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ORIGINAL PAPER

Synthesis and properties of poly(1,3-dialkoxybenzene)s from facile solvent-free grinding oxidative coupling polymerization

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Abstract Soluble conjugated aromatic poly(1,3-dialkoxybenzene)s were obtained in high yield up to 80% in 30 min by grinding 1,3-dialkoxybenzene with anhydrous $FeCl_3$ powder in a mortar at ambient and solvent-free condition. The polymers were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR, and gel permeation chromatography. The structure of the aromatic rings linkage at meta-position was confirmed. Thermogravimetric analysis, UV–Vis, fluorescence spectroscopy, and four-probe a.c. technique were used to probe the thermal, optical, and electrical properties of the polymers. The polymers displayed high thermostability with the decomposition temperatures at about 382–388 °C. The optical energy gap (E_g) of the polymers was 4.23 eV and electrical conductivity at room temperature was 10^{-6} S cm^{-1}. The fluorescence curve of the polymers displayed the maximum at 344 nm in CH_2Cl_2 solution. The morphology of the polymers was determined by X-ray diffraction and scanning electron microscope technique.

Keywords Poly(1,3-dialkoxybenzene)s · Conjugated polymer · Solvent-free grinding oxidative coupling polymerization

Introduction

Polyphenylenes are one class of conjugated polymers whose polymer chains are made of all phenyl rings linked at various positions. Extensive work on the

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para-polyphenylenes has been reported for their electrical conductivity and electroluminescence [1]. Different to the linear *para*-polyphenylenes, the poly(*m*-phenylene)s would be expected to have a helical conformation [2]. Although steric distortion can weaken the conjugation, the conformation of the polymer can not only influence its optical and electrical properties greatly [3], but also allow the polymers to undergo either intrachain self-organization or interchain self-assembly for materials applications [4, 5].

The homopolymer poly(*m*-phenylene) was first synthesized by Yamamoto reaction and shown to be crystalline [6]. Later, Fujioka reported the synthesis of poly(*m*-phenylene)s following the Ullmann reaction [7]. The Grignard reaction and Suzuki reaction also were used to prepare *m*-phenylene oligomers and polymers [8, 9]. However, there are some shortcomings such as complicated procedures, high cost, or expensive noble metal as catalyst.

Poly(1,3-dimethoxybenzene) have been directly prepared from 1,3-dimethoxybenzene by electrochemical polymerization and oxidative coupling polymerization [10, 11], while the material is insoluble in all common solvents. Oxidative coupling polymerization developed from Scholl reaction involves the coupling of aromatic nuclei by an oxidative process [12, 13]. Because the conjugated aromatic polymers are hardly soluble, it is necessary to introduce flexible side chain on the aromatic rings to increase the solubility of poly(*m*-phenylene)s [14]. Here we report the soluble poly(1,3-dialkyloxybenzene)s prepared by solvent-free grinding oxidative coupling polymerization. We had found that this method was facile and high-yield reaction. The structural properties, morphological and thermal performances, optical and electrical characters of the poly(*m*-phenylene)s have been discussed in this study.

