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Metal-Free Alkyne Polyhydrothiolation: Synthesis of Functional Poly(vinylenesulfide)s with High Stereoregularity by Regioselective Thioclick Polymerization

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A new synthetic route to sulfur-rich polymers has been developed. The alkyne polyhydrothiolations of 4,4′-thiodibenzenethiol (1) and arylene dipropiolates (2–5) mediated by amines proceed at room temperature in a regioselective fashion, furnishing sole anti-Markovnikov products of poly(vinylenesulfide)s (P1/2–P1/5) with high molecular weights (M_w up to 32 300) and high stereoregularities (Z content up to 81.4%) in high yields (up to 98.2%). Polymers P1/2–P1/4 are soluble in common organic solvents. They are optically transparent, allowing almost all visible and IR light to transmit through. Thanks to the high sulfur contents of the polymers, their films show high refractive indices ($n = 1.73–1.70$) in the wavelength region of 500–1700 nm as well as high Abbé numbers (v_D' up to 539) and low optical dispersions (D' down to 0.002) at wavelengths important for telecommunications. Their refractivities can be further enhanced (n up to 2.06) by metal complexation and their films can be crosslinked by UV irradiation, which enables ready fabrication of fluorescent photopatterns.

1. Introduction

The exploration of effective polymerization reactions for the synthesis of new polymers with novel structures and unique properties is an important area of research in macromolecular science. Addition polymerizations of olefinic monomers have been one of the main routes to synthetic polymers. In the olefinic polymerizations, the monomers are knitted together by carbon–carbon single bonds. Because of electronic saturation of the single bonds, the olefinic or vinyl polymers are electrically inactive and have thus been commonly used as commodity materials in contemporary society.

Polymerizations of acetylenic monomers can generate polymers with π-conjugated carbon–carbon double bonds that are expected to be electronically active. Indeed, polyacetylene has been found to show metallic conductivity upon doping—this seminal discovery has triggered much research activity in the utilization of alkynes as building blocks to construct functional polymers.[1] As a result of the enthusiastic efforts of polymer chemists, a large number of acetylenic polymers have been synthesized.[2] In almost all the acetylenic polymers, their monomer repeating units are strung together by carbon–carbon linkages. The polymerizations of acetylene monomers through carbon–heteroatom hookups are of great interest because the resultant heteroatom-containing acetylenic polymers may exhibit properties that are difficult, if not impossible, to access by the polymers with pure carbon-based skeletons.

Alkyne hydrothiolation is a reaction that is potentially useful for the synthesis of heteroatom-containing acetylenic polymers. The reaction was first reported by Truce and Simms in the 1950s: admixing alkynes with sodium thiolates resulted in the formation of vinyl sulfides.[3] The extensive studies on alkyne hydrothiolations in the past half century have revealed that the reactions proceed through Markovnikov and anti-Markovnikov addition routes to produce regio- and stereoisomers with branched and linear structures (Scheme 1).[4,5] One recent development in the area is the report by Yorimitsu and coworkers that certain cesium salts initiate hydrothiolations of aryl alkynes with alkyl thiols.[6] The inorganic bases, however, was not applicable to aryl thiols, while organic bases such as triethylamine completely failed to work as catalysts when the reactions were attempted at room temperature.

It is envisioned that alkyne hydrothiolation of alkyne and thiol with two triple bonds (diyne) and mercapto groups (dithiol) may produce a poly(vinylenesulfide) (PVS) with linear and branched conformations. The sulfur-containing polymer may exhibit properties uniquely associated with its high sulfur content, such as high light refractivity and excellent optical transparency, and

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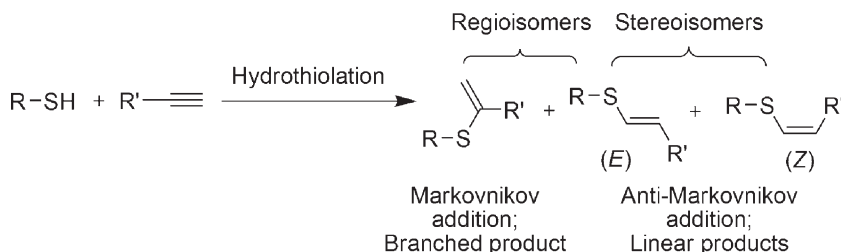
Scheme 1. Formation of 1,1- and 1,2-disubstituted olefins with branched and linear structures by Markovnikov and anti-Markovnikov routes of alkyne hydrothiolation, respectively.

thus find high-tech applications as a promising photonic material.[7] The PVS may readily react or coordinate with transition metals and the resultant macromolecular complexes may work as recyclable and reusable polymer catalysts[8] and serve as processable precursors to non-oxide ceramics upon pyrolysis.[9] Such possibilities, although attractive, have been virtually unexplored.

Our groups have been working on the development of alkyne polymerization reactions. Employing monoynes, diynes, and triynes as monomers, we have successfully synthesized a large variety of polyacetylenes, polyarylenes, polydiynes, and polytriazoles with linear and hyperbranched structures and regio- and stereoregularities by metathesis, cyclotrimerization, coupling, and click polymerizations.[10] In our previously investigated click polymerization systems, azide–alkyne cycloaddition (or 'azido-click') reactions were utilized. Thiol–alk*ene* addition is another well-known click reaction and has been used by several research groups to synthesize saturated macromolecules such as dendrimers and star polymers.[11,12] In contrast, thiol–alk*yne* addition or alkyne hydrothiolation remains unexploited, although it has the potential to be developed into a new "thioclick" polymerization technique for the synthesis of sulfur-containing unsaturated polymers.

In this work, we have extended our acetylene-based research to a heteroatom-mediated system and have developed alkyne hydrothiolation into a versatile polymerization technique for the preparation of sulfur-rich acetylenic polymers. In this paper, we show that alkyne polyhydrothiolations of 4,4′-thiodibenzenethiol (**1**) and arylene dipropiolates (**2–5**) are mediated by organobases such as secondary amines at room temperature to afford regioregular linear PVSs (**P1/2–P1/5**) with high molecular weights and high stereoregularities in high yields (Scheme 2). This represents the first example of a metal-free, organobase-mediated, thioclick polymerization reaction. The PVSs are optically
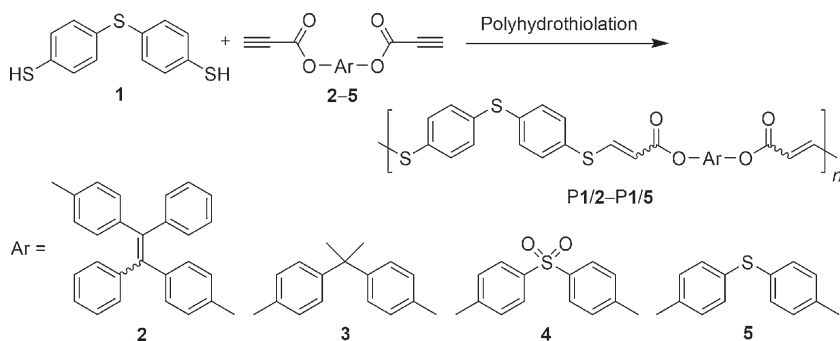
transparent and are readily metallized by complexation with cobalt carbonyls to furnish organometallic polymers with high refractive indexes ($n = 2.106$–1.708) and low chromatic aberrations (D' down to 0.002).

