

Synthesis and Characterization of Polyparaphenylene from *cis*-Dihydrocatechol

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ABSTRACT: Conducting polymer polyparaphenylene (PPP) was synthesized from *cis*-dihydrocatechol (DHCD) obtained from bacterial transformation of benzene. Results showed that the DHCD to DHCD-DA (diacetate) synthesis process produced some byproducts as impurities including trace amounts of phenol, quinone, and phenyl acetate derived from phenol. These impurities played a negative role in the polymerization process of DHCD-DA to P(DHCD-DA). In this study, a distillation fractionation method was employed to obtain monomer DHCD-DA with high purity and high yield. Four different polymerization methods using the purified DHCD-DA, including bulk polymerization initiated by different catalyst systems, solution polymerization as well as emulsion polymerization, were compared. A very high P(DHCD-DA) yield of 92% with a molecular weight of 84,500 was obtained

under an optimized condition using the bulk polymerization process initiated by (di)benzoyl peroxide (BPO) and ferrous sulfate. A standard curve was established to evaluate the aromatization degree of P(DHCD-DA) to PPP under different temperatures based on the intensity of FTIR absorption and functional groups on the PPP. The glass transition temperature and the crystallinity of PPP increased with the degree of aromatization of the prepolymer P(DHCD-DA). Thermal analysis indicated that the PPP possessed high thermal stability both in nitrogen and in air atmospheres. All these results would help the synthesis of PPP. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2085–2093, 2008

Key words: polyparaphenylene; conducting polymers; *cis*-dihydrocatechol; crystallization; thermal properties

INTRODUCTION

The discovery of highly conducting polyacetylene and the flexibility of doping it to achieve the full range properties from an insulator to a metal are the landmark of conductive materials.^{1–3} This type of polymers known as synthetic metal possesses not only the electrical, electronic, magnetic, and optical properties of a metal, but also preserves some mechanical properties and processability commonly associated with a conventional polymer.⁴ The conjugated bonds between the carbon atoms on the backbone are single and double alternatively, together with extended π electrons and large carrier charge concentration that enable the polymers to exhibit electrical conductivity.⁵ Polyacetylene (PA), polythiophene (PT), poly-

pyrrole (PPy), polyparaphenylene (poly-*p*-phenylene or PPP), and polyaniline (PANI) can best exemplify the properties of the conductive polymers.^{6–12}

PPP, as one of the most ordinary conductive polymers, has been attracting some attentions for its high thermal stability and versatile electron structures achieved via different preparation technologies^{13,14} and for its wide ranges of electrical conductivity obtained by doping. More importantly, it was reported that PPP had more stable properties and higher ability to endure corrosion when compared with thin film made of PPy and PANI.^{8,11,12}

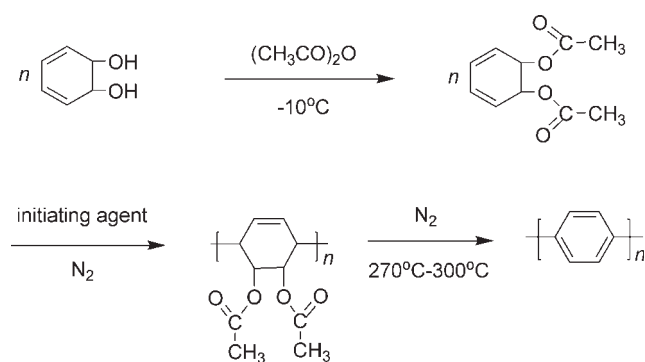
Versatile synthetic routes of PPP were reported, which included radical polymerization and typical organic chemistry procedures. Among these methods, one successful polymerization route studied widely is the bulk polymerization of benzene using aluminum chloride-copper (II) chloride system and iron (III) chloride as catalyst.^{11,15–17} However, the reaction requires large quantities of cupric chloride and the yield of PPP based on the metal salt was always very low.^{18,19} Furthermore, the chain growth can only be accomplished with 10–15 phenylene units, which indicate a relatively low molecular weight. Another influential way to synthesize

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Scheme 1 Synthesis of PPP from *cis*-dihydrocatechol.

polyphenylene originated from benzene bromide using nickel as a catalyst also encountered the aforementioned problems²⁰ and still not be well solved. Alternatively, Natori et al.²¹ attempted to synthesize PPP stemmed from 1,3-cyclohexadiene using ionic polymerization. The product poly(cyclohexene) was a mixture containing 1,4 and 1,2 units. The extreme reaction conditions in ionic polymerization may be a challenge for the large-scale production. Ballard et al.²² prepared PPP using the derivations of *cis*-dihydrocatechol (DHCD) obtained from bacterial fermentation using benzene as transformation substrate in a homopolymerization way in 1988. However, they achieved a yield of only 60%. We speculate that the possible reasons resulted into this phenomenon were due to the impurity of the DHCD diacetate (DHCD-DA) and the polymerization method as well as catalysts used in the polymerization process. Therefore, we tried to optimize the PPP synthesis (Scheme 1) to achieve high molecular weight, yield and purity based on Ballard et al.'s method. In this article, fractionation technique was used to purify the DHCD-DA with a high yield and a high purity. At the same time, we systematically investigated four different DHCA-DA polymerization methods using different reaction conditions to obtain an optimal reaction process. At the end, a more effective approach was found for the evaluation of aromatization conversion of P(DHCD-DA) to PPP as a function of temperature by comparing FTIR peak absorption intensity (R) of their blends using a standard curve. Through the optimal synthesis routine, thermal stable PPP with a high yield, a high purity, and a reasonably high molecular weight was successfully prepared. This process shows the possibility for large-scale production of PPP.

