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A soluble ladder copolymer from *m*-phenylenediamine and ethoxyaniline

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Abstract

A series of partial ladder copolymers were synthesized by chemically oxidative polymerization of *m*-phenylenediamine (MPD) and *o*-ethoxyaniline (EOA) using inorganic oxidants in inorganic acidic aqueous media. The polymerization yield, intrinsic viscosity, solubility, and thermal property of the copolymers were systematically studied by changing the comonomer ratio, initial polymerization temperature, polymerization time, oxidant, monomer/oxidant ratio, and acidic medium. As-prepared fine powder of the MPD/EOA copolymers was characterized by IR, UV–vis, and high-resolution ^{1}H NMR spectroscopies and DSC. Circular dichroism technique was firstly used to characterize chain structure of the copolymers. The results showed that the oxidative polymerization from MPD and EOA is exothermic and the resulting copolymers exhibit a remarkably enhanced solubility in all of the organic and inorganic solvents chosen as compared with totally insoluble MPD homopolymer. The polymers obtained by the oxidative polymerization are real copolymers containing MPD and EOA units but do not contain MPD and EOA homopolymers based on a careful solubility comparison. The actual MPD/EOA molar ratio calculated based on ^{1}H NMR spectra of the polymers is different from element analysis results. Element analysis indicated that denitrogenation happens during the polymerization linkage among MPD units and the structure consisting of MPD units is different from that reported. The ladder degree of the copolymers might be monitored by controlling MPD/EOA ratio. The DSC measurement indicates that the copolymers do not exhibit melt transition.

Keywords: Phenylenediamine/phenetidine copolymer; Macromolecular structure; Property

1. Introduction

Conducting polymers have attracted much scientific and technological interest in recent years. Most of these studies have been devoted to polyaniline (PAN) for its characteristics of easy preparation, high stability, good electroconductivity, high gas-separation ability, and extensively promising application in electrode material, microelectronics, electrochromic material, radiation shielding and recordable optical discs [1–7]. However, the commercial exploitation of PAN materials has been hampered to some extent by its intractable nature, as it is normally synthesized as an insoluble powder chemically or as thin and brittle films electrochemically [1–3]. The polymers from many substituted anilines, including halogenated aniline [8], alkyl and alkoxy aniline [9], aminoaniline (phenylenediamine, PD) [10], have been widely studied for the improvement of the solubility and processibility. Furthermore, the polymers of the aniline derivatives, which bear various functional groups, may exhibit some unique properties; especially polymers from PD [10]. The considerable difference in

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properties of aniline derivative polymers will greatly extend their application field.

The oxidative polymers of three isomers of *o*-, *m*-, *p*-PDs have become an important subject of active investigation owing to not only their better performances of electroactivity, permselectivity, and electrochromism but also their possible important utility for a variety of applications including electrocatalyst, electric and electronic materials, sensors, detectors, and heavy metal ion complex [10–12]. In general, homopolymerization of the three isomers by simple oxidative polymerization yields a ladder-like polymer containing phenazine ring that may be a new rigid-rod and heat-resistant polymer [10], while most of the other ladder-like polymers such as poly(benzimidazobenzophenanthroline) can be prepared only through a complicated polycondensation at an elevated temperature and high vacuum for a long time. As for *m*-phenylenediamine(MPD) homopolymer, there are two typical structures including rigid rod-like ladder or network type, depending on the coupling orientation in the MPD monomer [10]. Apparently, the thermal stability of the ladder MPD homopolymer is better than that of PAN, but unfortunately much worse solubility. As a matter of fact, the MPD homopolymer is entirely insoluble in almost all solvents including NMP, DMSO, and concentrated H_2SO_4 that are believed to be good solvents of PAN.

In an attempt to improve its solubility but simultaneously maintain partial ladder structure and original functionalities and provide additionally new interesting performances, several aromatic amines such as aniline, anisidine and xylidine have been introduced as comonomers [10–15], and modified copolymers have been obtained. However, up to now, the effect of improving solubility through copolymerization is not very satisfactory. Even if terpolymerization of MPD with anisidine and xylidine, the solubility of the terpolymers obtained could not be over 80% even in NMP [15].

So far, little attention has been paid to the chemically oxidative copolymerization of MPD except for a few reports [10,15]. However, the polymerization process is of particular importance since this is the most feasible route for the production on a large scale. Moreover, few systematic studies have been reported on the relationship between polymerization conditions and principal macromolecular structure/properties of the MPD homopolymer or its copolymers, such as intrinsic viscosity (I.V.), solubility, and fusibility, partly due to the intractability (insolubility and infusibility) of the MPD homopolymer, which has impeded quantitative solution characterization and processing of the polymers.

It is challenging to design structures with the aim of enhancing the solubility and fusibility, therefore improving the processability of MPD polymer. Fortunately, it is known that longer side-substituents in polymer chain may cause greater distortions of the polymer chains, and decrease the interchain van der Waals force owing to steric hindrance, which is favorable for improvement of the solubility. In addition, side groups in the polymer chains provide more solvation sites, which also increase the solubility furthermore.

The purpose of this paper is to synthesize a soluble copolymer, to initiate a systematic investigation aimed at establishing the relationship between polymerization conditions and characteristics of the MPD/*o*-ethoxyaniline (EOA) copolymers, and to explicate the structural and property modifications induced by copolymerization. The effects of comonomer ratio, polymerization temperature and time, acidic medium, oxidant, monomer/oxidant ratio on polymerization yield, I.V., solubility, and thermal transition of the copolymers have been systematically investigated for the first time.

