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# Preparation and solubility of a partial ladder copolymer from *p*-phenylenediamine and *o*-phenetidine

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**Abstract**

A series of copolymers were synthesized by chemically oxidative polymerization of *p*-phenylenediamine (PPD) and *o*-phenetidine (PHT) in acidic aqueous media. The polymerization yield, intrinsic viscosity, and solubility of the copolymers were comprehensively studied by changing the comonomer ratio, polymerization time and temperature, oxidant, monomer/oxidant ratio, and acidic medium. As-prepared fine powder of the PPD/PHT copolymers was characterized by FT-IR, UV–vis, high-resolution $^1$H-NMR, and DSC techniques. A circular dichroism technique was firstly used to characterize the macromolecular structure of the copolymers. The results showed that the oxidative copolymerization from PPD and PHT is exothermic and the resulting copolymers exhibit an enhanced solubility in most of the organic solvents as compared with poly(*p*-phenylenediamine), sometimes also with poly(*o*-phenetidine). The polymer obtained is a real copolymer containing PPD and PHT units, and the actual PPD/PHT ratio calculated by $^1$H-NMR spectra of the polymers is very close to the feed ratio. The DSC measurement indicates that the copolymers are amorphous and chemically instable at elevated temperature.


*Keywords:* Aniline derivative copolymer; Oxidative polymerization; Ladder polymer

## 1. Introduction

There is a growing interest in the investigation on new aromatic nitrogenous polymers because of their versatility, easy preparation, and very attractive property—cost performance [1–3]. *p*-Phenylenediamine (PPD) homopolymer, one of the most important derivatives of polyaniline, is more attractive because of its unique flat ladder structure (Fig. 1a and b) and a wide application potential in electrocatalysis, electrochromics, sensors and electrode materials [1,4–10]. However, the commercial exploitation of the PPD homopolymer has been hampered by its intractable nature. Normally, the homopolymer is chemically or electrochemically produced as powder or as thin and brittle film, respectively, which is difficult to dissolve in common organic solvents or melt at elevated temperature, possibly due to its rigid ladder structure containing mostly phenazine rings [1,11]. In order to improve the solubility of the phenazine ring-containing polymers, the copolymers of phenylenediamine with aniline derivatives have been synthesized and alkyl and alkoxyl side groups have been introduced into the rigid ladder main chain. It is found that incorporation of the substituent groups will induce distortions in the ladder chain, reducing the conjugation and increasing the chain flexibility (Fig. 1c and d). In addition, because alkyl and alkoxyl substituents on the polymer chains must exhibit an affinity to organic solvents, the solubility of the polymers is also significantly improved. Two representative aniline derivatives such as 2,3-xylidine (XY) and *o*-anisidine (AS) have been selected as the comonomers for the preparation of the partial ladder copolymers containing methyl and methoxy side groups

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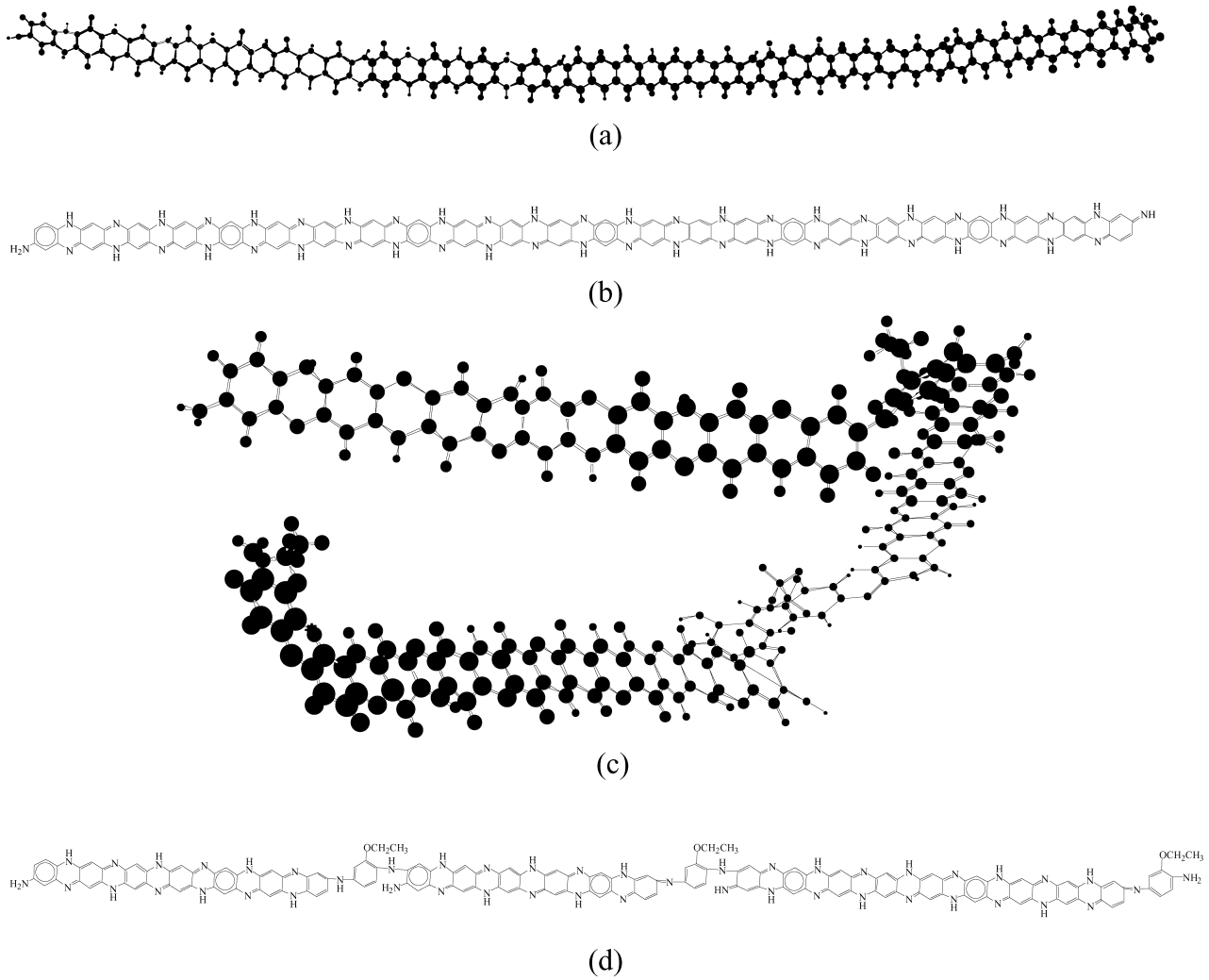



Fig. 1. The chemical structure of the PPD-containing polymers (DP = 24): (a) a steric structure and (b) a molecular structure of PPD homopolymer, (c) a steric structure and (d) a molecular structure of PPD/PHT (88/12) copolymer (DP = 25). The steric structures in (a) and (c) are simulated by the CS Chem3D Pro developed by CambridgeSoft, 1999.

[1,12,14,15]. It is found that the partial ladder copolymers indeed possess appreciably higher solubility in common organic solvents compared to the whole ladder polymers [12–14]. It can be predicted that longer substituents may cause larger distortions in the polymer chains, greater distance between the polymer chains, as well as stronger affinity to organic solvents, finally leading to more tremendous improvement of polymer solubility. In order to examine the effect of slightly longer substituent, *o*-phenetidine (PHT), for the first time, is chosen to copolymerize with PPD. Furthermore, the copolymerization of PPD with PHT is also believed to take advantage of the combination of good solubility of poly(PHT) with the novel ladder structure of poly(PPD). In this paper, PPD/PHT copolymers with seven monomer ratios were prepared by a chemically oxidative polymerization. The dependence of the polymerization yield and intrinsic viscosity of the copolymers on the polymerization conditions such as comonomer ratio, time, temperature, monomer/oxidant ratio, oxidant variety, acid concentration and its species, and reaction medium, has been the first elaborated. Their macromolecular structure, solubility, and thermal behavior are investigated systematically.

