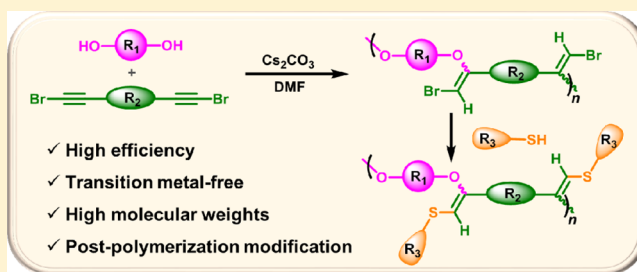


Transition-Metal-Free Polymerization of Bromoalkynes and Phenols

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Supporting Information

ABSTRACT: Exploration of efficient and powerful polymerization methodologies is of crucial importance for polymer science. Among the established polymerization methodologies, the polymerization of internal alkynes is less developed and still in its infancy stage. In this work, a new polymerization of internal alkynes of bromoalkynes and phenols is established, and polymers with high weight-average molecular weights (up to 47 600) are obtained in excellent yields (up to 95.2%) in as short as 1 h without using a complex transition-metal catalytic system. The resultant polymers possess good solubility, exhibit high thermal stability, and could display typical aggregation-induced emission (AIE) characteristics upon introduction of tetraphenylethylene, a typical AIE-active luminogen. Moreover, the polymers could be post-modified by a thiophenol derivative because they contain bromovinyl groups in each repeating unit, enabling it to possess a higher refractive index than that of the pristine one. Therefore, it displays a convenient platform for polymer functionalization. This work not only establishes a new polymerization of bromoalkynes and phenols but also provides a powerful strategy for the preparation and modification of functional polymers under mild reaction conditions without using transition-metal catalysts.



INTRODUCTION

Exploration of efficient and powerful polymerization methodologies has drawn increasing attention among researchers in the field of polymer science.^{1,2} In recent years, triple-bond monomers, such as alkynes,^{3–5} isocyanides,^{6–10} and nitriles,^{11–13} have been used for the construction of functional polymers with advanced structures.^{14,15} Among these triple-bond building blocks, alkynes are the most commonly employed monomers for the development of diverse polymerizations, which include azide–alkyne click polymerization,^{16–20} thiol–yne click polymerization,^{21–24} amino–yne click polymerization,^{25,26} phenol–yne click polymerization,²⁷ multi-component polymerization,² and so on.^{28–32} However, the research on phenol–yne polymerizations, especially based on internal alkynes, is rarely reported.^{33,34} In the few reported polymerizations of activated internal diynes and diols, the scope of diol monomers, the unpleasant smell of catalysts, and harsh anaerobic conditions have limited their applications. Very recently, our groups successfully reported a new polymerization of internal diynes and diphenols in the presence of Pd₂(dba)₃, bathophenanthroline, AgOAc, and Cu(OAc)₂·H₂O at 130 °C.³⁵ However, the complex transition-

metal catalytic system and long reaction time (48 h) also limit its further applications.

Inspired by the previous research and based on our experience, we try to make further progress in the polymerization of internal alkynes and phenols. We were attracted by a reported elegant organic reaction that the phenols and bromoalkynes could be reacted in the presence of K₂CO₃ instead of transition-metal catalyst to facilitate produce functional (Z)-2-bromovinyl phenyl ethers.^{36–38} It is worth noting that bromoalkynes, a kind of internal alkynes, could be easily prepared from terminal alkynes. We also have used it as a building block to establish new polymerizations.^{6,39} Therefore, we tried to develop the reported reaction of bromoalkynes and phenols into a powerful polymerization, although it is much difficult to convert an organic reaction into a useful polymerization for several important issues have to be addressed.³ Thanks to the features of readily available reactants and inorganic base, simple procedures, and high efficiency of the above organic reaction, polymerization was successfully