EXPERIMENTAL

Materials

DHCD was provided by Tsinghua University (Beijing, China) via a microbial fermentation process that

converted benzene to DHCD.²³ Analytically pure chloroform, *n*-hexane, pyridine, acetic anhydride, ethyl ether, and tetrahydrofuran were purchased from Damao Chemical Reagent Company (Tianjin China). Chemically pure azodiisobutyronitrile (AIBN) and (di)benzoyl peroxide (BPO) were received from Sinopharm Group Chemical Reagent Co., Ltd. Chemically pure ferrous sulfate, sodium hydrogen carbonate, and sodium sulfate were obtained from Guangzhou Chemical Factory Co., Ltd (Guangzhou, China). Commercial bulk-grade emulsifier MGS-65 was received from Cognis (Shanghai, China). All other chemicals were used as received.

Synthesis of DHCD-DA

The derivatization of DHCD into DHCD-DA was carried out according to Ballard et al.²² First, raw material DHCD was purified before derivatization by dissolving it in chloroform and recrystallizing it. Typically, the reactants with molar ratio of DHCD : pyridine : acetic anhydride fixed about 1 : 3.23 : 3.08 were prepared, and acetic anhydride was added dropwise at -10°C . After finishing the acetic anhydride addition, the system was kept stirring at -10°C for 2 h and then allowed to warm up to room temperature. The product solution was concentrated on a rotary evaporator at 40°C to remove pyridine followed by pouring it to ethyl ether. The mixture was transferred into a dropping-funnel for the following treatment: saturated sodium hydrogen carbonate solution was used to neutralize organic acids generated from the reactions until no bubble was produced, and the neutralized mixture was washed three times using distilled water. The organic phase was dried in the presence of anhydrous sodium sulfate and was filtered. Subsequently, the solvent was removed by evaporation, yielding DHCD-DA as a slightly yellow liquid.

Fractionation

The above obtained DHCD-DA was purified carefully to remove small amounts of impurities, including traces of phenol, quinone, and phenyl acetate derived from phenol. Different fractions which were sensitive to temperature were collected via distillation of the raw materials in a round-bottom flask with a Vigreux fractionation column under a vacuum of 3 mmHg. The fraction collected under $35\text{--}40^{\circ}\text{C}$ was denoted as Fraction A. Then Fraction B was collected in a temperature range of $60\text{--}65^{\circ}\text{C}$. The residual portion in the flask known as Fraction C was collected directly with 92% of total weight. The structures of components in all fractions along with the original product were verified by NMR (Fig. 1).

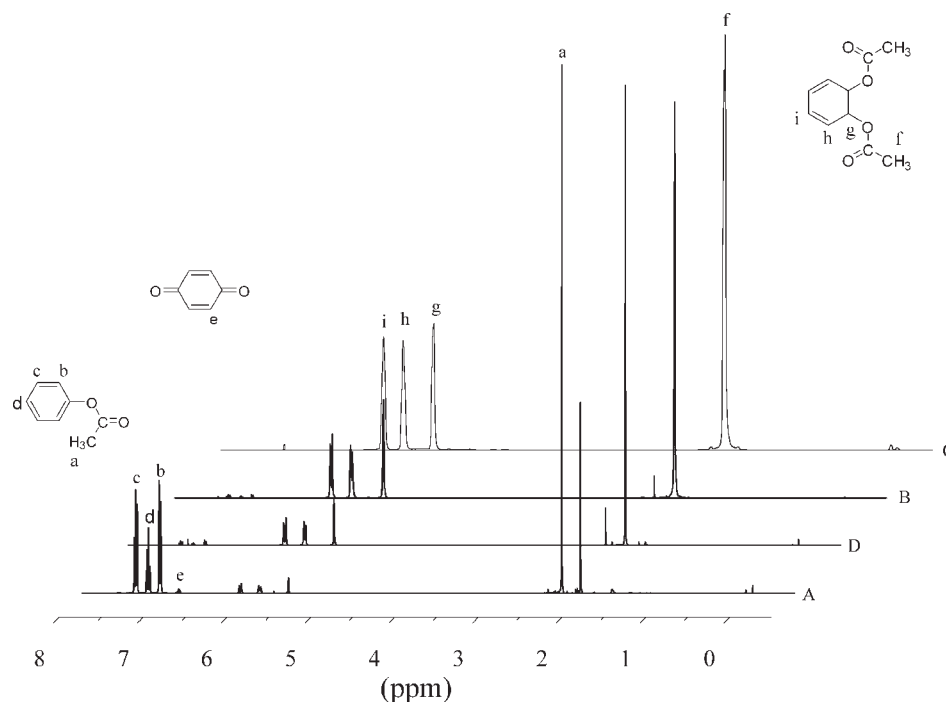


Figure 1 ^1H NMR spectra of raw DHCD-DA and each individual fraction after fractionation. (A) fraction A was collected at 35–40°C; (B) fraction B was collected at 60–65°C; (C) product remained in round-bottom flask; and D original product DHCD-DA.

