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Development of transition metal-free polymerization route to functional conjugated polydiynes from haloalkyne-based organic reaction

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The development of efficient transition metal-free polymerization route has been an active research topic in polymer science owing to its low synthetic cost and decreased metal residue and hence elevated material performance in the products. In this work, we report a new such method for constructing conjugated polydiynes based on the organic reaction of 1-haloalkyne. In the presence of potassium iodide, the polymerizations of 1,2-bis[4-(iodoethynyl)phenyl]-1,2-diphenylethene (**1**), 1,4-bis(2-iodoethynyl)benzene (**2**) and 4,4'-bis(2-iodoethynyl)-1,1'-biphenyl (**3**) proceed smoothly in *N*,*N*-dimethylformamide at 120 °C under nitrogen, producing P**1**–**3** consisted of alternate aromatic and 1,3-diyne moieties in moderate to satisfactory yields. While P**1** possesses good solubility in common organic solvents, P**2** and P**3** are insoluble due to their rigid structures. All the polymers are thermally stable, losing 5% of their weight at high temperature of up to 352 °C. Homogeneous film of P**1** can be readily obtained by spin-coating its solution, which shows high and UV-tunable refractive index (*n* = 2.1125–1.7747) in a wide wavelength range (400–900 nm). A well-defined fluorescent photopattern can be generated by UV irradiation of the polymer film through a copper mask. This work thus opens a new avenue for constructing conjugated polymer with advanced functionalities.

Introduction

Synthetic polymeric materials are gaining increasing attention due to their superior properties, such as high mechanical strength, good thermal stability and excellent macroscopic processability, and hence potential high-tech applications. Development of facile and efficient methodologies towards various polymers is thus a long-standing research topic and the pursuit of both scientists and engineers. Currently, most of the polymerizations are derived from organic reactions of small molecules. For an ideal organic reaction to be developed into a new polymerization method, several criteria should be satisfied, which include but are not limited to high reaction efficiency and conversion rate, wide monomer scope and high regio-/stereo-selectivity. In this way, the derived polymerization reaction can afford polymers in good yields with high molecular weights and specific structures. Furthermore, to ensure the polymers obtained are practically useful, sensible monomer design is necessary, which is closely related to the properties of the polymers obtained.

Triple bond reactions constitute a considerable portion of the organic reactions and $C\equiv C$ serves as a versatile building block in the construction of various functional structures. In many triple-bond reactions, such as cyclotrimerization, addition and metathesis, the triple bonds are transformed to aromatic rings or double bonds, affording conjugated products with novel electronic and optical properties. Therefore, triple-bond-derived polymerization reactions are powerful methods for the preparation of conjugated polymers.[1-11] Our research group are interested in constructing functional conjugated macromolecules from alkyne monomers.[12-17] We have prepared hyperbranched polyarylenes with unique optical and photophysical properties by polycyclotrimerization of diynes $R-(C\equiv CH)_2$ catalyzed by tantalum or cobalt complexes.[18-22] As an extension of this system, we have developed a polymerization route to construct nitrogen-rich hyperbranched polytriazines by polycyclotrimerization of dinitriles $R-(C\equiv N)_2$.[23] Besides, we also utilized alkyne-azide cycloaddition to construct functional poly(triazole)s with heteroatom-containing backbones.[15,24] Specifically, we successfully developed various click polymerization systems conducted in the absence or presence of metal or non-metal catalyst. [24-30] Additionally, we embarked on the development of thiol-yne click polymerization based on alkyne hydrothiolation for the synthesis of sulfur-containing unsaturated polymers.[31] Due to the high efficiency of the thiol-yne addition reaction, functional poly(vinylene sulfide)s can be readily obtained via rhodium-catalyzed,

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*† Electronic supplementary information (ESI) available: crystal data for model compound **7**.*

secondary amine-mediated and catalyst-free thiol-yne click polymerizations.[32-34]

In the above examples, the triple bonds open and new double bonds form during the polymerization process. We also developed other polymerization reactions, in which the triple bonds of the monomers remain intact after the polymerization. The preservation of C≡C results in conjugated structures and endows the polymeric products with potential thermal, electronic and optical properties.[35,36] For example, luminescent poly(arylene ethynylene)s with tetraphenylethene (TPE) and silole moieties were prepared by palladium-catalyzed Sonogashira polycoupling of terminal alkynes and aryl halides.[37] Compared with those containing ethynylene units, polymers with 1,3-diyne functionalities demonstrate better performance as semiconductors, optical materials and molecular recognition systems.[2,38,39] Generally, diyne-containing polymers can be readily obtained by homo-polycoupling reactions of diyne monomers catalyzed by transition metal catalyst, such as copper and palladium. For example, under Glaser-Hay oxidative coupling conditions and in the presence of CuCl, soluble linear and hyperbranched polydiynes were produced in almost quantitative yields with high molecular weights.[40-43] These two tools have been widely used to produce triple bond-containing polymers but they show some disadvantages. While the Sonogashira polycoupling reaction requires strict stoichiometric balance between monomers in order to generate high molecular weight polymer, the copper residue in the polymers generated by Glaser-Hay homo-polycoupling may deteriorate their material properties.

