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Transition-Metal-Free Multicomponent Polyannulations of Dimethyl Sulfoxide, Amines, and Aldehydes toward Poly(phenylquinoline)s

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Electronic Supplementary Information

Abstract Dimethyl sulfoxide (DMSO) possessing strong solvency and high boiling point is a very important aprotic polar solvent in organic and polymer synthesis. Notably, it is also a useful synthon in organic chemistry. However, the direct incorporation of DMSO in polymer synthesis remains challenging. In this work, DMSO was successfully converted to nitrogen-containing heterocyclic polymers as a monomer *via* multicomponent polymerizations (MCPs) with dialdehydes and diamines in the presence of $K_2S_2O_8$/*t*-BuOK at 120 °C in 6 h. A series of poly(phenylquinoline)s with high M_w values (up to 5.11×10^4) were obtained in satisfactory yields (up to 82%), performing good solubility, good thermal and morphological stability as well as excellent film-forming ability. The thin films of poly(phenylquinoline)s exhibit high refractive index value in a wide wavelength range of 400–1700 nm. Thus, this work not only enriches the family of MCPs but also provides an efficient strategy for the conversion of DMSO into functional polymeric materials that are potentially applicable in diverse areas.

Keywords Transition-Metal-Free; Multicomponent polymerization; Poly(phenylquinoline)s

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INTRODUCTION

A solvent is generally a liquid capable of dissolving a solid, liquid, or gaseous solute without causing a chemical reaction with the solute, the function of which is not limited to dissolution, preservation, separation, purification, or reaction. It is essential for the development of life sciences, medicine, agriculture, materials, and chemistry, particularly synthetic chemistry. The solvent properties often determine the success or failure of the reaction. Common solvents include water, alcohols, haloalkanes, amides, nitriles, and suloxides.

In addition to being the solvent of the reaction, some solvents can also participate in the reaction as synthons and even in polymerization reactions to prepare functional polymers with complex structures.[1−7] For example, water is a very good monomer in some polymerizations. Qin and coworkers established a multicomponent polymerization (MCP) of water, diisocyanides, and bis(bromoalkyne) to prepare polyamides with good stereoregularity.[8] They also developed an MCP of water, isocyanides, and chlorooximes under simulated physiological conditions (in phosphate-buffered saline) to prepare functional polyamides.[9] Tang and coworkers prepared a luminescent polymer film *via* the interfacial polymerization of water and trifunctional ester-activated alkynes in the presence of bicyclo[2.2.2]-1,4-diazaoctane (DABCO).[10] In addition to water, some organic solvents can also be used as monomers in polymerization reactions. Matyjaszewski and coworkers used trimethysilyl trifluoromethanesulfonate to initiate the ring-opening polymerization of tetrahydrofuran (THF).[11] Zheng and coworkers realized a *t*-BuOK-catalyzed multicomponent polymerization (MCP) of chloroform ($CHCl_3$), elemental sulfur (S_8) and diamine to prepare functional polythiourea via sequential reactions of isothiocyanation and nucleophilic addition.[12] Hu and coworkers used another haloalkane solvent, dichloromethane (CH_2Cl_2), as a monomer to polymerize with S_8 and aromatic amines to prepare functional aromatic polythioureas with the assistance of fluoride.[13] Cong and coworkers developed a Cu(II)-catalyzed “one-pot, two-step, three-component” tandem polymerization of CS_2, amines and 2-iodoaniline for the efficient preparation of fused-heterocyclic polybenzothiazoles.[14] It is important to use solvents as monomers to prepare functional polymers because of their low cost, abundant sources, and diverse structures.

Dimethyl sulfoxide (DMSO) is a sulfur-containing, colorless, odorless transparent liquid at room temperature. Possessing high polarity, high boiling point, good thermal stability, aprotic property, and water miscibility, DMSO can be dissolved in ethanol, propanol, benzene, chloroform, and most other or-

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ganic matter, known as "universal solvent".[15] Because of its unique chemical structure, DMSO was used as a synthon for many well-known small molecular reactions, such as nucleophilic substitution,[16] elimination,[17] electrophilic,[18] and substitution reactions.[19] With the recent trend in polymer chemistry of using common solvents as monomers to prepare functional polymers and the rich chemical properties of DMSO, could DMSO be used as a comonomer to construct polymers with unique structures and advanced functionalities?

Recently, Liu and coworkers reported that arylamines, arylaldehydes, and DMSO could undergo a multicomponent reaction to afford 3-arylquinolines in high yield *via* annulation.[20] Inspired by this efficient small molecular reaction and our previous work on MCP,[21,22] in this work, DMSO was utilized successfully as a monomer to realize transition-metal-free multicomponent polyannulations with dialdehydes and diamines in the presence of $K_2S_2O_8$/*t*-BuOK. A series of ring-fused polymers, poly(phenylquinoline)s (PPQs), with high M_w values (up to 5.11×10^4), were obtained in satisfactory yields (up to 82%) (Fig. 1a). The resulting PPQs exhibited good solubility, thermal stability, and morphological stability.

