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Multicomponent Tandem Reactions and Polymerizations of Alkynes, Carbonyl Chlorides, and Thiols

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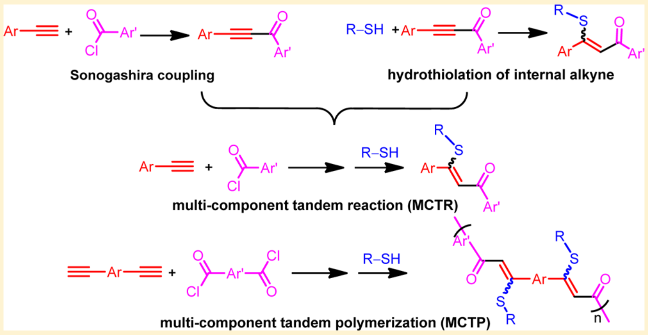
Supporting Information

ABSTRACT: Multicomponent tandem reactions (MCTRs), with multiple bonds formed in a highly concise fashion in a single vessel, have been noted as one of the most powerful and popular synthetic strategies in modern organic chemistry. Attracted by their operational simplicity, synthetic efficiency, high atom economy, and environmental benefit, the MCTRs and the corresponding multicomponent tandem polymerizations (MCTPs) of alkynes, carbonyl chlorides, and aliphatic/aromatic thiols were developed. By combining the Sonogashira coupling reaction between alkynes and carbonyl chlorides, and the hydrothiolation reaction of electron-deficient alkynone intermediates, high atom economy was achieved in such one-pot, two-step, three-component reactions/polymerizations. The MCTPs can proceed efficiently under mild conditions near room temperature to afford sulfur-rich polymers with high molecular weight, high yield, high regioselectivity, and good stereoselectivity. Through the MCTPs of different combination of monofunctional and bifunctional monomers, polymers with tunable backbone structures and photophysical properties can be obtained. These polymers generally possess good solubility and film-forming ability. Their thin films enjoy high refractivity, and their photosensitivity enables easy modulation of the thin film refractive indices.



INTRODUCTION

Tandem reactions represent one of the most powerful and popular synthetic masterpieces in modern organic chemistry.[1] In contrast to traditional "step-by-step" operations, multiple steps are combined into one synthetic operation and occur in a specific order without isolation of reactive intermediates, which directly undergo next reaction *in situ*, delivering compact and elegant syntheses of complex products.[2] Such one-pot operation can avoid time-consuming and costly synthetic steps, tedious separation and purification of intermediates, and protection/deprotection procedures, enabling high-throughput synthesis of structurally complex compounds from simple and readily available substrates.[3] With their high atom economy and environmental benefit, tandem reactions are sought after for both their academic interest and industrial relevance,[4] especially in heterocyclic chemistry,[5] biological systems,[6] combinatorial chemistry, and diversity-oriented synthesis.[7] The pace of development of tandem reactions has conspicuously quickened recently, witnessed by abundant literatures.[8]

Of the various tandem reactions, there are generally two types.[9] In domino/cascade reactions, the reagents and catalysts are mixed together and undergo a transformation via two or more intrinsically coupled reactions under the same reaction conditions one after another in an inseparable fashion. They are generally fast intramolecular reactions with unstable intermediates, where the functional groups must be precisely located, which may offset some of the potential benefits of the methodology. On the other hand, sequential/consecutive reactions are considered to be stepwise reactions with relatively stable, yet reactive, intermediates, where the individual steps can be performed separately. External reagents or changes in reaction conditions are required in such reactions to facilitate the tandem process,[10] enabling multicomponent tandem reactions (MCTRs).

To meet the demands for the continuing development of green chemistry, it is highly desirable to promote the elegance of efficient synthesis in polymerizations. For example, scientists have made great endeavor to develop efficient multicomponent polymerizations (MCPs), including the step-growth Passerini

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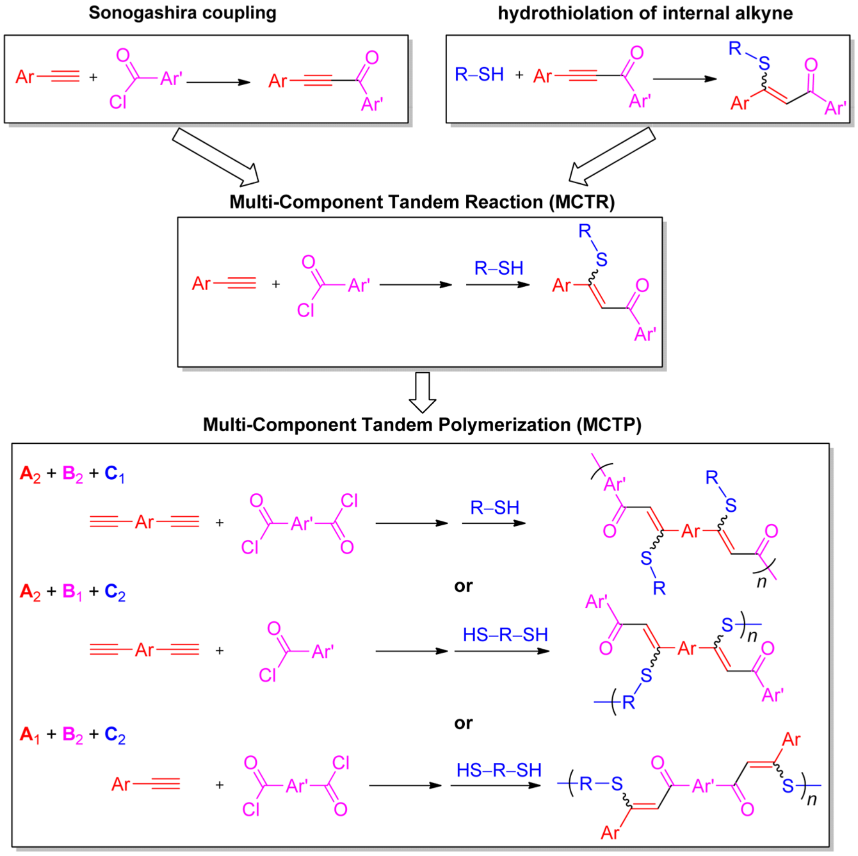
Scheme 1. MCTRs and MCTPs of Alkynes, Carbonyl Chlorides, and Thiols



polymerization of a dialdehyde, a diisocyanide, and a carboxylic acid to afford polyamides,[11] the four-component polymerization of a dicarboxylic acid, a dialehyde, a diisocyanide, and a monocarboxylic acid for the preparation of highly branched functional polymers,[12] and the four-component Ugi polymerizations of isocyanohexanes, aldehydes, acids, and amines for the preparation of diversely substituted polyamides.[13] Several alkyne-based MCPs have also been developed such as the MCP of alkynes, aldehydes, and amines[14] and the MCP of alkynes, azides, and amines/alcohols.[15] On the other hand, pioneering work about the synthesis of nonconjugated polymers through tandem catalysis and tandem polymerization has been reported,[16] such as the preparation of ordered poly(amide—thioether) through tandem type polymerization of 2,4-dichlorophenyl acrylate, 4,4′-thiobis(benznenthiol), and 4,4′-oxidianiline,[17] the surface modification of silica nanoparticles through tandem reversible addition−fragmentation chain transfer polymerization and click chemistry,[18] the tandem ring-opening/ring-closing metathesis polymerization of various cycloalkenes and terminal alkynes-containing monomers,[19] the tandem phosphine-mediated thiol−ene/radical-mediated thiol−yne sequence to prepare multifunctional thioethers,[20] etc. However, conjugated polymers with optoelectronic properties have seldom been prepared through such approaches because of the narrow monomer scope of MCPs/tandem polymerizations, the various side reactions, the rigid structure, and poor solubility of the polymers. In particular, alkyne-based tandem polymerizations are rarely reported to prepare conjugated polymers,[21] despite the rich chemistry of alkynes.[22]

With the compelling advantages of MCPs and tandem polymerizations, it is attractive to combine them and develop efficient multicomponent tandem polymerizations (MCTPs) to explore the general applicability for the preparation of macromolecules with novel structures and unique properties. The maximization of the structural diversity, reaction efficiency, and atom- and step-economy can be expected from MCTPs, which are hence in great and continued demand for the synthesis of conjugated polymers. In our previous work, the three-component tandem polymerization of alkyne, aroyl chloride, and ethyl 2-mercaptoacetate was explored as an efficient polymerization technique for the preparation of conjugated polythiophenes with structural regularity, processability, and advanced functionality.[23]

In this work, by combining the Sonogashira coupling reaction between alkynes and carbonyl chlorides and the hydrothiolation reaction of electron-deficient alkynone intermediates, the one-pot, two-step, three-component coupling-addition tandem reactions and polymerizations are investigated (Scheme 1). Their general applicability to aliphatic and aromatic thiols is explored. It is noteworthy that the hydrothiolation additions of C≡C bonds can be facilely controlled to stop at the first stage, producing products with conjugate C═C bonds. The MCTRs and MCTPs of alkynes, carbonyl chlorides, and aliphatic/aromatic thiols can proceed efficiently under mild conditions near room temperature to afford sulfur-rich polymers with high regioselectivity, good stereoselectivity, and high molecular weight (M_w) in high yield. Through different combination of monomers, polymers with tunable backbone structures can be obtained, which can easily form thin films with high and tunable refractivity.