2. Results and Discussion

2.1. Monomer Preparation

To explore the possibility of utilizing alkyne hydrothiolation to construct sulfur-containing macromolecules, we adopted an $A_2 + B_2$ approach and used dithiol **1** and dipropiolates **2–5** as building blocks for the synthesis of linear PVSs. The advantage of this strategy is that the monomers can be synthesized with ease and can be kept for a long time on the shelf under ambient conditions, which circumvents the self-oligomerization problem met by the AB_2 approach.

Arylene dipropiolates **2–5** were prepared by esterifications of their corresponding diols with propiolic acid in the presence of 1,3-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), and *p*-toluenesulfonic acid (TsOH). All the monomers were characterized by spectroscopic techniques, from which satisfactory analysis data corresponding to their expected molecular structures were obtained (see Experimental section for details).

2.2. Polymer Synthesis

The development of non-metallic and metal-free polymerization reactions has attracted much interest among polymer chemists in recent years because of their remarkable advantages, such as environmental benignity, economic benefit, and ease in polymer purification.[13] The reactions are free of the detrimental effects of metallic ions in the catalyst residues on polymer properties, such as light emission and optical non-linearity. In addition, functional groups that are toxic to transition metals can be used, which helps widen the variety of polymers that can be synthesized by the reactions.

In our previous investigations, we found that bis(aroylacetylene)s and dipropiolates could be polycyclotrimerized in the presence of secondary amines or in refluxing N,N-dimethylformamide (DMF).[10] We thus tried to synthesize PVS from **1** and **3** under metal-free conditions. After stirring in DMF at room temperature for 24 h, a PVS with an M_w of 5200 was isolated in a yield of ∼92% (Supporting Information, Table S1, run 1). Changing the solvent to tetrahydrofuran (THF), toluene, and dioxane had little effect on the yield of the PVS but decreased its molecular weight. Both yield and M_w dropped when the polymerization was preformed in 1,2-dichlorobenzene.

In the presence of organobase, the nucleophilicity of the thiol group will be increased, which may enhance the efficiency of its
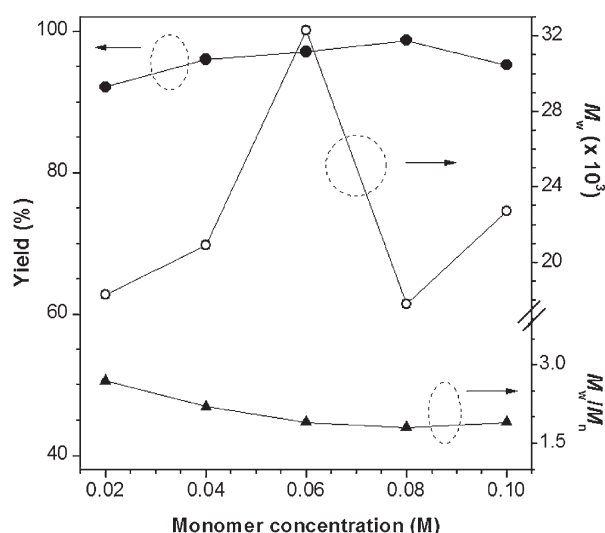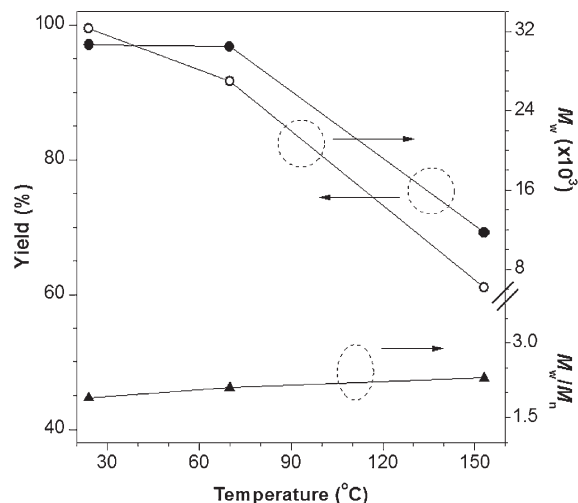

Scheme 2. Synthesis of PVSs **P1/2–P1/5** by polyhydrothiolation of dithiol **1** and diynes **2–5**.

Table 1. Effect of organobase on polyhydrothiolation of **1** and **3**.

Run [a]	Base	Yield [%]	M_w [b]	M_w/M_n [b]
1	piperidine	Gel		
2	methylpiperazine	Gel		
3	diethylamine	37.0	17 100	3.2
4	triethylamine	71.7	6300	1.7
5	diphenylamine	97.1	32 300	1.9
6	triphenylamine	97.1	6800	1.7
7	morpholine	81.8	3900	1.7
8	diphenylamine	97.8	30 100	2.1

[a] Carried out at room temperature in DMF under nitrogen for 24 h; [**1**] = [**3**] = 0.06 M; [base] = 0.6 M (except for run 8, where [base] = 1.2 M). [b] Estimated by gel permeation chromatography (GPC) in THF on the basis of a polystyrene calibration.

addition reaction. With this consideration in mind, we tested the effects of different amines on the alkyne polyhydrothiolation. Insoluble gels are formed when the polymerizations are initiated by piperidine and methylpiperazine (Table 1, runs 1 and 2). Soluble polymers, however, are obtained in moderate to high yields when other amines are used. Among them, diphenylamine works efficiently for the reaction, producing a PVS with a high molecular weight (M_w 32 300) in a nearly quantitative yield (97%). Doubling the amount of diphenylamine to 1.2 M gives similar results, because the thiol group of **1** is already converted into thiolate in the reaction mixture containing 0.6 M diphenylamine.

We then tried to determine the optimal monomer concentration [M] in the polymerization of **1** and **3** in the diphenylamine/DMF mixture. In all the runs, an equimolar ratio of **1** and **3** was used. With an increase in [M], the M_w of the polymer is enhanced and reaches its maximum value of ~32 000 at [M] = 0.06 M (Fig. 1). Further increasing [M] has an adverse effect on the molecular weight. The polymer yield remains high at all [M]s studied, which demonstrates of the high efficiency of the polymerization reaction.

Figure 2. Effect of temperature on the polyhydrothiolation of **1** and **3** in DMF under nitrogen in the presence of 1.2 M of diphenylamine for 24 h; [**1**] = [**3**] = 0.06 M.