Haloalkynes exhibit both controllable electrophilic and nucleophilic properties. Because of such functionality, they have emerged as powerful and versatile synthons in synthetic organic chemistry.[44] In 2010, Jiang and co-workers discovered a transition metal-free homocoupling reaction to synthesize symmetrical 1,3-diynes from 1-haloalkynes (Scheme 1).[45] This reaction is mediated by potassium iodide without employing any transition metal, base or oxidant, and is different from previous protocols, which use terminal alkynes as reactants and transition-metal complexes or reactive alkynylmagnesium compounds as catalysts. Taking advantages of inexpensive additive used, simple procedure and high product yield, we tend to develop the KI-mediated coupling reaction of 1-haloalkyne into a novel polymerization route in this work. With such regard, bis(iodoalkyne)s **1**–**3** were prepared and used as monomers for constructing polymers. All the monomers can be polymerized in the presence of KI, generating P**1**–**3** in moderate to satisfactory yield in a short time. While P**1** readily dissolves in common organic solvents, P**2** and P**3** are insoluble. We herein report the synthesis of the polymers and present the material properties of P**1** in this work.

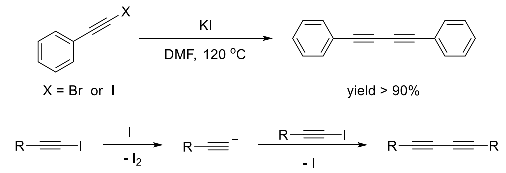
Results and Discussion

Monomer design

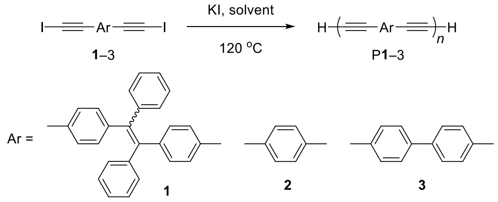
The first step in developing a polymerization reaction from a small molecular reaction is the design and synthesis of monomers bearing two reactive functional groups. We thus prepared 1,2-bis[4-(iodoethynyl)phenyl]-1,2-diphenylethene (**1**) by reaction of 1,2-bis(4-ethynylphenyl)-1,2-diphenylethene (**4**) with *N*-iodosuccinimide in alkaline medium (Scheme 3).[46,47] We also synthesized 1,4-bis(2-iodoethynyl)benzene (**2**), 4,4'-bis(2-iodoethynyl)-1,1'-biphenyl (**3**) by the same reaction route, using 1,4-diethynylbenzene (**5**) and 4,4'-diethynylbiphenyl (**6**) as starting materials.[48] All the monomers were obtained in high yields. Their structures were characterized by standard spectroscopic methods with satisfactory results. Details can be found in the experimental section.

Polymerization

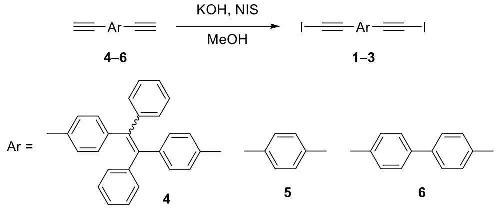
We first used monomer **1** to optimize the conditions for the polymerization. We initially investigated the solvent effect on the polymerization. According to the small molecular reaction, the polymerization is better to be conducted at high temperature. Various solvents with high boiling point and different solvating power and polarity are thus tested. Among all the tested solvents, *N*,*N*-dimethylformamide (DMF) was the most appropriate one for the polymerization, yielding a soluble polymer with the highest molecular weight (M_w = 18 700) in a higher yield (69%). Satisfactory yield (53%) was also obtained when the polymerization was conducted in dimethylsulfoxide (DMSO), but the molecular weight of the product became lower (M_w = 7 100). The polymerizations in non-polar solvents, such as 1,4-dioxane and *o*-xylene, however, generate oligomers in poor yields, indicating that they are not suitable for the polymerization.



Scheme 1 Transition metal-free homocoupling of 1-haloalkyne and its plausible mechanism.



Scheme 2 Construction of conjugated polydiynes by KI-mediated transition metal-free homo-polycoupling of bis(iodoalkyne)s.



Scheme 3 Synthetic route to monomers **1**–**3**.

We then followed the time course of the polymerization by calculating the isolation yield of the polymer obtained and measuring its molecular weight by GPC analysis. As shown in Table 2, within the first 6 h, the yield rises from 13% to 72% and the molecular weight of the polymer also increases from 2 900 to 20 100. Further prolonging the reaction time to 24 h, however, leads to no further increase in the isolation yield and molecular weight. Instead, some insoluble gel-like substances are formed when the reaction time exceeds 6 h (Table 2, no. 4 and no. 5), which have lowered the overall yield and the polymer's molecular weight. The time course study suggests that 6 h is the most suitable time for the polymerization (Table 2, no. 3).