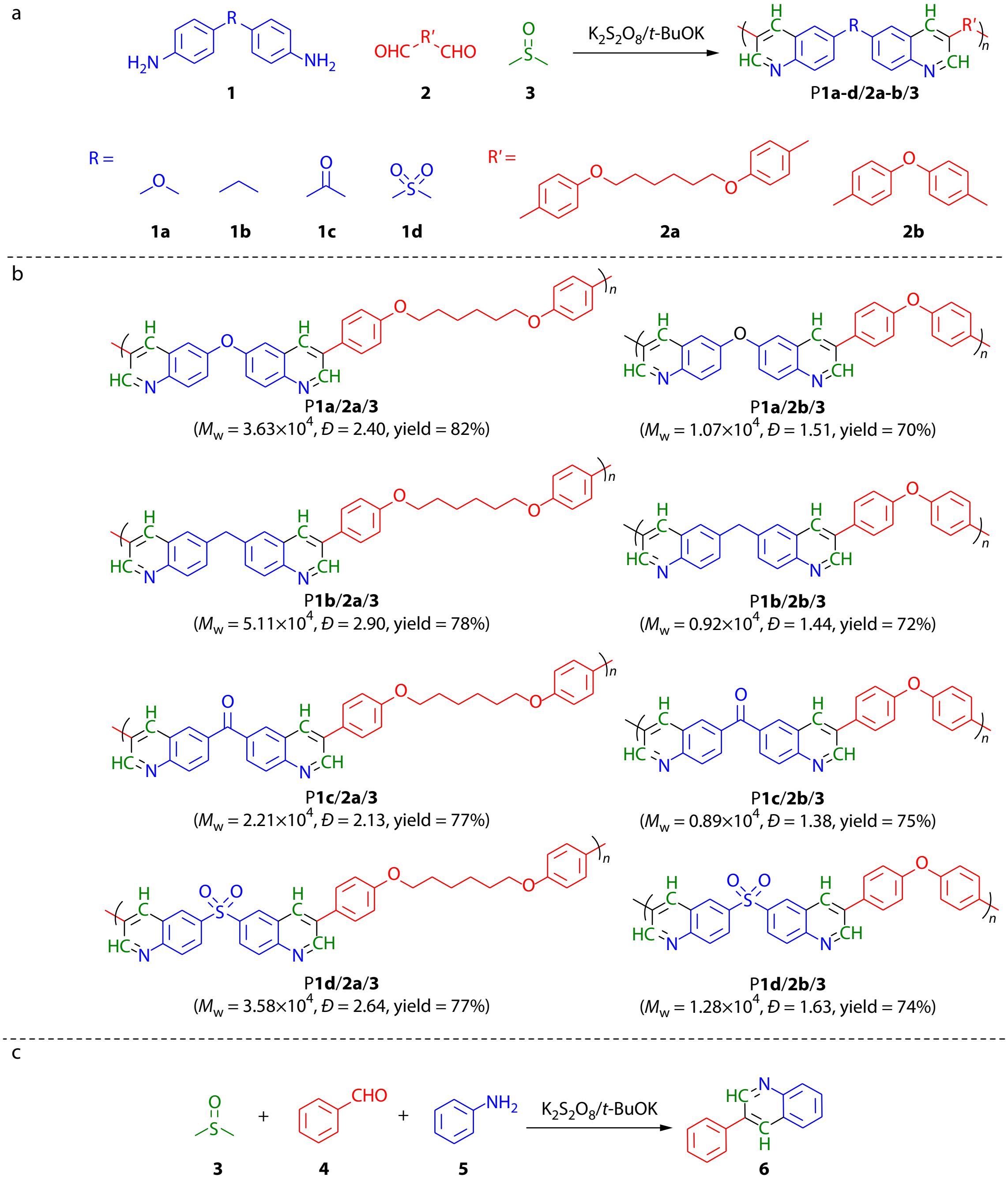


Fig. 1 (a) MCP of diamines **1**, dialdehydes **2**, and DMSO. (b) Chemical structures and polymerization results of PPQs. M_ws are determined by GPC in DMF based on PMMA standard samples. (c) Synthetic routes to model compound **6**.

In addition, the PPQs showed excellent film-forming ability, and their thin films showed high refractive index values (n589 nm to 1.7795).

EXPERIMENTAL

Materials

Benzaldehyde, aniline, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenylmethane, extra dry dimethyl sulfoxide (DMSO), extra dry *N*,*N*-dimethylformamide (DMF), 4,4'-diaminobenzophenone, 4,4'-diaminodiphenyl sulfone, 1,6-dibromohexane, *p*-hydroxybenzaldehyde, ammonium chloride, potassium carbonate, and potassium peroxodisulfate were obtained from Energy Chemicals. 4,4'-Oxydibenzaldehyde was obtained from Bide Pharmatech Ltd. Methanol, chloroform, and ethyl acetate were purchased from Chron Chemical. All the chemicals and reagents were used as received without further purification.