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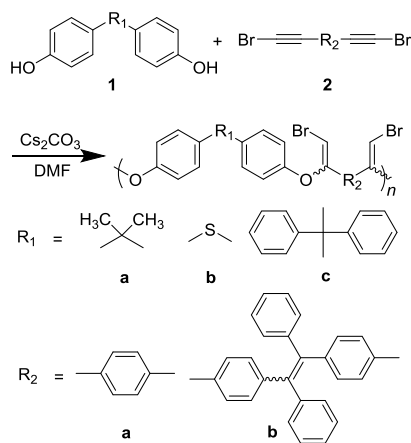
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established in this work. Based on our systematically optimized reaction conditions, bis(bromoalkyne)s and diphenols could be polymerized in *N,N*-dimethylformamide (DMF) in the presence of an inorganic base of Cs_2CO_3 under ambient conditions and polymers with high molecular weights could be produced in excellent yields in a short time. Moreover, when tetraphenylethylene (TPE), a star luminogen exhibiting the unique aggregation-induced emission (AIE) characteristics,^{40–43} is readily introduced into the polymer chains, the resultant polymer is imparted with an AIE feature, too. In addition, these resultant polymers could be easily post-modified by a thiophenol derivative through a conventional substitution reaction because they contain bromovinyl groups. A new polymer that possesses a higher refractive index than the pristine one could be obtained. Therefore, this work not only develops an efficient and powerful polymerization of bis(bromoalkyne)s and diphenols but also provides a convenient platform for polymeric functionalization, which would greatly enrich the structures and properties of the polymeric materials.

RESULTS AND DISCUSSION

Polymerization. To accumulate the experiences for this polymerization, preliminary experiments were carried out. We first studied the reaction time of the polymerization using **1a** and **2a** as model monomers while keeping other conditions similar to the organic reaction (Scheme 1). The results showed

Scheme 1. Polymerization of Diphenols **1 and Bis(bromoalkyne)s **2****



that the polymerization proceeded for 3 h and could furnish a product with the highest weight-average molecular weight (M_w , Table S1). Next, we optimized the used inorganic base. According to the model reaction, the polymerization is better to be conducted under an alkaline environment. Thus, other two alkaline salts of CsF and Cs_2CO_3 were tested. A trace amount of the product was obtained when CsF was used to mediate the polymerization, whereas Cs_2CO_3 could furnish the best results, and a soluble polymer with highest M_w (10 300) was produced in the highest yield (92.1%). Thus, Cs_2CO_3 was used for following investigation.

Encouraged by the preliminary results, we systematical optimized the polymerization conditions continually using **1a** and **2a** as model monomers. We first investigated the reaction time again. As shown in Table 1, as time shortened, the M_w of products remained almost unchanged. However, their yields dropped dramatically when the reaction time was shortened to

Table 1. Time Course of the Polymerization of **1a and **2a**^a**

entry	<i>t</i> (h)	yield (%)	M_w^b	\bar{D}^b
1	3	92.1	10 300	1.40
2	2	99.7	10 300	1.44
3	1	93.8	11 700	1.52
4	0.5	69.3	11 300	1.48

^aCarried out in DMF at 110 °C in air ($[\mathbf{1a}]/[\mathbf{2a}] = 1$, $[\text{Cs}_2\text{CO}_3]/[\mathbf{2a}] = 2$, $[\mathbf{2a}] = 0.1$ M). ^bWeight-average molecular weight (M_w) and polydispersity index (\bar{D} , M_w/M_n) of polymers were estimated by gel permeation chromatography (GPC) using THF as the eluent on the basis of a polymethyl methacrylate calibration.

half an hour probably because of the uncompleted reaction. In view of satisfactory M_w and the yield of the product, 1 h was selected as the optimal polymerization time.

Next, other parameters including the monomer concentration, the amount of Cs_2CO_3 , reaction temperature, and solvent were optimized, and the results are listed in Table 2.

Table 2. Effect of Reaction Conditions on the Polymerizations of **1a and **2a**^a**

entry	$[\mathbf{2a}]$	$[\text{Cs}_2\text{CO}_3]/[\mathbf{2a}]$	<i>T</i> (°C)	solvent	yield (%)	M_w^b	\bar{D}^b
1	0.05	2	110	DMF	36.1	7700	1.26
2	0.10	2	110	DMF	93.8	11700	1.52
3	0.20	2	110	DMF	90.3	28500	2.30
4	0.20	1	110	DMF	86.5	19100	1.88
5	0.20	0.5	110	DMF	67.5	9900	1.51
6	0.20	2	90	DMF	83.2	24800	2.20
7	0.20	2	70	DMF	98.4	19600	1.85
8	0.20	2	50	DMF	53.3	5000	1.22
9	0.20	2	110	DMAc	74.5	12000	1.57
10	0.20	2	110	DMSO	90.7	8000	1.25

^aCarried out in 2 mL of solvent for 1 hour under air condition. ^bWeight-average molecular weight (M_w) and polydispersity index (\bar{D} , M_w/M_n) of polymers were estimated by GPC using THF as the eluent on the basis of a polymethyl methacrylate calibration. DMAc = *N,N*-dimethylacetamide.