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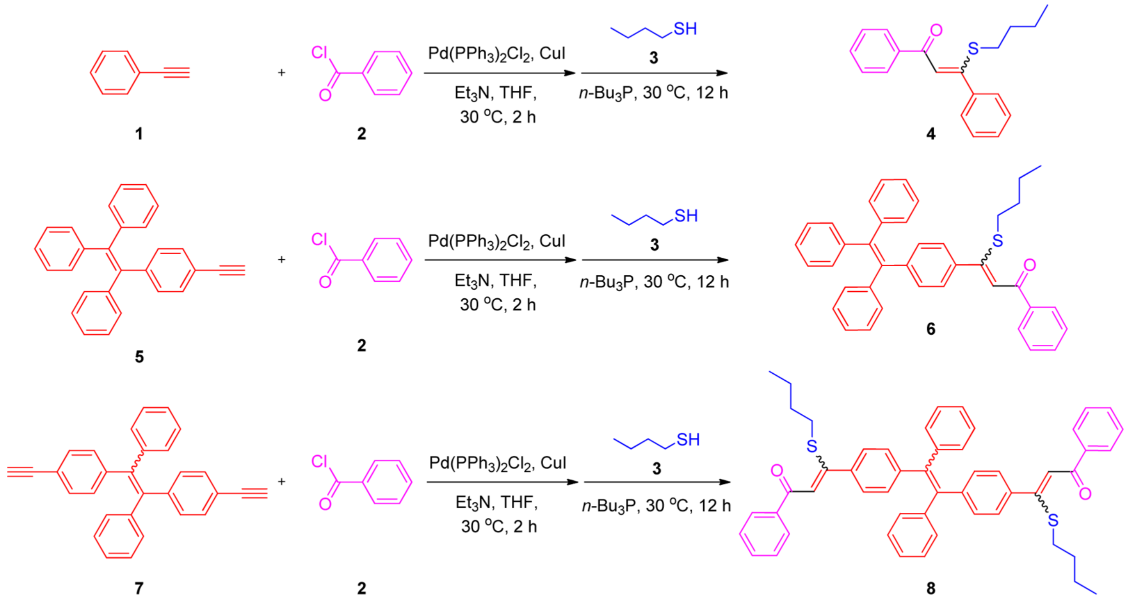
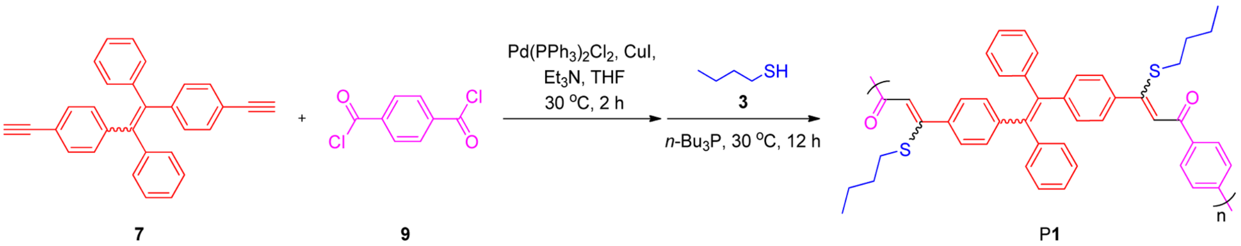
Scheme 2. Synthesis of 4, 6, and 8 through MCTRs of Alkynes 1, 5, or 7, Carbonyl Chloride 2, and Thiol 3



Scheme 3. Synthesis of Polymer P1 through MCTP of TPE-Diyne 7, Terephthaloyl Chloride 9, and Butylthiol 3



RESULTS AND DISCUSSION

Multicomponent Tandem Reactions. To combine Sonogashira coupling reaction of carbonyl chloride and alkyne and hydrothiolation of activated internal alkyne in a one-pot, two-step, three-component manner, tandem reaction of commercially available phenylacetylene **1**, benzoyl chloride **2**, and *n*-butylthiol **3** was first investigated. Tetraphenylethene (TPE)-containing monoyne **5** and diyne **7** were also chosen as alkyne reactants because the twisted structure of TPE unit could prevent the intermolecular interactions and hence increase the solubility of the product. The Sonogashira coupling reactions of **1**, **5**, or **7**, with **2** were first carried out at 30 °C under nitrogen in THF in the presence of $Pd(PPh_3)_2Cl_2$, CuI, and triethylamine (Et_3N) to afford the activated alkynone intermediates after 2 h. The third component, *n*-BuSH **3**, and n-Bu_3P were then added by syringes to proceed the second step addition reaction without oxygen or air, converting the alkynones to the corresponding thiol-addition product **4**, **6**, and **8**, respectively (Scheme 2). The existence of oxygen in the reaction system might lead to radical additions which afforded regioisomeric mixtures. Among all the tested additives of the second step such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), *n*-tributylphosphine (n-Bu_3P), and Et_3N, n-Bu_3P provides the best results with fast and efficient reaction, high conversion, less side reaction, and relatively low catalyst loading ratio.[24] The catalyst loading ratio of the thiol addition of alkynone is relatively high compared with the typical thiol−Michael addition of acrylic and acrylate derivatives, probably due to the high steric hindrance of the internal alkyne structure and the possible side reactions which may deactivate the phosphine catalyst.[25]

Generally, the addition reaction of thiol and C≡C will not stop at the first stage because of the higher addition activity of thiol with C═C than that with C≡C.[26] However, under the catalysis of n-Bu_3P, the Michael addition reaction rate of thiol and C≡C is 3 orders of magnitude higher than that of thiol and C═C.[27] The reaction affords single addition product with C═C bond retained in the structure, even with excess amount of *n*-BuSH, which is independent of the monomer structure. The MCTRs proceeds regioselectively with exclusive addition products at the 3-position of the alkynone moiety and stereoselectively with up to 89% *Z*-conformation of the resultant C═C bond obtained in high yield of 87%−92%.

Multicomponent Tandem Polymerization. With the success experience of the highly efficient MCTRs of alkynes, carbonyl chloride, and thiol, the reaction was further explored as tandem polymerization for the convenient preparation of conjugated polymer with regular structures. The MCTPs was developed based on the optimized condition of MCTRs (Scheme 3), wherein TPE-containing diyne **7**, terephthaloyl dichloride **9**, and *n*-butylthiol **3** were used as monomers to afford alkylthiol-substituted conjugated linear polymer P**1**. Similar to the MCTRs, the polymerization was conducted in two separate steps. Poly(aryleneynonylene) intermediate with relatively poor solubility was obtained from the first step, Sonogashira reaction of **7** and **9**, which was directly reacted with the third component, thiol **3**, to afford alkylthiol-substituted polymer product with improved solubility and high yield.

The polymerization conditions including reaction time, the amount of transition-metal catalysts, and n-Bu$_3$P were optimized. The reaction time of the first step is 2 h because elongated reaction time of Sonogashira coupling reaction might lead to intermediate with poor solubility which is difficult to convert completely in the next step. The reaction time of the second step, hydrothiolation of alkynone, was investigated as shown in Table 1, suggesting that high yield and high M_w can be obtained in a few hours. Increasing the reaction time has a positive effect on yield, M_w, and PDI (M_w/M_n). Further optimization was performed with second step reaction time of 12 h for the sake of energy conservation and time-saving. Furthermore, the effect of the amount of Pd(PPh$_3$)$_2$Cl$_2$ and CuI was systematically investigated through a series of parallel reactions (Table 2). While polymer with high M_w were generated in high yield in all the cases, the ratio between Pd(PPh$_3$)$_2$Cl$_2$ and CuI does affect the M_w of the resultant polymer. The polymerization carried out in the presence of 4 mol % of Pd(PPh$_3$)$_2$Cl$_2$ and 16 mol % of CuI presents the best result with the highest M_w of 57 900 and high yield of 96%. The influence of the amount of n-Bu$_3$P on the polymerization was then optimized as shown in Table 3. Of the tested conditions, the polymerization catalyzed by 20 mol % of n-Bu$_3$P provided polymer with the highest M_w (Table 3).