Instruments

^{1}H- and ^{13}C-NMR spectra were measured on a Bruker AV 500 spectrometer in DMSO-d_6 using tetramethylsilane (TMS) as an internal reference. FTIR spectra were recorded on a PerkinElmer Spectrum 3 FTIR Spectrometer as thin films on the KBr pellets. Thermogravimetric analysis was carried out on a Netzsch STA 449 F3 instrument under a nitrogen atmosphere at a heating rate of 20 °C/min. The weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity index ($Đ$) of the polymers were evaluated using a Waters 1515 Associates gel permeation chromatography (GPC) system equipped with an RI detector. DMF treated with LiBr was used as a solvent to dissolve the polymers (~5 $mg \cdot mL^{-1}$). The solutions were filtered through 0.22 μm PTFE syringe-type filters before being injected into the GPC system, and DMF treated with LiBr was used as the eluent at a flow rate of 1.0 $mL \cdot min^{-1}$. A set of linear polymethyl methacrylate (PMMA) standards (Waters) covering the M_w range of 10^3–10^7 was utilized for M_w and PDI calibration. The refractive indices of the polymers were measured on a J. A. Woollam V-VASE variable-angle ellipsometry system in the range of 400–1700 nm. The thin films of polymers for refractive index measurements were prepared by spin coating dichloromethane solutions of the polymers (30 $mg \cdot mL^{-1}$) on clean silicon slices using an EZ4 Spin Coater.

Monomer Synthesis

The monomer **2a** was synthesized according to our previously published paper.[23] Monomer **1a**, **1b**, **1c**, **1d**, **2b** and **3** were purchased from Energy Chemical and used as received without further purification.

Model Compound

A 10 mL reaction tube equipped with a magnetic stirrer was capped with a rubber plug and placed with *t*-BuOK (2.0 mmol, 224.4 mg), and $K_2S_2O_8$ (1.0 mmol, 270.3 mg). After removing the air with N_2, a mixture of benzaldehyde (0.75 mmol, 79.6 mg), aniline (0.5 mmol, 46.6 mg) and DMSO (2.0 mL) was injected into the reaction tube. The reaction mixture was then stirred at 150 °C for 2 h. After completion of the reaction, the mixture was cooled to room temperature and extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with an aqueous saturated brine solution (10 mL), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude products were separated by flash column chromatography (eluent:15:1 petroleum ether (PE)/ethyl acetate (EA)) on silica gel to obtain the desired products in 70% yield (72 mg). Yellow oil; FTIR (KBr), ν (cm^{-1}): 1640, 1491, 1187, 1122, 1027, 902, 783, 761, 697; ^{1}H-NMR (DMSO-d_6), δ (TMS, ppm): 9.26 (s, 1H), 8.66 (s, 1H), 8.07 (s, 2H), 7.90 (d, 2H), 7.78 (t, 1H), 7.65 (t, 1H), 7.56 (m, 2H), 7.47 (t, 1H). ^{13}C-NMR (125 MHz, DMSO-d_6), δ (TMS, ppm): 149.49, 146.82, 137.11, 132.89, 129.57, 129.28, 128.68, 128.46, 128.29, 127.69, 127.32, 127.06, 124.90.

Polymerization

A typical procedure for the synthesis of P**1a/2a/3** is provided below. A 10 mL reaction tube equipped with a magnetic stirrer was capped with a rubber plug and placed with **1a** (20.0 mg, 0.1 mmol), **2a** (32.6 mg, 0.1 mmol), *t*-BuOK (0.8 mmol, 89.8 mg) and $K_2S_2O_8$ (0.4 mmol, 108.1 mg). After removing the air with N_2, 2 mL of DMSO was injected into the tube using a hypodermic syringe, and the resultant solution was stirred for 6 h at 120 °C. After cooling to room temperature, the reaction mixture was diluted with 2 mL DMSO and centrifuged. The liquid supernatant was added dropwise to 200 mL of methanol using a cotton file under stirring. The precipitate was allowed to stand overnight and was collected by filtration. The polymer was washed with methanol and dried to a constant weight under vacuum at room temperature.

Characterization data of P**1a/2a/3**. A brown solid was obtained in 82% yield; M_w: 3.63×10^4; $Đ$: 2.40. FTIR (KBr), ν (cm^{-1}): 2924, 2863, 1598, 1496, 1303, 1238, 1171, 1112, 1008, 949, 829, 519. ^{1}H-NMR (500 MHz, DMSO-d_6), δ (TMS, ppm): 9.28 (s, CH), 7.98–6.69 (Ar—H), 3.96 (s, OCH_2), 1.70 (s, CH_2), 1.44 (s, $C\underline{H}_2$). ^{13}C-NMR (125 MHz, DMSO-d_6), δ (TMS, ppm): 149.48, 134.62–125.96, 113.73, 67.07, 28.03, 24.55.