Employing similar reaction conditions listed in entry 3, Table 1, we first investigated the influence of monomer concentration on the polymerization results. Diluting the monomer concentration from 0.1 to 0.05 M resulted in a lower M_w and yields of products, whereas increasing the monomer concentration to 0.2 M led to the product with an excellent M_w (28 500) and higher yield (90.3%) because of more effective intermolecular collisions. Interestingly, further exploration of other reaction conditions suggested that the original ones are the best (entry 3, Table 2, $[\mathbf{2a}] = 0.2$ M, $[\text{Cs}_2\text{CO}_3]/[\mathbf{2a}] = 2$, $T = 110$ °C).

By using these optimized reaction conditions, we performed the polymerization using other phenols **1b–1c** and aromatic bromoalkynes **2b** to show its robustness and universality (Scheme 1). All the polymerization reactions propagated smoothly, and the polymers of PII–PIV with high M_w (up to 47 600) were produced in excellent yields (up to 95.2%), manifesting the universality of this powerful and efficient polymerization (Table 3).

Table 3. Polymerization of 1 and 2^a

polymer	monomer	yield (%)	M_w^b	\bar{D}^b	Z/E (%)
PI	1a + 2a	90.3	28 500	2.30	72.3
PII	1b + 2a	95.2	47 600	3.08	72.0
PIII	1c + 2a	76.5	41 500	2.45	71.8
PIV	1a + 2b	85.5	23 800	2.11	^c

^aCarried out in DMF under air condition for 1 h ($[1]/[2] = 1$, $[Cs_2CO_3]/[1] = 2$, $[1] = 0.2$ M). ^bWeight-average molecular weight (M_w) and polydispersity index (\bar{D} , M_w/M_n) of polymers were estimated by GPC using THF as the eluent on the basis of a polymethyl methacrylate calibration. ^cAs PIV contains other double bonds and the ratio is hard to be obtained.

All the resultant polymers PI–PIV are soluble in commonly used organic solvents, such as dimethylsulfoxide (DMSO), DMF, chloroform, and tetrahydrofuran (THF). They are also thermally stable. As revealed by the thermogravimetric analysis (TGA) under nitrogen, the temperatures for the 5% loss of their weights are all above 357 °C (Figure 1).

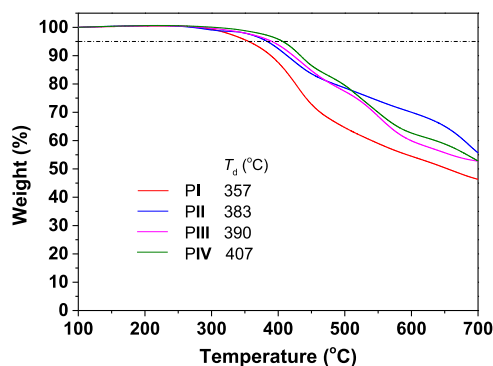


Figure 1. TGA thermograms of PI–PIV. T_d represents the temperature of 5% weight loss of the polymers.