Temperature strongly influences the polymerization reaction. Both the yield and M_w of the PVSs are decreased when the temperature is raised from 23 to 150 °C (Fig. 2). As mentioned above, dipropiolates can undergo polycyclotrimerization in refluxing DMF.[10] Some portion of monomer **3** may self-polymerize at high temperatures to form low-molecular-weight hyperbranched oligomers that may have been removed during the purification process of the reaction product. The concentration of **3** in the solution is thus lowered, which leads to the formation of polymers with lower molecular weights in lower yields. Figure 3 shows the time course of the alkyne polyhydrothiolation. After 12 h, a polymer with a M_w of 25 000 is obtained, which is high enough for practical applications. Prolonging the reaction time to

Figure 1. Effect of monomer concentration on the polyhydrothiolation of **1** and **3** at room temperature in DMF under nitrogen for 24 h in the presence of 1.2 M of diphenylamine.
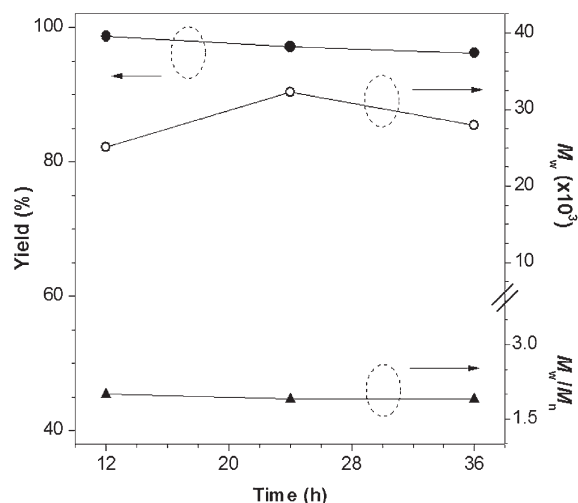

Figure 3. Time course of polyhydrothiolation of **1** and **3** at room temperature in DMF under nitrogen in the presence of 1.2 M of diphenylamine; [**1**] = [**3**] = 0.06 M.

Table 2. Polyhydrothiolation of **1** with **2–5**.

Run [a]	Monomers	Yield [%]	S [b]	M_w [c]	M_w/M_n [c]	Z [d] [%]
1	**1 + 2**	73.5	√	21 000	2.9	78.1
2 [e]	**1 + 3**	97.2	√	29 000	1.7	80.2
3	**1 + 3**	97.1	√	32 300	1.9	81.4
4	**1 + 4**	87.2	√	7500	2.1	68.9
5	**1 + 5**	98.2	×			

[a] Carried out at room temperature in DMF in the presence of 1.2 M diphenyl-amine under nitrogen for 24 h unless stated otherwise; [monomer] = 0.06 M. [b] Solubility (S) tested in common organic solvents such as toluene, DCM, chloroform, and THF: √ = completely soluble, × = insoluble. [c] Estimated by GPC in THF on the basis of a polystyrene calibration. [d] Determined by ^{1}H NMR spectroscopy. [a] Conducted in air.

24 h slightly lowers the yield of the PVS but increases its M_w to 33 000.

The above systematic studies enable us to polymerize **1** with **2–5** under optimal conditions. Table 2 summarizes the polymerization results. All the polymerizations proceed smoothly, giving P**1**/**2**– P**1**/**5** in good yields. Comparing the polymerization results of **1** and **3** obtained under nitrogen and in air, it is clear that oxygen and moisture exert little effect on the alkyne polyhydrothiolation reaction (Table 2, runs 2 and 3). The oxygen and moisture tolerances greatly help simplify the reaction procedures.

2.3. Structural Characterization

To verify that dithiol **1** and dipropiolates **2**−**5** have indeed been polymerized in an alkyne polyhydrothiolation mechanism, we conducted a model reaction using thiophenol (**6**) and phenyl propiolate (**7**) as reactants (Scheme 3). While a thiol can undergo Markovnikov addition to an alkyne to give a branched vinyl sulfide, the reaction can also proceed in an anti-Markovnikov fashion to yield linear adducts with E and Z conformations (cf., Scheme 1). When **6** and **7** are reacted under conditions similar to those given in Table 2, run 2, product **8** is isolated in a high yield (94%). Spectroscopic analysis reveals that **8** is a linear anti-Markovnikov product with a predominant Z conformation (Z : E = 4 : 1). No branched product is obtained at all, which indicates that the reaction proceeds in a regioselective fashion.

To collect direct structural information, we characterized the polymers by spectroscopic methods. Examples of the IR spectra of P**1**/**3** and its monomers **1** and **3** are given in Figure 4. The S−H stretching vibration of **1** is observed at 2600 cm^{-1}, while the =C−H and C=C stretchings of **3** occur at 3266 and 2124 cm^{-1},
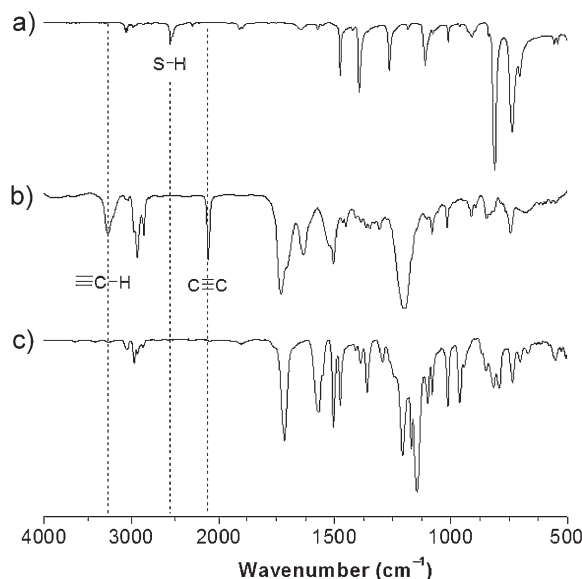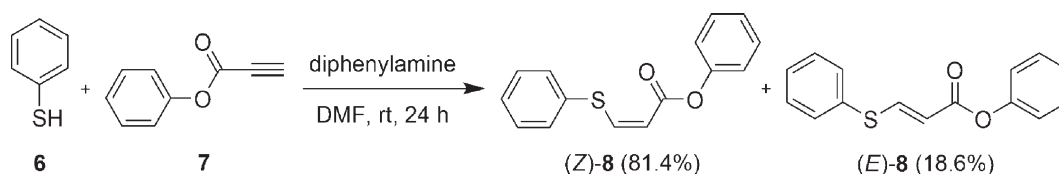

Figure 4. IR spectra of monomers a) **1**, b) **3**, and c) their polymer P**1**/**3**.

respectively. No such peaks are observed in the spectrum of P**1**/**3**. Instead, new peaks associated with C=C stretching and bending vibrations are observed at 1580 and 940 cm^{-1}, and reveal that all the mercapto groups and triple bonds of **1** and **3** have been transformed by the polymerization reaction into vinyl sulfide units in P**1**/**3**.