Characterization data of P**1a/2b/3**. A black solid was obtained in a 70% yield. M_w: 1.07×10^4. $Đ$: 1.51. FTIR (KBr), ν (cm^{-1}): 3343, 3035, 1591, 1495, 1233, 1162, 1100, 1008, 872, 832, 616, 505. ^{1}H-NMR (500 MHz, DMSO-d_6), δ (TMS, ppm): 9.29 (s, CH), 7.96–6.09 (Ar—H). ^{13}C-NMR (125 MHz, DMSO-d_6), δ (TMS, ppm): 135.65–125.68, 123.71–113.17.

Characterization data of P**1b/2a/3**. A black solid was obtained in a 78% yield. M_w: 5.11×10^4. $Đ$: 2.90. FTIR (KBr), ν (cm^{-1}): 3359, 2928, 2858, 1600, 1507, 1245, 1171, 1116, 1014, 829, 628, 514. ^{1}H-NMR (500 MHz, DMSO-d_6), δ (TMS, ppm): 9.27 (s, $C\underline{H}$), 7.86–6.49 (Ar-$\underline{H}$), 3.92 (s, $OC\underline{H}_2$), 1.69 (s, CH_2), 1.44 (s, $C\underline{H}_2$). ^{13}C-NMR (125 MHz, DMSO-d_6), δ (TMS, ppm): 133.49–126.62, 114.86, 67.83, 48.73, 28.97, 25.68.

Characterization data of P**1b/2b/3**. A brown solid was obtained in a 72% yield. M_w: 9200. $Đ$: 1.44. FTIR (KBr), ν (cm^{-1}): 3344, 3028, 2912, 1597, 1495, 1236, 1165, 1011, 867, 829, 619, 511. ^{1}H-NMR (500 MHz, DMSO-d_6), δ (TMS, ppm): 9.27 (s, CH), 7.99–6.46 (Ar—H). ^{13}C-NMR (125 MHz, DMSO-d_6), δ (TMS, ppm): 135.37–124.08, 122.48–114.39.

Characterization data of P**1c/2a/3**. A black solid was obtained in a 77% yield. M_w: 2.21×10^4. $Đ$: 2.13. FTIR (KBr), ν (cm^{-1}): 3356, 2923, 2850, 1597, 1507, 1470, 1245, 1168, 1007, 829, 764, 511. ^{1}H-NMR (500 MHz, DMSO-d_6), δ (TMS, ppm): 9.30 (s, CH), 7.89–6.15 (Ar—H), 3.93 (s, OCH_2), 1.70 (s, CH_2), 1.45 (s, CH_2). ^{13}C-NMR (125 MHz, DMSO-d_6), δ (TMS, ppm): 173.09, 134.81–126.34, 114.86, 67.83, 28.97, 25.68.

Characterization data of P**1c/2b/3**. A purple solid was obtained in a 75% yield. M_w: 8900. $Đ$: 1.38. FTIR (KBr), ν (cm^{-1}):

3351, 3043, 1594, 1498, 1236, 1165, 1011, 924, 835, 767, 687, 508. ^{1}H-NMR (500 MHz, DMSO-d$_6$), δ (TMS, ppm): 9.34 (s, CH), 7.94–6.58 (Ar—H). ^{13}C-NMR (125 MHz, DMSO-d$_6$), δ (TMS, ppm): 138.85–125.02, 123.52–115.24.

Characterization data of **P1d/2a/3**. A black solid was obtained in a 77% yield. M_w: 3.58×10^4. $Đ$: 2.64. FTIR (KBr), v (cm^{-1}): 3351, 2919, 2858, 1594, 1504, 1304, 1242, 1146, 1103, 1020, 829, 548. ^{1}H-NMR (500 MHz, DMSO-d$_6$), δ (TMS, ppm): 9.28 (s, CH), 7.99–6.23 (Ar—H), 3.94 (s, OCH$_2$), 1.71 (s, CH$_2$), 1.45 (s, CH$_2$). ^{13}C-NMR (125 MHz, DMSO-d$_6$), δ (TMS, ppm): 151.96, 132.70–125.22, 113.61, 66.98, 29.31, 24.27.

Characterization data of **P1d/2b/3**. A black solid was obtained in a 74% yield. M_w: 1.28×10^4. $Đ$: 1.63. FTIR (KBr), v (cm^{-1}): 3351, 2912, 1590, 1498, 1411, 1310, 1242, 1125, 1032, 952, 832, 616. ^{1}H-NMR (500 MHz, DMSO-d$_6$), δ (TMS, ppm): 9.28 (s, CH), 7.95–6.14 (Ar—H). ^{13}C-NMR (125 MHz, DMSO-d$_6$), δ (TMS, ppm): 135.08–123.93, 123.33–113.83.