Polymerization

Pure DHCD-DA (Fraction C) was polymerized employing different polymerization methods and initiators to obtain an optimal PPP production, including a comparison with bulk polymerization initiated by AIBN reported previously by Ballard et al.²²

Bulk polymerization

Pure DHCD-DA (2.5 g, 13 mmol), BPO (0.024 g, 0.1 mmol), and ferrous sulfate (0.06 g, 0.4 mmol) were placed in a three-neck flask and degassed by flushing with nitrogen gas three times. BPO and ferrous sulfate here together were used as initiators via the redox reaction process. Reaction temperature was set at 31, 34, 37, and 40°C using a sensitive thermo sensor (DF-101S, Yuhua Instrument Co., Ltd. Gongyi, China) for 72 h, respectively, for the optimal condition for DHCD-DA polymerization. The recovery and purification of poly(*cis*-dihydrocatechol diacetate) or P(DHCD-DA) were conducted in chloroform and recovered by precipitation into *n*-hexane.

Solution polymerization

The tetrahydrofuran (THF) solution of DHCD-DA (v/m, 50 mL/10 g, 51 mmol) was placed in four-neck flask and degassed by flushing with nitrogen gas three times. AIBN (0.05 g, 0.3 mmol) dissolved

in 20 mL dried THF was used as an initiator and added with a hypodermic syringe. The polymer was collected and purified as the method mentioned above after the system maintained at 70°C for 72 h.

Emulsion polymerization

Distilled water (10 g) and emulsifier (1 g) (MGS-65, Cognis) were placed in a four-neck flask and degassed by pumping followed by flushing with nitrogen three times. The potassium peroxydisulfate (0.1 g, 0.37 mmol dissolved in 5.0 g water) and ferrous sulfate (0.14 g, 0.92 mmol dissolved in 5.0 g water) were used as a catalyst system. The initiator aqueous solutions and pure DHCD-DA (5.0 g, 25 mmol) were added dropwise from two sides of the flask under constant temperature at 40°C for 72 h. The resulting emulsion was centrifuged to demulsify. Subsequently, the polymer precipitates were collected by filtration, followed by dissolving in chloroform and recovering by precipitation into *n*-hexane.

The resultant products P(DHCD-DA) were compared with each other based on different polymerization methods and initiators used in the reaction processes in terms of molecular weights and yields.

Aromatization

Aromatization was carried out on P(DHCD-DA) samples with the highest molecular weight under

different isothermal points from 270 to 300°C with 10°C interval for 1 h under nitrogen protection. Finally, black and bright products PPP with different conversion depended on aromatization temperature were obtained.

Analytical techniques

Structure characterization

A Bruker AV 400 nuclear magnetic resonance (NMR) spectroscopy was used, CDCl_3 at room temperature was a solvent and tetramethylsilane was used as the internal reference. Chemical shift at 7.3 ppm was referred to the nondeuterated CHCl_3 .

UV/vis spectroscopic measurements were performed with scanning wavelengths ranging from 220 to 350 nm using a Beckman Coulter DU 800 and quartz cells. Samples dissolved in chloroform were used for the measurements.

A Nicolet IR 200 fourier transform infrared spectroscopy (FTIR) was used in this article. About 64 scans were performed with resolution of 4 cm^{-1} at room temperature. Samples were prepared by dispersing the polymers in KBr and compressing the mixtures into a disk.

Molar mass measurement

Average molecular weight and distribution were estimated by GPC using a Waters 1525 pump with a combination of four styragel columns series (Styragel HR, 5 μm). A differential refractive index detector (2414, Waters, USA) and UV detector (2487 Dual Wavelength, Waters, USA) were employed. Chloroform was used as an eluent at a flow rate of 1.0 mL/min. A polymer sample concentration of 2 mg/mL and an injection volume of 50 μL were used for GPC studies. The calibration curve was generated using polystyrene standards containing 1.22×10^3 , 2.85×10^3 , 1.35×10^4 , 2.96×10^4 , 1.97×10^5 , and 5.58×10^5 in number-average molecular weights, respectively.

Thermal properties

Differential scanning calorimetry (DSC) study was performed using a TA Instruments Q100 with an autocool accessory calibrated by indium under the following protocol: The samples were heated from -60°C to 300°C at a rate of $10^\circ\text{C min}^{-1}$, they were maintained at 300°C for 1 min, followed by rapid cooling to -60°C with the refrigerated cooling equipment and remained at -60°C for 1 min. The samples were reheated at $10^\circ\text{C min}^{-1}$ to 300°C . Glass transition temperature (T_g) was taken at the midpoint of the transition from the second heat run.

Thermogravimetric analyses (TGA) were performed on TA Instruments (TA Instruments Q50, TA, USA) under nitrogen and air atmospheres (50 mL min^{-1}), respectively, with a scan rate of $10^\circ\text{C min}^{-1}$ to 900°C .

Wide-angle X-ray diffraction

Wide-angle X-ray diffraction (WAXD) studies were carried out on a Bruker D8 ADVANCE diffractometer using Ni-filtered Cu K α radiation ($\lambda = 0.154\text{ nm}$). WAXD patterns were recorded in the 2θ range $5\text{--}50^\circ$ at a scan speed of $1.0^\circ\text{ min}^{-1}$ at room temperature.

Conductivity measurement

A four-point-probe device (CPS-06 contact probe, Alessi, Irvine, CA) was employed to measure the room temperature conductivity of the PPP. Samples were prepared by compressing PPP powder into disk under 15 Mpa for 5 min.