Table 1. **Time Course of the Second Step on the Polymerization**[a]

no.	t_2 (h)	yield (%)	M_w[b]	PDI[b]	Z/E[c]
1	6	87	38600	2.92	78/22
2	12	92	43300	2.87	70/30
3	24	100	44000	2.68	74/26

[a] Carried out in THF under nitrogen at 30 °C in the presence of Pd(PPh$_3$)$_2$Cl$_2$, CuI, and Et$_3$N. Monomer **7** was reacted with **9** for 2 h prior to the addition of **3** and n-Bu$_3$P. [**7**] = 0.04 M, [**9**] = 0.04 M, [**3**] = 0.16 M, [Pd(PPh$_3$)$_2$Cl$_2$] = 0.8 mM, [CuI] = 6.4 mM, [Et$_3$N] = 0.08 M, [n-Bu$_3$P] = 8 mM. [b] Estimated by GPC in THF on the basis of a polystyrene calibration. [c] Calculated from the integration ratios of ^{1}H NMR peaks at δ = 0.83 and 0.94. Abbreviations: t_2: the reaction time of the second step.

Table 2. **Concentrations Effect of Pd(PPh$_3$)$_2$Cl$_2$ and CuI on the Polymerization**[a]

no.	[Pd(PPh$_3$)$_2$Cl$_2$] (mM)	[CuI] (mM)	yield (%)	M_w[b]	PDI[b]	Z/E[c]
1	0.8	3.2	96	47100	2.85	81/19
2	0.8	6.4	92	43300	2.87	70/30
3	1.6	2.0	92	14300	1.90	78/22
4	1.6	3.2	98	16900	2.43	76/24
5	1.6	4.4	89	31000	2.37	81/19
6	1.6	5.2	92	20700	4.23	82/18
7	1.6	6.4	96	57900	3.44	76/24

[a] Carried out in THF under nitrogen at 30 °C for 12 h in the presence of Pd(PPh$_3$)$_2$Cl$_2$, CuI, and Et$_3$N. Monomer **7** was reacted with **9** for 2 h prior to the addition of **3** and n-Bu$_3$P. [**7**] = 0.04 M, [**9**] = 0.04 M, [**3**] = 0.16 M, [Et$_3$N] = 0.08 M, [n-Bu$_3$P] = 8 mM. [b] Estimated by GPC in THF on the basis of a polystyrene calibration. [c] Calculated from the integration ratios of ^{1}H NMR peaks at δ = 0.83 and 0.94.

Table 3. **Concentration Effect of n-Bu$_3$P on the Polymerization**[a]

no.	n-Bu$_3$P (mol %)	yield (%)	M_w[b]	PDI[b]	Z/E[c]
1	10	92	53200	3.86	79/21
2	20	96	57900	3.44	76/24
3	30	93	42300	2.87	82/18

[a] Carried out in THF under nitrogen at 30 °C for 12 h in the presence of Pd(PPh$_3$)$_2$Cl$_2$, CuI, and Et$_3$N. Monomer **7** was reacted with **9** for 2 h prior to the addition of **3** and n-Bu$_3$P. [**7**] = 0.04 M, [**9**] = 0.04 M, [**3**] = 0.16 M, [Pd(PPh$_3$)$_2$Cl$_2$] = 1.6 mM, [CuI] = 6.4 mM, [Et$_3$N] = 0.08 M. [b] Estimated by GPC in THF on the basis of a polystyrene calibration. [c] Calculated from the integration ratios of ^{1}H NMR peaks at δ = 0.83 and 0.94.

The MCTPs generally proceed fast and produce polymers with high M_w in high yield, demonstrating their high efficiency. The nucleophilic attack of the aliphatic thiol readily occurs in the MCTP to afford hydrothiolation product with complete conversion. To explore the general applicability of this MCTP, aromatic thiols with less nucleophilicity were then tested as the third component of the MCTP under the optimized condition (Scheme 4). The polymerization proceeded smoothly when p-toluenethiol **10** was used instead of n-butylthiol **3**, affording conjugated polymer **P2** with a similar chalcone-containing polymer backbone of **P1**. The second step, hydrothiolation reaction of alkynone intermediate and 4-methylbenzenethiol, proceeded efficiently to produce soluble polymer with high M_w of 59 100 in 98% yield, proving that the MCTP is applicable for both aliphatic thiols and aromatic thiols.

The high efficiency of this MCTP and the multicomponent nature of the polymerization enabled versatile monomer combinations such as "A$_2$ + B$_2$ + C$_1$", "A$_2$ + B$_1$ + C$_2$", or "A$_1$ + B$_2$ + C$_2$", which could lead to polymer products with different backbone structures and properties. For example, when using bifunctional thiol monomer, 4,4′-thiodibenzenethiol **12**, as the third component, to couple with diyne **7** and monofunctional 4-dimethylaminobenzoyl chloride **11**, **P3** with sulfur-rich polymer backbone was obtained. Similarly, when dithiol **12** was reacted with monoyne **5** and terephthaloyl dichloride **9** through the two-step polymerization, **P4** with both enone structure and sulfur-rich characteristics embedded in the polymer backbone was obtained. Both yield and M_w of **P3** are smaller compared with those of **P4** because the electron-donating dimethylamino group containing monomer **11** is less reactive in the Sonogashira coupling reaction, and the alkynone intermediate generated from **7** and **11** is less reactive in the thiol addition. Compared with that of **P2**, the yield and M_w of **P3**−**P4** was decreased, probably due to the severe steric hindrance of the addition step (Table 4).

Structural Characterization. The chemical structures of the butylthiol-substituted product **4**, **6**, and **8** as well as **P1**−**P4** were fully characterized by standard spectroscopic techniques, revealing their expected structures with high purity (see Experimental Section). The single crystal structure of **6** was obtained as show in Figure 1, revealing the desired structure of Z-isomer. The molecular packing mode suggested intermolecular sulfur−sulfur interactions in the crystals. The IR, ^{1}H NMR, and ^{13}C NMR spectra of monomers **7**, **9**, and **3**, small molecules **4**, **6**, and **8**, and **P1** are compared as examples in Figures 2−3 and Figure S1. In the IR spectra, the absorption bands of **7** associated with the ≡C−H and C≡C stretching vibrations emerged at 3271 and 2023 cm^{-1}, respectively. Both