## 2. Experimental

### 2.1. Polymerization

PPD, PHT, oxidants, acids, and solvents were commercially obtained and used as received. PPD/PHT copolymers were prepared by an oxidative polymerization through a previously described method [12,13,15–17]. A representative procedure for the preparation of the PPD/PHT (10/90) copolymer is as follows: 25 ml of a 1 M HCl solution was added with 0.22 g (2 mmol) PPD and 2.38 ml (18 mmol) PHT in a 100 ml glass flask in water bath and magneto-stirred vigorously for half an hour. Ammonium persulfate

$[(NH_4)_2S_2O_8]$, 4.657 g (20 mmol), was dissolved separately in 15 ml 1 M HCl to prepare an oxidant solution. The monomer solution was then treated with the oxidant solution, added drop wise at a rate of one drop for every 3 s at 12 °C in ca. 45 min (the total monomer/oxidant molar ratio is 1/1). Immediately, after the first few drops, the reaction solution turned black. The reaction mixture was stirred for 24 h at ambient temperature. The copolymer HCl salt was isolated from the reaction mixture by filtration and washed with an excess of distilled water to remove the oxidant and oligomers. The HCl salt was subsequently neutralized in 140 ml of 0.2 M ammonium hydroxide and stirred for 24 h to obtain the base form of PPD/PHT copolymer. The copolymer base was washed with excess water. A bluish-black solid powder was left to dry in ambient air for 1 week. The copolymer of 1.671 g was obtained with a yield of 62.8%. The PPD/PHT copolymers exhibit the following nominal partial ladder structure in Scheme 1.

### 2.2. Measurements

The intrinsic viscosity for the PPD/PHT copolymers in DMSO was measured with Ubbelodhe viscosimeter at 25 °C. The solubility of the copolymers was evaluated using the following method: polymer powder sample of 10 mg was added into the solvent of 1 ml and dispersed thoroughly. After the mixture was swayed continuously for 24 h at room temperature, the solubility was characterized. IR spectra were recorded on a Nicolet FT-IR 470 spectrophotometer at 2 $cm^{-1}$ resolution on KBr pellets. UV–vis spectra were measured on a U-3000 Spectrophotometer (Hitachi Ltd, Tokyo, Japan) in a range of 190–1100 nm with a homogeneous solution of the copolymers in DMSO. Circular dichroic (CD) spectra of polymers were taken with a JASCO J-715-150S Spectropolarimeter. $^1$H-NMR spectra were obtained in deuterated DMSO using a Bruker DMX 500 spectrometer operating at 500.13 MHz. DSC measurements were performed at a heating rate of 40 °C/min with a sample size of 4–7 mg using a Perkin-Elmer 7 Pyris Thermal Analyzer.

## 3. Results and discussion

### 3.1. Synthesis of the PPD/PHT copolymers

The oxidative copolymerization of PPD and PHT with ammonium persulfate as an oxidant in 40 ml 1 M HCl aqueous solution affords fine and uniform bluish-black particles with several micrometers as products after the oxidative polymerization of 24 h. The progress in copolymerization reaction was followed by measuring the solution temperature. It is found that with dropping oxidant solution slowly and regularly, the polymerization solution temperature rises and exhibits one peak and finally reaches a nearly constant temperature. PPD/PHT (50/50) copolymerization exhibits the strongest exothermic capability among the five-copolymerization systems, indicating the strongest polymerizing tendency and the most violent polymerization. The enhancement of the solution temperature is 9.6 °C for the PPD/PHT (50/50) system, as listed in Table 1. On contrary, PPD/PHT (90/10) copolymerization exhibits the weakest exothermic effect with an enhancement of the solution temperature of 3.0 °C. These results may be due to the highest initial polymerization temperature for PPD/PHT (50/50) and the lowest initial temperature for PPD/PHT (90/10). That is to say, the exothermic capacity from the PPD/PHT copolymerization is dependent on the initial temperature of reaction solution. In other words, initial solution temperature appears important for the oxidative copolymerization of PPD with PHT. It should be noted that different enhancement in solution temperature also be due to the slight difference in dropping rate of oxidant solutions. The exception of PPD/PHT (10/90) may be due to slightly slow dropping rate of oxidant solution.

It is found from Fig. 2 that the copolymerization of PPD and PHT is significantly dependent on the comonomer ratio. The yield and intrinsic viscosity of the copolymers are the highest at the feed PHT content ranging from 0 to 30 mol%, the second highest at the feed PHT content from 90 to 100 mol%, but the lowest at the feed PHT content from 50 to 70 mol%. This must be attributable to the higher reactivity of the PPD monomer and the higher chain rigidity of the ladder structure from PPD unit than PHT monomer and PHT unit, respectively. On the other hand, the

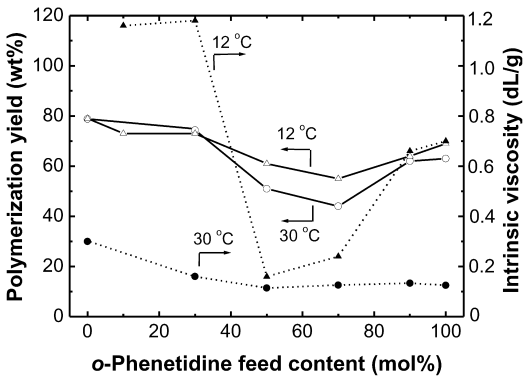
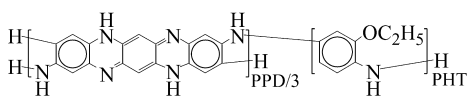



Fig. 2. Influence of *o*-phenetidine (PHT) feed content on polymerization yield (△12 °C, ○30 °C) and intrinsic viscosity (▲12 °C, ●30 °C) of *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) copolymers with monomer/$(NH_4)_2S_2O_8$ ratio of 1/1 for polymerization time of 24 h at two polymerization temperatures of 12 and 30 °C in 1 M HCl.




**Unit PPD** **Unit PHT**

Scheme 1.

Table 1
Effect of PPD/PHT molar ratio on solubility of *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) copolymers obtained with oxidant $(NH_4)_2S_2O_8$/monomer molar ratio of 1/1 in 1 M HCl aqueous solution

| PPD/PHT feed molar ratio | Polymerization temperature | Solubility[a] and solution color[b] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Initial/top/$\Delta T$ (°C) | NMP (wt%) | DMSO (wt%) | DMF (wt%) | Formic acid (wt%) | *m*-Cresol (wt%) | $CHCl_3$ | THF | Toluene | Xylene | $H_2SO_4$ |
| | Solubility parameter ($J^{1/2}/cm^{3/2}$) | 23 | 27 | 25 | 25 | 23 | 19 | 20 | 18 | 18 | |
| | Polarity index | 6.7 | 7.2 | 6.4 | 6.5 | 7.4 | 4.1 | 4.0 | 2.4 | 2.5 | |
| 0/100[c] | 11.0/–/– | 100(bb) | 100(bb) | 100(bb) | 100 | 100 | MS(bb) | MS(bb) | PS(br) | PS(bl) | S(bb) |
| 10/90 | 11.4/15.1/3.7 | 100(bb) | 100(bb) | 100(bb) | 100(bl) | 100(bl) | S(bb) | MS(bb) | PS(br) | PS(bl) | S(bb) |
| 30/70 | 11.1/17.5/6.4 | 100(bb) | 100(bb) | 100(bb) | 100(bl) | 100(bl) | S(bb) | PS(bl) | PS(br) | PS(bb) | S(bl) |
| 50/50 | 12.4/22.0/9.6 | 100(bb) | 100(bb) | 100(bb) | 100(bl) | 100(bl) | MS(r) | PS(bl) | SS(r) | SS(r) | S(bl) |
| 70/30 | 10.8/17.0/6.2 | 100(br) | 56(br) | 42(br) | 100(bl) | 83(br) | PS(br) | PS(br) | IS | SS(r) | S(bl) |
| 90/10 | 10.4/13.4/3.0 | 53(br) | 19(br) | 14(br) | 100(br) | 20(br) | SS(br) | SS(br) | IS | IS | S(bl) |
| 100/0 | 30/–/– | 24(b) | 15(b) | 17(b) | 100(bl) | MS(bl) | IS | PS(b) | IS | IS | S(bl) |