RESULTS AND DISCUSSION

DHCD purification and derivatization

DHCD was unstable at room temperature, it could be converted to phenol and quinone.²² The heat released during the synthesis of DHCD-DA could increase the amount of phenol and quinone which were negative factors for DHCD-DA polymerization, leading to only 40% polymerization of DHCD-DA as described in previous report.²⁴ To remove impurities in DHCD-DA reactant, a fractionation method was developed, DHCD-DA with various purities were obtained under different temperatures as monitored by ^1H NMR spectra (Fig. 1 and Table I).

Fraction A collected at $35\text{--}40^\circ\text{C}$ during the distillation fractionation was 5.9% in weight of the total distillation substrate. ^1H NMR spectrum confirmed the structure of phenyl acetate. The phenyl acetate was a byproduct of the reaction between phenol and acetic anhydride during the DHCD derivatization process to DHCD-DA. The signal shift at 6.86 ppm was the result of quinone. NMR analysis indicated that the majority of the byproduct phenyl acetate and all of the quinone were eliminated in this step [Fig. 1(A,B) and Table I]. Fraction B, collected at $60\text{--}65^\circ\text{C}$, took up 2.1 wt % of the original distillation substrate. ^1H NMR revealed that the residual phenyl acetate was completely distilled during this distillation process [Fig. 1(B) and Table I]. DHCD-DA which was 92% of the original distillation mixture was thus eventually left in the flask, this was namely Fraction C which was confirmed by ^1H NMR as DHCD-DA with very high purity [Fig. 1(C)].

TABLE I
Fractionation of DHCD-DA Containing Impurity and ^1H NMR Study of Each Individual Fraction

	DHCD-DA (%)	Phenyl acetate (%)	Quinone (%)	Weight (%)
Fraction A	10.7	87.6	1.7	5.9
Fraction B	97.1	2.9	0	2.1
Fraction C	100	0	0	92
Raw material	94.7	5.2	0.1	100

Fraction A: collected at 35–40°C; Fraction B: collected at 60–65°C; Fraction C: left in the flask; Raw material: DHCD-DA before distillation.

Polymerization of DHCD-DA

To obtain PPP with a high molecular weight and a high yield, different methods were employed to polymerize DHCD-DA. Bulk polymerization using BPO and ferrous sulfate as redox catalysts, solution polymerization of DHCD-DA in THF and emulsion polymerization were carried out, respectively, to compare molecular weights (M_w) and yields of final poly(DHCD-DA) or P(DHCD-DA) obtained from these methods. Because of the insolubility of PPP, its molecular weight could only be characterized via the molecular weight of its soluble precursor P(DHCD-DA). It showed clearly that the polymerization methods and the type of initiators imposed profound effect on degree of polymerization and polymer yield (Samples A–D) (Table II). The lowest P(DHCD-DA) M_w of 3500 was observed from the solution polymerization in THF initiated by AIBN. The bulk polymerization initiated by BPO and ferrous sulfate as a redox catalyst system was the most effective method for polymerizing DHCD-DA, leading to the highest M_w of 84,500 and the highest yield in this study (Table II B). Results also demonstrated that the polymer M_w and polydispersity were sensitive to the reaction temperature (Table III). For instance, P(DHCD-DA) M_w increased from 71,800 to 84,500 with increasing temperature from 31 to 34°C, the M_w also decreased from 84,500 to 48,900 with the temperature increased from 34 to 40°C. Compared

TABLE II
Molecular Weights of P(DHCD-DA) obtained using various polymerization methods

Samples	M_n	M_w/M_n	Yield (%)
A	34,500	1.52	99
B	84,500	3.57	99
C	3,500	1.49	90
D	59,100	2.68	56

A, Bulk polymerization, initiated by AIBN, reaction temperature 70°C; B, Bulk polymerization, initiated by BPO and FeSO_4 , reaction temperature 34°C; C, Solution polymerization, initiated by AIBN, dissolved in THF, reaction temperature 70°C; D, Emulsion polymerization, initiated by $\text{K}_2\text{S}_2\text{O}_8$ and FeSO_4 , reaction temperature 40°C.

with the properties of the polymer from bulk polymerization initiated by AIBN and results reported by Ballard et al.²² (Table II A), P(DHCD-DA) with higher molecular weight and yield could be achieved by the bulk polymerization initiated by BPO and ferrous sulfate as a redox catalyst system. With a M_w and a yield of 84,500 and 99%, respectively, the bulk polymerization process was significantly better than others, including the high purity as shown by the ^1H NMR spectrum of P(DHCD-DA) (Table II B). Figure 2 shows the ^1H NMR spectrum of P(DHCD-DA) (Table II B) with structural assignments. Typical signals of P(DHCD-DA) were detected. The signal of the methyl (e, 1.98 ppm), the broad signal (f, 2.5 ppm) can be considered to be the hydrogen atoms which bound to main chain, and the other hydrogen atoms noted as g, h can be considered to be the broad band in 4.8 to 6.0 ppm, respectively. Any other impurity signals could not be found in Figure 2, which indicated that the high purity of the P(DHCD-DA) was harvested by bulk polymerization initiated by BPO and ferrous sulfate as redox catalyst system. The P(DHCD-DA) structure was also further confirmed by UV/vis (Fig. 3) and FTIR [Fig. 4(A)].