Structural Characterization. Thanks to their excellent solubility in most organic solvents, the structures of PI–PIV were characterized by spectroscopic methods. As the spectral profiles of PI–PIV are similar (Figures 2 and S1–S3), the Fourier transform infrared (FT-IR) spectra of PI and its monomers 1a and 2a are discussed here as an example (Figure 2). The absorption peaks at 3290 and 2261 cm^{-1} are readily

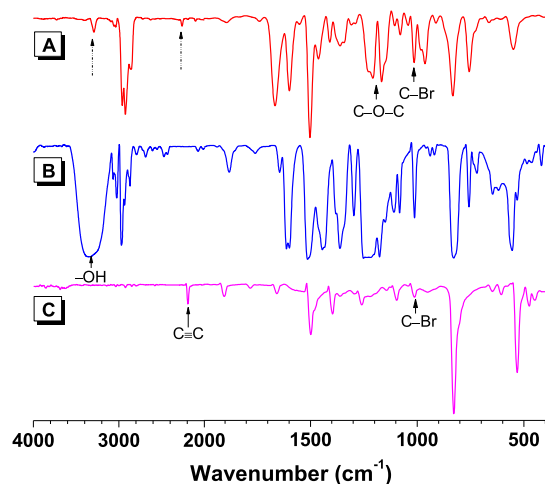


Figure 2. FT-IR spectra of PI (A), 1a (B), and 2a (C).

assigned to the stretching vibration of phenolic hydroxyl group in 1a and ethynyl group in 2a, respectively. In the spectrum of PI, these two characteristic signals weakened or disappeared. Meanwhile, there are two sets of new peaks arising at 1205 and 1170 cm^{-1} , which belong to the stretching vibration of C–O–C, respectively. All these results indicate that monomers 1a and 2a had been polymerized and ether linkage had been formed accordingly.

More detailed structural information of polymers could be obtained from the 1H and ^{13}C NMR spectra (Figures 3, 4 and

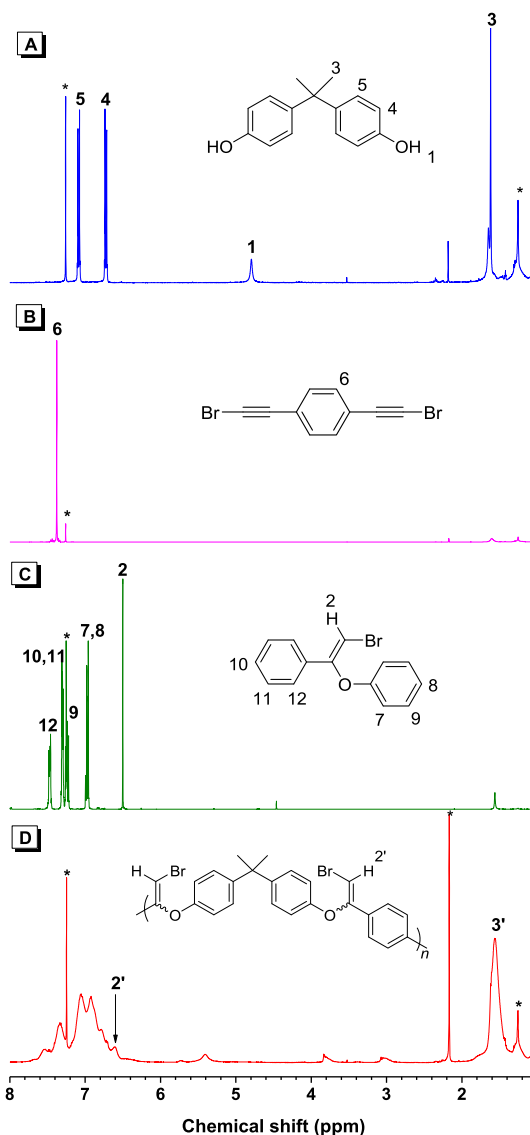


Figure 3. 1H NMR spectra of 1a (A), 2a (B), model compound (C), and PI (D) in $CDCl_3$. The solvent peaks are marked with asterisks.

S4–S9). To facilitate the structural characterization, model compound 3 was prepared under the same reaction conditions (Scheme S1). The 1H NMR spectra of PI, monomers 1a and 2a, and the model compound 3 in $CDCl_3$ are shown in Figure 3 as an example. Characteristic proton “2” of compound 3 resonated at δ 6.50 is observed in Figure 3C. Correspondingly, proton “2'” of PI was observed at δ 6.60 in Figure 3D. It is worth noting that we could hardly find the resonant peak associated with phenols from the spectrum of PI. The ^{13}C NMR spectra were also measured to verify the structure of PI

