_2$), 1.01 (CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 151.1, 135.9−123.3, 113.8, 111.5, 69.5, 32.1, 20.1, 14.6.

Characterization Data of PId. Pale yellow powder; yield: 90%. M_w 53 900; M_w/M_n 2.40. IR (thin film), ν (cm^{-1}): 2918, 1593, 1504, 1473, 1325, 1278, 1178, 1095, 1068, 1010, 953, 812, 756, 694, 525. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.41−7.00 (Ar−H), 6.72 (d, J = 16.0 Hz, =C−H from the *E*-vinylene unit), 6.70 (d, J = 16.0 Hz, =C−H from the *E*-vinylene unit), 6.53 (d, J = 9.6 Hz, =C−H from the *Z*-vinylene unit), 6.34 (d, J = 9.6 Hz, =C−H from the *Z*-vinylene unit). ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 147.1, 146.5, 135.6, 133.4, 132.0−129.4, 127.8, 127.1, 125.0, 123.6, 120.1.

Characterization Data of PIe. Yellow powder; yield: 97%. M_w 9100; M_w/M_n 2.48. IR (thin film), ν (cm^{-1}): 3292, 2974, 1597, 1574, 1473, 1442, 1388, 1180, 1099, 1068, 1010, 939, 914, 848, 816, 758, 700, 628, 491. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.26−7.01 (Ar−H), 6.71 (=C−H), 6.65 (=C−H), 6.46 (=C−H), 6.37 (=C−H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 143.5, 142.7, 140.8, 134.5, 131.5, 130.4, 128.2, 126.6, 125.5.

Characterization Data of PII. White powder; yield: 95%. M_w 21 300; M_w/M_n 1.49. IR (thin film), ν (cm^{-1}): 2966, 1606, 1575, 1508, 1319, 1240, 1180, 1157, 1084, 1012, 829, 766, 630, 580, 509. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.83 (Ar−H), 7.50−7.37 (Ar−H), 7.12 (Ar−H), 6.90 (d, J = 15.6 Hz, =C−H from the *E*-vinylene unit), 6.84 (Ar−H and =C−H from the *E*-vinylene unit), 6.74 (d, J = 10.4 Hz, =C−H from the *Z*-vinylene unit), 6.44 (d, J = 10.4 Hz, =C−H from the *Z*-vinylene unit), 5.01 (CH$_2$), 1.62 (CH$_3$). ^{13}C NMR

(100 MHz, CDCl$_3$), δ (ppm): 156.5, 143.4, 136.8, 135.3, 132.3, 130.7−126.5, 121.6, 119.0, 114.1, 69.5, 41.7, 31.0.

Characterization Data of **PIII.** White powder; yield: 75%. M_w 6200; M_w/M_n 1.65. ^{1}H NMR (500 MHz, CDCl$_3$), δ (TMS, ppm): 7.48−7.28 (Ar−H), 7.12 (Ar−H), 6.85 (Ar−H), 6.69 (d, J = 16.0 Hz, =C−H from the *E*-vinylene unit), 6.47 (=C−H from the *E*-vinylene unit), 6.44 (d, J = 10.5 Hz, =C−H from the *Z*-vinylene unit), 6.23 (d, J = 10.5 Hz, =C−H from the *Z*-vinylene unit), 5.00 (CH$_2$), 3.07 (≡ C−H), 2.78 (S−CH$_2$−), 1.71 (CH$_2$), 1.62 (CH$_3$), 1.56 (CH$_2$), 1.33 (−SH). ^{13}C NMR (125 MHz, CDCl$_3$), δ (ppm): 156.7, 143.4, 138.1, 136.7, 135.5, 132.4, 128.8−125.2, 114.2, 69.8, 41.7, 35.7, 31.1, 29.9.

CONCLUSION

In summary, we have developed a facile and efficient catalyst-free thiol−yne click polymerization. The polymerization of aromatic diynes and dithiols could be carried out under very mild reaction conditions without any external stimulus and readily furnished PVSs of PIa−PIe, PII, and PIII in high yields with high M_w values at 30 °C after 2 h. Furthermore, this catalyst-free thiol−yne click polymerization is regioselective, and solely anti-Markovnikov addition products were obtained. The PVSs enjoy good solubility, thermal stability, and film-forming ability. Thin solid films of PVSs exhibit higher RI values (n > 1.63) than commercially important optical plastics. The AIE-active TPE moiety containing PVS of P**Ie** also possesses the AIE feature. Thus, this catalyst-free thiol−yne click polymerization provides a powerful tool for the preparation of functional materials for the application in diverse areas.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed synthetic routes of monomer **1b−1e** and **3**; FTIR, ^{1}H NMR, and ^{13}C NMR spectra of PVSs P**Ib−PIe**, **PII**, and **PIII**; GC-MS spectrum of crude product from the model reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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