2. Experimental

2.1. Reagents

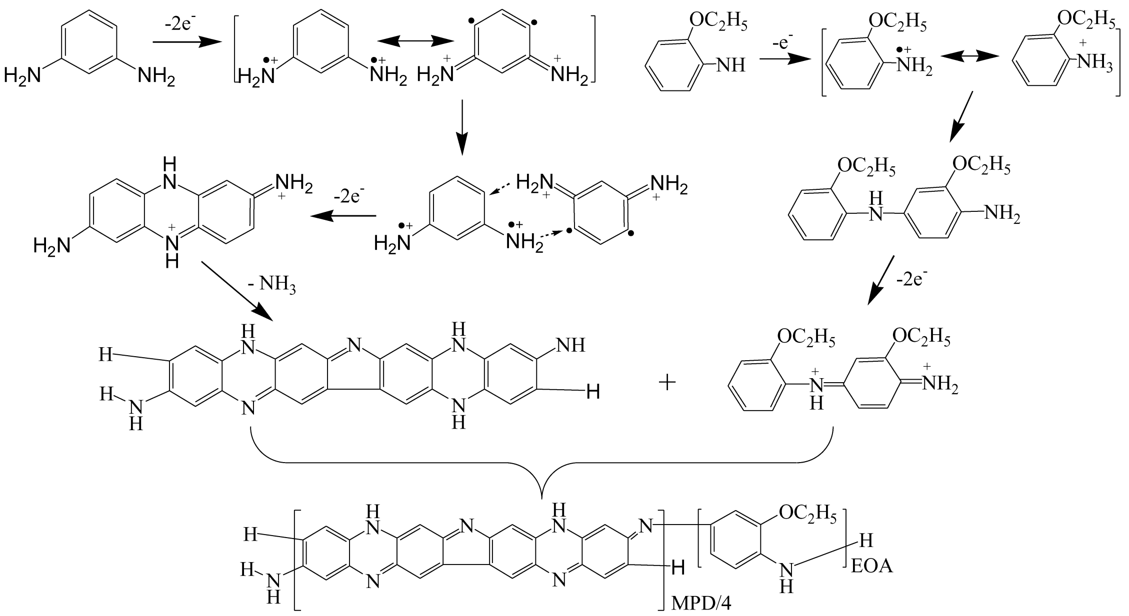
EOA (Acros Organics) as well as MPD, oxidants, and all solvents (Shanghai Reagent Factory of China) were reagent grade and used as received.

2.2. Polymerization

MPD/EOA copolymers were prepared by an oxidative polymerization in Scheme 1 [11,12,15–17]. A representative procedure for the preparation of the MPD/EOA (10/90) copolymer is as follows: to 25 ml 1 M HCl was added 0.22 g (2 mmol) MPD and 2.38 ml (18 mmol) EOA 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 three seconds at 9.5 °C in ca. 45 min. Immediately, after the first few drops, the reaction solution turned black. The reaction mixture was magneto-stirred for 24 h at 9.5 °C. 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 0.2 M ammonium hydroxide and stirred for 24 h to obtain the emeraldine base of MPD/EOA copolymer. The copolymer base was washed with excess water. A fine bluish-black powder was left to dry. The copolymer of 1.99 g was obtained with a yield of 75%.

2.3. Measurements

The I.V. was measured in DMSO with Ubbelodhe viscosimeter at 25 °C. The solubility was evaluated using the following method: polymer sample of 10 mg was added into the solvent of 1 ml and dispersed thoroughly. After the



Scheme 1. The copolymerization mechanism of *m*-phenylenediamine and *o*-ethoxyaniline

mixture was swayed continuously for 24 h at room temperature, the solubility was characterized qualitatively for low-boiling-point solvents or quantitatively for high-boiling-point solvents (solubility = soluble fraction(mg)/10) × 100%). The polymer bases were submitted to C, H, N, and S analyses in a Perkin–Elmer Series 2 Elemental Analyzer. IR spectra were recorded on a Spectrum One Spectrometer at 4 cm^{-1} resolution on KBr pellets. UV–vis spectra were measured on a U-3000 Spectrophotometer (Hitachi Ltd, Tokyo, Japan) in a wavelength range of 190–1100 nm with a homogeneous copolymer solution in DMSO. Circular dichroic (CD) spectra of the copolymer solutions were taken with a JASCO J-715-150S Spectropolarimeter. ^1H NMR spectra were obtained in DMSO-d_6 using a DMX500 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 MPD/EOA polymers

EOA is chosen as comonomer to copolymerize with MPD because the oxidation potential of EOA (0.98 V vs. SCE) is slightly lower than that of MPD (1.05 V vs. SCE), as shown in Fig. 1. The mixtures of MPD/EOA monomers with molar ratios of 30/70 and 10/90 exhibit one major oxidation peak at 0.82 and 0.88 V vs. SCE, respectively. Therefore under a suitable condition, the copolymerization between EOA and MPD should occur. Although the bulkier ethoxy group might increase the difficulty of polymerization, especially that of coupling due to steric hindrance, the electronic effects from the ethoxy group will play an important role. The monomer reactivity increases with increasing electron-donating ability of the substituent. This facilitates the coupling reaction during polymerization and may weaken the steric hindrance.