Tracking the conversion of DHCD-DA to the P(DHCD-DA)

UV/vis spectroscopy was used to track the transformation of monomer DHCD-DA to polymer P(DHCD-DA) (Fig. 3). As expected, DHCD-DA exhibited a strong absorption band in the region from 240 to 290 nm, the maximum point ($\lambda_{\text{max}}^{\text{ab}}$) on the absorption was approximately at 260 nm (Fig. 3

TABLE III
Relationship between Molecular Weights and Polymerization Temperatures

Reaction temperature/°C	M_n	M_w/M_n
31	71,840	5.14
34	84,480	3.57
37	57,980	6.38
40	48,890	3.9

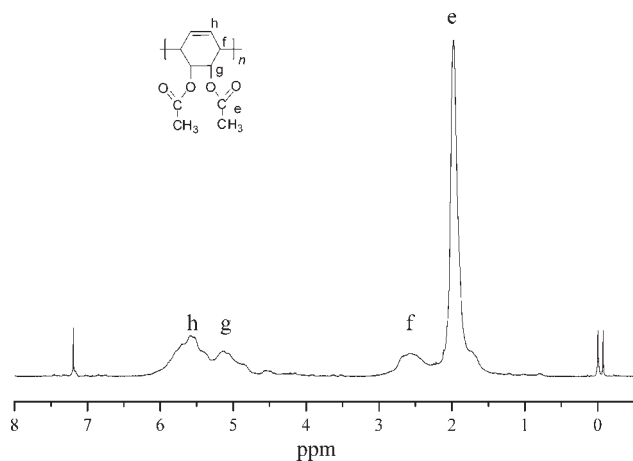


Figure 2 ^1H NMR spectrum of P(DHCD-DA) synthesis in bulk polymerization in CDCl_3 .

Curve A). On the other hand, the broad peak at 260 nm which represents the conjugated bonds in DHCD-DA was disappearing when compared with UV spectra of P(DHCD-DA) (Fig. 3 Curves A and B). The results proved that the disappearance of conjugate bonds DHCD-DA was in accordance with the polymerization of them.

Aromatization of P(DHCD-DA)

To study the most suitable temperature for aromatization of P(DHCD-DA), aromatization was conducted for 1 h under nitrogen atmosphere at different temperatures ranging from 270 to 300°C (Fig. 5). The aromatization temperature strongly affected the polymer color which was turned yellow at 270°C, brown at 280°C, dark brown at 290°C, or flaming black at 300°C. P(DHCD-DA) showed significant difference with its 300°C aromatization product on their FTIR spectra (Fig. 4). A strong benzene

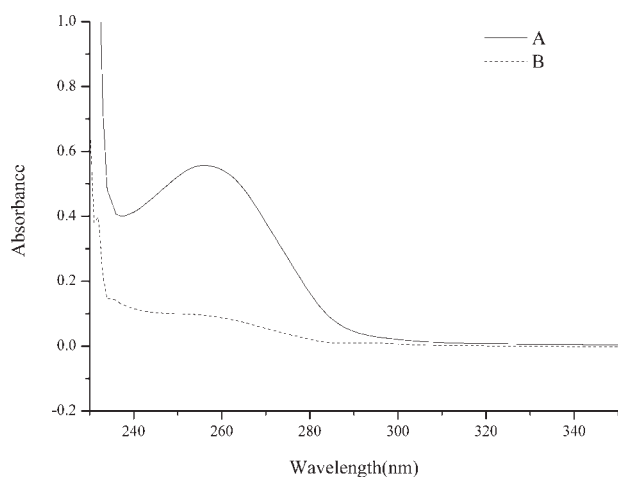


Figure 3 UV/vis spectra of (A) the monomer DHCD-DA and (B) the polymer P(DHCD-DA).

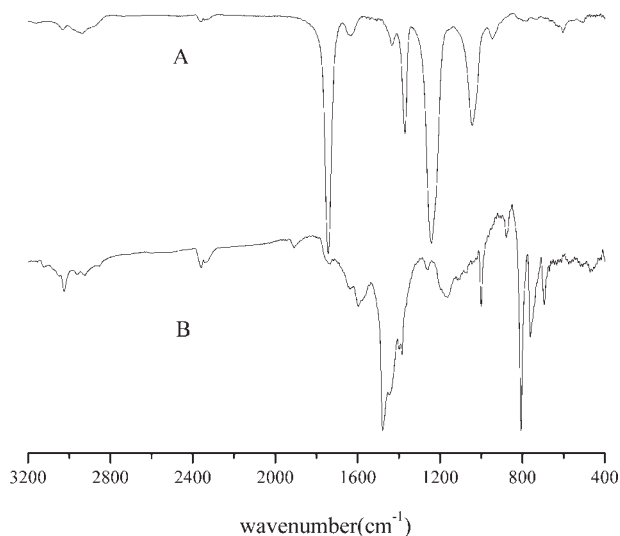


Figure 4 IR spectra of PPP (B) and its precursor P(DHCD-DA) (A).