According to the mechanism shown in Scheme 1, KI plays an important role in the polymerization and serves as an additive to remove the iodine cation from the monomer. Therefore, we studied the effect of its amount on the polymerization (Table 3). At a KI concentration two times higher than that of **1**, a polymer with the highest molecular weight (M_w = 20 100) was obtained in a satisfactory yield (72 %, Table 3, no. 2). By further increasing the KI amount, the molecular weight of the polymeric product drops dramatically but the isolated yield remains pretty high. On the other hand, reducing the amount of KI to a value equal to the monomer concentration decreases both the yield and molecular weight. Therefore, the ratio of KI and monomer **1** was kept at 2:1 in the following experiments.

Table 1 Solvent effect on the polymerization[a]

no.	solvent	yield (%)	M_w[b]	M_w/M_n[b]
1	DMF	69	18 700	2.3
2	DMSO	53	7 100	1.6
3	1,4-dioxane	26	2 800	1.3
4	*o*-xylene	18	3 400	1.3

[a] Carried out in different solvents using **1** as monomer under nitrogen in the presence of KI at 120 °C for 24 h. [**1**] = 0.1 M. [KI]/[**1**] = 2. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration.

Table 2 Time course of the polymerization[a]

no.	time (h)	yield (%)	M_w[b]	M_w/M_n[b]
1	1	13	2 900	1.2
2	3	55	7 100	1.5
3	6	72	20 100	2.4
4	12	63	16 800	1.8
5[c]	24	69	18 700	2.3

[a] Carried out in DMF using **1** as monomer under nitrogen in the presence of KI at 120 °C. [**1**] = 0.1 M. [KI]/[**1**] = 2. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration. [c] Data taken from Table 1, no. 1.

Table 3 Effect of additive on the polymerization[a]

no.	[KI]/[**1**]	yield (%)	M_w[b]	M_w/M_n[b]
1	1	52	6 700	1.4
2[c]	2	72	20 100	2.4
3	3	77	11 600	2.0
4	4	75	8 600	1.6

[a] Carried out in DMF using **1** as monomer under nitrogen in the presence of KI at 120 °C for 6 h. [**1**] = 0.1 M. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration. [c] Data taken from Table 2, no. 3.

Table 4 Effect of monomer concentration on the polymerization[a]

no.	[**1**]	yield (%)	M_w[b]	M_w/M_n[b]
1	0.05	47	5 000	1.3
2[c]	0.10	72	20 100	2.4
3	0.15	79	10 300[d]	1.6
4	0.20	91	10 700[d]	1.9

[a] Carried out in DMF using **1** as monomer under nitrogen in the presence of KI at 120 °C for 6 h. [KI]/[**1**] = 2. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration. [c] Data taken from Table 2, no. 3. [d] Soluble fraction.

We then investigated the influence of monomer concentration on the polymerization reaction. Generally speaking, a higher monomer concentration will facilitate intermolecular collision between monomers, leading to better polymerization result. As shown in Table 4, when the monomer concentration was increased from 0.05 M to 0.20 M, the isolation yield was enhanced from 47% to 91 % accordingly. The dependence of molecular weight on the monomer concentration, however, was different. Increasing the monomer concentration from 0.10 M to 0.20 M results in partial gelation, yielding a partially soluble polymer with a molecular weight of merely 10 700. These results demonstrate that the present polymerization is efficient and does not require the use of reacting monomers in high concentration.

Many polymerization reactions are sensitive to oxygen, especially those involving radical species. To check the sensitivity of the present polymerization to air, we compared the polymerization results obtained under nitrogen and in open air (Table 5). The polymerization conducted in the open air gives a poorer result than that obtained under nitrogen, presumably due to the high sensitivity of the iodine radical involved in the reaction mechanism to oxygen. Clearly, nitrogen environment is essential for efficient polymerization.

To sum up, the homo-polycoupling of **1** is better to be carried out in DMF under nitrogen at a monomer concentration of around 0.10 M and KI/**1** ratio of 2. Thus, we used the same conditions for polymerizing **2** and **3**. While both monomers can be polymerized in moderate yields, the polymers obtained are insoluble. The rod-like, aromatic structures of the monomers may impact their resulting polymers with tight molecular packing and rigid conformation, thus dramatically lowering their processability. On the other hand, P**1** may show weak interaction and large free volume between the polymer chains due to the twisted conformation of the TPE unit of **1**. This may explain why it can dissolve readily in common organic solvents, such as THF, dichloromethane, chloroform, etc.