[a] IS, insoluble; MS, mainly soluble; PS, partially soluble; S, soluble; SS, slightly soluble.
[b] The solution color is indicated in the parentheses with the following abbreviations: b, brown; bb, bluish black; bl, black; br, brownish red; g, green; r, red; v, violet; vr, violet red.
[c] Copolymerization time is 13 h.

enhancement of the intrinsic viscosity may be also responsible for the elevation of the molecular weight of the copolymers. The fact that the copolymers usually exhibit lower yield and lower intrinsic viscosity than the two homopolymers implies a retarding effect between PPD and PHT monomers each other during the copolymerization, i.e. the copolymerizing ability between the both monomers is lower than the respective homopolymerizing ability of the both monomers alone. Furthermore, this retarding effect seems the strongest at almost the same molar content of the two monomers. This clearly suggests a strong interaction between the two monomers, leading to the formation of a real copolymer containing both PPD and PHT units.

The change of polymerization yield and intrinsic viscosity with polymerization time is listed in Table 2. It can be seen that the polymerization yield and intrinsic viscosity of PPD/PHT (50/50) copolymer reach the highest value of 67% and 0.15 dl/g, respectively, at 10 h, and exhibit a decreasing tendency with prolongating polymerization time from 10 to 48 h. This could be due to a gradually increased polymerization and propagation rates and not apparent hydrolysis with increasing time up to 10 h. After 10 h, both the yield and the intrinsic viscosity decrease slowly with further prolongation of polymerization time due to a gradually apparent hydrolysis in acidic media. From Table 2, it can be concluded that 10 h might be the optimal polymerization time for copolymerization of PPD and PHT and too long polymerization time may result in the decrease of the yield and molecular weight.

As shown in Fig. 3, by elevating the polymerization temperature from −20 to 30 °C, both the polymerization yield and intrinsic viscosity of the PPD/PHT copolymers exhibit a substantially decreasing tendency. It appears that −20 °C is more suitable for the preparation of PPD/PHT (50/50) copolymer with relatively high molecular weight possibly due to lower chain terminating rate of oxidative polymerization at low temperature. Both lower yield and lower intrinsic viscosity of the polymers obtained at higher temperature should be attributed to higher hydrolysis rate, especially from the PHT units. Similarly, both higher yield

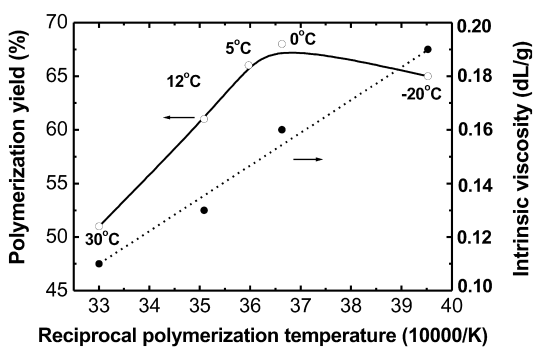



Fig. 3. The effect of polymerization temperature on polymerization yield and intrinsic viscosity of *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) (50/50) copolymers with monomer/$(NH_4)_2S_2O_8$ ratio 1/1 in 1 M HCl aqueous solution and polymerization time 24 h.

Table 2
The effect of polymerization time on yield, intrinsic viscosity, and solubility of *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) (50/50) copolymers With monomer/$(NH_4)_2S_2O_8$ ratio 1/1 in 1 M HCl aqueous solution

| Polymerization | | | Solubility in solvents and solution color[a] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (h) | Yield (%) | Polymer intrinsic viscosity (dl/g) | NMP (wt%) | DMSO (wt%) | DMF (wt%) | Formic acid (wt%) | $H_2SO_4$ | *m*-Cresol | $CHCl_3$ | THF | Toluene | Xylene | Xylene/*n*-butanol (9/1, vol) | Toluene/DMSO (9/1, vol) |
| 5 | 51 | 0.14 | 100(br) | 100(br) | 100(br) | 100(bl) | S(g) | S(bl) | PS(br) | PS(br) | SS(b) | SS(b) | PS(br) | PS(br) |
| 10 | 67 | 0.15 | 100(r) | 100(r) | 100(r) | 100(bl) | S(g) | S(bb) | PS(b) | PS(br) | SS(r) | IS | MS(b) | SS(r) |
| 15 | 54 | 0.12 | 100(br) | 100(br) | 100(br) | 100(bl) | S(bb) | MS(bb) | PS(br) | PS(br) | PS(br) | SS(b) | MS(b) | PS(br) |
| 20 | 53 | 0.11 | 100(br) | 100(br) | 100(br) | 100(bl) | S(bb) | S(bb) | PS(br) | PS(br) | PS(br) | SS(b) | PS(b) | PS(br) |
| 24 | 61 | 0.13 | 100(bb) | 100(bb) | 100(b) | 100(bl) | S(bl) | S(bl) | MS(b) | PS(b) | SS(r) | SS(r) | PS(b) | MS(bl) |
| 48 | 50 | 0.06 | 100(b) | 100(br) | 100(b) | 100(bl) | S(bb) | MS(bb) | PS(b) | PS(b) | SS(bl) | SS(b) | PS(b) | PS(b) |

[a] The full name of the abbreviations is referred to the footnotes of Table 1.

and higher intrinsic viscosity for the copolymers with PHT monomer feed content from 50 to 100 mol% were found at 12 than 30 °C in Fig. 2, due to relatively significant hydrolysis from the PHT units in all molecular-weight fractions of the polymers at 30 °C. Note that much higher intrinsic viscosity but practically the same yield for the copolymers with PHT monomer feed content from 0 to 30 mol% are observed at 12 than 30 °C, possibly owing to relatively low hydrolysis from more PPD units at relatively high temperature.

The effect of monomer/oxidant (ammonium persulfate) molar ratio on the copolymerization of PPD/PHT (50/50) in 1 M HCl in a temperature range from 12 to 16 °C was studied. It can be seen from Table 3 that with changing monomer/oxidant molar ratio from 4/8 to 4/2 the copolymerization yield exhibits a maximum of 99% at 4/6 whereas the intrinsic viscosity of the copolymer decreases significantly. When less oxidant was added, the oxidant will be consumed fast and some monomers may not be further oxidized to polymerize, leading to low polymerization yield and even intrinsic viscosity. It suggests that the optimal monomer/oxidant molar ratio might be 4/8 for the preparation of PPD/PHT (50/50) copolymer with both relatively high molecular weight and high polymerization yield. However, as listed in Table 3, the solubility of the PPD/PHT (50/50) copolymer in most solvents is better with monomer/oxidant molar ratio 4/4 than 4/6–4/8. Therefore, the following investigation has been done by using equivalent molar contents of monomers and oxidant.