band was observed in the spectrum of the aromatization product at 1479 cm^{-1} and in the fingerprint region from 650 to 900 cm^{-1} ,^{25,26} which could not be found in P(DHCD-DA) prior to aromatization (Fig. 4). The weak bands at around 3000 cm^{-1} were attributed to C—H telescopic vibration in the benzene backbone. There were also some weak band overlap at 1744 cm^{-1} and 1044 cm^{-1} with P(DHCD-DA), demonstrating an incomplete aromatization process (Fig. 4). The degree of aromatization of P(DHCD-DA) to PPP could be estimated by comparing the intensity of carbonyl absorption at 1744 cm^{-1} with that of the phenylene ring at 1479 cm^{-1} in the FTIR spectra based on Lambert-Beer law $A_\lambda = \epsilon_\lambda bc$, where A_λ is the absorbance, ϵ_λ is a molar absorption or extinction coefficient of the chromophore at wavelength λ , ϵ_λ is a property of a given material and

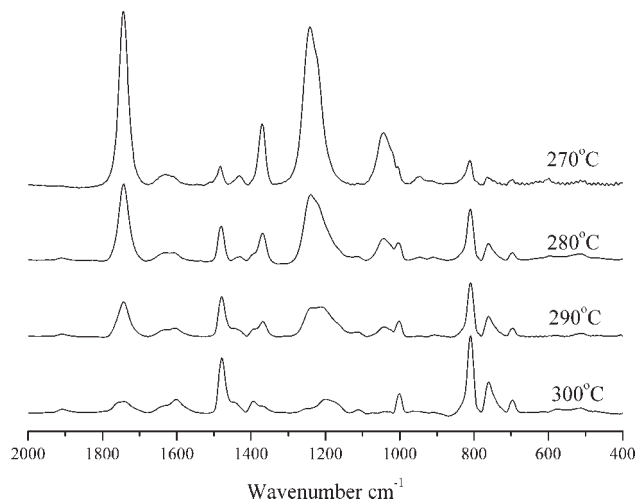


Figure 5 IR spectra of PPP obtained at different aromatization temperatures.

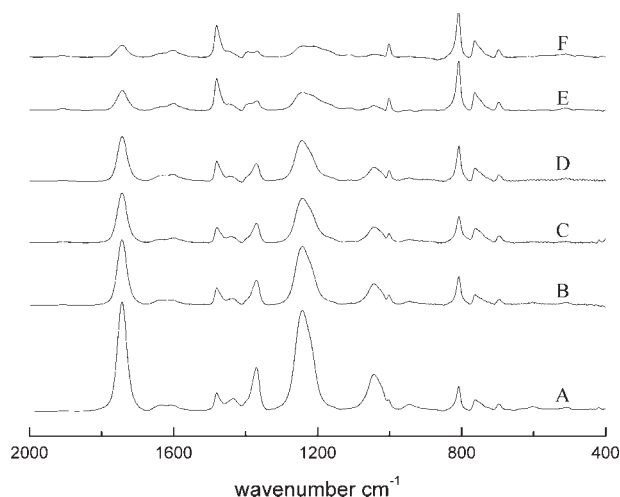


Figure 6 IR spectra of the blends with different ratios of PPP and P(DHCD-DA). Weight fractions of PPP and P(DHCD-DA) in the aromatization system were represented by c_x and c_y . (A) $c_x/c_y = 1.10$; (B) $c_x/c_y = 1.80$; (C) $c_x/c_y = 2.81$; (D) $c_x/c_y = 3.97$; (E) $c_x/c_y = 5.86$; and (F) $c_x/c_y = 8.15$.

given solvent, b is a sample path length measured in centimeters, c is concentration of the given compound in the sample measured in mol L^{-1} .²⁶ Assuming that the absorption bands of 1479 and 1744 cm^{-1} satisfy the Lambert-Beer law, absorbance at 1479 and 1744 cm^{-1} are represented A_x and A_y , weight fractions of PPP and P(DHCD-DA) in the aromatization system were represented by c_x and c_y , respectively, then clearly,

$$c_x + c_y = 1 \quad (1)$$

Therefore, the ratio (R) of the two absorbance is:

$$R = A_x/A_y = \varepsilon_x c_x / \varepsilon_y c_y = K(c_x/c_y) \quad (2)$$

Thus, $c_x = R/(K + R)$ and $c_y = K/(K + R)$. A standard curve was thus established by mixing known amount of P(DHCD-DA) with known amount of highly purified PPP to establish the relationship between aromatization conversion and ratios of the blends (Figs. 6 and 7). It was found that PPP with

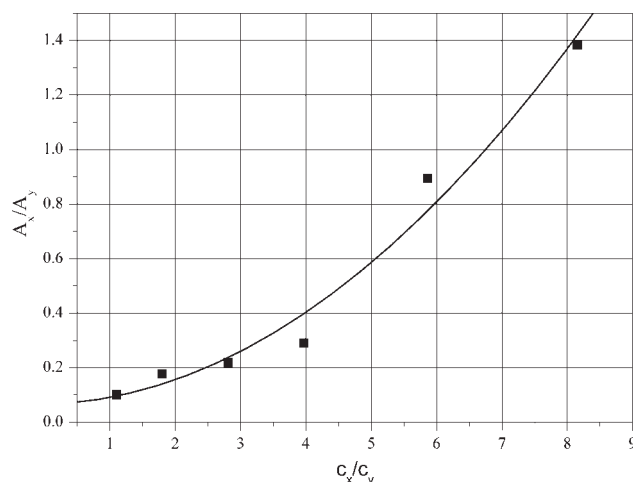


Figure 7 A standard curve used to estimate ratios of PPP and P(DHCD-DA) mixtures. Absorbance at 1479 and 1744 cm^{-1} are represented as A_x and A_y ; weight fractions of PPP and P(DHCD-DA) in the aromatization system were designated as c_x and c_y . A_x/A_y : ratio of the absorbance at 1479 to that at 1744 cm^{-1} ; c_x/c_y : ratio of the weight fractions of PPP to that at P(DHCD-DA).

high purity without residual DHCD-DA could be obtained when aromatization of P(DHCD-DA) was conducted under 350°C in nitrogen environment for 2 h (data not shown).