RESULTS AND DISCUSSION

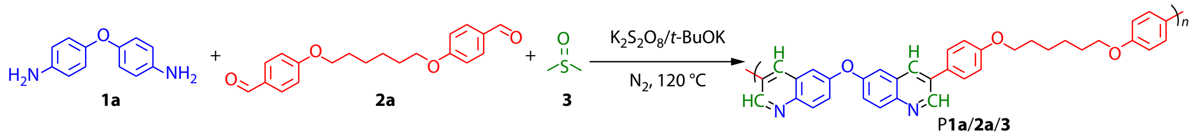
Multicomponent Polymerization

DMSO, diamine (**1a**–**1d**) and dialdehyde (**2b**) were commercially available at low cost, and dialdehyde **2a** was prepared using a simple Williams ether synthesis method. According to our experience in the development of new polymerizations, the conditions for organic reactions are not fully suitable for polymerization. Thus, to obtain polymers with a high M_w in high yields, we systematically investigated the polymerization conditions using commercially available diamines **1a**, **2a**, and DMSO as model monomers (Fig. 1). Considering that DMSO is a common and inexpensive organic solvent, we chose DMSO as the solvent for the following experiments.

According to a literature report,[20] a small molecule reaction was conducted at 150 °C to afford arylquinolines, which resulted in high energy consumption, therefore, we decided to investigate the effect of temperature first. As shown in Table 1, entries 1–6, polymerization was greatly affected by temperature. When the temperature was lower than 80 °C, no product was obtained (Table 1, entry 1). Both yield and M_w increased dramatically with increasing temperature (entries 2–5). However, when the temperature was set to 130 °C, an insoluble product was obtained, which impeded the characterization of the products (entry 6). Thus, 120 °C was selected as the optimal temperature.

Next, we followed the time course of polymerization. As listed in Table 1, entries 7–14, in the first 6 h, with a gradual increase in the reaction time, the yield and M_w of the polymer increased correspondingly from 49% to 79% and 1.45×10^4 to 3.2×10^4 (entries 7–9), respectively. Subsequently, the yield and M_w values stabilized. When the reaction time was pro-

Table 1 Optimization of polymerization conditions for **1a**, **2a** and **3**.^{a}



Entry	[M] (mol/L)	[$K_2S_2O_8$] (equiv.)	t (h)	T (°C)	S^b	yield (%)	$M_w{}^c \times 10^{-4}$	$Đ^c$
				Screening of temperature				
1	0.05	4	6	70	–	–	–	–
2	0.05	4	6	80	√	19	1.51	1.52
3	0.05	4	6	100	√	59	2.50	2.26
4	0.05	4	6	110	√	69	2.61	2.30
5	0.05	4	6	120	√	82	3.63	2.62
6	0.05	4	6	130	×	–	–	–
				Screening of time				
7	0.05	4	4	120	√	49	1.45	1.74
8	0.05	4	5	120	√	65	2.59	2.17
9	0.05	4	6	120	√	79	3.23	2.63
10	0.05	4	7	120	√	79	3.20	2.60
11	0.05	4	8	120	√	81	3.41	2.61
12	0.05	4	10	120	√	80	3.43	2.62
13	0.05	4	12	120	√	81	3.44	2.62
14	0.05	4	24	120	√	82	3.60	2.68
				Screening of monomer concentration				
15	0.025	4	8	120	√	35	1.12	1.53
16	0.05	4	8	120	√	79	3.42	2.61
17^d	0.1	4	8	120	Δ	76	2.61	2.16
				Screening of $K_2S_2O_8$/t-BuOK loading				
18	0.05	3	8	120	√	69	1.59	1.50
19	0.05	4	8	120	√	82	3.40	2.61
20^d	0.05	5	8	120	Δ	92	2.72	2.18
21	0.05	6	8	120	×	–	–	–

^{a} The polymerization was carried out under a N_2 atmosphere, [**1a**] = [**2a**], [t-BuOK] = 2[$K_2S_2O_8$]. ^{b} Solubility (S) tested in common organic solvents such as DMF and DMSO: × = insoluble; √ = completely soluble; Δ = partially soluble. ^{c} Determined by GPC with DMF as the eluent based on linear polymethyl methacrylate (PMMA) calibration. M_w = weight-average molecular weight; polydispersity index ($Đ$) = M_w/M_n. ^{d} The molecular weights belong to soluble fractions.

longed from 6 h to 24 h, both the yield and M_w of the resultant polymers increased inconspicuously (entries 10–14). Considering the M_w and yield of the products, 6 h was selected as the reaction time.