Influence of oxidant variety and its standard reduction potential on polymerization yield and intrinsic viscosity of the PPD/PHT (50/50) copolymers obtained is listed in Table 4. It seems that $K_2Cr_2O_7$ is the best oxidant to prepare the copolymer with the highest intrinsic viscosity. However, the copolymer obtained using $K_2Cr_2O_7$ exhibits the yield higher than 100% as well as the poorest solubility in nonacid solvents, indicating a presence of Cr-containing inorganic impurity in the copolymer. When $FeCl_3$ with the lowest reduction potential was used as an oxidant, the copolymer obtained exhibits both the lowest intrinsic viscosity and the lowest yield. Too low reduction potential of $FeCl_3$ to promote the polymerization efficiently must be one of the reasons. High yields of copolymerization are observed when $K_2S_2O_8$, $Na_2S_2O_8$, and $(NH_4)_2S_2O_8$ are employed as oxidants because their reduction potentials are high enough to achieve a fast rate of copolymerization of PPD and PHT. That is to say, oxidant plays an important role in copolymerization yield of PPD/PHT. On the other hand, it appears that $K_2S_2O_8$ is the best oxidant for the preparation of the copolymer with high yield and high intrinsic viscosity. However, the solubility of the PPD/PHT (50/50) copolymer formed using $K_2S_2O_8$ is slightly poorer than that using $(NH_4)_2S_2O_8$. Moreover, the solubility of $K_2S_2O_8$ itself in acidic aqueous solution is much poorer than that of $(NH_4)_2S_2O_8$. Therefore, $(NH_4)_2S_2O_8$ is still used as oxidant in the posterior study.

Table 3
The effect of $(NH_4)_2S_2O_8$ content on yield, intrinsic viscosity, and solubility of *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) (50/50) copolymers at polymerization temperature 13–16 °C in 1 M HCl aqueous solution and polymerization time 24 h

| Monomer/oxidant feed molar ratio | Yield (%) | Intrinsic viscosity (dl/g) | Solubility in solvents and solution color[a] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | NMP (wt%) | DMSO (wt%) | DMF (wt%) | Formic acid (wt%) | $H_2SO_4$ | *m*-Cresol | $CHCl_3$ | THF | Toluene | Xylene | Xylene/*n*-butanol (9/1, vol) | Toluene/DMSO (9/1,vol) |
| 4/8 | 92 | 0.27 | 100(vr) | 100(b) | 75(vr) | 100(bl) | S(bl) | S(bl) | PS(br) | PS(b) | IS | IS | SS(r) | PS(r) |
| 4/6 | 99 | 0.11 | 42(b) | 100(b) | 100(vr) | 100(bl) | S(bb) | MS(bb) | PS(br) | PS(br) | IS | IS | PS(b) | SS(br) |
| 4/4 | 61 | 0.13 | 100(bb) | 100(bb) | 100(bl) | 100(bl) | S(bl) | S(bl) | MS(bl) | PS(bl) | SS | SS | PS(b) | MS(bl) |
| 4/3 | 25 | 0.09 | 100(br) | 100(br) | 100(br) | 100(bl) | S(bb) | S(bb) | PS(br) | PS(br) | PS(br) | SS(br) | PS(b) | MS(br) |
| 4/2 | 4 | 0.07 | 100(vr) | 100(b) | 99(bl) | 99(bl) | S(bl) | S(bl) | PS(b) | PS(br) | PS(br) | PS(b) | MS(b) | MS(b) |

[a] The full name of the abbreviations is referred to the footnotes of Table 1.

Table 4
The effect of HCl concentration on yield, intrinsic viscosity, and solubility of *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) (50/50) copolymers with monomer/oxidant ratio 1/1 in 1 M HCl aqueous solution

| Polymerization | | | Intrinsic viscosity (dl/g) | Solubility in solvents and solution color[a] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Oxidant | Standard reduction potential (V) | Yield (%) | | NMP (wt%) | DMSO (wt%) | DMF (wt%) | Formic acid (wt%) | $H_2SO_4$ | *m*-Cresol | $CHCl_3$ | THF | Toluene | Xylene | Xylene/*n*-butanol (9/1,vol) | Toluene/DMSO (9/1, vol) |
| $FeCl_3$ | 0.77 | 6 | 0.14 | 98(bb) | 95(bb) | 91(bb) | 100(bl) | S(bl) | S(bb) | PS(br) | PS(br) | SS(r) | SS(r) | PS(br) | PS(br) |
| $K_2Cr_2O_7$ | 1.33 | 212 | 0.68 | 12(r) | 24(br) | 35(r) | 100(br) | S(bl) | SS(bl) | SS(r) | SS(r) | IS | IS | SS(r) | SS(r) |
| $(NH_4)_2S_2O_8$ | 2.01 | 61 | 0.13 | 100(bb) | 100(bb) | 100(b) | 100(bl) | S(bl) | S(bl) | MS(b) | MS(b) | SS(r) | SS(b) | PS(b) | MS(bl) |
| $Na_2S_2O_8$ | 2.01 | 62 | 0.10 | 100(r) | 100(br) | 99(b) | 100(bl) | S(bl) | S(bb) | PS(br) | PS(br) | SS(br) | SS(b) | PS(br) | PS(br) |
| $K_2S_2O_8$ | 2.01 | 71 | 0.17 | 100(bb) | 100(b) | 97(b) | 100(bl) | S(g) | S(bb) | PS(br) | PS(br) | SS(br) | SS(br) | PS(br) | PS(br) |

[a] The full name of the abbreviations is referred to the footnotes of Table 1.

Adding some water-soluble organic solvents into the polymerization medium can significantly influence the polymerization yield although the intrinsic viscosity is not significantly influenced (Table 5). It is interesting that the yield increases slightly with adding organic solvent (ethanol) with high nucleophilicity into acidic water. On contrary, the addition of solvent with low nucleophilicity results in a decrease in the yield. The possible reason is that the organic aromatic amine monomers have better solubility in ethanol than acidic water, leading to more uniform dispersion of the monomers and then more sufficient chain initiation. Very analogical intrinsic viscosity of the copolymers listed in Table 5 could be due to similar insolubility of the active polymer chains in the four-polymerization media.

Table 6 lists the dependence of the polymerization yield and intrinsic viscosity of PPD/PHT (50/50) copolymer on acidic medium variety. When $H_2SO_4$ was employed, the highest yield and highest intrinsic viscosity of the copolymer are observed. The second highest yield and intrinsic viscosity of the copolymer is obtained if $HNO_3$/$H_2SO_4$ (1/1 vol) was used as a polymerization medium. Therefore, it is concluded that the copolymers obtained in $H_2SO_4$ and/or $H_2SO_4$-containing media exhibit both higher yield and intrinsic viscosity. Contrarily, the copolymer formed in HCl exhibits lower yield, and the copolymer formed in HCl/$HNO_3$ (1/1 vol) exhibits lowest yield and lowest intrinsic viscosity. It appears that HCl is not good acidic medium for the copolymerization though HCl is very frequently used as polymerization of aniline.

In addition, not only the nature of protonic acid but also its concentration affects the copolymerization of PPD and PHT monomers, as listed in Table 7. With increasing HCl concentration from 0.5 to 2.0 M, the yield exhibits a maximum together with a higher intrinsic viscosity in 1 M HCl, since $H^+$ concentration in 0.5 M HCl is not high enough to maintain a stable chain propagation due to a weak protonation but $H^+$ concentration in 2.0 M HCl is high enough to result in slight degradation due to hydrolysis. The dependence of the intrinsic viscosity, i.e. molecular weight, of PPD/PHT copolymers on the acidity of the reaction medium clearly indicates that two competing processes (polymerization and hydrolysis) control the formation of the copolymers. It appears that 1.0 M HCl is the best for the formation of PPD/PHT copolymers with high yield and high intrinsic viscosity.