P(DHCD-DA) to PPP conversion increased with increasing aromatization temperature from 72.3% at 270°C to 98.2% at 300°C (Table IV), indicating that the higher the aromatization temperature, the easier the elimination of the pendant acetate group. Interestingly, the conductivity of undoped PPP was much better when the aromatization was conducted at 290°C accompanied with a conversion of 92.4% (Table IV). This better conductivity might be due to the unaromatized residues that formed a mixed conjugated polymeric network in the conducting polymer.²⁷

Thermal properties

DSC and WAXD measurements were carried out to investigate the glass transition temperatures (T_g) and crystallization behavior of the different PPP

TABLE IV
Studies on Glass Transition Temperatures, Crystallinity Degree of Aromatization, and the Conductivity of PPP

Sample No.	Aromatization Temperature (°C)	PPP Conversion (%)	T_g (°C)	Crystallinity (%)	Conductivity ($\text{S} \times \text{m}^{-1}$)
A	300	98.2	232	13.4	1.1E-7
B	290	92.4	223	12.4	1.64E-5
C	280	84.7	215	9.4	8.3E-8
D	270	72.3	173	4.7	9.1E-7

conversion (Figs. 8, Table IV). The T_g of PPP obtained from aromatization of P(DHCD-DA) increased with increasing conversion of P(DHCD-DA) to PPP (Table IV). As PPP content increased in a mixture of P(DHCD-DA) and PPP, more rigid phenylene units were formed via fully extended π bond conjugation. On the other hand, flexible pendant acetate group reduced T_g of the polymer by acting as internal diluents before aromatization, and thus provided molecular chain flexibility and reduced the rotational energy requirements in the backbone. This explains the increased T_g with increasing aromatization temperature. Although the T_g of P(DHCD-DA) obtained at 201°C was higher than that of PPP obtained at 173°C which had also a low aromatization degree (72.3%). As the P(DHCD-DA) molecular chains were more regular compared with those of the PPP with low degree of aromatization which could lower the T_g of PPP. The relationship between PPP conversion and crystallinity of each sample revealed three characteristic maxima at 2θ values of 19.5°, 22.5°, and 27.7° for PPP crystallinity, respectively, (Fig. 8 and Table IV). The crystallinity increased with the growth of the aromatization degree, indicating the more the rigid phenylene units, the higher the crystallinity.

Thermal stability of the PPP was evaluated using TGA in nitrogen and air atmospheres, respectively, (Fig. 9). PPP with low molecular weight started degradation at ~250°C under air atmosphere and 300°C under nitrogen atmosphere, respectively. Therefore, it is beneficial to conduct the aromatization process under nitrogen at 300°C to avoid PPP oligomer degradation. The results also indicated that thermal stability increased with increasing PPP M_w , as PPP with a high molecular weight showed much higher thermal stability from a degradation temperature of

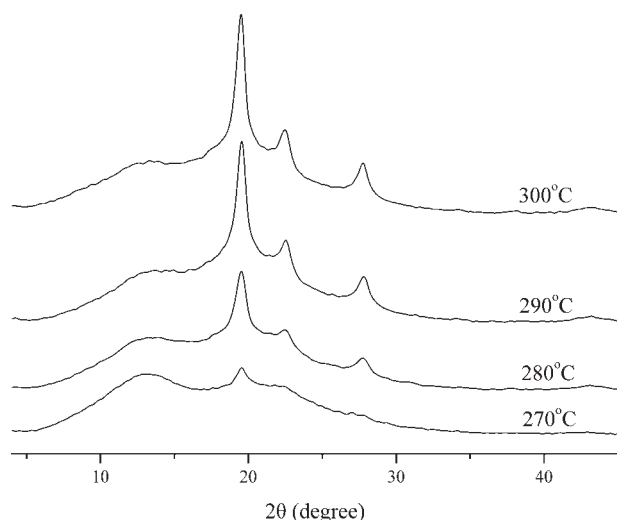


Figure 8 X-ray diffraction patterns of PPP with different degrees of aromatization.

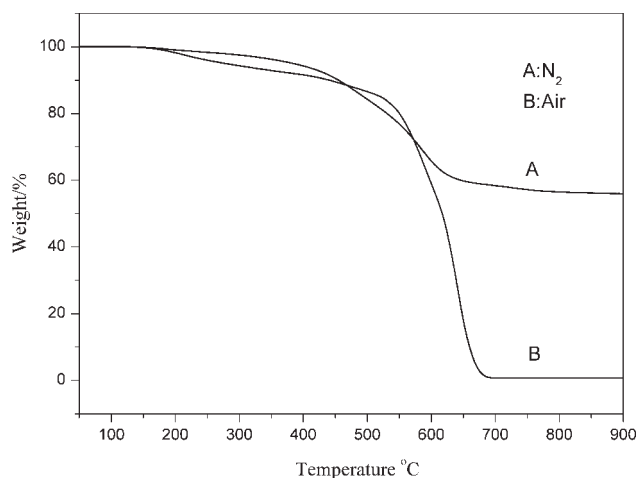


Figure 9 TGA thermograms of PPP. (A) under a nitrogen atmosphere and (B): under an air atmosphere.