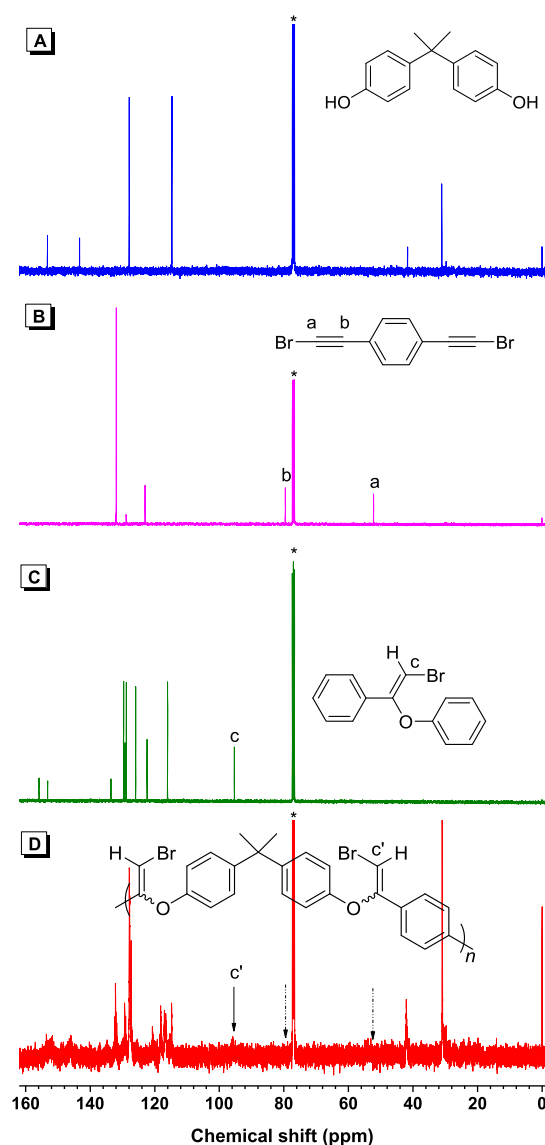


Figure 4. ^{13}C NMR spectra of **1a** (A), **2a** (B), model compound (C), and **PI** in CDCl_3 . The solvent peaks are marked with asterisks.

(Figure 4). The peaks representing carbons “a” and “b” in **2a** disappeared in the spectrum of **PI**, whereas the resonance of the carbonyl carbon “c” in model compound **3** was observed in the spectrum of **PI** at δ 95.75. These results suggested that **1a** and **2a** had been polymerized, and **PI** was indeed obtained, further substantiating the conclusion drawn from the FT-IR and ^1H NMR spectral analysis.

Theoretically, there will be two *E*- and *Z*-isomers in the polymers according to the reaction mechanism, although only one *Z*-isomer derivative was reported.^{36–38} As the peaks in the ^1H NMR of protons in the vinyl groups are severely overlapped, we thus used the Raman spectra of **PI**–**PIV** to identify the ratio of *Z*- and *E*-isomers. As shown in Figure S10A–D, two peaks at 1602 and 1668 cm^{-1} were recorded for **PI**–**PIV**. By comparing with the model compound with *Z*-stereoregularity (Figure S10E), the peaks at 1602 cm^{-1} of **PI**–**PIV** were assigned to *Z*-isomers. Accordingly, the peaks at 1668 cm^{-1} could be assigned to the *E*-isomers. Based on Raman spectral analysis, the ratio of the *Z*-/*E*-isomers in **PI**–**PIV** was deduced to be ~72% via integration of the peaks (Table 3).

Photoluminescence Properties. Thanks to its excellent functional group tolerance, the AIE-active TPE moiety could be readily incorporated into the polymer chains of **PIV** by our developed polymerization. After confirming its structure, we investigated its photoluminescence (PL) behavior. As shown in Figure 5, the THF solution of **PIV** is almost nonemissive, while the emission of its THF/water mixtures is intensified gradually with increasing the water fraction (f_w). The emission intensity reaches the highest in the THF/water mixture with f_w of 90%, which was 11-fold higher than that in THF (Figure 5B), demonstrating a typical AIE feature.