### 3.2. Solubility of the PPD/PHT copolymers

It can be seen from Tables 1–8 that the solubility of PPD/PHT copolymers is strongly influenced by PPD/PHT molar ratio and oxidant variety, but slightly influenced by polymerization time, polymerization temperature, monomer/oxidant ratio, organic additive, acid variety, and acid concentration. It is seen that all copolymers and two homopolymers are completely soluble in formic acid and

Table 5
The effect of organic solvent as an additive on yield, intrinsic viscosity, and solubility of *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) (50/50) copolymers with monomer/$(NH_4)_2S_2O_8$/HCl molar ratio of 1/1/2 in 1 M HCl solution for 24 h

| Polymerization media HCl/organic solvent = 1/1 (vol) | Nucleophilicity of solvent (kcal/mol) | Polymer | | Solubility in solvents and solution color[a] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Yield (%) | Intrinsic viscosity (dl/g) | NMP (wt%) | DMSO (wt%) | DMF (wt%) | Formic acid (wt%) | $H_2SO_4$ | *m*-Cresol | $CHCl_3$ | THF | Toluene | Xylene |
| Acetonitrile | 14.1 | 34 | 0.11 | 99(br) | 86(b) | 99(br) | 100(bl) | S(bl) | S(bl) | PS(b) | MS(b) | SS(b) | SS(b) |
| Acetone | 17.0 | 52 | 0.07 | 100(br) | 100(bl) | 100(bl) | 100(bl) | S(bl) | S(bl) | PS(bl) | PS(bl) | PS(br) | SS(br) |
| Water | | 61 | 0.13 | 100(bb) | 100(bb) | 100(b) | 100(bl) | S(bl) | S(bl) | MS(b) | PS(b) | SS(r) | SS(r) |
| Ethanol | 31.5 | 63 | 0.12 | 100(br) | 100(b) | 99(bl) | 100(bl) | S(bl) | S(bl) | PS(b) | PS(b) | PS(b) | SS(b) |

[a] The full name of the abbreviations is referred to the footnotes of Table 1.

Table 6
Influence of acid variety on yield, intrinsic viscosity, and solubility of *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) (50/50) copolymers at oxidant/monomer molar ratio of 1/1 in 1 M acidic aqueous solution at about 13 °C

| Polymerization | | Intrinsic viscosity (dl/g) | Solubility in solvents and solution color[a] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Medium | Yield (%) | | NMP (wt%) | DMSO (wt%) | DMF (wt%) | Formic acid (wt%) | $H_2SO_4$ | *m*-Cresol | $CHCl_3$ | THF | Toluene | Xylene | Xylene/*n*-butanol (9/1, vol) | Toluene /DMSO (9/1, vol) |
| $HCl/HNO_3$ (1/1 vol) | 53 | 0.10 | 100(br) | 100(br) | 100(br) | 100(bl) | S(bb) | MS(bb) | PS(br) | PS(br) | SS(b) | SS(b) | PS(br) | PS(b) |
| HCl | 61 | 0.13 | 100(bb) | 100(bb) | 100(b) | 100(bl) | S(bl) | S(bl) | MS(b) | PS(b) | SS(r) | SS(r) | PS(b) | MS(bl) |
| $HNO_3$ | 64 | 0.14 | 100(br) | 100(br) | 100(br) | 100(bl) | S(bl) | MS(bl) | PS(br) | PS(br) | PS(br) | PS(br) | PS(br) | PS(br) |
| $H_3PO_4$ | 75 | 0.12 | 100(br) | 100(br) | 99(br) | 100(bl) | S(bl) | S(bl) | PS(b) | PS(br) | PS(br) | PS(br) | PS(bl) | PS(b) |
| $HCl/H_2SO_4$ (1/1 vol) | 77 | 0.12 | 100(br) | 100(b) | 100(br) | 100(bl) | S(bl) | S(bl) | PS(b) | PS(b) | PS(br) | PS(br) | PS(br) | PS(b) |
| $HNO_3/H_2SO_4$ (1/1 vol) | 78 | 0.16 | 100(br) | 100(b) | 100(br) | 100(bl) | S(bb) | S(bb) | PS(br) | PS(br) | PS(b) | SS(b) | MS(b) | PS(br) |
| $H_2SO_4$ | 81 | 0.20 | 94(b) | 100(b) | 100(b) | 100(bl) | S(bl) | S(bl) | PS(b) | PS(b) | PS(b) | SS(b) | PS(bl) | PS(br) |

[a] The full name of the abbreviations is referred to the footnotes of Table 1.

Table 7
The effect of HCl concentration on the yield, intrinsic viscosity, and solubility of *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) (50/50) copolymers with monomer/$(NH_4)_2S_2O_8$ molar ratio of 1/1

| Polymerization | | Intrinsic viscosity (dl/g) | Solubility in solvents and solution color[a] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [HCl] (M) | Yield (%) | | NMP (wt%) | DMSO (wt%) | DMF (wt%) | Formic acid (wt%) | $H_2SO_4$ | *m*-Cresol | $CHCl_3$ | THF | Toluene | Xylene | Xylene/*n*-butanol (9/1, vol) | Toluene/DMSO (9/1, vol) |
| 0.5 | 43 | 0.04 | 100(br) | 100(br) | 100(r) | 100(bl) | S(bb) | S(bb) | PS(br) | PS(br) | SS(br) | SS(b) | PS(br) | PS(br) |
| 1.0 | 61 | 0.13 | 100(bb) | 100(bb) | 100(b) | 100(bl) | S(bl) | S(bl) | MS(b) | PS(b) | SS(r) | SS(b) | PS(b) | MS(bl) |
| 1.25 | 44 | 0.14 | 100(r) | 100(br) | 100(r) | 100(bl) | S(bl) | S(bl) | PS(br) | PS(br) | PS(r) | SS(b) | PS(b) | MS(b) |
| 1.5 | 45 | 0.13 | 100(r) | 100(br) | 99.7(r) | 100(bl) | S(bl) | S(bl) | PS(br) | PS(b) | PS(r) | SS(r) | PS(br) | PS(br) |
| 2.0 | 46 | 0.10 | 100(b) | 100(b) | 100(b) | 100(bl) | S(bb) | S(bb) | PS(b) | PS(b) | SS(b) | IS | PS(b) | SS |

[a] The full name of the abbreviations is referred to the footnotes of Table 1.

Table 8
The effect of polymerization temperature on solubility of *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) (50/50) copolymers with monomer/$(NH_4)_2S_2O_8$ molar ratio 1/1 in 1 M HCl aqueous solution and polymerization time 24 h

| Polymerization temperature (°C) | Solubility in solvents and solution color[a] | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | NMP (wt%) | DMSO (wt%) | DMF (wt%) | Formic acid (wt%) | $H_2SO_4$ | *m*-Cresol | $CHCl_3$ | THF | Toluene | Xylene | Xylene/*n*-butanol (9/1, vol) | Toluene/DMSO (9/1, vol) |
| −20 | 100(bl) | 100(bl) | 100(bl) | 100(bl) | S(bl) | S(bb) | PS(bl) | PS(bl) | SS(bb) | SS(r) | PS(bb) | PS(bl) |
| 0 | 100(bb) | 91(bb) | 100(bl) | 100(bl) | S(bl) | PS(bb) | MS(br) | PS(br) | SS(br) | SS(r) | MS(bb) | PS(bl) |
| 12 | 100(bb) | 100(bb) | 100(bb) | 100(bl) | S(bl) | S(bl) | MS(b) | PS(bl) | SS(r) | SS(r) | PS(b) | MS(bl) |
| 30 | 100(br) | 100(br) | 98(br) | 100(v) | S(bl) | S(br) | PS(b) | PS(b) | IS | IS | SS(b) | PS(br) |

[a] The full name of the abbreviations is referred to the footnotes of Table 1.