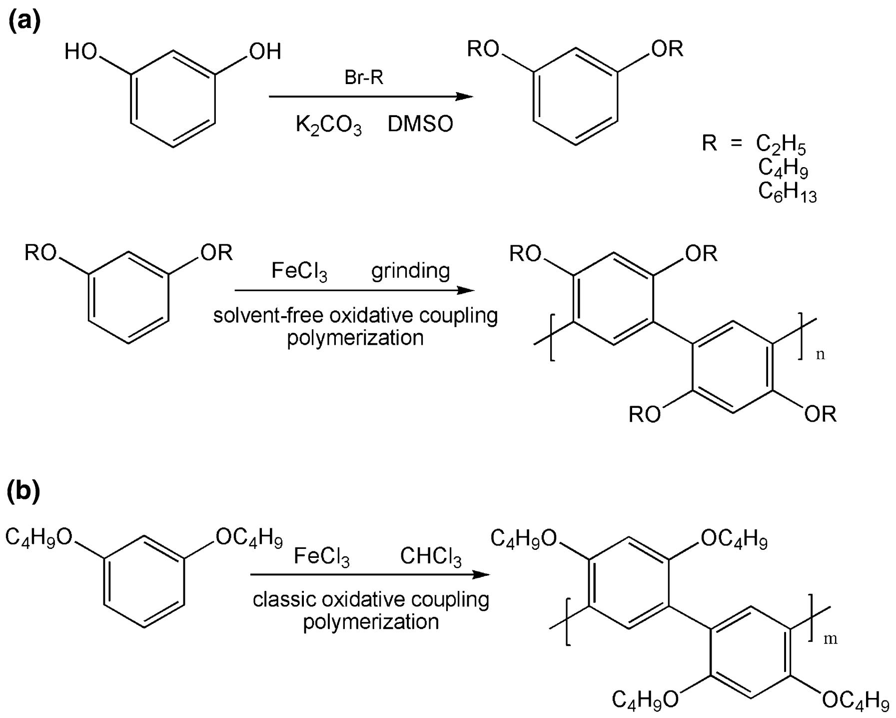
Experimental

Materials

Resorcinol, alkyl bromide (bromoethane, bromobutane, bromohexane), potassium carbonate, dimethyl sulfoxide (DMSO), anhydrous $FeCl_3$, dichloromethane, chloroform, methanol, and ethanol were all A. R. and purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. 1,3-Dialkoxybenzenes were synthesized using an etherification procedure from resorcinol and alkyl bromide.

General polymerization

A typical polymerization is shown in Scheme 1a. For example, the synthetic procedure of poly(1,3-dibutoxybenzene) was as follows: 0.44 g (2 mmol) 1,3-dibutoxybenzene and 0.97 g (6 mmol) anhydrous $FeCl_3$ powder were put into a mortar. After grinding for about 30 min, the mixture was put into the cold ethanol which contains 5% hydrochloric acid. Then the crude polymer was collected by



Scheme 1 Different oxidative coupling polymerization of 1,3-dialkoxybenzenes: **a** solvent-free grinding polymerization, **b** classic polymerization in solution

filtration and then washed by ethanol until the filtrate was colorless. The dry residue dissolved into 5 mL chloroform and precipitated in 30 mL ethanol. The refined polymer was filtrated and washed with ethanol, and then dried overnight. Lastly, the polymer was extracted with ethanol by Soxhlet Extractor for 24 h. 0.33 g brown powder was obtained and the yield was 75%. FT-IR (KBr, cm^{-1}): 2955, 2930, 2870 (C–H), 1648, 1600, 1500, 1463 (C–C, Ar), 1381 (C–H), 1171, 1029 (C–O–C), 824 (C–H, Ar). ^{1}H-NMR spectrum (500 MHz, $CDCl_3$, δ, ppm): 7.20–7.08 (m, 1H, Ar), 6.65–6.45 (m, 1H, Ar); 3.92–3.27 (m, 4H, OCH_2), 1.88–1.07(m, 8H, CH_2–CH_2), 1.07–0.60 (m, 6H, CH_3). ^{13}C-NMR spectrum (500 MHz, $CDCl_3$, δ, ppm): 156.51, 135.06, 120.41, 99.02, 68.62, 31.74, 19.40, 14.06. Gel permeation chromatography (GPC) [tetrahydrofuran (THF), polystyrene (PS) standard]: $M_n = 4{,}100$; $M_w = 8{,}204$.

For comparison, poly(1,3-dibutoxybenzene) was also prepared by oxidative coupling polymerization in solution according to the procedure of previous reports [11]. The anhydrous $FeCl_3$ was activated by thionyl chloride and chloroform was purified by distillation after dried with calcium chloride first. Then 1.30 g (8 mmol) anhydrous $FeCl_3$ powder were added to a solution of 0.44 g (2 mmol) 1,3-dibutoxybenzene in 20 mL $CHCl_3$ at room temperature. The mixture was stirred for 48 h under N_2 atmosphere. Then the mixture was put into the cold ethanol which contains 5% hydrochloric acid. The crude polymer was collected by filtration. The residue was extracted with ethanol by Soxhlet Extractor for 24 h. 0.23 g (yield 52%) brown powder was obtained and named as P0 (Scheme 1b).