500 to 650°C under both nitrogen and air atmosphere. These results were in good agreement with the data reported previously.²²

CONCLUSIONS

Fractionation distillation was effective for obtaining pure PPP monomer DHCD-DA by removing traces of phenol, quinone, and phenyl acetate, which were inhibitors of DHCD-DA polymerization to P(DHCD-DA). Among the four different polymerization methods employed for P(DHCD-DA) synthesis including bulk polymerization initiated by different catalysts, solution polymerization, and emulsion polymerization, the bulk polymerization initiated by BPO and ferrous sulfate redox system showed most effective for DHCD-DA polymerization, leading to the highest molecular weight and the highest yield. A standard curve was established to calculate the degree of aromatization based on FTIR absorptions of different function groups in P(DHCD-DA) and PPP. Results demonstrated that the aromatization degree increased with increasing aromatization temperature. The glass transition temperature and the crystallinity of PPP increased with the aromatization degree. Moreover, thermal property study revealed that PPP had thermostability both in nitrogen and in air atmospheres. All these results provided useful information for synthesis of conductive polymer PPP.

References

- Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J Chem Soc Chem Com* 1977, 16, 578.
- Chiang, C. K.; Fincher, C. R., Jr. Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. *J Phys Rev Lett* 1977, 39, 1098.
- Heeger, A. *J Synth Met* 2002, 125, 23.
- MacDiarmid, A. G. *Synth Met* 2002, 125, 11.
- Adam, P.; Patrice, R. *Prog Polym Sci* 2002, 27, 135.
- Han, G. Y.; Shi, G. Q. *Sens Actuators B* 2004, 99, 525.

7. Han, G. Y.; Shi, G. Q.; Qu, L. T.; Yuan, J. Y.; Chen, F. E.; Wu, P. Y. *Polym Int* 2004, 53, 1554.
8. Goto, H. *Macromol Chem Phys* 2006, 207, 1087.
9. Wan, M. X.; Li, J. C. *J Polym Sci Part A: Polym Chem* 1998, 36, 2799.
10. Zhang, Z. M.; Deng, J. Y.; Shen, J. Y.; Wan, M. X.; Chen, Z. *J Macromol Rapid Commun* 2007, 28, 585.
11. Li, Z.; Li, Q. Q.; Qin, A. J.; Dong, Y. Q.; Lam, J. W. Y.; Dong, Y. P.; Ye, C.; Qin, J. G.; Tang, B. Z. *J Polym Sci Part A: Polym Chem* 2006, 44, 5672.
12. Xie, Z. L.; Peng, H.; LAM, J. W. Y.; Chen, J. W.; Zheng, Y. H.; Qiu, C. F.; Kwok, H. S.; Tang, B. Z. *Macromol Symp* 2003, 195, 179.
13. Öpik, A.; Golovtsov, I.; Lobanov, A.; Kerm, K. *Synth Met* 1993, 55, 4924.
14. Shacklette, L. W.; Chance, R. R.; Ivory, D. M.; Miller, G. G.; Baughman, R. H. *Synth Met* 1980, 1, 307.
15. Ivory, D. M.; Miller, G. G.; Sowa, J. M.; Shacklette, L. W.; Chance, R. R.; Baughman, R. H. *J Chem Phys* 1979, 71, 1506.
16. Kovacic, P.; Wu, C. *J Polym Sci* 1960, 47, 448.
17. Kovacic, P.; Jones, M. B. *Chem Rev* 1987, 87, 357.
18. Kovacic, P.; Kyriakis, A. *J Phys Soc Jpn* 1963, 85, 454.
19. Kovacic, P.; Koch, F. W. *J Org Chem* 1963, 28, 1864.
20. Yamamoto, T.; Hayash, Y.; Yamamoto, Y. *Bull Chem Soc Jpn* 1978, 2091, 51.
21. Natori, I.; Natori, S.; Sato, H. *Macromolecules* 2006, 39, 3168.
22. Ballard, D. G. H.; Curtis, A.; Shirley, J. M.; Taylor, S. C. *Macromolecules* 1988, 21, 294.
23. Ouyang, S. P.; Sun, S. Y.; Liu, Q.; Chen, J. C.; Chen, G. Q. *Appl Microbiol Biotechnol* 2007, 74, 43.
24. Ballard, D. G. H.; Blacker, A. J.; Woodley, J. M.; Taylor, S. C. In *Plastics from Microbes: Microbial Synthesis of Polymers and Polymer Precursors*; Mobley, D. P., Ed.; Hanser, New York, 1994; p 139.
25. Ma, Q. X. Bio-Production of *Cis*-3,5-dihydroxycyclohexa-1,2-diene by Recombinant *Escherichia coli* JM109 and Synthesis of Polyparaphenylene), M.Sc. Thesis, Tsinghua University, Beijing, China, 2004.
26. Potts, W. J., Jr. *Chem Infrared Spectroscopy*; Wiley: New York, 1963.
27. Ravindranath, R.; Ajikumar, P. K.; Bahulayan, S.; Hanafiah, N. B. M.; Baba, A.; Advincula, R. C.; Knoll, W.; Valiyaveetil, S. *J Phys Chem B* 2007, 111, 6336.