Third, the effect of monomer concentration on polymerization was investigated. As shown in Table 1, entries 15–17, the monomer concentration had a significant influence on the polymerization. When we halved the monomer concentration from 0.05 mol·L^{-1} to 0.025 mol·L^{-1}, the yields and M_w values decreased significantly from 79% to 35% and from 3.42×10^4 to 1.12×10^4 (entries 15 and 16), respectively. While we doubled the monomer concentration from 0.05 mol·L^{-1} to 0.1 mol·L^{-1}, the solubility of the resultant polymer became poor (entry 17). Thus, the monomer concentration was set as 0.05 mol·L^{-1} and used for further polymerization.

Subsequently, we monitored the influence of $K_2S_2O_8$ and *t*-BuOK loading on the polymerization. The molar ratio of the oxidizer ($K_2S_2O_8$) to the base (*t*-BuOK) was fixed at 1:2. By increasing the molar ratio of $K_2S_2O_8$ to monomers from 3 equiv. to 4 equiv., not only did the M_w values increase from 1.59×10^4 to 3.40×10^4, but the isolated yields also increased from 69% to 82% (entries 18, 19). However, further addition of the oxidizer resulted in products with poor solubilities (entries 20, 21). Thus, the molar ratio of $K_2S_2O_8$ to monomer of 4 equiv. is much more suitable.

With the optimized polymerization conditions in hand, we polymerized different monomers to verify the universality and diversity of the MCP. Various aromatic diamines **1a**–**1d** and aromatic dialdehyde **2a**–**2b** were designed as monomers for polymerization with DMSO (Fig. 1a). All monomer combinations in the polymerization proceeded smoothly, and soluble polymers with different chemical structures were obtained in good yields (70%–82%) with high molecular weights ranging from 8900 to 5.11×10^4 (Fig. 1b, Fig. S1 in the electronic supplementary information, ESI), indicating the universality and diversity of MCP. It is worth noting that aromatic amine monomers can obtain better polymerization results regardless of whether the benzene ring contains an electron-donating or electron-withdrawing group in the para position. On the other hand, because the flexible alkyl chain can enhance the solubility of PPQs, monomer **2a** with a long alkyl chain can obtain better polymerization results than monomer **2b** with a rigid structure. When phthalaldehyde was used as the dialdehyde monomer, an insoluble product was obtained because of its rigid structure.

Structural Characterization

To confirm the expected polymer structures of the PPQs, a small molecular model compound **6** was designed and synthesized under similar conditions (Fig. 1c). The Fourier transform infrared (FTIR), ^{1}H-, and ^{13}C-NMR spectra of the polymers were compared with those of the monomers and model compounds.

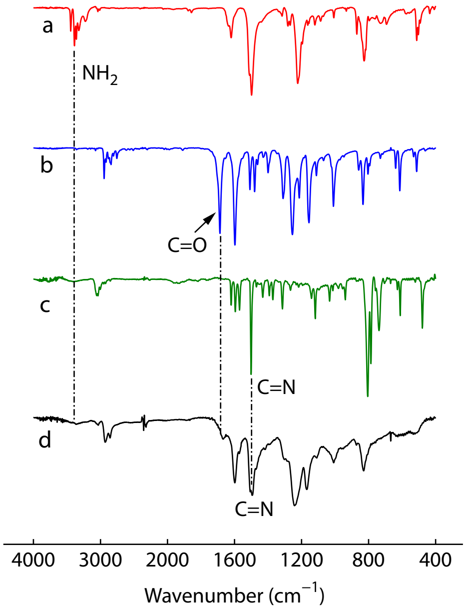


Fig. 2 FTIR spectra of (a) monomer **1a**, (b) monomer **2a**, (c) model compound **6**, and (d) polymer P**1a**/**2a**/**3**.

The FTIR spectra of model compound **6**, polymer P**1a/2a/3**, and their corresponding monomers **1a** and **2a** are shown in Fig. 2. The absorption band of **1a** associated with —NH$_2$ stretching vibration, was observed at 3387 cm^{-1}. The C=O stretching vibration of **2a** was observed at 1688 cm^{-1}. However, in the spectra of model compound **6** and P**1a/2a/3**, the C=O and —NH$_2$ stretching vibrations become very weak. Meanwhile, a new peak corresponding to the —C=N stretching vibration appeared at 1496 cm^{-1}. These results indicate that the transformation of aldehydes and amino groups in **1a** and **2a** and the formation of quinoline in P**1a/2a/3** occurred via polymerization. Similar results were obtained in the FTIR spectra of the other polymers (Figs. S2–S8 in ESI).

More detailed information regarding polymer structures can be obtained from NMR spectroscopy. Fig. 3 shows the ^{1}H-NMR spectra of model compound **6**, polymer P**1a/2a/3**, and their corresponding monomers **1a** and **2a**. The amino protons of **1a** and aldehyde protons of **2a** resonating at δ =4.80 and 9.97 could not be found in the spectra of model compound **6** and P**1a/2a/3**, respectively. Instead, new peaks at δ=9.26, assigned to the resonances of the newly formed quinoline group, appeared in the spectra of model compound **6** and P**1a/2a/3**.[24] These results suggest that PPQs were successfully obtained using this MCP. Similar results were obtained for the ^{1}H-NMR spectra of the other polymers (Figs. S9–S15 in ESI).