Instrumental

FT-IR spectra were recorded on a Nicolet 5700 FT-IR. The spectra of polymers were performed in KBr pellets. ^{1}H-NMR and ^{13}C-NMR spectra of polymers were taken on a Varian Unity 500 NMR spectrometer at 500 MHz in $CDCl_3$ using tetramethylsilane as reference. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) were determined by GPC using a Waters 510 high-performance liquid chromatography with THF as the eluent (1 mL min^{-1}). Calibration was accomplished with monodispersed PS standards. The absorption spectra were recorded on a VARIAN CARY 50Bio UV Spectrophotometer. The fluorescence spectra were obtained on a Hitachi F-7000 fluorescence spectrophotometer with CH_2Cl_2 as the solvent. The conductivity of the polymer was measured using the four-probe a.c. technique. Thermogravimetric analysis (TGA) was carried out by a METTLER TGA/SDTA851 under nitrogen atmosphere with a heating rate of 10 °C min^{-1}. The morphology of the polymer was characterized by scanning electron microscope (SEM) with a JSM-7500F instrument operating at 15 kV. X-ray diffraction (XRD) analysis was carried out by the X’Pert PRO MPD diffractometer, which configures with a Cu radiation X-ray source.

Results and discussion

Table 1 shows the yields of different poly(1,3-dialkoxybenzene)s obtained depending on the reaction time and the molecular ratio of 1,3-dialkoxybenzenes and $FeCl_3$. As shown in Table 1, anhydrous $FeCl_3$ as oxidation could give yields of about 40% at room temperature when the molecular ratio is 1:2 and the reaction time is more than 30 min. The result indicates that the reaction was initiated by grinding, which generated cation radicals mechanically. In addition, the solvent-free oxidative reaction could offer a high yield when three times of oxidant was used. The yields of 75, 80, and 68% were obtained for 1,3-dibutoxybenzene, 1,3-diethoxybenzene, and 1,3-dihexyloxybenzene, respectively (entries 3, 7, and 10). It also can be seen that the ratio of the oxidation and the reaction time could not effect the reaction obviously. Compared with the insoluble poly(1,3-dimethoxybenzene)s, the polymers in our study were readily soluble in common organic solvents such as chloroform, dichloromethane, toluene, and THF. Compared with the classic oxidative coupling polymerization in solution (Scheme 1b), the solvent-free grinding oxidative coupling polymerization process at ambient condition in 30 min and is easier to handle with $FeCl_3$ used directly from purchased chemicals without further purification. However, the solution polymerization required strict anhydrous procedures and vacuum distilled anhydrous $FeCl_3$ [11]. The solvent-free grinding oxidative coupling polymerization is a facile, time saving, “green-chemistry” method.

Table 1 Preparation of poly(1,3-dialkoxybenzene)s by solvent-free grinding oxidative coupling polymerization

Entry	Monomer	Ratio[a]	Time (min)	Yield (%)
1	DBB	1:2	30	40
2	DBB	1:2	40	42
3	DBB	1:3	30	75
4	DBB	1:3	40	77
5	DBB	1:4	30	76
6	DBB	1:4	40	76
7	DEB	1:3	30	80
8	DEB	1:3	40	82
9	DEB	1:4	30	82
10	DHB	1:3	30	68
11	DHB	1:4	30	69