In fact, the copolymerization of MPD and EOA with ammonium persulfate as an oxidant in 1 M HCl for 24 h afforded fine and uniform bluish-black particles with the diameter of several microns as products. The progress in copolymerization reaction was followed by measuring the solution temperature. It was 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. MPD/EOA (70/30) copolymerization, having an enhancement of the solution temperature of 7.0 °C, exhibits the strongest exothermic capability among the five-copolymerization systems, as listed in Table 1. Other polymerizations show similar exothermic effect with a temperature enhancement of

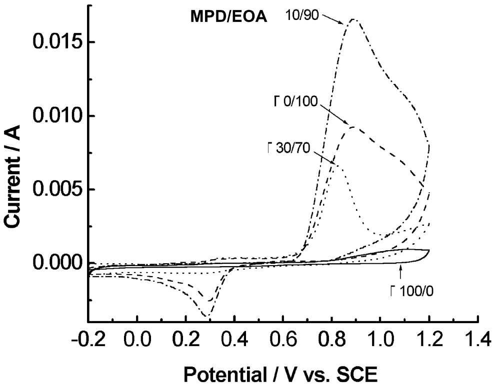


Fig. 1. The first cycles of the cyclic voltammogram of *m*-phenylenediamine and *o*-ethoxyaniline and their mixtures in H_2SO_4.

Table 1
Effect of *m*-phenylenediamine(MPD)/*o*-ethoxyaniline(EOA) molar ratio on the copolymerization characteristics and solubility of the copolymers obtained with oxidant $(NH_4)_2S_2O_8$/monomer molar ratio of 1/1 in 1 M HCl for the polymerization time of 24 h

MPD/EOA molar ratio		Polymerization		Polymer Intrinsic viscosity, I.V. (dL/g)	Solubility[a] and solution color[b]									
Feed	Calculated by ^{1}H NMR[c]	Temperature initial/top/ΔT(°C)	Yield (%)		NMP (wt%)	DMSO (wt%)	DMF (wt%)	Formic acid (wt%)	H_2SO_4	*m*-Cresol (wt%)	$CHCl_3$	THF	Toluene	Xylene
		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[d]	0/100	9.0/–/–	80	0.18	100(bb)	100(bb)	100(bb)	100(bb)	S(bb)	100(bb)	MS(bb)	MS(bb)	PS(br)	PS(b)
10/90	7/93	9.3/11.4/2.1	75	0.16	100(bl)	100(bl)	100(bl)	100(bl)	S(bl)	100(bl)	S(bl)	MS(bl)	PS(r)	PS(r)
30/70	45/55	10.6/12.5/1.9	71	0.22	100(bl)	100(bl)	100(bl)	100(bl)	S(bl)	100(bl)	MS(r)	PS(br)	SS(r)	SS(r)
50/50	59/41	12.3/14.3/2	62	0.18	100(bl)	100(bl)	100(bl)	100(bl)	S(bl)	100(bl)	PS(r)	PS(br)	SS(r)	SS(r)
70/30	54/46	8.7/15.7/7.0	57	0.17	100(br)	100(b)	100(bl)	100(bl)	S(bl)	100(bl)	PS(r)	SS(br)	IS	IS
90/10	–	14.6/17.5/2.9	50	0.33	79(br)	80(b)	34(bl)	100(bl)	MS(bl)	83(bl)	SS(bl)	SS(r)	IS	IS
100/0[e]	100/0	24.3/27.5/3.2	79	–	0	0	0	0	0	0	IS	IS	IS	IS

[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.

[c] MPD/EOA molar ratio calculated based on the ^{1}H NMR spectra shown in Fig. 4.

[d] Polymerization time is 13 h.

[e] For *m*-phenylenediamine homopolymer from Refs. [10,15]

1.9–3.2 °C regardless of the difference of initial temperature. An analogical temperature enhancement was observed for the MPD/anisidine/xylidine terpolymerization [15]. Smaller fluctuation of the solution temperature during the addition of an oxidant solution is beneficial to the preparation of a polymer with a narrower molecular weight distribution.

3.1.1. Effect of comonomer ratio

It was found that the copolymerization yield of MPD with EOA was significantly dependent on the monomer ratio as shown in Table 1, suggesting a copolymerization effect between MPD and EOA. It seems that MPD and EOA monomers are retardant of the other polymerization each other because both homopolymerizations exhibit the highest yield. The yield for other MPD/EOA copolymerization systems monotonically decreases from 80 to 50% with an increase in feed MPD content from 10 to 90 mol%. In fact, the MPD/EOA (90/10) copolymerization shows the lowest yield, indicating that addition of 10 mol% EOA monomer strongly hinders the polymerization of MPD because of the steric hindrance of EOA. A different relationship between the I.V. and comonomer ratio (Table 1) is observed. With increasing feed MPD content from 0 to 70 mol% the I.V. remains a nearly constant low value of around 0.20 dL/g. At MPD content up to 90 mol% the I.V. reaches a highest value of 0.33 dL/g, which may be due to the higher rigidity of the ladder phenazine structure consisting of MPD units. The fact that the MPD/EOA (90/10) copolymer is not completely soluble in NMP, DMSO and DMF is another evidence of its higher chain rigidity. Note that few reports on the I.V. of MPD homopolymer are found because it is insoluble in nearly all of the solvents. Therefore, it is impossible to compare the intrinsic viscosities of MPD/EOA copolymers with MPD homopolymer. The MPD/EOA (90/10) copolymer with the lowest yield exhibits the highest I.V. and MPD/EOA (10/90) copolymer with the higher yield exhibits the lowest I.V. Apparently high polymerization yield and high I.V. cannot be realized at the same time for the copolymers. It can be concluded that the polymerization yield and I.V. of the MPD/EOA copolymers were significantly but reversely influenced by the monomer ratio, demonstrating that copolymerization mechanism is complicated.