Scheme 4. MCTPs of Alkynes, Carbonyl Chlorides, and Aromatic Thiols

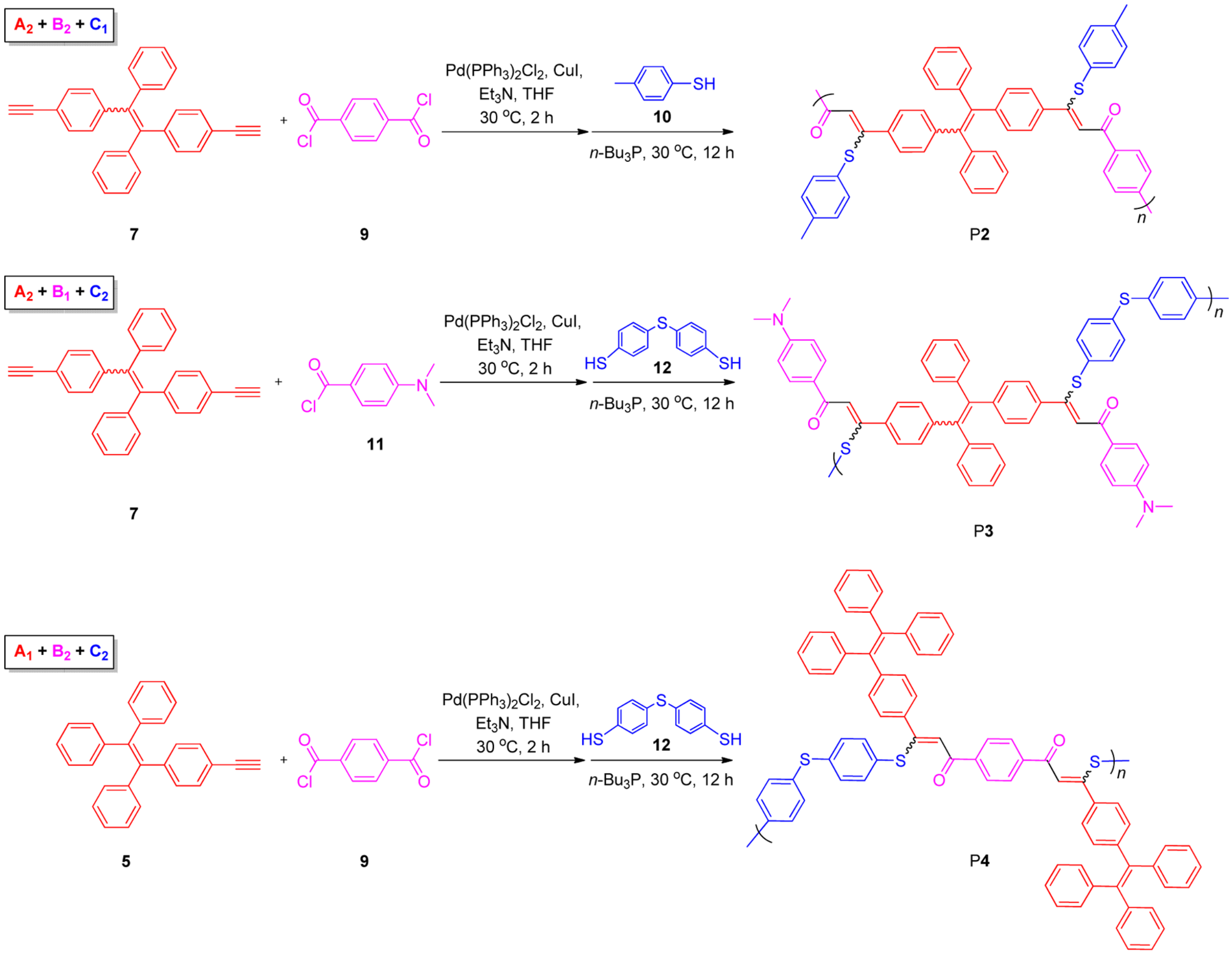


Table 4. Polymerization Results of the MCTPs of Alkynes, Carbonyl Chlorides, and Aromatic Thiols[a]

no.	polymer	yield (%)	M_w[d]	PDI[d]	Z/E[e]
1	P2[b]	98	59100	3.66	63/37
2	P3[c]	74	5900	1.42	
3	P4[c]	85	11100	2.17	

[a] Carried out in THF under nitrogen at 30 °C in the presence of $Pd(PPh_3)_2Cl_2$, CuI, and Et_3N. Alkynes were reacted with carbonyl chlorides for 2 h prior to the addition of aromatic thiols and n-Bu_3P. [b] [**7**] = 0.04 M, [**9**] = 0.04 M, [**10**] = 0.16 M, [$Pd(PPh_3)_2Cl_2$] = 1.6 mM, [CuI] = 6.4 mM, [Et_3N] = 0.08 M, [n-Bu_3P] = 8 mM, t_2 = 12 h. [c] [**7**] = [**9**] = [**12**] = 0.02 M, [**5**] = [**11**] = 0.04 M, [$Pd(PPh_3)_2Cl_2$] = 0.8 mM, [CuI] = 1.6 mM, [Et_3N] = 0.04 M, [n-Bu_3P] = 8 mM, t_2 = 24 h. [d] Estimated by GPC in THF on the basis of a polystyrene calibration. [e] Calculated from the integration ratios of ^1H NMR peaks at δ = 2.33 and 2.41.

peaks disappear in the spectra of **8** and P**1**, indicating that the terminal C≡C−H group of **7** has been completely consumed in the tandem reaction/polymerization. The absorption band of **9** associated with the carbonyl stretching vibrations was observed at 1724 cm^{-1}, which shifted to ~1631 cm^{-1} in the spectra of P**1** after butylthiol-substituted chalcone formed. The absorption peaks of **3** located at 2965 and 2882 cm^{-1} are attributed to the stretching vibrations of CH_2 and CH_3 groups, both of which emerge in the spectra of **4**, **6**, **8**, and P**1**, confirming the substitution of the butylthiol groups.

Their ^1H NMR spectra were also compared in Figure 3. The resonance of the acetylene protons of **7** at δ 3.03 and the thiol proton of **3** at δ 1.33 disappear in the spectra of **4**, **6**, **8**, and P**1**. New peaks emerge at δ 7.05 and 6.72 in the spectrum of **4**, which are attributed to the newly formed olefinic protons of *Z*- and *E*-isomers, respectively, in good accordance with the literature.[24] No other olefinic proton peak was observed in the range of δ 5.50−7.24, indicating 100% regioselectivity of the addition reaction. The *Z*- and *E*-isomers can be further distinguished from the aromatic protons next to the carbonyl groups at δ 7.97 (*Z*-**4**) and 7.84 (*E*-**4**), the CH_2 groups next to the sulfur atom at δ 2.84 (*E*-**4**) and 2.40 (*Z*-**4**), and the methyl groups at δ 0.93 (*E*-**4**) and 0.73 (*Z*-**4**). These four groups of peaks all emerged in the ^1H NMR spectra of **6**, **8**, and P**1**, which can be correlated with the stereoselectivity. ^1H NMR spectra analysis reveals that the hydrothiolation addition product was obtained exclusively at the 3-position of the alkynone moieties of the intermediates in the MCTRs and MCTPs, and high stereoselectivity of up to 89% was achieved. Similarly, in ^{13}C NMR spectra, the resonance of the acetylene carbon of **7** at δ 83.7 is absent in the spectra of **8** and P**1**, while new peaks emerge at about δ 119.5 and 163.5, representing the newly formed ethylene carbons connecting to sulfur and

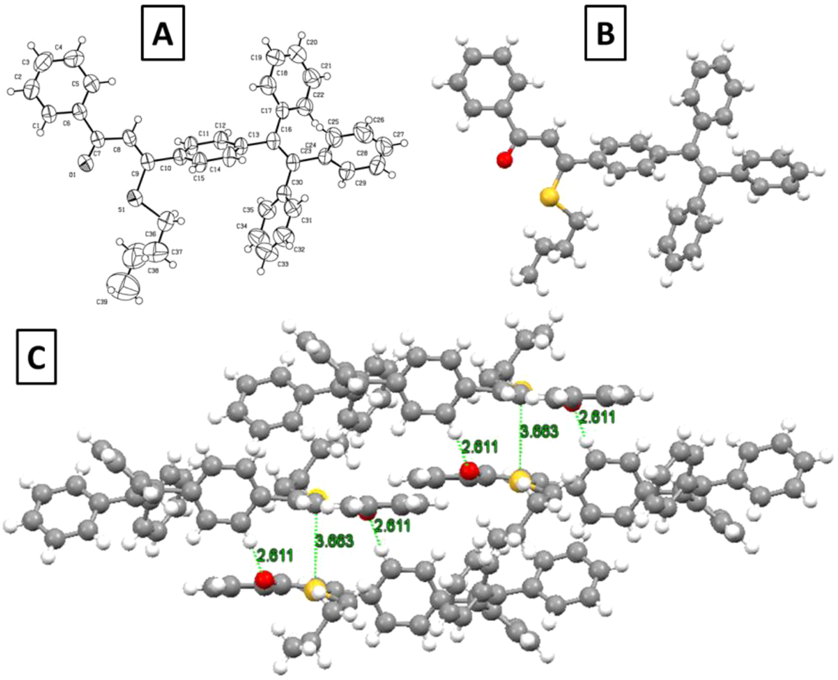


Figure 1. (A, B) Single crystal structure and (C) molecular packing of compound **6** (CCDC 1045141).