The model reaction suggests that the alkyne polyhydrothiolation is regioselective. To prove whether this is the real case, we analyzed the NMR spectra of the polymers. Figure 5 shows the ^{1}H NMR spectra of P**1**/**3** and its monomers **1** and **3** in chloroform-d; for better peak assignment, the spectrum of model compound **8** is also given in the figure. The thiol and acetylene protons of **1** and **3** resonate at δ 3.46 and 3.06, respectively, which completely disappear after the monomers have been subjected to alkyne polyhydrothiolation reaction. By comparison with the spectra of monomers **1** and **3** and model compound **8**, the resonance peaks in the spectrum of P**1**/**3** can be readily assigned. The resonances of the phenyl protons in P**1**/**3** are located at similar chemical shifts to those in **1** and **3**.

New peaks assigned to the proton resonances of the linear vinyl groups newly formed by the alkyne polyhydrothiolation are observed at δ 5.86, 6.15, and 7.92. While the first and third peaks stem from the resonances of the PVS segments with an E-conformation, the second one originates from the resonance of the chain segments that comprise Z-isomeric units. Thanks to the large difference in the chemical shifts of the stereoisomers, the

Scheme 3. Synthesis of model compound **8** with high stereoselectivity (Z : E = 4 : 1) through organobase-catalyzed regioselective alkyne hydrothiolation.
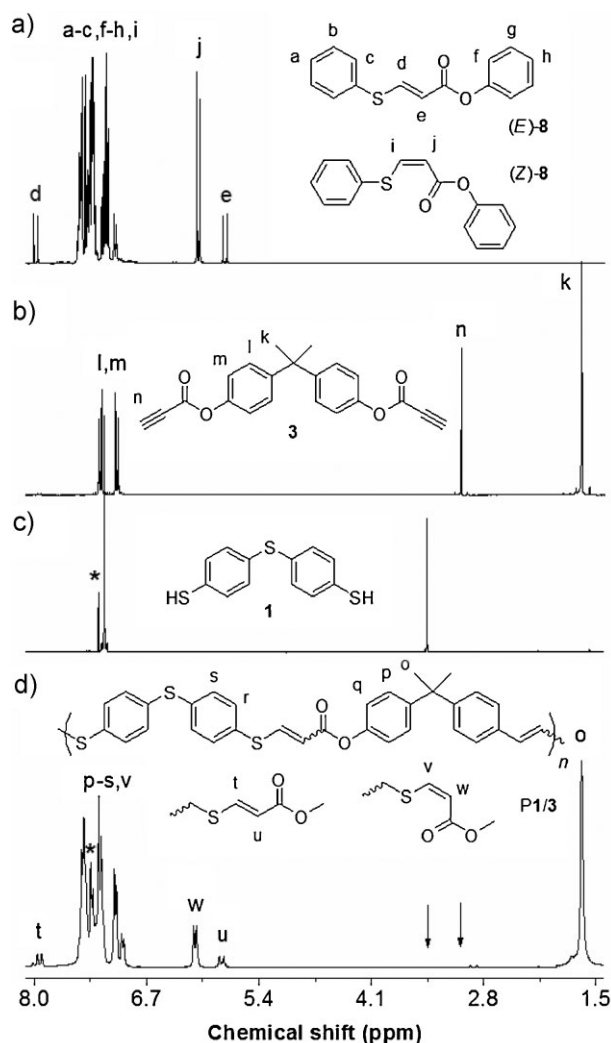
(Z)-**8** (81.4%)   (E)-**8** (18.6%)

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Figure 5. ^{1}H NMR spectra of a) model compound **8**, b) monomer **3**, c) monomer **1**, and d) polymer P**1**/**3** in CDCl$_3$. The solvent peaks are marked with asterisks.

Table 3. Thermal properties of P**1**/**2**–P**1**/**5** determined by thermogravimetric analysis under nitrogen at a heating rate of 10 °C min^{-1}.

Polymer	F_S [a] [wt %]	T_d [b] [°C]	W_r [c] [%]
P**1**/**2**	13.38	345	45.6
P**1**/**3**	16.51	335	42.0
P**1**/**4**	21.21	324	14.1
P**1**/**5**	22.39	333	32.9

[a] Sulfur content of PVS calculated from its repeat unit. [b] Temperature for 5% weight loss. [c] W_r = weight residue at 600 °C.

chloroform, THF, and dioxane, and can be readily fabricated into tough solid films by spin-coating and static-casting processes. Among the PVSs, P**1**/**5** has the highest sulfur content ($F_S > 22$ wt %; Table 3). Its intractability may thus be caused by the strong interaction between the sulfur atoms in different polymer chains, which leads to the formation of physical crosslink networks. This hypothesis is further supported by the good solubility of its sulfonylated counterpart of P**1**/**4**. The oxidation of the thio group between the phenyl rings reduces the likelihood of the formation of a disulfur bridge between the polymer chains, thus making P**1**/**4** soluble in common organic solvents.

All the polymers are thermally stable. As can be seen from Fig. S2 in the Supporting Information, the temperatures for 5% weight loss or the degradation temperatures (T_d) of the polymers are all higher than 320 °C under nitrogen, which is indicative of their strong resistance to thermolysis (Table 3). Except for P**1**/**4**, the residues of the polymers after pyrolysis at 600 °C are higher than 30%. The exceptionally low weight residue for P**1**/**4** (~14 wt %) is probably a result of the ready evaporation of the sulfur dioxide gas formed in the pyrolysis process of the sulfonylated polymer at the high temperature.

2.5. Metal Complexation

The polymers contain π-electron-rich aromatic rings and vinyl double bonds as well as metal-affinitive or metallophilic thio groups that are expected to form organometallic complexes with cobalt carbonyls.[14] Indeed, when the soluble PVSs (P**1**/**2**, P**1**/**3**, and P**1**/**4**) are admixed with Co$_2$(CO)$_8$ in THF, their solutions are darkened, which is accompanied by gas evolution. The solutions remain homogeneous throughout the whole process of the cobalt-complexation reaction. However, the isolated macromolecular complexes P**1**/**2**(Co)–P**1**/**4**(Co) are insoluble, possibly because of the formation of supramolecular aggregates during the product purification processes (precipitation into poor solvent and drying under vacuum).

We used elemental analysis (EA) and energy-dispersion X-ray analysis (EDX) to estimate the compositions of the PVS(Co) complexes. The cobalt contents of P**1**/**2**(Co), P**1**/**3**(Co), and P**1**/**4**(Co) determined by EA are 0.09, 6.25, and 1.86%, respectively (Table 4). The severe steric effect of the bulky, non-planar tetraphenylethene (TPE) units in P**1**/**2** may have greatly shielded the vinyl sulfide groups and hampered them from reacting with Co$_2$(CO)$_8$. On the other hand, the higher M_w value of P**1**/**3** together

E and Z contents of the polymer can be calculated using their integrals and the Z/E ratio is found to be 81.4%. Other polymers are also Z-rich. Evidently, the alkyne polyhydrothiolation produces polymers with high stereoregularity.