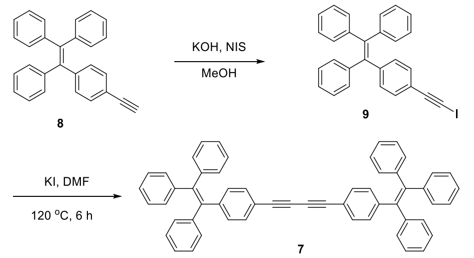
Table 5 Effect of air on the polymerization[a]

no.	yield (%)	M_w[b]	M_w/M_n[b]
1[c]	72	20 100	2.4
2[d]	42	4 600	1.3

[a] Carried out in DMF using **1** as monomer in Schlenk tube in the presence of KI at 120 °C for 6 h. [**1**] = 0.1 M, [KI]/[**1**] = 2. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration. [c] Under nitrogen flow. Data taken from Table 2, no. 3. [d] In open air.

Model reaction

In order to confirm the occurrence of the homo-polycoupling reaction and gain insight into the structure of the polymer, a model compound **7** was synthesized (Scheme 4). Compound **9** was prepared by iodination of 1-(4-ethylnylphenyl)-1,2,2-triphenylethene (**8**) using NIS in methanol. Its homo-coupling was carried out at conditions similar to those for preparing the polymers. The model compound **7** generated was purified by silica gel column chromatography using hexane/DCM mixture as eluent. Single crystals of **7** were obtained from its chloroform/hexane solution and analyzed by X-ray crystallography. The results are shown in Fig. 1 and Table S1 in the electronic supporting information. As shown in Fig. 1, the molecular structure clearly shows the linear 1,3-diyne unit, thus verifying the success of the reaction. Comparison between **7** and the resulting polymer will give a strong supportive information on the structural analysis of the later.



Scheme 4 Synthetic route to model compound **7**.

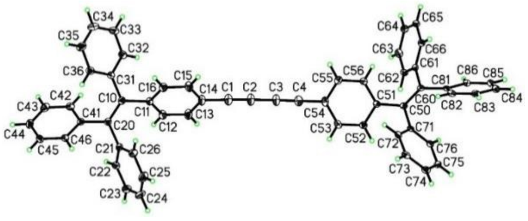


Fig. 1 ORTEP drawing of crystal structure of model compound **7**. (CCDC 1423561).

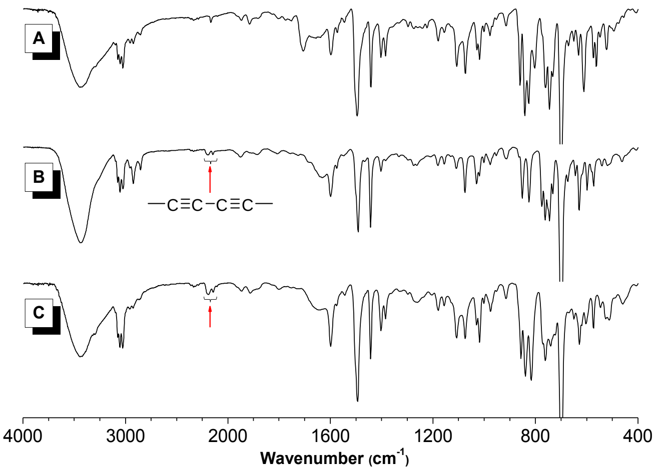


Fig. 2 IR spectra of (A) **1**, (B) **7** and (C) P**1** (Table 1, no. 1).

Structure characterization

Monomer **1**, model compound **7** and polymer P**1** were characterized by standard spectroscopic techniques, such as FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopies, from which satisfactory analysis data corresponding to their molecular structures were obtained. The featured peaks of P**1** in each spectrum are discussed in detail in the following text.

The IR spectrum of P1 is shown in Fig. 2C. For comparison, the spectra of monomer **1** and model compound **7** are also given in the same figure (Fig. 2A and B, respectively). The absorption peaks associated with the C≡C–C≡C stretching in model compound **7** are observed at 2199 and 2147 cm^{-1}, respectively. These two absorption peaks are also observed in the IR spectrum of the polymer, but are absent in monomer **1**. This confirms the success in the formation of 1,3-diyne structure in the polymer backbone and the occurrence of the homo-polycoupling reaction. Other peaks in the monomer are well reserved in the polymer.

Fig. 3 shows the ^{1}H NMR spectra of **1**, **7** and P**1** in deuterated DCM. Though all the protons resonate in the aromatic area, the peaks are well resolved and can be assigned due to their different chemical environments. As shown in Fig. 3, the peaks associated with the resonance of "a" protons are shifted from ~7.27 ppm in monomer **1** to ~7.70 ppm (a'proton) in **7** and P**1** due to the formation of new C≡C–C≡C unit after the polymerization (Table 1, no. 1). Compared with **7**, the peaks in P**1** are broader due to its polymeric nature. Interestingly, a small peak at ~3.0 ppm is observed in P**1**, which suggests that the end groups are triple-bond functionalities. From the integral of this peak and those of the aromatic ones, the molecular weight of the polymer is calculated to be ~8 270, which is consistent with the result (M_n = 8 130) by the GPC analysis (Table 1, no. 1).