3.1.2. Effect of polymerization time

The change of polymerization yield and I.V. with polymerization time is shown in Table 2. It can be seen that the polymerization yield of MPD/EOA (50/50) copolymer is almost constant for the polymerization time between 5 and 15 h although it reaches the highest value of 68% at 10 h. In the polymerization time between 15 and 24 h, the yield gradually decreases down to the lowest value at 20–24 h. On the contrary, the I.V. reaches the lowest value of 0.1 dL/g at 10 h but the highest value of 0.18 dL/g at 24 h. After 5 h EOA units begin to hydrolyze to shorter

Table 2
The effect of polymerization time on the copolymerization characteristics and solubility of *m*-phenylenediamine(MPD)/*o*-ethoxyaniline(EOA) (50/50) copolymer with monomer/$(NH_4)_2S_2O_8$ molar ratio of 1/1 in 1 M HCl aqueous solution at 13 °C

Polymerization Time (h)	Yield (%)	Intrinsic viscosity I.V. (dL/g)	Solubility[a] in solvents and solution color in the brackets[b] NMP (wt%)	DMSO (wt%)	DMF (wt%)	Formic acid (wt%)	H_2SO_4	*m*-Cresol	$CHCl_3$	THF	Toluene	Toluene/DMSO[c]	Xylene/*n*-butanol[c]
5	67	0.15	100(bl)	100(br)	100(bl)	100(bl)	S(bb)	S(bl)	PS(b)	PS(b)	SS(b)	PS(b)	PS(b)
10	68	0.10	100(bl)	100(b)	100(bl)	100(bl)	S(bb)	S(bl)	PS(bl)	PS(b)	IS	PS(bb)	MS(b)
15	66	0.12	100(bl)	100(bl)	100(bl)	100(bl)	S(bb)	S(bl)	PS(b)	PS(b)	IS	PS(b)	SS(br)
20	61	0.16	100(bl)	100(bl)	100(bl)	100(bl)	S(bb)	S(bl)	PS(b)	PS(b)	SS(r)	MS(b)	SS(b)
24	62	0.18	100(bl)	100(bl)	100(bl)	100(bl)	S(bb)	S(bl)	PS(b)	PS(br)	SS(b)	SS(b)	PS(bb)

[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.
[c] Volume ratio 90/10.

chains because EOA units are easier to hydrolyze than MPD unit exhibiting the rigid ladder structure [18], which also be proved by element analysis. At the same time, polymerization of MPD monomers gradually takes up the predominant role, which also explains why polymerization yields increase. After 10 h, with the continuous prolongation of polymerization time, the molecular chains become longer and more rigid by inserting MPD units into EOA units, resulting in an increase in the I.V. During the polymerization process of the MPD monomers, some shorter chains mostly containing EOA units will degrade due to hydrolysis, which decreases the yield [18]. Summarizing, the MPD/EOA (50/50) copolymer exhibits the highest yield and the lowest I.V. at 10 h but the lowest yield and the highest I.V. at 24 h.

3.1.3. Effect of polymerization temperature

As shown in Table 3, by elevating the polymerization temperature from −18 to 30 °C, both the polymerization yield and the I.V. of the copolymers exhibit a maximum value at 0 °C. It is certain that 0 °C is the optimal temperature for the preparation of high molecular weight MPD/EOA (50/50) copolymer with high yield, possibly due to lower chain terminating rate of oxidative polymerization from MPD monomer and lower hydrolyzing rate of the EOA units at lower temperature. The copolymer formed at −18 °C shows the lowest I.V. partly due to lower initiation rate and propagation rate and partly due to the precipitation of the polymer salt. Thus, it is concluded that too low or high temperature does not favor the oxidative copolymerization of MPD with EOA.

3.1.4. Effect of monomer/oxidant ratio

The effect of monomer/oxidant ratio on the copolymerization of MPD/EOA (50/50) was studied and listed in Table 4. It seems that with increasing the oxidant content the copolymerization yield increases monotonically and I.V. of the copolymers also exhibits an increasing tendency. When less oxidant was added, the oxidant will be consumed fast and some monomer cannot be further oxidized to polymerize, leading to low polymerization yield and I.V. More oxidant is beneficial for the copolymerization of MPD/EOA possibly by retarding chain-terminating reaction, which is favor for increasing polymerization yield, or promoting chain propagation reaction, which apparently increases the length of polymer chain, that is, I.V. Too high oxidant content is not necessary because too high concentration of oxidant will promote the formation of oligomers [2]. Apparently, the optimal monomer/oxidant molar ratio should be 4/8 for the formation of the MPD/EOA (50/50) copolymer with the highest yield and highest I.V. simultaneously. Relatively more oxidant is required because of the bifunction groups from MPD monomer.