$H_2SO_4$. The copolymers with PPD feed content of less than 90 mol% exhibit much better solubility in other eight solvents than PPD homopolymer (Table 1). In other words, with increasing feed PHT content, the PPD/PHT copolymers exhibit a monotonically enhanced solubility in the eight nonacid solvents. Finally, when PHT feed content is up to 50 mol%, the copolymers are totally soluble in NMP, DMSO, DMF, and *m*-cresol, and mainly soluble in $CHCl_3$. Apparently, good solubility of the copolymers results from the presence of a large number of ethoxyl substituents on the aniline ring, increasing the distance between the macromolecular chains and significantly reducing interactions between the chains of copolymers. On the other hand, the incorporation of PHT unit into PPD backbone can decrease the structural regularity and rigidity of the poly(PPD) chains as well as break the ladder structure of poly(PPD) to some extent (Fig. 1). Thus, it could be speculated that the improvement of the copolymer solubility with increasing PHT content might be due to the change of molecular structure rather than the change of intrinsic viscosity. In addition, improved solubility with inducing PPD unit into PHT polymer in $CHCl_3$ (Table 1) is a circumstantial evidence that the polymerization product is indeed copolymer containing PPD and PHT units rather than a simple mixture of two homopolymers. The solubility of PPD/PHT (50/50) copolymer in all nonacid solvents increases with the variation of the oxidant from $K_2Cr_2O_7$, $FeCl_3$, $Na_2S_2O_8$, $K_2S_2O_8$ to $(NH_4)_2S_2O_8$ (Table 4). This improvement of solubility should be attributed to the decrease of the molecular weight of the copolymer obtained. In conclusion, the PPD/PHT copolymers exhibit much better solubility in the solvents with the solubility parameter of 23–27 $J^{1/2}/cm^{3/2}$ and polarity index of 6.4–7.4 than with the solubility parameter of 18–20 $J^{1/2}/cm^{3/2}$ and polarity index of 2.4–4.1. The solvency of the solvents to the PPD/PHT copolymers becomes stronger in the following order

$$\text{Toluene} < \text{Xylene} < \text{THF} < CHCl_3 < \text{DMF} < \text{DMSO} < m\text{-Cresol} < \text{NMP} < \text{Formic acid} \leq H_2SO_4$$

### 3.3. FT-IR spectra of PPD/PHT copolymers

Representative FT-IR spectra for the copolymers with a whole PPD feed content from 0 to 100 mol% are shown in Fig. 4. A broad absorption band at ca. 3300–3500 $cm^{-1}$ can be described to N–H stretching [18,19], which suggests the presence of –NH– groups in PPD and PHT units. A weak peak at around 3055 $cm^{-1}$ should be due to aromatic C–H stretching vibrations. The two bands mentioned above become broader and shift to lower wave number with an increase in PPD feed content from 0 to 100 mol% because PPD unit contains less –NH– and aromatic C–H bonds. The systematical change also suggests the formation of a

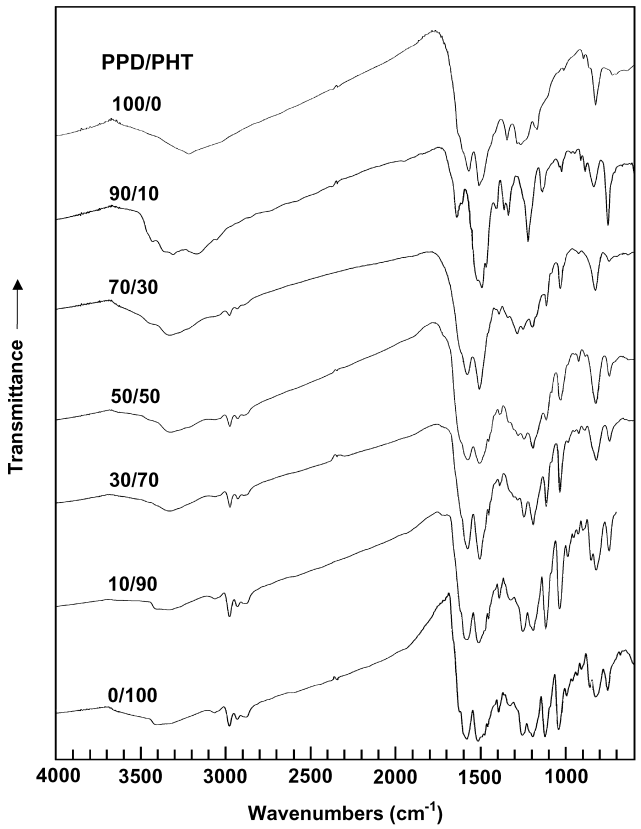



Fig. 4. FT-IR absorption spectra of the copolymers with seven *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) molar ratios of 0/100, 10/90, 30/70, 50/50, 70/30, 90/10 and 100/0.

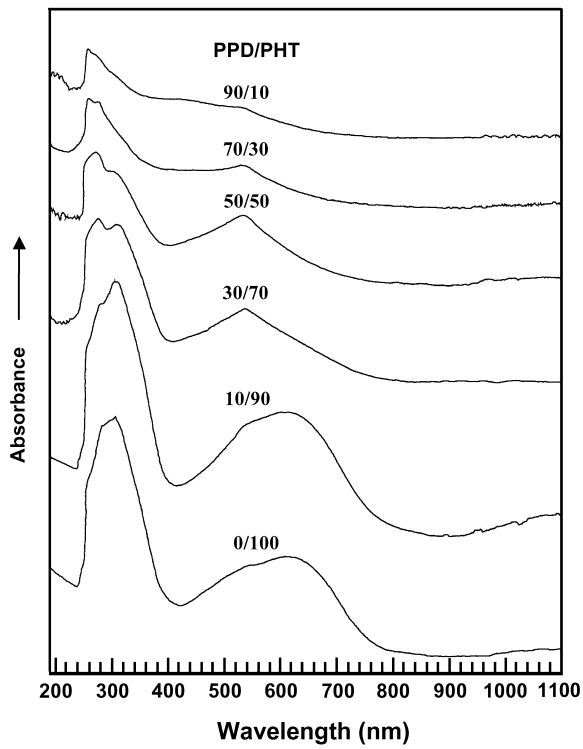



Fig. 5. UV–vis absorption spectra of the copolymers with *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) molar ratios of 0/100, 10/90, 30/70, 50/50, 70/30, and 90/10 in DMSO.

real copolymer between PPD and PHT units. Since PPD unit does not contain aliphatic C–H bond, the characteristics of IR absorption band of $-CH_3$ and $-CH_2-$ at 2800–3000 and 1460, 1380 $cm^{-1}$ should be ascribed to PHT unit. With increasing feed PPD content, the absorption intensity becomes weaker significantly and disappears in PPD homopolymer but the peak shape does not remarkably change. The reason is that the content of PHT in the copolymer decreases but the $-OCH_2CH_3$ in the polymer chain seems to keep the same form as that in the PHT homopolymer. The strong band at 1570 $cm^{-1}$ is attributed to quinonediimine unit while the band at 1511 $cm^{-1}$ is due to the stretching of benzenoid ring [18]. The imine –C=N– absorption locates at about 1300 $cm^{-1}$ and the out of plane bending of benzene ring locates at about 830 $cm^{-1}$. From Fig. 4, it can be seen that PHT homopolymer does not have the absorption at 1300 $cm^{-1}$. These are in agreement with the proposed structure in Scheme 1 and Fig. 1.