Photopatternability. As **PIV** is highly emissive in the solid state and contains the vinyl groups, we thus tested its photopatternability by UV irradiation of its spin-coated films on silicon wafers through a negative copper photomask. As depicted in Figure 6, a two-dimensional (2D) fluorescent photopattern was successfully generated after UV irradiation for 20 min in air. The unexposed parts (squares) remain bright green emission, while the exposed regions (lines) become nonemissive because of the strong photo-oxidative bleaching

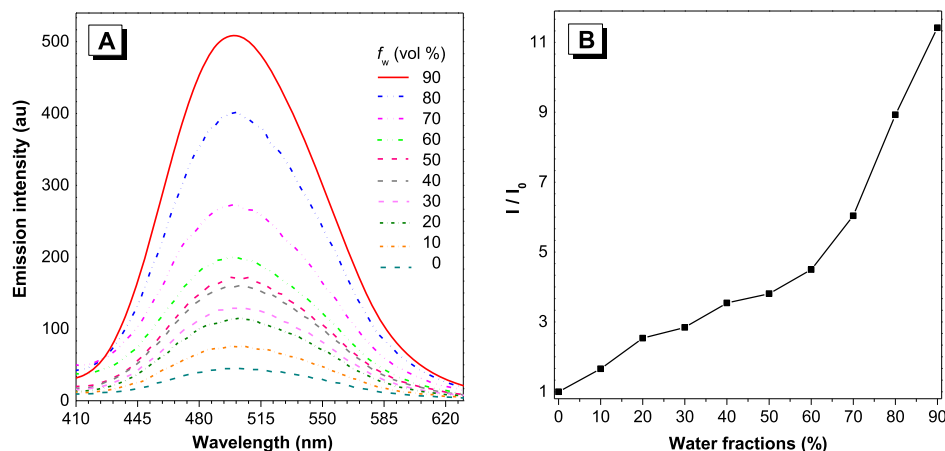


Figure 5. (A) PL spectra of **PIV** in THF/water mixtures with different water fractions (f_w). (B) Plot of the changes in the PL intensity of **PIV** vs f_w , where I_0 and I are the maximal PL intensities recorded before and after the addition of water into the THF solution, respectively. Concentration of **PIV**: 10 μM , λ_{ex} : 345 nm.

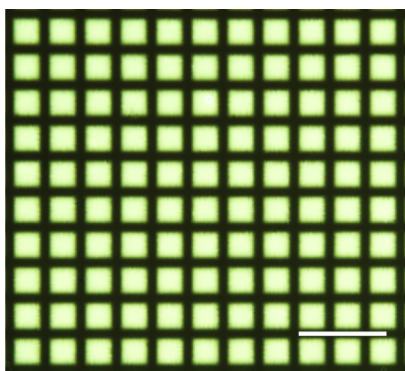
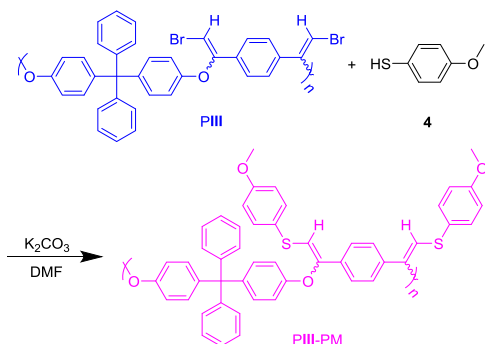


Figure 6. 2D fluorescent photopattern generated by photo-oxidation of PIV. The photograph was taken under UV illumination (330–385 nm). The scale bar is 50 μm .

effect. Therefore, PIV possesses good photosensitivity and could be used to fabricate a 2D fluorescent photopattern.

Post-Modification of Polymers. Post-modification is a powerful tool to enrich the family of poly(vinyl ether)s, and it also provides a convenient platform for polymers to be further functionalized. As PI–PIV contains bromovinyl groups in each repeating unit, they could be easily post-modified. For example, the substitution reaction of PIII (M_w : 32 800) and thiophenol **4** occurred under ambient conditions, generating PIII–PM with an M_w of 40 800 in 96% yield (Scheme 2 and Table S2). After modification, the maximum absorption peaks were shifted to 328 nm because of extension of the conjugation.