3.1.5. Effect of oxidant type

The influence of oxidant and its standard reduction

Table 3

The effect of polymerization temperature on the copolymerization characteristics and solubility of *m*-phenylenediamine(MPD)/*o*-ethoxyaniline (EOA) (50/50) copolymers with monomer/$(NH_4)_2S_2O_8$ molar ratio of 1/1 in 1 M HCl aqueous solution for the polymerization time of 24 h

Polymerization Temperature (°C)	Yield (%)	Intrinsic viscosity I.V. (dL/g)	Solubility[a] in solvents and solution color in the brackets[b]									
			NMP (wt%)	DMSO (wt%)	DMF (wt%)	Formic acid (wt%)	H_2SO_4	*m*-Cresol	$CHCl_3$	THF	Toluene/DMSO[c]	Xylene/*n*-butanol[c]
− 18	62	0.13	100(bl)	100(bl)	100(bl)	100(bl)	S(bl)	S(bl)	PS(bl)	PS(bl)	PS(bl)	PS(br)
0	72	0.32	100(bl)	100(bl)	100(bl)	100(bl)	S(bl)	PS(bl)	PS(br)	PS(br)	PS(bb)	PS(r)
13	62	0.18	100(bl)	100(bl)	100(bl)	100(bl)	S(bb)	S(bl)	PS(b)	PS(b)	PS(b)	SS(br)
30	57	0.14	100(b)	100(br)	58(br)	100(bl)	S(bb)	S(bl)	PS(b)	SS(b)	PS(b)	SS(b)

[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.

[c] Volume ratio 90/10.

Table 4

The effect of $(NH_4)_2S_2O_8$ content on the copolymerization characteristics and solubility of *m*-phenylenediamine(MPD)/*o*-ethoxyaniline(EOA) (50/50) copolymers at the polymerization temperature 13–16 °C in 1 M HCl for the polymerization time of 24 h

Monomer/oxidant feed molar ratio	Yield (%)	Intrinsic viscosity (dL/g)	Solubility[a] in solvents and solution color in the brackets[b]										
			NMP (wt%)	DMSO (wt%)	DMF (wt%)	Formic acid (wt%)	H_2SO_4	*m*-Cresol	$CHCl_3$	THF	Toluene	Toluene/DMSO[c]	Xylene/ *n*-butanol[c]
4/8	84	0.23	100(b)	83(b)	47(b)	100(bl)	S(bl)	PS(b)	IS	SS(b)	IS	SS	IS
4/6	83	0.17	100(bl)	100(bl)	100(b)	100(bl)	S(bl)	MS(bl)	IS	IS	IS	IS	PS(b)
4/4	62	0.18	100(bl)	100(bl)	100(bl)	100(bl)	S(bb)	S(bl)	PS(b)	PS(br)	SS(b)	SS(b)	PS(bb)
4/3	43	0.11	100(bl)	100(b)	100(b)	100(bl)	S(bb)	S(bl)	PS(b)	PS(b)	IS	PS(b)	PS(br)
4/2	29	0.12	100(b)	100(b)	100(b)	100(bl)	S(bl)	S(bl)	SS(b)	PS(b)	SS(b)	SS(b)	SS(br)

[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.

[c] Volume ratio 90/10.

potential on the yield and I.V. of the MPD/EOA (50/50) copolymers obtained is listed in Table 5. It appears that $K_2Cr_2O_7$ is optimal oxidant to prepare the copolymer with the highest I.V. However, the copolymer obtained using $K_2Cr_2O_7$ exhibits the yield higher than 100% as well as the poorest solubility in non-acid solvents, indicating a presence of $K_2Cr_2O_7$ and its reductive product in the copolymer because they are not completely soluble in water and the weight content of C, N, H, O elements in the copolymer is only 48.92% based on element analysis. Similar extremely high yield has been observed for the copolymerization of pyrrole(PY) and alkoxyl aniline with $K_2Cr_2O_7$ as oxidant [19]. On the basis of element analysis results calculated MPD/EOA molar ratio in MPD/EOA (50/50) copolymer obtained with $K_2Cr_2O_7$ as oxidant is 74/26, implying the presence of more rigid MPD unit in the copolymer than feed content, which could explain the highest I.V. However, $KClO_4$, which has a similar reduction potential (1.37 V) as $K_2Cr_2O_7$, did not initiate oxidative copolymerization of MPD with EOA under the same reaction conditions. Except for the $K_2Cr_2O_7$, the yield exhibits an enhancing tendency with elevating the reduction potential of the oxidants. Particularly, the MPD/EOA (50/50) copolymer obtained with $K_2S_2O_8$ as oxidant exhibits the highest yield. However, there was no obvious correlation between the I.V. and reduction potential of the oxidants. When $FeCl_3$ with the lowest reduction potential was used as an oxidant, the copolymer with the lowest I.V. was obtained at the lowest yield because $FeCl_3$ might lead to the formation of a large fraction of water-soluble oligomers. Perhaps the reduction potential of $FeCl_3$ is too low to effectively initiate the polymerization for the formation of high molecular weight polymers [9]. In addition, the oxidative ability of $FeCl_3$ is sensitive to temperature and it is reported that $FeCl_3$ could show higher oxidative ability at higher temperature (about 35 °C) [3]. High polymerization yields 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 MPD and EOA. On the other hand, almost the same I.V. was observed when $(NH_4)_2S_2O_8$, $Na_2S_2O_8$, and $K_2S_2O_8$ were used as oxidant because of their same reduction potential regardless of their different counter cations. Substantially similar relationship between polymerization yield or I.V. and the reduction potential of the oxidants has been observed for the copolymerization of PY and alkoxyl aniline [19]. That is to say, the reduction potential of the oxidants plays an important role in oxidative copolymerization. It should be noted that the copolymers obtained might undergo degradation reaction at high-applied potential, leading to low I.V. and good solubility, as listed in Table 5. These facts indicate that the mechanism of oxidative polymerization of MPD/EOA is complicated; not only the reduction potential but also the chemical structure of the oxidants influence the polymerization process.