[a] Molecular ratio of 1,3-dialkoxybenzenes and $FeCl_3$

DBB 1,3-dibutoxybenzene; *DEB* 1,3-diethoxybenzene; *DHB* 1,3-dihexyloxybenzene

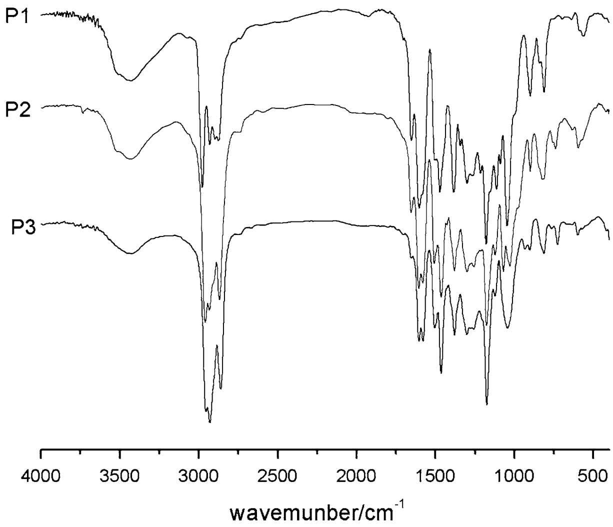


Fig. 1 FT-IR spectra of poly(1,3-dialkoxybenzene)s

The structure of the polymer was examined using IR spectroscopy with a pressed KBr pellet. Figure 1 shows the IR spectra of poly(1,3-dialkoxybenzene)s by the solvent-free grinding oxidative coupling polymerization (P1: poly(1,3-DEB); P2: poly(1,3-DBB); P3: poly(1,3-DHB)). At 2955, 2930, and 2870 cm^{-1}, it is possible to observe the stretching vibrations of C–H bonds of the methyl and methylene groups of the ether in the polymers. The breathing modes of the aromatic rings occur at 1,648 to 1,460 cm^{-1} for the polymers. Between 1,200 and 1,000 cm^{-1} strong absorption bands are observed which are assigned to the asymmetric stretching vibrations of the ether linkages. The peaks at 830 cm^{-1} are due to out-of-plane vibration of the isolated C–H.

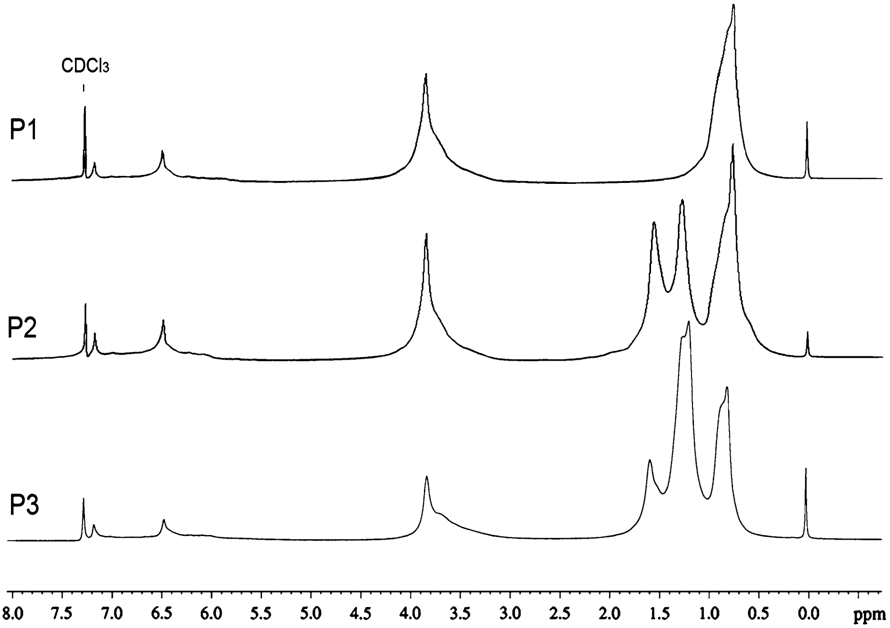


Fig. 2 ^{1}H-NMR spectra of poly(1,3-dialkoxybenzene)s in $CDCl_3$

The structures of polymers can be further deduced by 500 MHz ^{1}H-NMR and ^{13}C-NMR spectroscopy. The ^{1}H-NMR spectra of polymers (Fig. 2) exhibit two sets of lines originating in the aromatic protons between δ 6.48–7.20 and the aliphatic protons between δ 3.80–0.70, which were assigned to the aromatic and alkyl protons, respectively. Especially, the peaks at 6.48 and 7.17 are due to the absorptions of the isolated C–H of the aromatic rings.