A big difference between the spectra of PPD/PHT copolymers and poly(PPD) or poly(PHT) was found and might also suggest an occurrence of the copolymerization effect between PPD and PHT monomers.

### *3.4. UV–vis spectra of the PPD/PHT copolymers*

Fig. 5 shows the UV–vis absorption spectra of six copolymers with feed PPD content from 0 to 90 mol% in DMSO. The UV–vis spectrum of PPD homopolymer is not shown in Fig. 5 because its solubility in DMSO is too poor. Two strong bands at shorter wavelength and two weak bands at longer wavelength are observed. In the spectra of polyaniline emeraldine (both oxidized and reduced samples), there exist two bands at 634 and 320 nm [20]. When oxidized, the peak at 634 nm is replaced by other absorption whose peak from 570 to 600 nm and an additional peak, below 300 nm, appeared. Polyaniline pernigraniline exhibits absorption at 278, 320 and 528 nm[18]. A band at 320 nm due to $\pi \rightarrow \pi^*$ transition between conjugated adjacent benzenoid rings and a band at 528 nm may be assigned to electronic transition of quinoneimine (quinoid) structures. Therefore, combined with Fig. 5, it could be proposed that the band at 278 nm should be ascribed to $\pi \rightarrow \pi^*$ transition between quinoid rings and benzenoid rings. UV–vis spectrum of poly(PHT) has four bands at 284, 310, 546, 614 nm because the poly(PHT) has two or more oxidation states. The poly(PHT) exhibits the band at 310 nm corresponding to the band at 320 nm of polyaniline, because of a shift to shorter wavelength by the influence of $-OCH_2CH_3$. Particularly, with increasing feed PPD content, the wavelength of all four bands shifts to lower value continuously. Band at 284 nm becomes stronger while band at 310 nm becomes weaker and almost disappears in PPD/PHT(90/10) polymer, which suggests that quinoneimine increase with increasing feed

PPD content and the transition between adjacent benzenoid rings decreases. The band at 284 nm shifts to shorter wavelength due to decreasing of π electron in quinoid structures with PPD unit increasing. Bands at 546 and 641 nm become weaker and band at 641 nm almost disappears when PPD content up to 30%, which suggests that PPD/PHT copolymers become more oxidized with increasing PPD unit and quinoneimine structures predominate in polymer chain. All analysis is in agreement with the proposed structure in Scheme 1 and Fig. 1. Additionally, the continuous variation of wavelength and intensity of UV–vis bands may result from copolymerization effect of PPD with PHT monomers. In other words, the polymer formed by oxidative polymerization of PPD with PHT monomers is the copolymer of two monomers rather than the mixture of two homopolymers.

### 3.5. High-resolution $^1$H-NMR spectra of the PPD/PHT copolymers

$^1$H-NMR spectra of the PPD/PHT copolymers are characterized by three main signals or groups of signals, which are exactly corresponding to the aromatic protons and two kinds of ethoxyl protons, as shown in Fig. 6. Those peaks in a wide range from 6.4 to 7.6 ppm should be ascribed to the benzenoid and quinoid protons of the PPD and PHT units. The strong peaks in a range between 3.9 to 4.2 and 0.8 to 1.4 ppm are assigned to protons in $-CH_2-$ and $-CH_3$ groups, respectively. Two strongest peaks at 2.49 and 3.33 ppm are due to protons of DMSO and water in DMSO. Additionally, several peaks in 5.7–6.4 ppm could be due to the protons of –NH– and $-NH_2$ groups [1,14,19]. It appears that the $^1$H-NMR spectra of PPD/PHT copolymers do not change systematically with increasing feed PPD content. These spectra are not much informative on the calculation of sequence distribution of the comonomer units because of a very similar environment of the aromatic protons in PPD and PHT units. Fortunately, based on a comparison of the area of aromatic proton peak (6.4–7.6 ppm) on PPD and PHT units with ethoxyl proton peak (3.9–4.2 or 0.8–1.4 ppm) on PPD unit, the ratio of PPD to PHT units in the copolymers can be calculated. Because there are the same numbers of aromatic protons as those of methyl protons on every PHT unit in the polymer chains, the number of aromatic protons on PPD units may be calculated through the following equation

PPD proton area

= Total aromatic proton area − Methyl proton area

therefore, the ratio of PPD over PHT = (PPD proton area/(8/3)) ÷ (Methyl proton area/3)

The calculated PPD/PHT molar ratios are 15/85, 34/66, and 52/48 for the copolymers with feed PPD/PHT molar ratios of 10/90, 30/70, 50/50, respectively, suggesting that the monomer feed in copolymer is significantly affected by

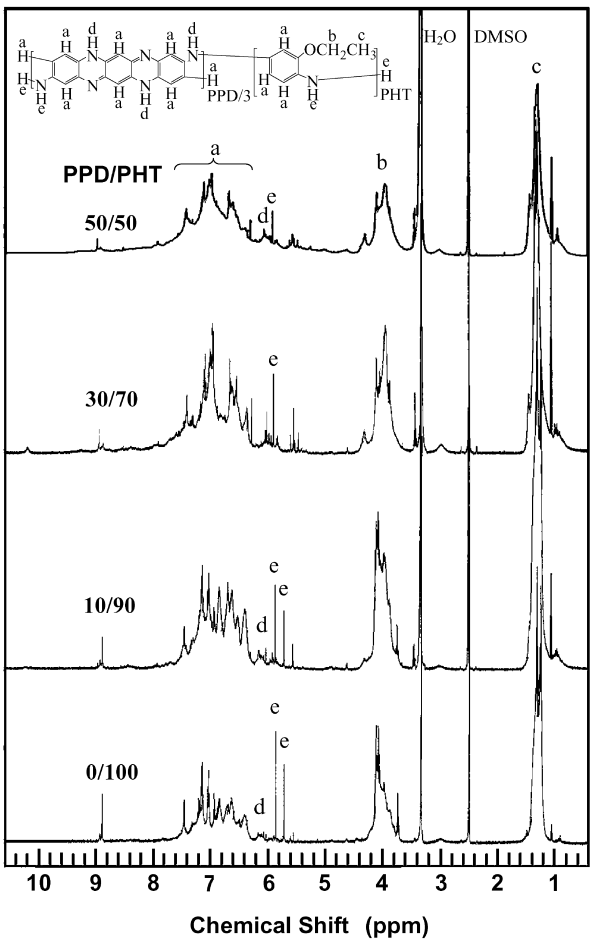



Fig. 6. 500 MHz $^1$H-NMR spectra of the copolymer solutions with *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) molar ratios of 0/100, 10/90, 30/70, and 50/50 in deuterated dimethylsulfoxide (DMSO-$d_6$).

the feed ratio of monomers. Apparently, the calculated PPD content is slightly higher than feed PPD content for PPD/PHT copolymers, implying a slightly high polymerizability of PPD monomer than PHT monomer, which was also confirmed by the polymerization yield and intrinsic viscosity of the PPD/PHT polymers shown in Fig. 2. Another one possible reason is that in 6.4–7.9 ppm there exist the resonance peaks of the protons of –NH– and $-NH_2$ groups [18].