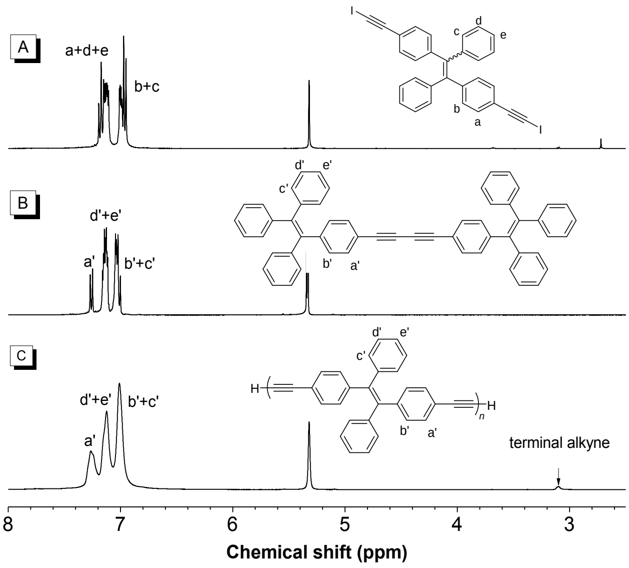


Fig. 3 ^{1}H NMR spectra of (A) **1**, (B) **7** and (C) P**1** (Table 1 no. 1) in dichloromethane-d_2.

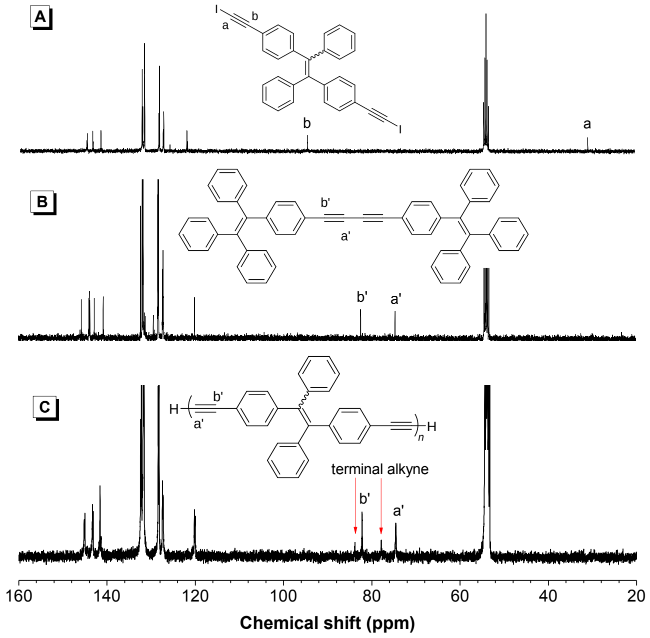


Fig. 4 ^{13}C NMR spectra of (A) **1**, (B) **7** and (C) P**1** (Table 1 no. 1) in dichloromethane-d_2.

The structure of the resulting polymer is further verified by ^{13}C NMR spectroscopy (Fig. 4). The peak representing the "a" carbon of the triple bond experiences a large shift from 30.7 ppm in **1** to 74.5 ppm in **7** and P**1**. Meanwhile, the "b" carbon of the triple bond shifts to higher field due to the formation of 1,3-diyne unit (from 94.5 ppm to 82.4 ppm). The end groups of P**1** are also proven to be terminal alkynes, as suggested by the resonance peaks observed at 77.8 and 83.8 ppm. Other peaks corresponding to the resonances of the phenyl rings and C=C double bond of the TPE unit inherited from the monomers are also observed. These results demonstrate the precise structure of the polymer and are well consistent with the results from the IR and ^{1}H NMR analyses.

Thermal stability

Thermogravimetric analysis (TGA) was employed to evaluate the thermal stability of the polymers. Thanks to their aromatic structure and 1,3-diyne unit, all the polymers show high thermal stability, losing merely 5 % of their weight at high temperatures of up to 352 °C (Fig. 5). Moreover, P**1** retains 60% of its weight after being heated to 800 °C. The high mass preservation suggests the potential application of P**1** as ceramic material.

Light refraction

Polymers with high refractive indices (RI or *n*) are promising candidate materials for photonic applications. Particularly, polymers whose RI can be manipulated by light irradiation are useful in permanent data storage and holographic recording. P**1** shows good film-forming ability and can be fabricated into tough thin film by spin coating its dichloroethane solution onto a silica substrate for RI measurement. As shown in Fig. 6, P**1** shows high RI value of 2.1125–1.7747 in a wide wavelength range of 400–900 nm. The RI value at 632.8 nm is 1.8070, which is much higher than those of many commercial optical plastics

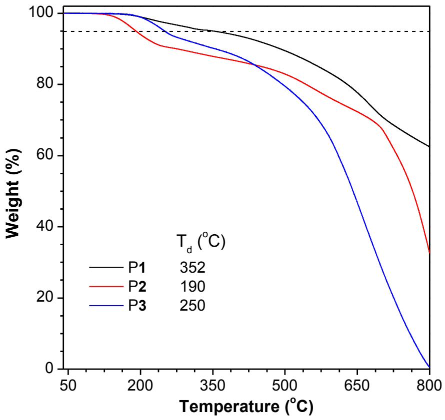


Fig. 5 TGA thermograms of P**1**–**3** recorded under nitrogen at a heating rate of 10 °C/min.