Table 5
The effect of oxidant on the copolymerization characteristics and solubility of *m*-phenylenediamine(MPD)/*o*-ethoxyaniline(EOA) (50/50) copolymers with monomer/oxidant ratio 1/1 in 1 M HCl aqueous solution at 13 °C for the polymerization time of 24 h

Oxidant		Polymn.	Intrinsic Viscosity I.V. (dL/g)	Solubility[a] in solvents and solution color in the brackets[b]											
Molecular formula	Standard reduction potential (V)	Yield (%)		NMP (wt%)	DMSO (wt%)	DMF (wt%)	Formic acid (wt%)	H_2SO_4	*m*-Cresol	$CHCl_3$	THF	Toluene	Xylene	Toluene/DMSO[c]	Xylene/*n*-butanol[c]
$FeCl_3$	0.77	13	0.05	100(bl)	100(bl)	83(b)	100(bl)	S(bl)	S(bl)	PS(b)	PS(b)	IS	IS	PS(b)	SS(b)
$K_2Cr_2O_7$	1.33	215	0.73	23(b)	10(bl)	35(b)	100(bl)	S(bl)	SS(bl)	SS(br)	PS(bl)	SS(bl)	SS(b)	SS(bl)	SS(bl)
$(NH_4)_2S_2O_8$	2.01	62	0.18	100(bb)	100(bb)	100(b)	100(bl)	S(bl)	S(bl)	MS(b)	MS(b)	SS(r)	SS(b)	MS(bl)	PS(b)
$Na_2S_2O_8$	2.01	63	0.19	100(b)	100(br)	100(b)	100(bl)	S(bl)	S(bl)	PS(b)	SS(b)	IS	IS	PS(b)	SS(b)
$K_2S_2O_8$	2.01	69	0.17	100(bl)	100(bl)	100(bl)	100(bl)	S(bb)	S(bl)	PS(br)	PS(bl)	PS(br)	SS(r)	PS(b)	PS(br)

[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.

[c] Volume ratio 90/10.

3.1.6. Effect of acidic medium

It is found that the polymerization yield of MPD/EOA (50/50) copolymer at oxidant($(NH_4)_2S_2O_8$)/monomer molar ratio of 1/1 in 1 M acidic aqueous solution at about 13 °C varies from 62, 57, 70 to 76% with changing acid from HCl, HCl + H_2SO_4, H_2SO_4 to HNO_3, whereas corresponding I.V. varies from 0.18, 0.16, 0.11 to 0.13 dL/g. Since the oxidative polymerization in acidic medium is accompanied by the transfer of proton [2], the nature of the protonic acid remarkably affects the quality of the polymers. It is noted that the polymerization yield and I.V. are strongly but reversely dependent on the nature of acid. When HCl and HCl + H_2SO_4 were employed, the lower yield but the higher I.V. of the copolymer were observed. For HNO_3 the highest yield and second lowest I.V. were obtained. The highest yield was also observed for the oxidative polymerizations of PY and alkoxyl aniline in HNO_3 [19]. Generally, the copolymers obtained in 1 M HCl and/or HCl-containing mediums exhibit higher I.V.

Not only acid nature but also acid concentration affects the characteristics of polymerization, as shown in Table 6. It shows that, in the pH range described, the yield exhibits a minimum value at HCl concentration of 1.25–1.5 M, while the I.V. decreases significantly with increasing HCl concentration from 0.5 to 2.0 M. It seems that an HCl concentration of 0.5 M produces MPD/EOA copolymer with the second highest yield together with the highest I.V. At the highest HCl concentration of 2 M, the copolymer formed exhibits the largest yield but the lowest I.V. These data show that high acidity accelerates hydrolysis of the copolymer chains with relatively high molecular weight. The dependence of the I.V., i.e. molecular weight, of MPD/EOA copolymers on the acidity of the reaction medium clearly indicated that two competing processes (polymerization and degradation due to hydrolysis) controlled the characteristics of the polymerization. Solubility of the copolymers prepared at higher HCl concentration is better than those prepared at lower HCl concentration (0.5 M), which also proves the conclusion above.

3.2. Structure analysis of the MPD/EOA polymers

3.2.1. Element analysis

The structure of the copolymers has been studied by the C/H/N ratio because a confirmed structure must be corresponding to a certain C/H/N ratio. Two series of C/H/N ratios have been calculated and listed in Table 7 according to two proposed formula of MPD unit listed in the footnotes. Apparently, the experiment C/H/N ratio computed by element analysis is very close to the ratio calculated from formula b or Fig. 2c, indicating an amine/imine ratio of around 2/3 and medium degree of susceptibility to protonation. Excrescent experimental H content must be due to the water and dopant (HCl) impurities absorbed firmly in the polymers, as revealed by DSC measurements later. From these results, it is concluded

Table 6
The effect of HCl concentration on the copolymerization characteristics and solubility of *m*-phenylenediamine(MPD)/*o*-ethoxyaniline(EOA) (50/50) copolymers with monomer/$(NH_4)_2S_2O_8$ ratio 1/1 in HCl at 13 °C for the polymerization time of 24 h

Polymerization		Intrinsic viscosity (dL/g)	Solubility[a] in solvents and solution color in the brackets[b]										
[HCl] (M)	Yield (%)		NMP (wt%)	DMSO (wt%)	DMF (wt%)	Formic acid (wt%)	H_2SO_4	*m*-Cresol	$CHCl_3$	THF	Toluene	Toluene/ DMSO[c]	Xylene/ *n*-butanol[c]
0.5	63	0.19	100(b)	65(bl)	50(b)	100(bl)	S(bb)	S(bl)	PS(b)	PS(b)	SS(b)	PS(br)	PS(b)
1.0	62	0.18	100(bl)	100(bl)	100(bl)	100(bl)	S(bb)	S(bl)	PS(b)	PS(br)	SS(b)	SS(b)	PS(bb)
1.25	60	0.14	100(b)	100(b)	100(b)	100(bl)	S(g)	S(bl)	PS(b)	SS(b)	IS	SS(b)	PS(b)
1.5	60	0.10	100(b)	100(b)	100(b)	100(bl)	S(g)	S(bl)	PS(b)	SS(b)	IS	PS(b)	PS(b)
2.0	69	0.10	100(b)	100(bl)	100(bl)	100(bl)	S(bb)	S(bl)	PS(b)	MS(b)	SS(b)	PS(br)	PS(b)

[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.