In order to confirm the structure of poly(1,3-dialkoxybenzene)s, the ^{13}C-NMR spectrum of poly(1,3-DBB) is shown in Fig. 3. From Fig. 3, four peaks (δ 99.02, 120.41, 135.06, and 156.51) appear in the aromatic region, related to the six aromatic carbon atoms of the polymer repeating unit. The concise peaks of ^{13}C-NMR spectrum indicated that in poly(1,3-DBB), the aromatic ring moieties linkage at meta-position, which agreed with the poly(1,3-DMB) by electrosynthesis in Bu_4NBF_4/CH_3CN [10].

The data of the GPC obtained are summarized in Table 2. Poly(1,3-DEB), poly(1,3-DBB), and poly(1,3-DHB) prepared by solvent-free grinding oxidative coupling polymerization had number-average molecular weights (M_n) of 4128, 4100, and 4092 (vs. PS standards) with M_w/M_n (M_w: weight-average molecular weight) values of 2.1, 2.0, and 1.8, respectively. The M_n values correspond to degrees of polymerization of about 25, 18, and 15, respectively. It is difficult to form the polymers with higher molecular weights because of steric hindrance of the longer side chain. While P0 from the classic oxidative coupling polymerization in solution had the M_n of 1,707, which could be assigned to the polymerization proceeded heterogeneously [15].

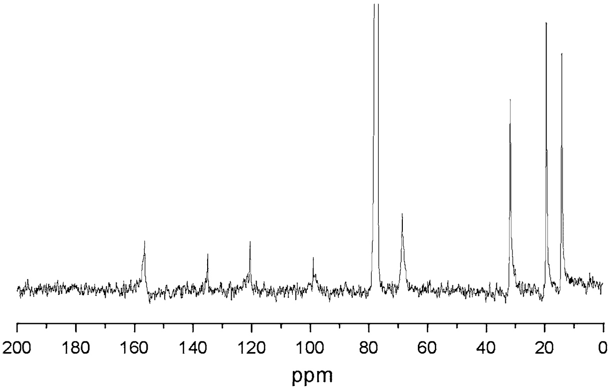


Fig. 3 ^{13}C-NMR spectrum of poly(1,3-DBB) in $CDCl_3$

Table 2 GPC data for the polymers

Polymer	M_n	M_w	M_w/M_n	DP
P0	1,707	7,852	4.6	8
P1	4,128	8,670	2.1	25
P2	4,100	8,204	2	18
P3	4,092	7,366	1.8	15

Table 3 Optical and electrical properties of the polymers

Polymer	λ_{UV-Vis} (nm)	$\lambda_{Flu\ ex}$ (nm)	$\lambda_{Flu\ em}$ (nm)	Conductivity (S cm^{-1})
P1	252 (293)	281	341	6.1×10^{-6}
P2	251 (294)	283	344	2.6×10^{-6}
P3	251 (294)	285	345	1.1×10^{-6}

Optical and electrical properties

The optical and photophysical properties of the polymers were investigated by UV–Vis and fluorescence spectrometries, and the optical data are shown in Table 3. The UV–Vis spectra of the polymers in CH_2Cl_2 solution were recorded and depicted in Fig. 4. The UV–Vis absorption spectra of all the polymers in CH_2Cl_2 solution exhibited the maximum absorption bands at around 293 and 251 nm. The polymers can be calculated by the absorption spectra [16] to show the same energy gap: 4.23 eV. The value is certainly smaller than the observations (5.0 eV) for *m*-oligophenyls [17], which can be attributed to the absorption of extended conjugation along the polymer chain of 1,3-linked polyphenylenes [8].