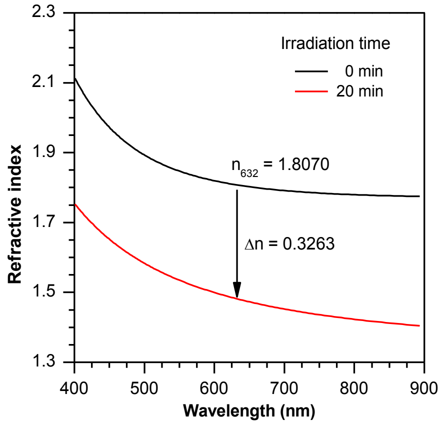


Fig. 6 Wavelength dependence of refractive indices of thin film of P**1** before and after UV irradiation.

at the same value. Such a high RI value may result from its high aromatic content and conjugation along the polymer backbone. Interestingly, P**1** is photosensitive. After exposing its thin film to UV light for 20 min, the RI value drops significantly to 1.7524–1.4044 in the wavelength range of 400-900 nm and decreases by 0.3263 at 632.8 nm.

Chromatic Dispersion

Chromatic dispersion (*D*) describes the optical frequency dependence or variation of the RI of a material with wavelength. Polymers with small *D* values are promising for optical applications to reduce chromatic aberration, while those with large *D* values may lead to unfavorable effect such as decreased image resolution. The Abbé number (ν_D) is a parameter used to measure the variation or dispersion in RI of a material with wavelength and is defined as (n_D−1)/(n_F−n_C), where n_D, n_F and n_C are the RI values at Fraunhofer D, F and C lines of 589.2, 486.1 and 656.3 nm, respectively. As shown in Table 6, the ν_D values of P**1** before and after UV irradiation are 7.4 and 3.9, respectively and the corresponding *D* values (the reciprocal of ν_D) are around 0.135 and 0.259, respectively. The RI values and the Abbé numbers of P**1** are quite low compared with many advanced organic materials, indicating that P**1** is a potential material for optical applications.

Table 6 Refractive indices and chromatic dispersions of P**1**[a]

Irradiation time	$n_{632.8}$	ν_D	D
0 min	1.8070	7.4	0.135
20 min	1.4807	3.9	0.259

[a] Abbreviation: n = refractive index, ν_D = Abbé number = $(n_D-1)/(n_F-n_C)$, where n_D, n_F and n_C are the RI values at wavelengths of 589.2, 486.1 and 656.3 nm, respectively, D = chromatic dispersion = $1/\nu_D$.

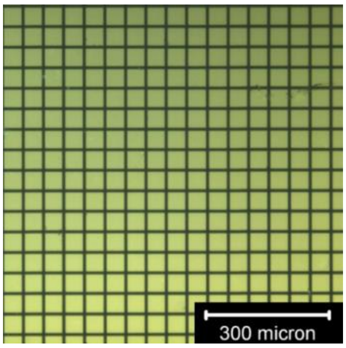


Fig. 7 Fluorescent photopattern generated by UV irradiation of P**1**. The photograph was taken under UV light illumination (330–385 nm).

Photopatterning

Fluorescent photopatterns are in urgent need in a variety of applications such as photonic and electronic devices and biological sensing and probing. Thanks to its good film-forming ability, light-emitting TPE unit and photosensitivity, P**1** was utilized to generate luminescent photopattern by photolithography. The thin film of P**1** prepared by solution spin-coating was subjected to irradiation with UV light in air for 20 min through a copper photomask. The unexposed region remains emissive (squares), while the fluorescence of the exposed regions was quenched (lines), presumably due to the photo-oxidation reaction. Thus, a fluorescent pattern with high resolution and sharp edges was observed under a fluorescence microscope (Fig. 7).

Conclusions

In this work, we developed a transition metal-free polymerization route to functional polydiynes from haloalkyne-based organic reaction. Mediated by an inexpensive additive of KI under nitrogen at 120 °C, the polymerizations of bis(haloalkyne)s proceed well, generating polydiynes in a short period of time in moderate to satisfactory yields. All the polymers are thermally stable with high degradation temperatures. Among the three polymers, only P**1** possesses good solubility in common organic solvents. It can form tough thin film which shows high, UV-tunable refractive indices ($n = 2.1125–1.7747$) in a wide range of wavelength (400–900 nm). A well-defined fluorescent photopattern of P**1** was acquired under UV light through photolithography process. Thus, the present result provides a facile and straightforward approach for the synthesis of conjugated polymers with extraordinary optical properties and high thermal stability.