Scheme 2. Post-Modification of PIII



To clearly characterize the post-modified structure of PIII–PM, model compound **9** was designed and readily prepared according to the route shown in Scheme S2. The ^1H NMR spectra of **9** and PIII–PM confirm the occurrence of the post-modification reaction (Figure 7B,C). From the ^1H NMR spectra shown in Figure 7, the grafting degree of PIII–PM was calculated to be 40%. It is worth noting that the refractive index of PIII–PM is slightly higher than that of PIII (Figure S11) at short wavelength, further indicative of the usefulness of the post-modification strategy.

CONCLUSIONS

In this work, we developed an efficient transition-metal-free polymerization of bromoalkynes and phenols. Mediated by an inexpensive inorganic base of Cs_2CO_3 at 110 $^\circ\text{C}$, the polymerization of bis(bromoalkyne)s and diphenols propagated smoothly, generating polymers with M_w up to 47 600 in

the yields up to 95.2% in as short as 1 h. All the resultant polymers are soluble in commonly used organic solvents and thermally stable with high degradation temperatures. The polymerization also exhibits functional group tolerance, and function moieties such as TPE could be readily introduced into the polymer, endowing it with AIE activity, too. PIV could be used to fabricate a 2D fluorescent photopattern with good resolution. Moreover, the resultant polymers could be easily post-modified because they contain bromovinyl groups in each repeating unit, and the post-modified polymer possesses a higher refractive index than the pristine one. Thus, this work not only establishes a novel polymerization of bromoalkynes and phenols but also provides a convenient platform for polymeric functionalization.

EXPERIMENTAL SECTION

Polymer Synthesis. All the polymerization reactions were carried out in air. A typical procedure for the polymerization of **1a** and **2a** is given below as an example.

Into a round-bottom flask were dissolved **1a** (45.6 mg, 0.2 mmol), **2a** (56.8 mg, 0.2 mmol), and Cs_2CO_3 (60.8 mg, 0.4 mmol) in DMF (1.0 mL). The mixture was stirred at 110 $^\circ\text{C}$ for 1 h. Afterward, the resultant mixture was added dropwise into 300 mL of CH_3OH through a cotton filter under stirring. The precipitate was allowed to stand overnight and then collected by filtration. The polymer was washed with CH_3OH three times and dried to a constant weight, affording a yellowish-brown powder product.

Characterization Data of PI. Yellowish-brown solid; yield 90.3% (entry 1, Table 3); M_w : 28 500. M_w/M_n : 2.30. FT-IR (KBr) ν (cm^{-1}): 3290, 3028, 2963, 2923, 2856, 2261, 1665, 1596, 1504, 1460–1289, 1205, 1170, 1011, 963, 833, 755, 549. ^1H NMR (500 MHz, CDCl_3): δ (TMS, ppm) 7.54, 7.48, 7.33, 7.05, 6.92, 6.79, 6.71, 6.60, 1.56. ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 156.89, 153.65, 153.56, 151.74, 146.00, 132.40–127.27, 120.71, 118.15, 116.98, 116.58, 115.23, 114.78, 95.75, 41.99, 31.02.

Characterization Data of PII. Yellowish-brown solid; yield 95.2% (entry 2, Table 3); M_w : 47 600. M_w/M_n : 3.08. FT-IR (KBr) ν (cm^{-1}): 3287, 2952, 2926, 2847, 1665, 1584, 1482, 1196, 1154, 1010, 823, 752, 522. ^1H NMR (500 MHz, CDCl_3): δ (TMS, ppm) 7.50, 7.32, 7.06, 6.81, 6.68, 6.56. ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 156.75, 155.58, 135.57, 134.60, 134.12–130.95, 129.36–125.56, 122.46, 121.77, 119.15, 117.83, 116.38.

Characterization Data of PIII. Yellowish-brown solid; yield 76.5% (entry 3, Table 3); M_w : 41 500. M_w/M_n : 2.45. FT-IR (KBr) ν (cm^{-1}): 2955, 2924, 2853, 1669, 1599, 1499, 1211, 1168, 1015, 962, 828, 755, 702. ^1H NMR (500 MHz, CDCl_3): δ (TMS, ppm) 7.49, 7.33, 7.15, 6.93, 6.68, 6.48. ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 152.75, 146.54, 142.40, 132.05, 130.95, 129.77, 127.50, 125.97, 117.49, 116.66, 96.44, 63.94.