The ^{13}C spectrum of P**1**/**3** shows no resonance peaks of the acetylenic carbons of monomer **3** at δ 76.6 and 74.3 (Supporting Information, Fig. S1). New peaks that correspond to the resonances of the olefinic carbons are observed at δ 164.8, 163.5, 115.0, and 112.8, because of the conversion of the acetylene triple bonds in **3** into the double bonds in P**1**/**3**.

2.4. Solubility and Stability

Except for P**1**/**5**, all other polymers are completely soluble in common organic solvents, such as toluene, dichloromethane,

Table 4. Chemical compositions of PSV(Co)s in units of at%.

Polymer complex	EA			EDX			XPS		
	C	H	Co	C	O	Co	C	O	Co
P**1**/**2**(Co)	72.95	3.92	0.09	85.85	2.72	0.16	83.99	8.59	0.12
P**1**/**3**(Co)	67.46	4.41	6.25	71.97	7.55	8.33	80.88	10.76	2.02
P**1**/**4**(Co)	59.18	3.33	1.86	65.78	3.93	1.62	73.70	15.73	0.87

with its less sterically hindered bisphenol-A moieties may have enabled more efficient metal complexations, which leads to the higher cobalt content in its complex. Similar results are obtained from the EDX measurements.

The analysis by X-ray photoelectron spectroscopy (XPS) offers information about chemical compositions on the surfaces of PVS(Co) powders. The cobalt contents estimated by the XPS analysis are generally lower than those obtained from the EA and EDX analyses, which suggests that the cobalt species are aggregated in the bulk rather than on the surface. The ceramic materials obtained from the pyrolyses of the PVS(Co) complexes are practically non-magnetic, in sharp contrast to the very high magnetizabilities of the ceramics obtained from the cobalt complexes of the hyperbranched polymers in our previous studies.[9] This is probably because of the formation of cobalt sulfides Co_xS_y by the pyrolysis of the PSV(Co) complexes, which are known to be magnetically insusceptible.[15]

2.6. Optical Transparency

Polymers with high optical clarity are promising candidate materials for advanced photonic applications.[16] The PVSs absorb little light in the visible spectroscopic region and allows almost all the light at wavelengths longer than 400 nm to transmit through (Fig. 6). For example, the light transmittance of P**1**/**3** is already 99% at a wavelength as short as 370 nm. Although the optical transparencies of the polymers are decreased after complexation with cobalt metal, the light transmittances are still higher than 90% beyond 400 nm. For example, the light transmittance of P**1**/**3**(Co) at 370 nm is 98%, just 1% lower than that of its parent form (P**1**/**3**). The excellent transparencies of the PVSs and PVS(Co)s may be attributed to the existence of two ester groups in every one of their repeat units, which weaken the electronic communications between the neighboring aromatic and vinyl groups, thereby decreasing their absorptivities in the long wavelength region.

2.7. Light Refractivity

The PVSs are comprised of polarizable aromatic rings, ester groups, and sulfur atoms and may show high refractive indices.[17] This is indeed the case: as shown in Figure 7a, P**1**/**2** displays high refractivities ($n = 1.7300–1.6569$) over a wide spectroscopic region (500–1700 nm). Polymers P**1**/**3** and P**1**/**4** display similarly high refractive indexes of 1.7148–1.6611 and 1.7345–1.7003, respectively, in the same spectroscopic region. It is noted that the n value
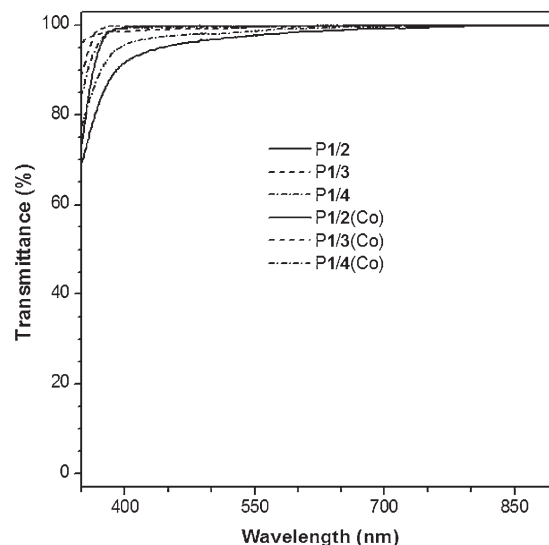

Figure 6. Light transmission spectra of THF solutions of P**1**/**2**−P**1**/**4** and thin solid films of P**1**/**2**(Co)−P**1**/**4**(Co). Solution concentration (μg mL^{-1}): 7.2 (for P**1**/**2**), 5.7 (for P**1**/**3**), 6.0 (for P**1**/**4**).
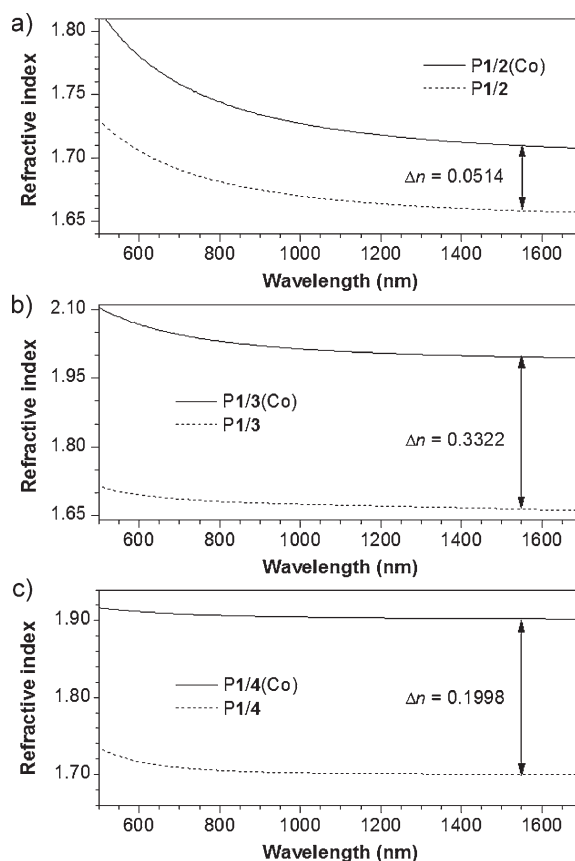
Figure 7. Wavelength dependence of refractive indexes of thin films of a) P**1**/**2** and P**1**/**2**(Co), b) P**1**/**3** and P**1**/**3**(Co), and c) P**1**/**4** and P**1**/**4**(Co); Δn values given in the figures are the differences in the refractive indexes at 1550 nm.

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Table 5. Refractive indices and chromatic dispersions of PVSs and PSV(Co)s.