### 3.6. Circular dichroism (CD) spectra of the PPD/PHT copolymers

The circular dichroism (CD) spectra of the PPD/PHT copolymers with six feed PPD content of 0, 10, 30, 50, 70 and 90 mol% are shown in Fig. 7, which confirms that they are chiroptically active. Poly(PHT) exhibits a positive band at ca. 200 nm, a negative band at 215 nm and some weak bands between 255 and 500 nm, while the spectra of PPD/PHT copolymers show remarkable differences. In contrast to poly(PHT), the band at 200 nm becomes negative and the band at 215 nm disappears in the spectra of PPD/PHT

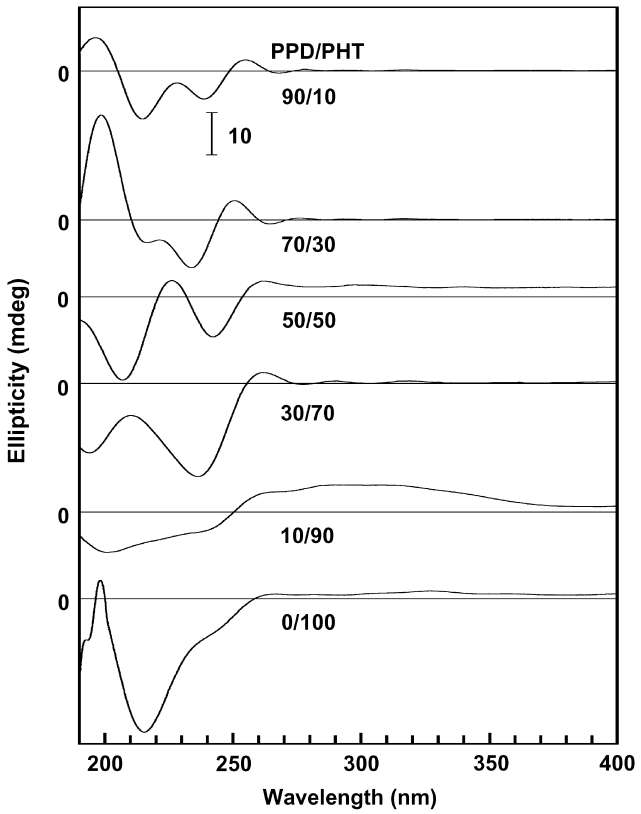



Fig. 7. Circular dichroic (CD) spectra of the copolymers with *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) molar ratios of 0/100, 10/90, 30/70, 50/50, 70/30, and 90/10 in DMSO.

(10/90). The different CD spectra confirm that the copolymers have a different conformation from the PHT homopolymer. The change in conformation of the polymer backbone is presumably due to the incorporation of rigid PPD ladder structure into poly(PHT) backbone that increases the rigidity of the polymer chains and thereby causes the polymer backbone to deviate from original arrangement. With increasing PPD feed content to 50 mol%, the CD spectra show similar chiroptical properties except for the change of the absorption intensities, indicating that the variation of the copolymer chain conformations becomes greater with increasing the content of PPD units, and the peaks at ca. 200, 210, and 235 nm shift to longer wavelength. When PPD content is up to 70 mol%, a remarkable wavelength shift was observed with CD bands at ca. 200, 220, 225, 235, and 250 nm. The reason may be that the PPD structures become predominated in the polymer chains with the PPD content of higher than 50 mol%, thereby resulting in a great change of the polymer conformations, further leading to the change of chiroptical characteristics of polymers. With increasing PPD feed content to 90 mol%, the CD spectra show similar chiroptical properties but the bands at 225, 235, 250 nm exhibit a 'red shift'. The weak bands at 255–500 nm exhibit a similar changing tendency of chiroptical properties to that in Fig. 7. A red shift of some CD bands to longer wavelength is found with increasing PPD content since an increase in PPD units brings a longer conjugating length. These results indicate that the conformation of copolymers has a close association with the comonomer ratio as well as the variation of wavelength and intensity of CD bands may result from copolymerization effect between PPD with PHT monomers. That is to say, the results confirm again that the polymer formed by oxidative polymerization of PPD with PHT is the copolymer of two monomers.

### *3.7. Thermal behavior of the PPD/PHT copolymers*

The DSC scans of the PPD/PHT copolymers with the PPD feed molar content from 10 to 90 mol% are shown in Fig. 8. All curves show a strong endothermic peak at ca. 80–100 °C and an exothermic peak at 150–200 °C. The endothermic peak is a result of the evaporation of water molecules trapped inside the copolymers, but the exothermic peak should attributed to a series of complex chemical reaction, involving bond scissoring (such as the exclusion of ethoxyl groups), followed immediately by new bond formation and crosslinking [21]. Similar exothermic phenomena were observed in the DSC curves of aniline and xylidine or ethylaniline copolymers [17,22]. This means that the copolymers of aniline derivatives are chemically unstable in 150–330 °C. The cooling curves seem featureless except for two small exothermic peaks at 288 °C and ca. 155 °C. When the temperature rises from 65 to 330 °C again

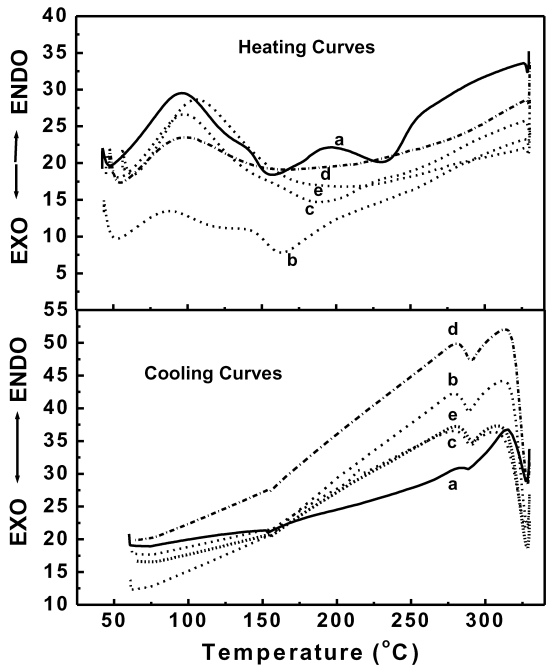



Fig. 8. DSC thermograms of the as-polymerized copolymer base powders with *p*-phenylenediamine (PPD)/*o*-phenetidine (PHT) molar ratios of 10/90(a), 30/70(b), 50/50(c), 70/30(d), 90/10(e). The heating and cooling cycles are as follows: (1) heating from 40 to 330 °C at 40 °C/min; (2) holding for 3 min at 330 °C; (3) cooling from 330 to 40 °C at 200 °C/min; (4) holding for 2 min at 40 °C; (5) heating from 40 to 330 °C at 20 °C/min; (6) holding for 1 min at 330 °C.

after the sample was allowed to maintain at 65 °C for half an hour, the curves seem not signal. Therefore the PPD/PHT copolymers do not appear to melt at the temperature below 330 °C. The fact that no melting peak is observed probably suggests an amorphous nature of the PPD/PHT copolymers.

## 4. Conclusions

A mutual retarding effect between PPD and PHT monomers occurs during the exothermic copolymerization. The polymerization yield, intrinsic viscosity, solubility, and thermal property of the PPD/PHT copolymers exhibit an obvious dependency of comonomer ratio. The available highest yield and intrinsic viscosity are 81% for PPD/PHT (50/50) copolymer and 1.18 dl/g for PPD/PHT (70/30) copolymer, which are much higher than those for PPD and PHT homopolymers. It is interesting that the PPD/PHT (10/90 and 30/70) copolymers exhibit better solubility in $CHCl_3$ than PHT homopolymer. Furthermore, almost all the PPD/PHT copolymers exhibit much better solubility in the most of the solvents than PPD homopolymer. The FTIR, UV–vis, $^1$H-NMR, CD and solubility investigations strongly suggest that the polymers obtained are actual copolymers consisting of two monomer units, and the calculated PPD content is slight higher than the feed PPD content because of a slightly high polymerizability of PPD monomer than PHT monomer. The DSC measurement indicates that the copolymers are amorphous and chemically instable in 150–330 °C. In conclusion, a series of new highly soluble and real PPD/PHT copolymers with partly ladder-like structure have been successfully synthesized by an oxidative polymerization.

## Acknowledgements

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