Experimental section

General information

Diyne **4** and monoyne **8** were synthesized according to previous published procedures, while compound **5** and **6** were prepared by using the literature methods.[46,48] All other reagents used for monomer synthesis and polymerization reactions were purchased from Aldrich and used as received without further purification. DMF used for the polymerization was purchased from J&K with molecular sieves in the sealed bottle. Other solvents including DMSO, 1,4-dioxane, *o*-xylene and methanol were purchased from Aldrich.

Weight- (M_w) and number-average (M_n) molecular weights and polydispersities (M_w / M_n) of the polymers were estimated by a Waters gel permeation chromatography (GPC) system equipped with a Waters 515 HPLC pump, a set of Styragel columns (HT3, HT4 and HT6; molecular weight range: 10^2 to 10^7), a column temperature controller, a Waters 486 wavelength-tunable UV-vis detector and a Waters 2414 differential refractometer. The polymers were dissolved in THF (~ 1 mg·mL^{-1}) and filtered through 0.45 µm PTFE syringe-type filters before being injected into the GPC system. THF was used as an eluent at a flow rate of 1.0 mL·min^{-1}. The column temperature was maintained at 40 °C and the working wavelength of the UV-vis detector was set at 254 nm. A set of monodispersed polystyrene standards (from Waters) covering the molecular weight range of 10^3 to 10^7 were used for the molecular weight calibration. IR spectra were recorded on a Perkin-Elmer 16 PC FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on Bruker ARX 400 NMR spectrometers using DCM-d_2 as solvent. High resolution mass spectra (HRMS) were recorded on a GCT Premier CAB 048 mass spectrometer operated in a MALDI-TOF model. Single crystal X-ray diffraction intensity data was recorded at room temperature on a Bruker-Nonices Smart Apex CCD diffractometer with graphite-monochromated Mo K$_\alpha$ radiation. Processing of the intensity data was carried out through the SAINT and SADABS routines and the structure and refinement were obtained by employing the SHELTL suite of X-ray programs (version 6.10). Thermogravimetric analyses (TGA) were conducted under nitrogen on a Perkin-Elmer TGA 7 analyzer at a heating rate of 10 °C·min^{-1}. Refractive indices (RI or *n*) were determined on a J A Woollam Variable Angle Ellipsometry System with a wavelength tunability from 400 to 900 nm. Photopatterning of the polymer film was conducted on a Spectroline ENF-280C/F UV lamp at a distance of 3 cm as light source. The incident light intensity was ∼18.5 mW·cm^{-2}. The films for RI measurement and photopattern were prepared by spin-coating the polymer solution (10 mg of P**1** in 1 mL of 1,2-dichloroethane) at 1000 rpm for 1 min on a silicon wafer. The polymer film was dried in a vacuum oven at room temperature overnight. The pattern was generated by UV irradiation of the polymer film through copper photomask for 20 min. The photo was taken on an optical microscope (Olympus BX 41) under a UV light source.

Monomer synthesis

Into a round-bottom flask was dissolved diyne **4** (5.0 mmol, 1.90 g) in methanol (30 mL). The mixture was cooled to 0 °C and 1.40 g (25.0 mmol) of KOH was then added. After stirring at 0 °C for 30 min, NIS (12.5 mmol, 2.81 g) was added. The reaction mixture was further stirred at 0 °C for 15 min. The ice bath was removed and the reaction mixture was stirred at room temperature for another 1 h. The reaction mixture was extracted by DCM and brine for 3 times. The organic layer was collected, dried over $MgSO_4$, filtered and evaporated. The crude product was purified by silica gel column chromatography using hexane/DCM as eluent to give monomer **1** as a pale yellow solid (2.88 g, 91%). IR (KBr), v (cm^{-1}): 3076, 3053, 3026, 2956, 2925, 2853, 2166, 1946, 1914, 1705, 1597, 1495, 1440, 1403, 1383. ^{1}H NMR (CD_2Cl_2, 400 MHz), δ (ppm): 7.21–7.12 (m, 10H), 7.02–6.97 (m, 8H). ^{13}C NMR (CD_2Cl_2, 100 MHz), δ (ppm): 144.82, 144.71, 143.47, 143.37, 141.60, 132.23, 132.09, 131.67, 131.65, 128.42, 128.27, 127.42, 127.29, 125.90, 122.04, 121.89, 94.56, 30.64. HRMS (MALDI-TOF): *m/z* 631.9492 (M$^+$, calcd 631.9498).

Monomers **2** and **3** and compound **9** were prepared by the same procedures using compounds **5**, **6** and **8** as starting materials. Below were their characterization data.

Monomer **2**. IR (KBr), v (cm^{-1}): 3034, 2160, 1905, 1657, 1501, 1484, 1401, 1363, 1232, 1118, 1102, 1059, 1016. ^{1}H NMR (CD_2Cl_2, 400 MHz), δ (ppm): 7.38 (s, 4H). ^{13}C NMR (CD_2Cl_2, 100 MHz), δ (ppm): 132.55, 132.47, 132.28, 124.01, 93.68, 29.50. HRMS (MALDI-TOF): *m/z* 377.8407(M$^+$, calcd 377.8402).