Film [a]	$n_{632.8}$	n_{1550}	v_D	$v_D{}'$	D	D'
P1/2	1.7004	1.6583	18.4	70.4	0.054	0.014
P1/3	1.6918	1.6640	22.8	69.6	0.044	0.014
P1/4	1.7317	1.7004	26.3	539.0	0.038	0.002
P1/2(Co)	1.7728	1.7097	13.6	50.7	0.074	0.020
P1/3(Co)	2.0593	1.9962	18.6	80.0	0.054	0.014
P1/4(Co)	1.9166	1.9002	156.5	643.0	0.006	0.002

[a] Abbreviations: n = refractive index, v_D = Abbé number (calculated from equation 1), $v_D{}'$ = modified Abbé number (calculated from equation 2), D = chromatic dispersion in the visible region, and D' = chromatic dispersion in the IR region.

increases with the sulfur content (F_S) in the polymer (cf., Table 3). When the F_S value is increased from ~13% in P1/2 to ~21% in P1/4, the n value at 1550 nm is increased from 1.6583 to 1.7004. The refractivity of the PVS can thus be tuned through molecular engineering endeavors. P1/5 has the highest sulfur content among the polymers but unfortunately its refractivity cannot be measured because of its insolubility in common organic solvents.

The n values of P1/2, P1/3, and P1/4 are around 1.7 at 632.8 nm and larger than 1.65 even at 1550 nm (Table 5), which are much higher than those of the commercially important optical plastics [e.g., $n \sim 1.49$ for poly(methyl methacrylate) (PMMA) and $n \sim 1.59$ for poly(ethylene terephthalate) (PET) and polycarbonate (PC)]. The PVSs are thus highly refractive polymers. No or little birefringence is detected, which is indicative of the amorphous nature of their thin solid films.

Interestingly, after metal complexation, the n values of the polymers are further enhanced (up to 2.0593). Inorganic and organometallic materials often show higher refractive indexes than pure organic materials.[17,18] The high refractive indexes of PSV(Co)s are thus likely because of their metallic components. The differences in the refractivity (Δn) between PVSs and PVS(Co)s at the telecommunication important wavelength of 1550 nm can be as large as 0.3322 (Fig. 7b). The Δn value of the P1/2 and P1/2(Co) pair is relatively small (0.0514), which is understandable because of the low cobalt content in P1/2(Co).

2.8. Chromatic Dispersion

For a material to be useful for practical applications, its optical aberrations should be small. The Abbé number (v_D) of a material is a measure of the variation or dispersion in its refractive index with wavelength, which is defined as

$$v_D = \frac{n_D - 1}{n_F - n_C} \tag{1}$$

where n_D, n_F, and n_C are the refractive indexes at wavelengths of the Fraunhofer D, F, and C spectroscopic lines of 589.2, 486.1, and 656.3 nm, respectively. A modified Abbé number ($v_D{}'$) has been proposed to evaluate the application potential of an optical

material, using its n values at the non-absorbing wavelengths of 1064, 1319, and 1550 nm.[19] The first two wavelengths are chosen in view of the practical interest of a commercial laser wavelength (Nd:YAG), while the last one is the wavelength of telecommunication importance. The modified Abbé number is defined as

$$v_D{}' = \frac{n_{1319} - 1}{n_{1064} - n_{1559}} \tag{2}$$

where n_{1319}, n_{1064}, and n_{1550} are the refractive indexes at 1319, 1064, and 1550 nm, respectively. The chromatic dispersion (D') is the constringence of the Abbé number ($v_D{}'$):

$$D' = \frac{1}{v_D{}'} \tag{3}$$

The v_D and $v_D{}'$ values of P1/4 are 26.3 and 643, which correspond to D and D' values of 0.038 and 0.002, respectively (Table 5). After metal complexation, the D and D' values of P1/4(Co) drop to 0.006 and 0.002, respectively, which are lower than those of PC ($D = 0.0297$) and PMMA ($D = 0.0175$),[20] and are comparable to our recently synthesized poly(triazole)s by the metal-free azido-click polymerizations ($D' = 0.006$–0.004).[10] Other PVS(Co)s also show small chromatic dispersions. The low spectroscopic aberrations of the polymers, coupled with their high optical transparencies and light refractivities, may enable them to find technological applications as coating materials in advanced optical display systems, such as microlens components for charge-coupled devices and high-performance complementary metal-oxide semiconductor image sensors.[7]

2.9. Photoresponsive Patterning

The PVSs contain a large number of photosensitive vinyl and ester groups. The polymers may be readily photo-crosslinked because of the formation of free radicals by UV irradiation and can thus be used as negative photoresist materials for pattern generation.[21] When a thin solid film of P1/2 spin-coated on a silicon wafer is irradiated in air through a copper photomask, the exposed region of the thin film is readily photo-crosslinked and a negative photoresist pattern with clear-cut edges is generated after the development of the irradiated polymer film by 1,2-dichloroethane (Fig. 8).

The TPE moieties in the backbone of P1/2 are well-known luminogenic units that exhibit an unusual phenomenon of aggregation-induced emission (AIE).[22,23] Although light emission of a 'conventional' luminophore is often quenched when its molecules are aggregated in the solid state and fabricated into a thin film, the film of P1/2 is still luminescent, thanks to its unique AIE feature. The photopattern generated by the photolysis of P1/2 emits a yellow light upon illumination with a handheld UV lamp, as evidenced by the luminescence image taken under a fluorescence microscope shown in Figure 8. Clearly, the polymer can be used as a photoresist material for the creation of fluorescent images.
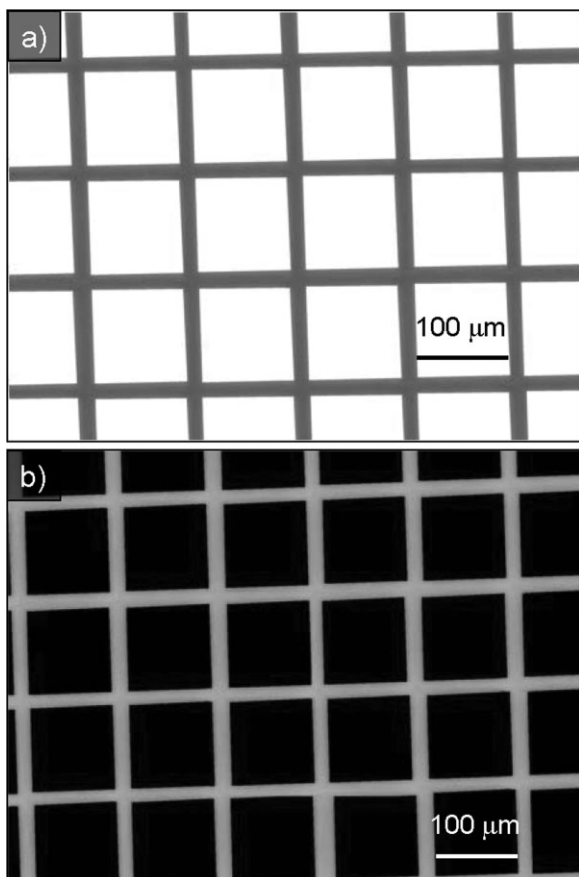
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Figure 8. Negative photoresist pattern generated by photolithography of P**1**/**2**; photographs taken under a) room lighting and b) UV illumination.