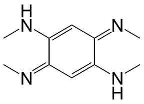
[c] Volume ratio 90/10.

Table 7
Elemental analysis of *m*-phenylenediamine(MPD)/*o*-ethoxyaniline(EOA) copolymers obtained with $(NH_4)_2S_2O_8$/monomer/HCl molar ratio of 1/1/2 in 1 M HCl aqueous solution at 13 °C for 24 h

MPD/EOA molar ratio		C/H/N/O[a]/Total (wt%)	Experimental formula	Calculated formula	
Feed	Experimental			b	c
0/100	0/100	68.47/7.18/9.20/11.90/96.75	$C_6H_{6.38}N_{0.69}O_{0.78}(H_2O)_{0.20}$	$C_6H_{6.38}N_{0.75}O_{0.75}$	$C_6H_{6.38}N_{0.75}O_{0.75}$
10/90	2.6/97.4	68.72/6.87/10.26/11.29/97.14	$C_6H_{6.28}N_{0.77}O_{0.74}(H_2O)_{0.18}$	$C_6H_{6.28}N_{0.77}O_{0.73}$	$C_6H_{6.29}N_{0.78}O_{0.73}$
30/70	23.4/76.6	67.16/6.84/12.03/9.73/95.76	$C_6H_{5.54}N_{0.92}O_{0.65}(H_2O)_{0.27}$	$C_6H_{5.54}N_{0.97}O_{0.58}$	$C_6H_{5.63}N_{1.04}O_{0.58}$
50/50	36.6/63.4	66.33/5.74/13.24/8.39/93.70	$C_6H_{5.07}N_{1.03}O_{0.57}(H_2O)_{0.39}$	$C_6H_{5.07}N_{1.09}O_{0.47}$	$C_6H_{5.21}N_{1.21}O_{0.47}$
70/30	51.7/48.3	64.28/5.48/14.47/6.68/90.91	$C_6H_{4.53}N_{1.16}O_{0.47}(H_2O)_{0.57}$	$C_6H_{4.53}N_{1.23}O_{0.36}$	$C_6H_{4.73}N_{1.4}O_{0.36}$
90/10	82.6/17.4	56.32/4.75/16.05/2.66/79.78	$C_6H_{3.42}N_{1.47}O_{0.21}(H_2O)_{1.26}$	$C_6H_{3.42}N_{1.5}O_{0.13}$	$C_6H_{3.46}N_{1.78}O_{0.13}$
100/0	100/0	49.21/4.18/15.90/0.00/69.29	$C_6H_{2.8}N_{1.61}(H_2O)_{1.6}(HCl)_{0.13}$	$C_6H_{2.8}N_{1.67}$	$C_6H_{3.2}N_2$

[a] It is the theoretic oxygen content calculated through the content of EOA unit in the polymers.

[b] Calculated from the MPD unit formula of Fig. 2(c) (DP = 30).



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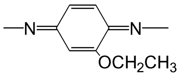
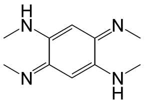


[c] Calculated from the MPD unit formula of



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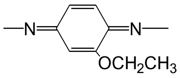


that a denitrogenation happens in MPD units during the oxidative polymerization, something like the denitrogenation observed during the homopolymerization of *sym*-triaminobenzene [10]. The macromolecular chain structures of MPD/EOA (90/10) copolymer and MPD homopolymer are simulated and shown in Fig. 2.

In addition, MPD/EOA ratio in the copolymers could be calculated on the basis of C/N ratio, as listed in Table 7. Comparing to feed monomer ratio, the MPD unit content in polymer chains is lower, partially similar to that by ^1H NMR. The difference between feed and observed MPD contents in the copolymers is over 20% until MPD feed content is up to 90 mol% where the difference is about 8%. It suggests that EOA monomer may exhibit higher reactivity than MPD monomer because of the electronic effects from ethoxy group, which plays a more important role than steric hindrance. The monomer reactivity increases with increasing electron-donating ability of the ethoxy group that enhances the electron density in polymer backbone and makes it more susceptible to the attack of oxidants. This facilitates the coupling reaction during polymerization.

The oxygen content in the copolymers could be calculated theoretically according to the content of EOA unit because oxygen element only exists in EOA units. From Table 7 it can be seen that the total content of C, H, O, and N elements is not 100%, and decreases with increasing MPD feed content. Since there exists denitrogenation in MPD units, the nitrogen loss will increase with increasing MPD feed content. This may explain a small part of the loss of element. In addition, some impurities such as dopants (anion) and proton could be responsible for a considerable part of the loss. PAN doped by proton acid is easily to be dedoped by treatment with NH_4OH solution. However, the ladder phenazine-like structure of MPD units provides many anion sorption and protonation sites which favor the sorption of anion and proton [20,21]; and the electron delocalization on the ladder polymer backbone makes polymer chain more stable and effectively obstructs the desorption of anion when dealt with NH_4OH. So MPD units introduce more impurities than EOA units. Furthermore, the H element content exceeds the highest content calculated theoretically according to formula b. This is also an evidence of the existence of the impurity in polymer chains.