Monomer **3**. IR (KBr), v (cm^{-1}): 3033, 2158, 1694, 1660, 1598, 1552, 1537, 1488, 1393, 1377, 1221, 1108, 1006. ^{1}H NMR (CD_2Cl_2, 400 MHz), δ (ppm): 7.57–7.56 (4H), 7.52–7.50 (4H). ^{13}C NMR (CD_2Cl_2, 100 MHz), δ (ppm): 140.72, 133.14, 132.94, 127.25, 127.17, 123.03, 94.02, 30.23. HRMS (MALDI-TOF): *m/z* 453.8702 (M$^+$, calcd 453.8715).

Compound **9**. IR (KBr), v (cm^{-1}): 3052, 3021, 2160, 1951, 1598, 1573, 1503, 1489, 1442, 1403, 1181, 1154, 1109, 1072, 1029, 1019. ^{1}H NMR (CD_2Cl_2, 400 MHz), δ (ppm): 7.20–7.18 (2H), 7.16–7.14 (9H), 7.07–7.05 (6H), 7.03–7.01 (2H). ^{13}C NMR (CD_2Cl_2, 100 MHz), δ (ppm): 142.27, 140.47, 131.92, 131.58, 131.54, 131.50, 128.16, 128.12, 128.02, 127.07, 126.97, 126.94, 121.45, 94.38, 31.95. HRMS (MALDI-TOF): *m/z* 482.0529 (M$^+$, calcd 482.0531).

Synthesis of model compound 7

Into a 50 mL Schlenk tube equipped with a stirring bar were added compound **9** (0.8 mmol, 386 mg) and KI (1.6 mmol, 265 mg). The Schlenk tube was then vacuumed and purged with nitrogen for 3 times. DMF (5 mL) was injected into the tube using a hypodermic syringe. The resulting mixture was stirred at 120 ^{o}C for 6 h under nitrogen environment. The reaction mixture was then cooled to room temperature, extracted with DCM and washed with brine for 3 times. The organic layer was collected, dried over $MgSO_4$, filtered and evaporated. The crude product was purified using silica gel column chromatography using hexane/DCM mixture as eluent to give model compound **7** as yellow solid (150 mg, 53 %). IR (KBr), v (cm^{-1}): 3074, 3053, 3025, 2923, 2853, 2196, 2146, 1949, 1630, 1598, 1491, 1443, 1403. ^{1}H NMR (CD_2Cl_2, 400 MHz), δ (ppm): 7.30 (d, 4H), 7.19–7.14 (m, 18H), 7.07–7.03 (m, 16H). ^{13}C NMR (CD_2Cl_2, 100 MHz), δ (ppm): 145.13, 143.43, 143.30, 143.18, 142.12, 140.08, 131.74, 131.37, 131.23, 131.15, 131.12, 127.83, 127.76, 127.64, 126.77, 126.63, 126.61, 119.34, 81.75, 73.92. HRMS (MALDI-TOF): *m/z* 710.2954 (M$^+$, calcd 710.2974).

Polymerization

All the polymerization reactions were carried out under nitrogen flow in Schlenk tube. A typical procedure for the polymerization of **1** under optimized conditions is given below as an example (Table 2, no. 3). In a 10 mL Schlenk tube with a two-way stopcock on the sidearm were charged with **1** (0.2 mmol, 126.4 mg) and KI (0.4 mmol, 66.4 mg) under nitrogen. After vacuum and purge with nitrogen for 3 cycles, 2 mL of DMF was injected into the tube using a hypodermic syringe. The resulting mixture was stirred at 120 ^{o}C for 6 h under nitrogen flow. Afterwards, the solution was added dropwise into 100 mL of methanol via a cotton filter under stirring. The precipitate was collected by centrifugation, washed with hexane and dried under vacuum at room temperature to a constant weight. A brownish yellow powder of polymer P**1** was obtained in 72% yield. M_w 20 100; M_w/M_n 2.4. IR (KBr), v (cm^{-1}): 3077, 3053, 3025, 2959, 2923, 2191, 2142, 1946, 1911, 1641, 1598, 1492, 1441, 1403, 1384. ^{1}H NMR (CD_2Cl_2, 400 MHz), δ (ppm): 7.26, 7.12, 7.01, 3.10. ^{13}C NMR (CD_2Cl_2, 100 MHz), δ (ppm): 145.19, 145.03, 143.30, 143.14, 141.60, 132.38, 132.19, 131.77, 131.64, 128.40, 128.21, 127.45, 127.27, 120.22, 120.02, 83.81, 82.19, 77.86, 74.63.

P**2**: yield 53%. No characterization could be done due to the insolubility of the polymer.

P**3**: yield 44%. No characterization was done as the polymer was insoluble.

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Table of Contents Entry

Construction of Functional polydiynes by transition metal-free homo-polycoupling of bis(iodoalkyne)s.