The ^{13}C-NMR spectra of **1a**, **2a**, model compound **6**, and P**1a/2a/3** further substantiated the conclusions drawn from the FTIR and ^{1}H-NMR spectra. The aldehyde carbon atom of monomer **2a**, which resonated at δ=193.42 could not found in the spectra of model compound **6** and P**1a/2a/3** (Fig. 4). Meanwhile, new peaks are found at δ=149.49, which are assignable to the resonances of the newly formed C=N group in the quinoline ring.[24] These results again confirm the transformation of the amino and aldehyde groups in **1a** and **2a**, the formation of quinoline in P**1a/2a/3**, and the success of the MCP. Similar results were obtained for the ^{13}C-NMR spectra of the other polymers (Figs. S16–S22 in ESI).

Plausible Polymerization Mechanism

Based on the literature,[20] a plausible polymerization mechanism for MCP was proposed (Scheme S1 in ESI). First, DMSO underwent disproportionation to provide dimethyl sulfide (DMS) and dimethyl sulfone (MSM) at a high temperature.[25] Meanwhile, **I** was formed by the condensation of aldehyde with DM-

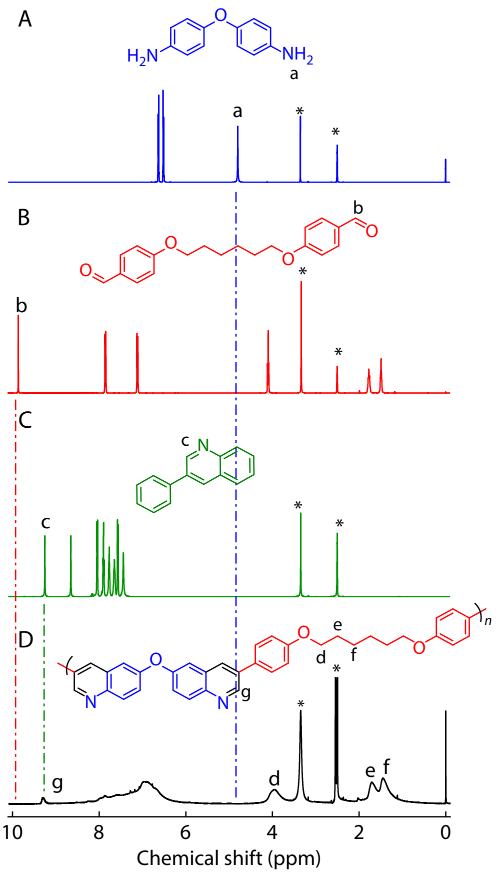


Fig. 3 ^{1}H-NMR spectra of (A) **1a**, (B) **2a**, (C) model compound **6**, and (D) polymer P**1a**/**2a**/**3** in DMSO-d$_6$. The solvent peaks are marked with asterisks.

SO, which was then reduced by DMS to form **II**.[26,27] Second, **III** was formed by the reaction of amine with DMSO in the presence of $K_2S_2O_8$.[28] Afterwards, **II** and **III** underwent a [4+2] cycloaddition to form **IV**. Subsequently, quinoline **V** is formed by the aromatization of **IV**. Repeating the above procedure generates PPQs in a step-growth manner.

Thermal Stability

Owing to the rigid aromatic groups in the polymer structures, the resulting PPQs are thermally stable. As evaluated by thermogravimetric analysis (TGA), the degradation temperatures (T_ds) of PPQs at 5% weight loss were in the high temperature range of 266–311 °C (Fig. 5). Moreover, because of the high content of rigid ring-fused structures, PPQs show high char yields (38.24%–66.79%) at 800 °C. P**2b**s, with more rigid structures, showed higher T_ds and char yields than P**2a**s. The morphological stability of the polymers was investigated using differential scanning calorimetry (DSC). The melting points (T_m) of the polymers were in the range 207–233 °C in the second heating scan (Fig. S23 in ESI). Owing to the existence of a flexible chain in P**2a**s, the melting points of P**2a**s are lower than those of P**2b**s. These results demonstrate that PPQs possess both high thermal and morphological stabilities.