The fluorescence spectra of the polymers are recorded in Fig. 5. When excited at 281 nm, P1 in CH_2Cl_2 solution displayed the fluorescence curves with maximum at

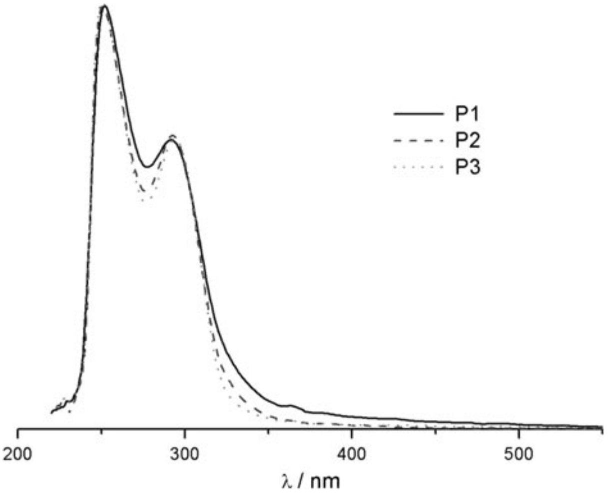


Fig. 4 UV–Vis absorption spectra of poly(1,3-dialkoxybenzene)s in CH_2Cl_2

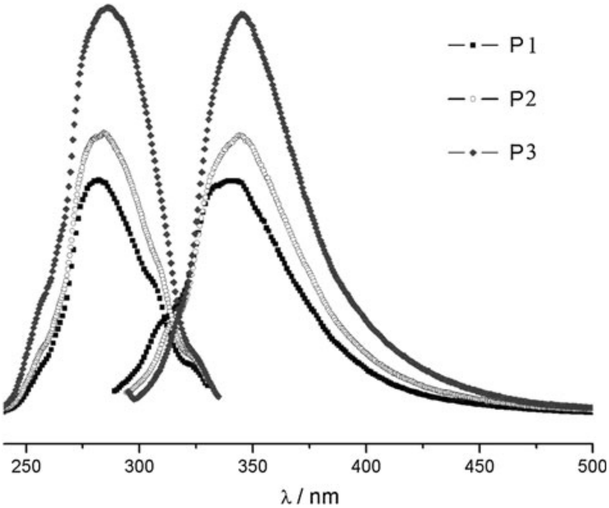


Fig. 5 Fluorescence spectra of poly(1,3-dialkoxybenzene)s in CH_2Cl_2

341 nm. The fluorescence emission bands of P2 and P3 are similar with only 3–4 nm red shift of the spectrum of P1. The red shift is due to the different alkoxy chain length. These results are different to that of poly(*p*-phenylene), which showed the emission with maximum at around 400 nm [13]. Steric distortion is possibly responsible for the weaker conjugation [2, 18].

Conductivity measurements were performed on pressed pellets of poly (1,3-dialkoxybenzene)s at room temperature. The measured conductivity value of polymers obtained were 6.1 × 10^{-6} S cm^{-1} (poly(1,3-DEB)), 2.6 × 10^{-6} S cm^{-1} (poly(1,3-DBB)), 1.1 × 10^{-6} S cm^{-1} (poly(1,3-DHB)), respectively. The conductivity value obtained places this material in the semiconducting range. However, the values are two order of magnitude lower than that reported for the poly(1,3-dimethoxybenzene) [10]. This can be attributed to the steric hindrance of the alkoxy substituents and the residual metal ions of the catalytic oxidants.

Thermal and morphological properties

The thermal properties of the polymers were characterized by TGA. TGA measurements carried out at a heating rate of 10 °C min^{-1} under nitrogen. The TGA curves are shown in Fig. 6. The high onset decomposition temperatures (5% weight loss) (~382–388 °C) indicated that polymers take a good thermal stabilities. Moreover, the survival rate of the polymers at 700 °C decreased with the increasing of the alkyl chain length.

The SEM micrographs were used to investigate the morphology of poly(1,3-DBB) (P2). The morphology is generally dependent on the reaction and purification conditions [19]. As seen in Fig. 7, the appearance of P2 exhibits grains of irregular granular shape. That is different from the morphology of poly(1,3-DMB) synthesized via the electrochemical oxidation [10].

The wide-angle X-ray scattering curves of poly(1,3-dialkoxybenzene)s are shown in Fig. 8. XRD patterns show that the polymers were amorphous structure with broad diffraction peaks [20]. There are two main diffraction peaks centered at $2\theta = 6°$, and 21°, indicating the presence of heterogeneous amorphous feature.