3. Conclusions

In this work, we have developed a thioclick polymerization technique for the synthesis of heteroatom-containing acetylenic polymers. The alkyne polyhydrothiolations of dithiol **1** and dipropiolates **2**–**5** proceed smoothly in the presence of diphenylamine at room temperature, producing sulfur-rich polymers P**1**/**2**–P**1**/**5** with high molecular weights in high yields. The organobase-mediated alkyne hydrothiolation reaction is strictly regioselective and furnishes polymers with high stereoregularities. The polymerization reaction is tolerant to functional groups as well as air and moisture. All these advantageous attributes make the alkyne polyhydrothiolation a true click reaction.[11]

Polymers P**1**/**2**–P**1**/**4** are completely soluble, film-forming, thermally stable, and optically transparent. Their films exhibit high refractive indices and low chromatic aberrations. Their refractivities can be tuned by their sulfur contents and greatly enhanced by complexation with transition-metal compounds such as cobalt carbonyls. The PVSs are photoresponsive and their films can be readily photo-crosslinked to create negative photoresist patterns that emit strong visible light upon photoexcitation. These unique features make the polymers promising photonic materials for high-tech applications.

4. Experimental

Materials: THF (Labscan), toluene (BDH), and dioxane (Aldrich) were distilled under nitrogen from sodium benzophenone ketyl immediately prior to use. Dichloromethane was distilled under nitrogen over calcium hydride. DMF was stirred with calcium hydride overnight, distilled under reduced pressure, and kept under nitrogen. Other solvents, such as triethylamine and dimethyl sulfoxide (DMSO), were purified using standard procedures. All the chemicals used in this work, such as 4,4′-thiodibenzenethiol (**1**), were purchased from Aldrich and used as received without further purification. 1,2-Bis(4-hydroxyphenyl)-1,2-diphenylethene was prepared according to our previously published procedures [23b].

Instrumentation: IR spectra were recorded on a Perkin–Elmer 16 PC FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on Bruker ARX 300 NMR spectrometers using CDCl$_3$ or DMSO-d_6 as solvents. Light transmission spectra were measured on a Milton Roy Spectronic 3000 array spectrophotometer. MALDI-TOF spectra were recorded on a GCT Premier CAB048 mass spectrometer operating in a chemical ionization (CI) mode with methane as carrier gas. M_w, M_n, and M_w/M_n values of the polymers were estimated by a Waters Associates GPC system equipped with refractive index (RI) and UV detectors. THF was used as eluent at a flow rate of 1.0 mL min^{-1}. A set of monodisperse linear polystyrenes were used as standards for the molecular weight calibration.

EA experiments were conducted on an Elementary Vario EL analyzer. XPS measurements were conducted on a PHI 5600 spectrometer (Physical Electronics), and the core level spectra were measured using a monochromatic Al Kα X-ray source (hv = 1486.6 eV). The analyzer was operated at 23.5 eV pass energy and the analyzed area was 800 μm in diameter. EDX analyses were preformed on a JEOL-6300 SEM system with quantitative elemental mapping and line scan capacities operating at an accelerating voltage of 15 kV. Thermogravimetric analyses (TGA) were carried out under nitrogen on a Perkin–Elmer TGA 7 analyzer at a heating rate of 10 °C min^{-1}.

Refractive indices of the polymers were determined on a J. A. Woollam variable angle ellipsometry system with a wavelength tunable from 300 to 1700 nm. To fit the acquired Ψ and Δ curves with the data obtained from the three-layer optical model that consisted of a crystalline silicon substrate, a 2 nm silicon dioxide layer, and a uniform polymer film, the Levenberg–Marquardt regression algorithm was employed. The Cauchy dispersion law was applied to describe the polymer layer from the visible to the IR spectroscopic region.

Monomer Preparation: Dipropiolates **2**–**4** were prepared by the esterification reactions of propiolic acid with 1,2-bis(4-hydroxyphenyl)-1,2-diphenylethene, bisphenol A, 4,4′-sulfonyl diphenol, and 4,4′-thiodiphenol, respectively. The synthetic procedures were similar to those described in our previous publications [10c].

Characterization Data for 4,4′-(1,2-Diphenylethenylene)diphenyl Dipropiolate (2): White solid; yield 63.5%. IR (thin film) v = 3276, 3054, 2934, 2856, 2124, 1732, 1650, 1502 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, TMS, δ): 8.04 (s, 1H), 8.05 (s, 1H), 6.91 (t, 4H), 7.02 (m, 8H), 7.11 (m, 6H). ^{13}C NMR (75 MHz, CDCl$_3$, TMS, δ): 150.71, 148.25, 142.89, 141.77, 140.46, 132.23, 131.21, 129.45, 128.47, 127.76, 126.77, 120.39, 94.08, 76.83, 76.65, 74.15. HRMS (MALDI-TOF, m/z): [M + H]$^+$ calcd for C$_{32}$H$_{21}$O$_4$, 469.4988; found, 469.1034. Anal. calcd for C$_{32}$H$_{20}$O$_4$: C 82.04, H 4.30; found: C 82.00, H 4.50.

Characterization Data for 4,4′-Isopropylidenediphenyl Dipropiolate (3): White solid; yield 53.2%. IR (thin film), v = 3266, 2934, 2124, 1730, 1634 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, TMS, δ): 7.26 (d, 2H), 7.05 (d, 2H), 3.06 (s, 1H), 1.67 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$, TMS, δ): 151.0, 148.5, 147.7, 127.9, 120.6, 76.6, 74.3, 42.6, 30.8. HRMS (MALDI-TOF, m/z): [M + H]$^+$ calcd for C$_{21}$H$_{17}$O$_4$, 333.3493; found, 333.1080. Anal. calcd for C$_{21}$H$_{16}$O$_4$: C 75.89, H 4.85; found: C 75.17, H 5.01.

Characterization Data for 4,4′-Sulfonyldiphenyl Dipropiolate (4): White solid; yield 62.3%. IR (thin film) v = 3268, 2126, 1734, 1656, 1588, 1490, 1410, 1324, 1294 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6, TMS, δ): 8.20 (d, 2H), 7.66 (d, 2H), 5.03 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, TMS, δ): 153.2, 150.0, 139.0, 129.7, 123.4, 82.3, 74.0. HRMS (MALDI-TOF, m/z): [M + H]$^+$ calcd for C$_{18}$H$_{11}$O$_6$ S, 355.6681; found, 355.3334. Anal. calcd for C$_{18}$H$_{10}$O$_6$S: C 61.01, H 2.84; found: C 61.62, H 3.05.