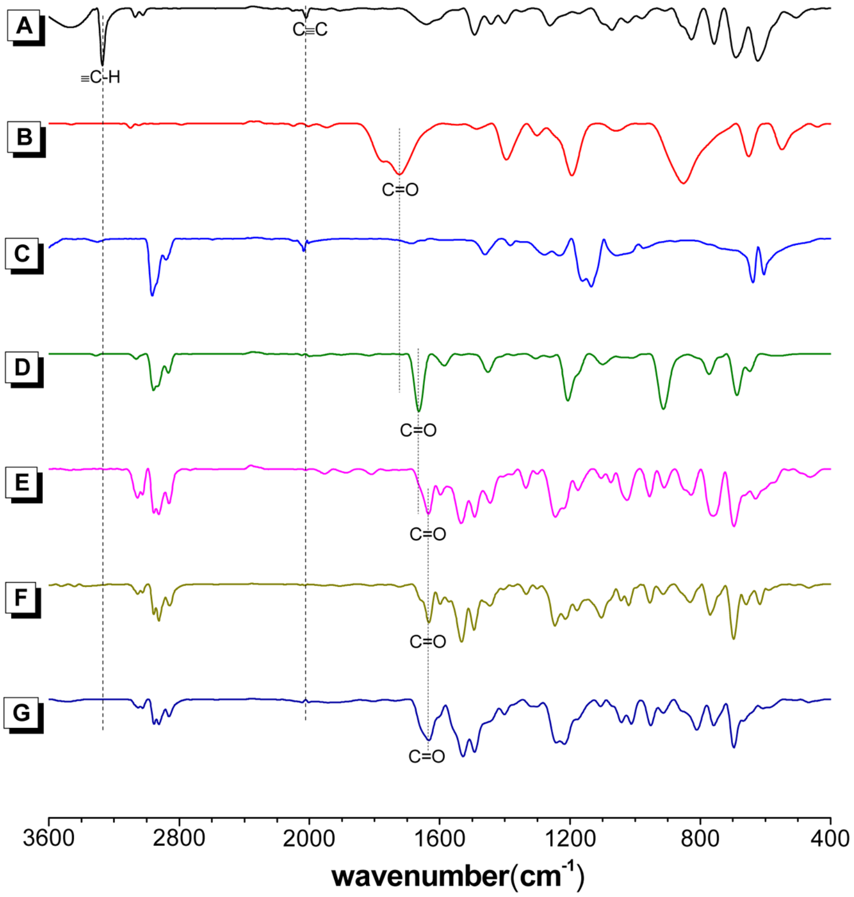


Figure 2. IR spectra of (A) **7**, (B) **9**, (C) **3**, (D) **4**, (E) **6**, (F) **8**, and (G) P**1**.

carbonyl group, respectively. The resonance of the carbonyl group of **9** also shifts from *δ* 167.5 to *δ* 188.3 after the reaction.

Furthermore, **4**, **6**, and **8** give M + H^+ peaks at m/z 297.1323 (calcd for **4**, 297.1308), 551.2426 (calcd for **6**, 551.2403), and 769.3190 (calcd for **8**, 769.3168) in their high-resolution mass spectra (Figures S2−S4). The elemental analysis of **6** and **8** were also measured, proving their desired molecular formula and high purity.

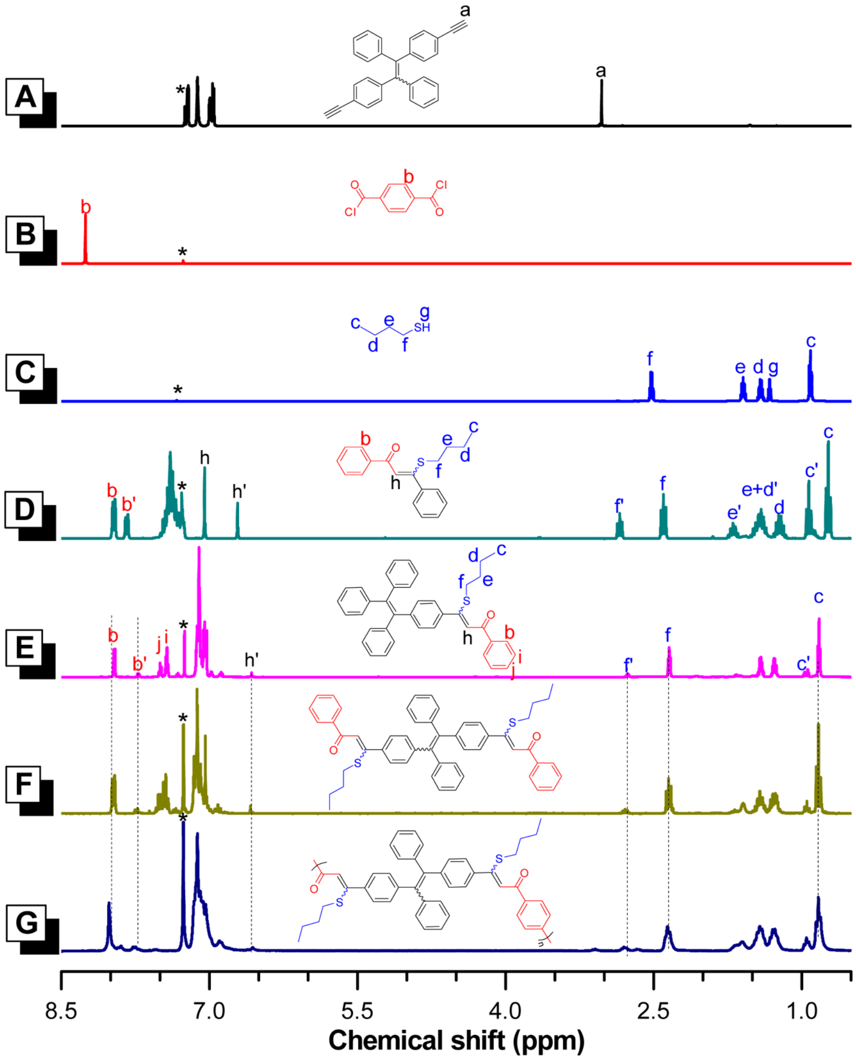


Figure 3. ^{1}H NMR spectra of (A) **7**, (B) **9**, (C) **3**, (D) **4**, (E) **6**, (F) **8**, and (G) **P1** in $CDCl_3$. The solvent peaks were marked with asterisks; the peaks from the *E*-isomers of **4**, **6**, **8**, and **P1** peaks are marked with asterisks.

Solubility and Thermal Stability. Despite the rigid structure of **P1**−**P4**, they all enjoy satisfactory solubility in organic solvents such as THF, 1,2-dichloroethane, chloroform, and DMF, owing to the twisted conformation of the TPE units embedded in the polymer and the butylthiol substitution side chains of **P1**.[28] They all possess good film-forming ability and can be facilely prepared into tough thin films by spin-coating or drop-casting methods. In addition, **P1**−**P4** generally show high thermal resistance with decomposition temperature at 5% weight loss under N_2 to be 292−315 °C (Figure S6).

Photophysical Properties. **P1**−**P4** possess different polymer backbones and conjugated structures; their photophysical properties were thus studied. The UV−vis absorption spectra of **6** and **P1**−**P4** in dilute THF solutions were compared in Figure 4. The absorption maximum of **6** is located at 341 nm, while that of **P1**−**P2** bathochromically shifted to 366 nm, suggesting a better conjugation of the polymers. **P3** with dimethylamino groups attached as electron donor and chalcone units as electron acceptor possesses an absorption maximum at 375 nm in THF solution. **P4**, on the other hand, have a hypsochromically shifted absorption maximum at 357 nm due to the nonconjugated polymer backbone. Unlike the previous reported TPE-containing compounds,[29] compounds **6**, **8**, and **P1**−**P4** are almost nonemissive under UV irradiation in both solution and solid

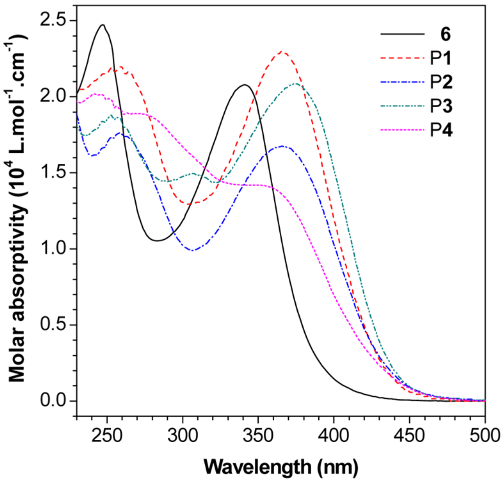


Figure 4. Absorption spectra of THF solutions of **6** and **P1**−**P4**. Concentration: 1 × 10^{-5} M.

state, probably due to the intersystem crossing processes promoted by sulfur atoms.[30]