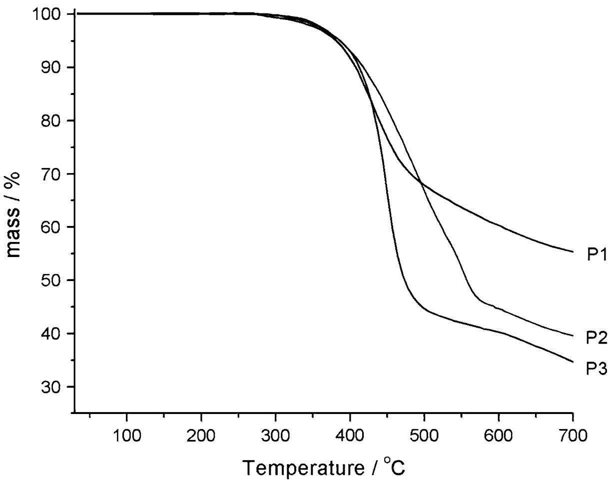


Fig. 6 TGA curves of poly(1,3-dialkoxybenzene)s under N_2

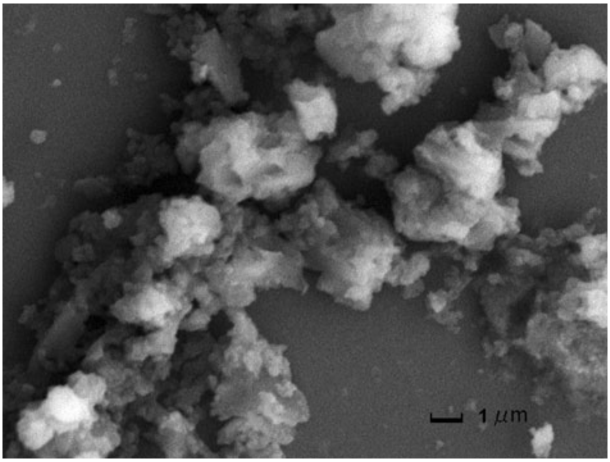


Fig. 7 SEM image of poly(1,3-DBB)

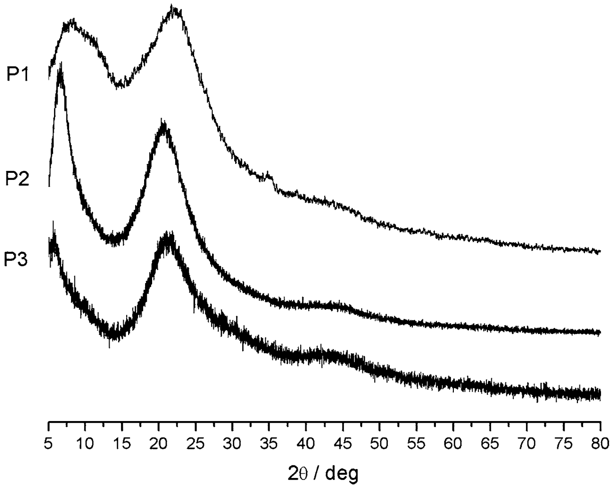


Fig. 8 XRD patterns of poly(1,3-dialkoxybenzene)s

Conclusions

The solvent-free grinding oxidative coupling polymerization is a facile, green-chemistry method. The obtained poly(1,3-dialkoxybenzene)s are found to have a good solubility in conventional organic solvents and an excellent thermostability. The polymers had higher number-average molecular weights with lower M_w/M_n values than those of the polymer by classic oxidative coupling polymerization in solution. The energy gap of the polymers is 4.23 eV. The conductivity values obtained are in the order of 10^{-6} S cm^{-1}, placing this compound in the range of a semiconductor. The photoluminescent emission of the polymers in CH_2Cl_2 solution has maximum at around 344 nm. The morphology of the polymer exhibits grains of irregular granular shape. XRD patterns show that the polymers are heterogeneous amorphous structure.

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