Light Refractivity

High refractive index polymers (RI value $n \geq 1.6$) are materials that possess the unique ability to bend or refract light in a highly efficient manner. These polymers play a crucial role in various applications, including optical waveguides, photosensitive microlenses, high-performance complementary image sensors, and antireflective coatings.[29,30] Therefore, the design and syn-

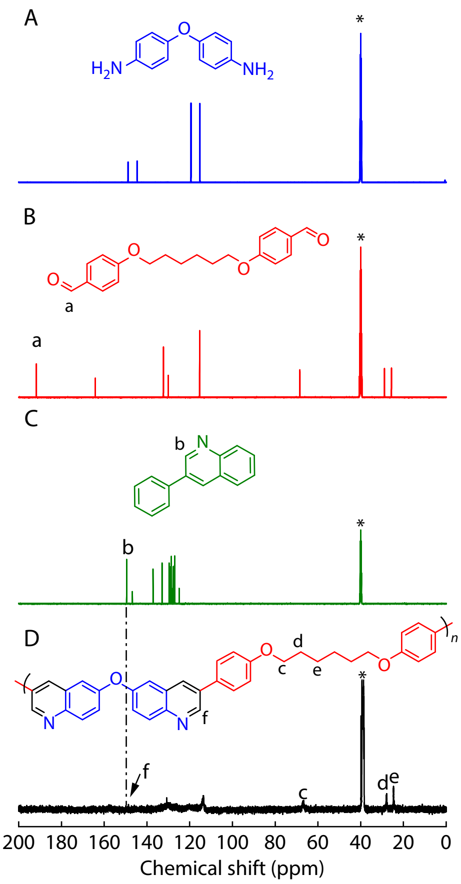


Fig. 4 ^{13}C-NMR spectra of (A) **1a**, (B) **2a**, (C) model compound **6**, and (D) polymer P**1a**/**2a**/**3** in DMSO-d$_6$. The solvent peaks are marked with asterisks.

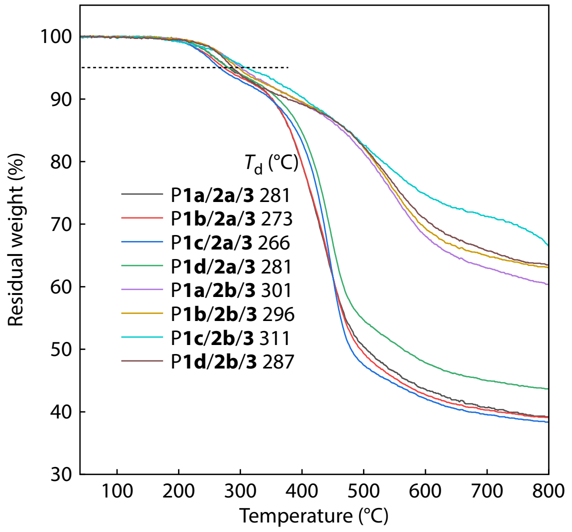


Fig. 5 TGA thermograms of polymers PPQs. T_d represents the temperatures of 5% weight loss.

thesis of new polymers with high refractive indices are of great importance in materials science. The light refraction properties of PPQs were studied using a rigid ring-fused structure and heteroatoms. The polymers could form tough thin films through spin-coating and these films of P**1a/2a/3**, P**1b/2a/3**, P**1c/2a/3**, P**1d/2a/3**, P**1a/2b/3**, P**1b/2b/3**, P**1c/2b/3** and P**1d/2b/3** display high RI with values of 1.7087, 1.6856, 1.6824, 1.6732, 1.7478, 1.7795, 1.7357 and 1.6944 at 589 nm, respectively, and their chromatic dispersions were 0.0429–0.0923, suggesting their higher refractive indices and lower chromatic dispersion compared with commercial optical plastics (*n*=1.49–1.59) (Fig. 6, Table S1 in ESI).

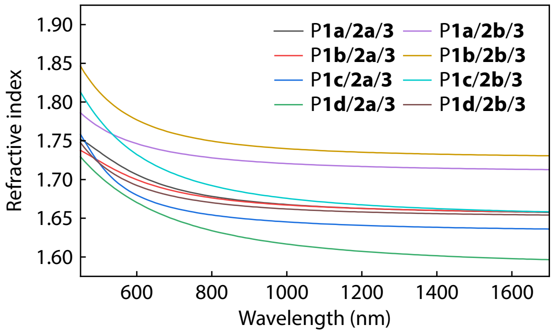


Fig. 6 Light refraction spectra of thin solid films of PPQs.

CONCLUSIONS

In this study, an efficient one-pot MCP of easily available dialdehydes, diamines, and the common organic solvent DMSO was successfully developed. This MCP can be applied to versatile aromatic aldehydes and aromatic amines to produce a series of PPQs with high M_w values (up to 5.11×10^4) in satisfactory yields (up to 82%) at 120 °C. The resultant PPQs are soluble in DMF or DMSO and possess good thermal stability with T_d up to 311 °C as well as high morphological stability. In addition, the PPQs showed excellent film-forming ability, and their thin films exhibited a high RI of up to 1.7795 at 589 nm. Thus, this work not only enriches the family of MCPs, but also provides an efficient way to transform DMSO into functional polymer materials with potential applications in various fields.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-025-3349-z.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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