Light Refractivity and Chromatic Dispersion. Organic materials with high refractive index (n) are highly desirable because of their applications in complementary metal oxide semiconductor, ophthalmic lenses, filters, etc.[31] Compared with inorganic semiconductors and chalcogenide glasses with high refractive index, they are less expensive and toxic, easier to fabricate into optical devices, making them promising candidates for a series of practical applications.[32] **P1**−**P4** possess abundant polarizable aromatic benzene rings, ketone groups, and sulfur atoms; therefore, high refractive indices can be expected. The wavelength-dependent refractive indices of spin-coated thin film of **P1**−**P4** are shown in Figure 5. The thin film of **P1** displays high refractive index value of 1.9102−1.6538 in a wide wavelength region of 400−1700 nm. **P2** with similar polymer backbone structure and sulfur content possesses similar value of 1.8818−1.6532 in the same wavelength region. When the sulfur content of the polymer increased in **P3** and **P4**, their n values increased accordingly to 1.8570−1.6577 and 1.9578−1.6704 in the wavelength region of 400−1700 nm, respectively. The refractivity of the polymers can thus be tuned through molecular engineering endeavors. Compared with the commercially important optical plastics such as poly(methyl methacrylate) (n = 1.49), poly(ethylene terephthalate) (n = 1.59), polycarbonate (n = 1.59), and polystyrene (n = 1.59), the polymers generally possess high refractivity.[33]

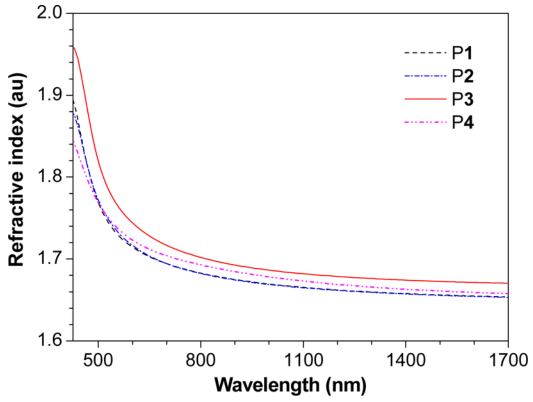


Figure 5. Wavelength dependence of refractive indices of thin films of **P1**−**P4**.

The chromatic dispersion of n value with wavelength is another critical parameter for optomaterials. The Abbé number (ν_D) of a material is a measure of the variation or dispersion in its refractive index with wavelength, which is defined as $\nu_D = (n_D - 1)/(n_F - n_C)$, where n_D, n_F, and n_C are the n values at Fraunhofer D, F, and C lines of 589.3, 486.1, and 656.3 nm, respectively.[34] A modified Abbé number (ν_D') has also been proposed using its n values at the nonabsorbing wavelengths of 1064, 1319, and 1550 nm and defined as $\nu_D' = (n_{1319} - 1)/(n_{1064} - n_{1550})$. The chromatic dispersion (D') is the constringence of the Abbé number: $D' = 1/\nu_D'$. The Abbé numbers and chromatic dispersions of **P1**−**P4** are summarized in Table 5. The D' values of **P1**−**P4** are in the range of 0.017−0.022, which are comparable with those of commercial optical plastics.[35]

Furthermore, the n values of the thin films can be modulated by UV irradiation, probably due to photoassisted reactions of the chalcone units or sulfur atoms of **P1**−**P4**, which change the chemical structure as well as the refractivity of the film.[36] As shown in Figure 6, upon exposure under UV light, the refractive index of the thin film of **P1** gradually decreases until irradiated for 55 min. After 65 min UV irradiation, the difference in the n value of the thin film at 632.8 nm and at the telecommunication important wavelength of 1550 nm is 0.1253 and 0.1118, respectively, demonstrating the efficient modulation of the n value of the film.

Table 5. Refractive Indices and Chromatic Dispersions of P1−P4[a]

film	$n_{632.8}$	ν_D	ν_D'	D	D'
P1	1.7093	8.5	58.4	0.118	0.017
P2	1.7082	8.4	58.8	0.119	0.017
P3	1.7338	6.3	58.8	0.159	0.017
P4	1.7159	10.5	44.6	0.095	0.022

[a] Abbreviations: n = refractive index, ν_D = Abbé number = $(n_D - 1)/(n_F - n_C)$, where n_D, n_F, and n_C are the refractive indices at wavelengths of 589.2, 486.1, and 656.3 nm, respectively. ν_D' = the modified Abbé number = $(n_{1319} - 1)/(n_{1064} - n_{1550})$, D = chromatic dispersion in the visible region, and D' = chromatic dispersion in the IR region.

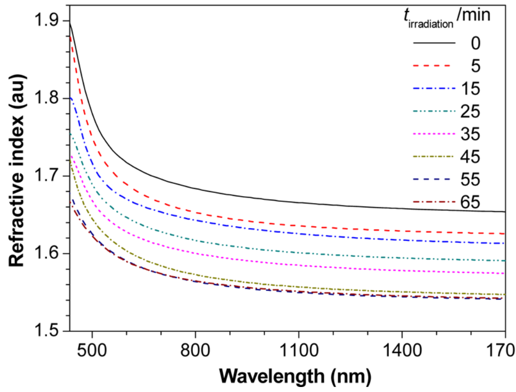


Figure 6. Wavelength dependence of thin film refractive indices of **P1** with different UV irradiation time. Film thickness: 70 nm.

When the spin-coated thin films of **P1**−**P4** prepared from their 1,2-dichloroethane solutions were exposed to UV irradiation in air through a copper photomask for 20 min, the chemical compositions of the exposed region were changed, resulting in well-resolved two-dimensional positive photopatterns with good resolution (Figure 7). In addition, when the patterns were developed in 1,2-dichloroethane for 40 s, the unexposed parts of the films were washed away, leaving the three-dimensional negative photopatterns (Figure S7). The patterns were observed under UV irradiation, and the photos were taken with elongated exposure time because of the weak emission of the polymers.

■ CONCLUSIONS

In this work, an efficient multicomponent tandem reaction was developed through combining the Sonogashira coupling reaction between alkynes and carbonyl chlorides and the hydrothiolation addition reaction of internal activated alkynes in a sequential manner. The reaction proceeded smoothly and produced desired product with high yield, high regioselectivity, and good stereoselectivity. This MCTR was then developed into an efficient one-pot, two-step, three-component tandem

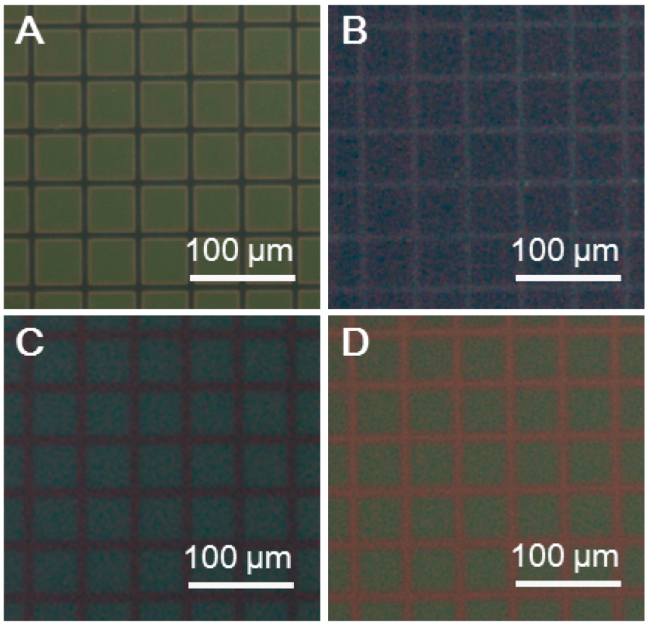


Figure 7. Positive photopatterns generated by photolithography of (A) P**1**, (B) P**2**, (C) P**3**, and (D) P**4**. Photographs were taken under UV illumination (330−385 nm).

polymerization of alkynes, carbonyl chlorides, and thiols, to afford polymers in high yield with high M_w, high regioselectivity, and good stereoselectivity. The MCTP showed general applicability of aliphatic and aromatic thiols. Through different monomer strategies such as "$A_2 + B_2 + C_1$", "$A_2 + B_1 + C_2$", or "$A_1 + B_2 + C_2$", the MCTPs can generate polymers with tunable polymer backbones as well as optical/photophysical properties. These polymers generally possess good solubility and can be facilely processed into thin films with high and tunable refractivity.

■ EXPERIMENTAL SECTION

Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. Triethylamine was dried by 4 Å molecular sieves and stored under nitrogen prior to use. TPE-containing alkynes **5** and **7** were prepared according to our previous reported literature.[37] Monomer **7** used in the polymerizations was 95% of *E*-isomer calculated from ^{1}H NMR prepared from recrystallization. $Pd(PPh_3)_2Cl_2$ was purchased from TCI, *n*-butylthiol **3** was purchased from Energy chemical, terephthaloyl dichloride **9** was purchased from Alfa Aesar, *n*-Bu_3P, CuI, and *p*-toluenethiol **10** were purchased from J&K Scientific Ltd., and 4,4′-thiodibenzenethiol **12** was purchased from Sigma-Aldrich. All these commercial available reactants and reagents were used as obtained without further purification.