Characterization Data of PIV. Yellowish-brown solid; yield 85.5% (entry 4, Table 3); M_w : 23 800. M_w/M_n : 2.11. FT-IR (KBr) ν (cm^{-1}): 2958, 2922, 2854, 1667, 1599, 1501, 1225, 1206, 1167, 1145, 1015, 962, 830, 758, 699. ^1H NMR (500 MHz, CDCl_3): δ (TMS, ppm) 7.03, 6.76, 6.58. ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 152.77, 145.64, 143.40, 140.92, 131.35, 127.80, 126.84, 117.82, 116.85, 115.34, 97.08, 42.07, 30.89.

Preparation of Model Compound. To verify the occurrence of the polymerization of bis(bromoalkyne)s with diphenols and to confirm the structures of polymeric products, model compound **3** was synthesized according to previous report.³⁸ Its synthetic route is shown in Scheme S1. Following is its characterization data. ^1H NMR (400 MHz, CDCl_3): δ (TMS, ppm) 8.17 (d, J = 9.2 Hz, 2H), 7.45 (m, 2H), 7.36 (m, 3H), 7.07 (d, J = 9.2 Hz, 2H), 6.65 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 160.73, 152.73, 132.49, 129.86, 129.12, 126.04, 125.49, 118.81, 116.06, 96.57.

Preparation of PIII–PM. Into a 10 mL tube were placed PIII (50 mg, 0.079 mmol) and K_2CO_3 (11 mg, 0.079 mmol). Then, DMF (4 mL) and thiophenol **4** (39 μL , 0.3 mmol) were injected into the tube.

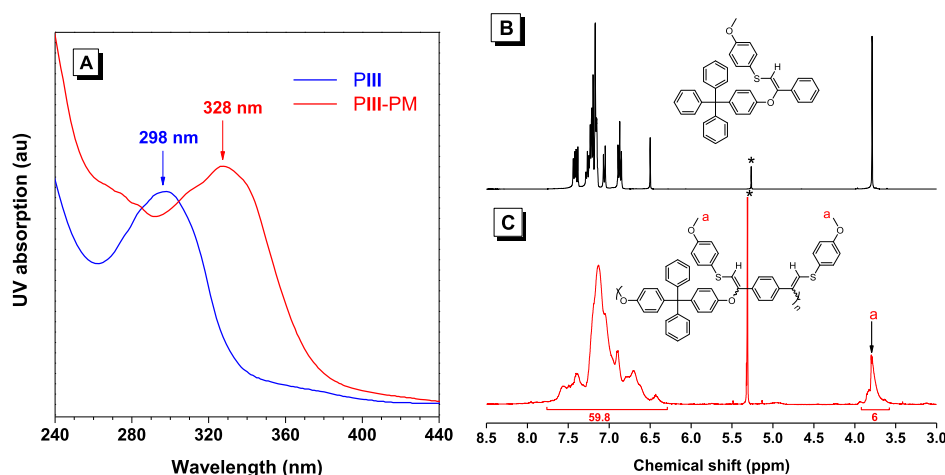


Figure 7. (A) UV–visible absorption spectra of PIII and PIII–PM in THF. Concentration: 10 μ M. (B,C) ^1H NMR spectra of PIII and PIII–PM in DCM-d_2 .

The mixture was stirred at 50 $^\circ\text{C}$ for 2 h. The resultant solution was added dropwise into 300 mL of CH_3OH through a cotton filter under stirring. The precipitate was allowed to stand overnight and then collected by filtration. The product was washed with CH_3OH three times and dried to a constant weight. A yellowish-brown powder product was obtained in 96% yield (57.3 mg, Table S2). ^1H NMR (500 MHz, CD_2Cl_2): δ (ppm) 7.56, 7.50, 7.40, 7.13, 7.04, 6.90, 6.79, 6.70, 6.43, 3.80.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.9b00306.

Detailed synthetic procedures to monomers, preliminary polymerization results, FT-IR, ^1H and ^{13}C NMR spectra of PII–PVI, and light refraction spectra of PIII and PIII–PM (PDF)

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Notes

The authors declare no competing financial interest.

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