Characterization Data for 4,4′-Thiodiphenyl Dipropiolate (5): Pale yellow solid; yield 57.3%. IR (thin film) $\nu = 3273$, 2934, 2126, 1732, 1585, 1487 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, TMS, δ): 7.37 (d, 2H), 7.13 (d, 2H), 3.90 (s, 1H). ^{13}C NMR (75 MHz, CDCl$_3$, TMS, δ): 150.6, 149.0, 135.8, 132.3, 122.8, 77.1, 74.0. HRMS (MALDI-TOF, m/z): [M + H]$^+$ calcd for C$_{18}$H$_{11}$O$_4$S, 323.3346; found, 323.0307. Anal. calcd for C$_{18}$H$_{10}$O$_4$S: C 67.07, H 3.13; found: C 67.07, H 3.65.

Polymer Synthesis: All the polymerization reactions were carried out under dry nitrogen using a standard Schlenk technique, unless otherwise specified. A typical procedure for the polymerization of **1** and **2** is given below as an example. In a 15 mL Schlenk tube with a three-way stopcock on the sidearm was placed 40 mg of **1** (0.15 mmol) and 70 mg of **2** (0.15 mmol) under nitrogen in a glovebox. Diphenylamine (0.5 g, 3 mmol) and DMF (2.5 mL) were added to dissolve the monomers using a hypodermic syringe. After stirring at room temperature for 24 h, the mixture was added dropwise to about 300 mL of a hexane/diethyl ether (v/v, 1 : 1) mixture through a cotton filter under stirring. The precipitate was allowed to stand overnight and then collected by filtration. The product was washed with the hexane/diethyl ether mixture and dried under vacuum at room temperature to a constant weight.

Characterization Data for P1/2: White powder; yield 73.5%. M_w 21 000, M_w/M_n 2.9 (GPC, polystyrene calibration). IR (KBr), $\nu = 3050$, 2936, 2860, 1714, 1672, 1524, 1502, 1478, 1386, 1358, 1204, 1142, 1096, 1012, 960, 814, 788, 700 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.99, 7.41, 7.34, 7.26, 7.09, 7.03, 6.09, 5.81. ^{13}C NMR (75 MHz, CDCl$_3$, TMS, δ): 168.1, 164.5, 163.2, 151.9, 149.0, 143.5, 141.0, 140.3, 135.9, 135.0, 134.1, 133.7, 132.2, 131.3, 128.3, 127.8, 127.7, 120.7, 114.8, 112.8.

Characterization Data for P1/3: White powder; yield 97.2%. M_w 29 000, M_w/M_n 1.7 (GPC, polystyrene calibration). IR (thin film), $\nu = 3061$, 2965, 2926, 2866, 1714, 1574, 1505, 1475, 1392, 1359, 1205, 1169, 1144, 1100, 1080, 1012, 961, 818, 734 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, TMS, δ): 8.02, 7.96, 7.91, 7.45, 7.43, 7.40, 7.32, 7.26, 7.23, 7.08, 7.05, 6.99, 6.96, 6.16, 6.12, 5.83, 5.81, 1.78. ^{13}C NMR (75 MHz, CDCl$_3$, TMS, δ): 164.8, 151.6, 148.5, 148.4, 146.9, 135.9, 135.2, 133.7, 132.5, 132.1, 132.0, 131.8, 131.8, 131.3, 128.4, 120.9, 114.9, 122.8, 42.5, 31.0.

Characterization Data for P1/4: White powder; yield 87.2%. M_w 7500; M_w/M_n 2.1 (GPC, polystyrene calibration). IR (thin film), $\nu = 3062$, 2092, 1724, 1568, 1474, 1388, 1356, 1324, 1296, 1210, 1134, 1102, 1012, 958, 818, 734 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, TMS, δ): 8.00, 7.98, 7.95, 7.77, 7.74, 7.52, 7.49, 7.44, 7.41, 7.38, 7.35, 7.32, 7.26, 6.25, 7.23, 7.08, 7.05, 6.90, 6.87, 6.14, 6.11, 5.81, 5.77. ^{13}C NMR (75 MHz, CDCl$_3$, TMS, δ): 167.5, 163.1, 162.5, 161.2, 154.4, 154.2, 153.7, 153.5, 150.6, 138.4, 136.1, 135.1, 134.9, 134.6, 134.1, 133.8, 133.5, 132.6, 131.8, 131.3, 130.4, 129.9, 129.3, 128.9, 128.3, 122.5, 122.3, 116.2, 113.6, 111.8.

Characterization Data for P1/5: White powder; yield 98.2%. IR (thin film), $\nu = 3058$, 2924, 2856, 1708, 1570, 1486, 1386, 1358, 1202, 1136, 1098, 1012, 960, 816, 788 cm^{-1}. (No GPC and NMR data due to insolubility of the polymer.)

Model Reaction: Phenyl 3-(phenylthio)acrylate (**8**) was designed and prepared as a model compound by alkyne hydrothiolation of thiophenol (**6**) and phenyl propiolate (**7**; Scheme 2). The experimental procedures were similar to those described above for the synthesis of P1/2. A white solid of **8** was obtained 94.0% yield. ^{1}H NMR (300 MHz, CDCl$_3$, TMS, δ): 8.01, 7.48, 7.45, 7.34, 7.179, 7.15, 7.08, 6.09, 5.82; ^{13}C NMR (75 MHz, CDCl$_3$, TMS, δ): 164.5, 163.4, 152.6, 150.4, 135.6, 133.0, 131.0, 129.7, 129.2, 128.3, 125.6, 121.5, 114.2, 112.1.

Cobalt Complexation: In a 30 mL test tube was dissolved 58 mg of P1/3 in 10 mL of THF under nitrogen. Into the mixture, a THF solution of Co$_2$(CO)$_8$ (5 mL, 17 mg) was added. The solution was stirred at room temperature for 1 h, after which the solvent was evaporated to about half of its original volume under reduced pressure. The solution was then added dropwise into a large volume of hexane ($\sim$200 mL) under stirring. The precipitate was washed with hexane several times to remove the unreacted octacarbonyldicobalt and then dried under vacuum to a constant weight. A pale purple powder of P1/2(Co) was obtained.

Photoresist Patterning: Photo-crosslinking reactions of the polymer films were conducted in air at room temperature using a 365 nm light

obtained from a Spectroline ENF-280C/F UV lamp as light source at a distance of 1 cm. The incident light intensity was $\sim$18.5 mW cm^{-2}. The film was prepared by spin-coating the polymer solution (10% w/w in 1,2-dichloroethane) at 2000 rpm for 1 min on a silicon wafer. The polymer film was dried in a vacuum oven at room temperature overnight. The photoresist patterns were generated by irradiating the polymer films for 3 min through a copper photomask. The films were developed in 1,2-dichloroethane for 40 s and dried at room temperature overnight under reduced pressure. The three-dimensional patterns were images on an optical microscope (Olympus B202) using a normal light and a fluorescent optical microscope (Olympus BX41) with a 330–385 wideband UV excitation.

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