Instruments. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance 600 MHz NMR spectrometer using deuterated chloroform as solvent and tetramethylsilane (TMS, $\delta = 0$) as internal reference. FT-IR spectra were recorded on a Bruker Vector 33 FT-IR spectrometer. Elemental analyses were carried out through a Vario EL-III elemental analyzer. High resolution mass spectrometry measurements were performed on a GCT premier CAB 048 mass spectrometer. The number- (M_n) and weight-average (M_w) molecular weights and polydispersity indices (PDI = M_w/M_n) of polymers were estimated by a Waters Associates 515 gel permeation chromatography (GPC) system. THF was used as eluent at a flow rate of 1 mL/min. A set of monodispersed linear polystyrenes coving the M_w range of 10^3–10^7 g/mol were utilized as standards for molecular weight calibration. Thermogravimetric analysis was carried out on a SHIMADZU TGA-50 analyzer under a nitrogen atmosphere at a heating rate of 10 K/min. UV−vis absorption spectra were recorded on a SHIMADZU UV-2600 spectrophotometer. Refractive indices (RI) of polymer films were determined by a J.A. Woolam V-VASE spectroscopic ellipsometer in a wavelength range of 400−1700 nm. The RI modulation was conducted using a 254 nm light irradiated from a Spectroline ENF-280C/F ultraviolet hand lamp at a distance of 5 cm, using polymer films prepared on quartz by a RF Generator KW-4A spin coater. Photopatterning of the spin-coated polymer films on silicon wafers were performed under 365 nm using a Spectroline ENF-280C/F UV lamp at a distance of 3 cm as light source. The incident light intensity was about 18.5 mW/cm^2. UV irradiation of the films through a copper photomask for 20 min afforded two-dimensional positive photopattern, which then developed in 1,2-dichloroethane for 40 s to afford three-dimensional negative photopattern. The photos were taken on a fluorescent optical microscope (Olympus BX41) under UV illumination (330−385 nm).

Multicomponent Tandem Reactions. 3-Butylthio-1,3-diphenyl-2-propenone (**4**): Into a 50 mL two-necked round-bottom flask equipped with magnetic stirrer was added $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol) and CuI (15 mg, 0.08 mmol), followed by 20 mL of distilled THF, phenylacetylene **1** (220 μL, 2 mmol), Et_3N (293 μL, 2.1 mmol), and benzoyl chloride **2** (230 μL, 2 mmol) under nitrogen. After stirring at 30 °C for 2 h, *n*-BuSH **3** (430 μL, 4 mmol) and *n*-Bu_3P (50 μL, 0.2 mmol) were then injected. The mixture was stirred for an additional 12 h, and 60 mL of water was then added. The organic layer was extracted with dichloromethane (3 × 40 mL). The solvent was removed under reduced pressure to afford the crude product which was purified by column chromatography on silica gel using a hexane/dichloromethane mixture (4:1) as eluent. A brown liquid was obtained in 92% yield, $Z/E = 64/36$. IR (KBr thin film), ν (cm^{-1}): 3065, 2959, 2934, 2866, 1661, 1586, 1452, 1206, 1101, 912. ^{1}H NMR (600 MHz, $CDCl_3$), δ (TMS, ppm): 7.96 (d, $J = 7.6$ Hz) + 7.84 (d, $J = 7.8$ Hz) (2H), 7.55−7.25 (m, 8H), 7.05 (s) + 6.71 (s) (1H), 2.84 (t, $J = 7.3$ Hz) + 2.40 (t, $J = 7.4$ Hz) (2H), 1.70 (m) + 1.41 (m) + 1.23 (m) (4H), 0.93 (t, $J = 7.3$ Hz) + 0.73 (t, $J = 7.3$ Hz) (3H). ^{13}C NMR (150 MHz, $CDCl_3$), δ (TMS, ppm): 188.56, 188.21, 163.81, 160.11, 139.18, 138.94, 138.65, 137.80, 132.16, 132.13, 128.92, 128.77, 128.46, 128.37, 128.26, 128.06, 128.01, 127.99, 119.65, 116.75, 32.56, 32.51, 31.42, 30.00, 22.08, 21.73, 13.61, 13.43. HRMS: *m*/*z* 297.1323 (M + H$^+$, calcd 297.1308).

3-Butylthio-3-(4-(1,2,2-triphenylvinyl)phenyl)-1-phenyl-2-propenone (**6**): Into a 50 mL two-necked round-bottom flask equipped with magnetic stirrer was added TPE-monoyne **5** (713 mg, 2 mmol), $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol), and CuI (15 mg, 0.08 mmol), followed by 20 mL of distilled THF, Et_3N (293 μL, 2.1 mmol), and benzoyl chloride **2** (230 μL, 2 mmol) under a dry nitrogen atmosphere. After stirring at 30 °C for 2 h, *n*-BuSH **3** (430 μL, 4 mmol) and *n*-Bu_3P (50 μL, 0.2 mmol) were injected. The mixture was stirred for an additional 12 h, and 60 mL of water was then added. The organic layer was extracted with dichloromethane (3 × 40 mL). The solvent was removed under reduced pressure to afford crude product which was purified by column chromatography on silica gel using hexane/dichloromethane mixture (4:1) as eluent. A yellow solid was obtained in 89% yield; $Z/E = 89/11$. IR (KBr thin film), ν (cm^{-1}): 3055, 3026, 2957, 2926, 2862, 1634, 1597, 1533, 1493, 1445, 1335, 1244, 1213, 1177, 1024, 957. ^{1}H NMR (600 MHz, $CDCl_3$), δ (TMS, ppm): 7.96 (d, $J = 7.2$ Hz) + 7.72 (d, $J = 7.9$ Hz) (2H), 7.50 (t, $J = 7.3$ Hz) + 7.43 (t, $J = 7.6$ Hz) + 7.32 (t, $J = 7.7$ Hz) (3H), 7.16−7.01 (m) + 6.57 (s) (20H), 2.76 (t, $J = 7.4$ Hz) + 2.34 (t, $J = 7.5$ Hz) (2H), 1.66 (m) + 1.41 (m) + 1.28 (m) (4H), 0.94 (t, $J = 7.4$ Hz) + 0.83 (t, $J = 7.4$ Hz) (3H). ^{13}C NMR (150 MHz, $CDCl_3$), δ (TMS, ppm): 190.60, 188.30, 165.98, 163.74, 158.52, 144.68, 144.59, 143.53, 143.29, 143.22, 141.89, 140.14, 138.74, 137.03, 132.13, 131.90, 131.41, 131.34, 131.30, 131.28, 131.25, 131.12, 128.66, 128.47, 128.26, 128.13, 128.08, 127.81, 127.72, 127.62, 127.59, 127.45, 126.69, 126.48, 119.49, 32.61, 32.50, 31.54, 30.30, 22.12, 21.92, 13.72, 13.63. HRMS: *m*/*z* 551.2426 (M + H$^+$ calcd 551.2403). Elemental Analysis: C 85.35%, H 6.30%, S 6.17% (calcd C 85.05%, H 6.22%, S 5.82%).

3,3′-[(1,2-Diphenylethene-1,2-diyl)-bis(4,1-phenylene)]-bis(3-butylthio-1-phenyl-2-prop-enone) (**8**): Into a 50 mL two-necked round-bottom flask equipped with magnetic stirrer was added TPE-diyne **7** (761 mg, 2 mmol), $Pd(PPh_3)_2Cl_2$ (56 mg, 0.08 mmol), and CuI (30 mg, 0.16 mmol), followed by 20 mL of distilled THF, Et_3N (0.59 mL, 4.2 mmol), and benzoyl chloride (**2**) (460 μL, 4 mmol) under nitrogen. After stirring at 30 °C for 2 h, *n*-BuSH **3** (860 μL, 8 mmol) and *n*-Bu_3P (100 μL, 0.4 mmol) were injected. The mixture was stirred for an additional 12 h, and 60 mL of water was then added. The organic layer was extracted with dichloromethane (3 × 40 mL). The solvent was removed under reduced pressure to afford crude product which was purified by column chromatography on silica gel using hexane/dichloromethane mixture (4:1) as eluent. A yellow solid was obtained in 87% yield; Z/E = 85/15. IR (KBr thin film), ν (cm^{-1}): 3055, 3026, 2957, 2924, 2860, 1634, 1599, 1533, 1495, 1445, 1335, 1246, 1213, 1179, 1103, 1020, 955. ^{1}H NMR (600 MHz, $CDCl_3$), δ (TMS, ppm): 7.97 (d, J = 7.7 Hz) + 7.74 (d, J = 7.8 Hz) (4H), 7.48 (m) + 7.34 (t, J = 7.5 Hz) (6H), 7.20−6.97 (m) + 6.58 (s) (20H), 2.79 (t, J = 7.4 Hz) + 2.35 (t, J = 7.4 Hz) (4H), 1.68 (m) + 1.42 (m) + 1.28 (m) (8H), 0.95 (m) + 0.83 (m) (6H). ^{13}C NMR (150 MHz, $CDCl_3$), δ (TMS, ppm): 188.29, 163.52, 144.13, 143.04, 141.06, 138.71, 137.31, 132.16, 131.96, 131.46, 131.40, 131.35, 131.29, 131.26, 131.05, 128.63, 128.47, 128.29, 128.16, 128.08, 127.90, 127.69, 127.53, 127.43, 126.98, 119.57, 118.22, 32.61, 32.53, 31.55, 30.26, 22.13, 21.93, 13.73, 13.63. HRMS: m/z 769.3190 (M + H$^+$ calcd 769.3168). Elemental Analysis: C 81.50%, H 6.54%, S 7.98% (calcd C 81.21%, H 6.29%, S 8.34%).

Multicomponent Tandem Polymerizations. All the polymerization procedures and manipulations were conducted under nitrogen using standard Schlenk technique except the purification of the final products.

A typical procedure of the MCTP to synthesize **P1** is given below. Into a 25 mL Schlenk tube equipped with magnetic stirrer was placed with TPE-diyne **7** (76 mg, 0.2 mmol), terephthaloyl dichloride **9** (41 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (6 mg, 0.008 mmol), and CuI (6 mg, 0.032 mmol) under nitrogen. 5 mL of freshly distilled THF and anhydrous Et_3N (60 μL, 0.42 mmol) were then injected by syringes. After stirring at 30 °C for 2 h, *n*-BuSH **3** (86 μL, 0.8 mmol) and *n*-Bu_3P (12 μL, 0.04 mmol) were injected to react for another 12 h at 30 °C under nitrogen. The mixture was then added dropwise to 300 mL of methanol through a cotton filter to precipitate the polymer. The precipitate was allowed to stand overnight and then filter. The product was washed with methanol (3 × 30 mL) and dried under vacuum at 50 °C to a constant weight. A yellow solid was obtained in 96% yield. M_w: 57 900. PDI: 3.44. Stereoselectivity: Z/E = 76/24. IR (KBr thin film), ν (cm^{-1}): 3053, 3024, 2955, 2924, 2864, 1632, 1528, 1493, 1400, 1242, 1217, 1042, 1011, 953. ^{1}H NMR (600 MHz, $CDCl_3$), δ (TMS, ppm): 8.01, 7.76, 7.20−6.95, 6.57, 2.79, 2.36, 1.67, 1.42, 1.28, 0.94, 0.83. ^{13}C NMR (150 MHz, $CDCl_3$), δ (TMS, ppm): 187.48, 165.09, 144.27, 142.98, 141.29, 141.08, 137.14, 131.41, 131.29, 131.11, 128.29, 128.20, 127.94, 127.81, 127.47, 127.34, 127.05, 126.95, 126.81, 119.22, 32.72, 32.65, 31.50, 30.20, 22.13, 21.92, 13.80, 13.62.

P2: Into a 25 mL Schlenk tube equipped with magnetic stirrer was placed with TPE-diyne **7** (76 mg, 0.2 mmol), terephthaloyl dichloride **9** (41 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (6 mg, 0.008 mmol), and CuI (6 mg, 0.032 mmol) under nitrogen. 5 mL of freshly distilled THF and anhydrous Et_3N (60 μL, 0.42 mmol) were then injected by syringes. After stirring at 30 °C for 2 h, *p*-toluenethiol **10** (99 mg, 0.8 mmol) and *n*-Bu_3P (12 μL, 0.04 mmol) were injected to react for another 12 h at 30 °C under nitrogen. The mixture was then added dropwise to 300 mL of methanol through a cotton filter to precipitate the polymer. The precipitate was allowed to stand overnight and then filter. The product was washed with methanol (3 × 30 mL) and dried under vacuum at 50 °C to a constant weight. A yellow powder was obtained in 98% yield. M_w: 59 100. PDI: 3.66. Stereoselectivity: Z/E = 63/37. IR (KBr thin film), ν (cm^{-1}): 3052, 3022, 2956, 2922, 2855, 1635, 1598, 1560, 1530, 1492, 1443, 1401, 1302, 1247, 1214, 1180, 1110, 1041, 1013, 954. ^{1}H NMR (600 MHz, $CDCl_3$), δ (TMS, ppm): 8.10, 7.90, 7.64, 7.45, 7.20−6.65, 6.16, 2.41, 2.33.

P3: Into a 10 mL Schlenk tube equipped with magnetic stirrer was placed with TPE-diyne **7** (38 mg, 0.1 mmol), 4-(*N*,*N*-dimethalamino)-benzoyl chloride **11** (37 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (3 mg, 0.004 mmol), and CuI (1.5 mg, 0.008 mmol) under nitrogen. 5 mL of freshly distilled THF and anhydrous Et_3N (30 μL, 0.21 mmol) were then injected by syringes. After stirring at 30 °C for 2 h, 4,4′-thiodibenzenethiol **12** (25 mg, 0.1 mmol) and *n*-Bu_3P (12 μL, 0.04 mmol) were added to react for another 24 h at 30 °C under nitrogen. The mixture was then added dropwise to 300 mL of methanol through a cotton filter to precipitate the resultant polymer. The precipitate was allowed to stand overnight and then filter. The polymer was washed with methanol (3 × 30 mL) and dried under vacuum at 50 °C to a constant weight. A pale brown powder was obtained in 74% yield. M_w: 5900. PDI: 1.42. IR (KBr thin film), ν (cm^{-1}): 3074, 3051, 3023, 2953, 2920, 2859, 2804, 1633, 1595, 1550, 1526, 1498, 1474, 1443, 1368, 1334, 1255, 1182, 1169, 1012, 944. ^{1}H NMR (600 MHz, $CDCl_3$), δ (TMS, ppm): 7.95, 7.75, 7.60, 7.50, 7.38, 7.24−6.46, 6.37, 3.06.

P4: Into a 10 mL Schlenk tube equipped with magnetic stirrer was placed with TPE-monoyne **5** (71 mg, 0.2 mmol), terephthaloyl dichloride **9** (20 mg, 0.1 mmol), $Pd(PPh_3)_2Cl_2$ (3 mg, 0.004 mmol), and CuI (1.5 mg, 0.008 mmol) under nitrogen. 5 mL of freshly distilled THF and anhydrous Et_3N (30 μL, 0.21 mmol) were then injected by syringes. After stirring at 30 °C for 2 h, 4,4′-thiodibenzenethiol **12** (25 mg, 0.1 mmol) and *n*-Bu_3P (12 μL, 0.04 mmol) were added to react for another 24 h at 30 °C under nitrogen. The mixture was then added dropwise to 300 mL of methanol through a cotton filter to precipitate the resultant polymer. The precipitate was allowed to stand overnight and then filter. The product was washed with methanol (3 × 30 mL) and dried under vacuum at 50 °C to a constant weight. A yellow powder was obtained in 85% yield. M_w: 11 100. PDI: 2.17. IR (KBr thin film), ν (cm^{-1}): 3075, 3052, 3022, 2956, 2927, 2869, 1637, 1599, 1564, 1530, 1493, 1475, 1443, 1402, 1389, 1321, 1297, 1247, 1206, 1181, 1096, 1074, 1012, 956. ^{1}H NMR (600 MHz, $CDCl_3$), δ (TMS, ppm): 8.10, 7.88, 7.65, 7.44, 7.25−6.75, 6.25.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Single crystal data for compound **6** (CCDC 1045141), ^{13}C NMR spectra of compounds **3**, **4**, **6**−**9**, and **P1**, HR-MS spectra of **4**, **6**, and **8**, IR spectra of **P2**−**4**, thermogravimetric curve of **P1**−**P4**, and negative photopattern of **P1**−**P4**. 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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