3.2.2. FT-IR spectra

FT-IR spectra for the copolymers with six MPD/EOA ratios are shown in Fig. 3. Apparently, a broad and strong band centered at 3342 cm^{-1} for four MPD/EOA copolymers and at 3435 cm^{-1} for MPD homopolymer due to the characteristic free –NH– stretching vibration suggests the presence of secondary amino groups (–NH–) in five MPD unit-containing polymers [10,15,22]. There is a comparatively weak –NH– vibration peak at 3410 cm^{-1} in the IR spectrum of EOA homopolymer, suggesting a small amount of –NH– groups in its molecular chains. The weak peak at 3050 and 2977 cm^{-1} for all polymers except for MPD homopolymer should be attributed to C–H stretching on the aromatic rings and ethoxyl groups, respectively. The both peaks will become stronger with increasing feed EOA contents. All the polymers exhibit two weak peaks at 2930 and 2865 cm^{-1}, possibly due to aliphatic C–H stretching vibrations on the ethoxyl groups as well as impurity [9,15] because there are no ethoxyl groups in the MPD homopolymer. The four copolymers and EOA homopolymer exhibit two strongest peaks in 1510–1624 cm^{-1} that are associated with C–C stretching vibration in the aromatic rings [11,12,22]. It is believed that the peak at

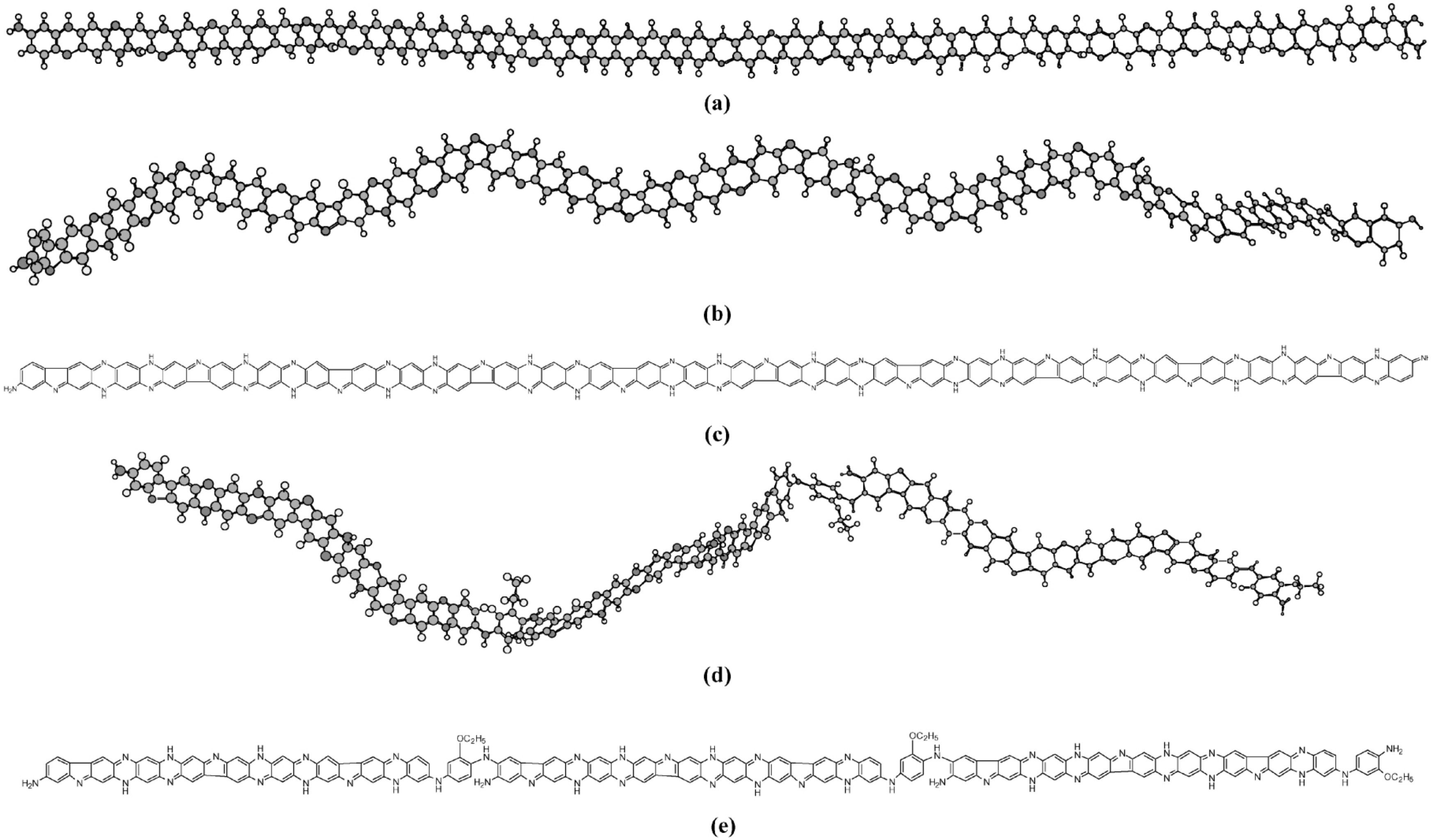


Fig. 2. The chemical structure of the MPD polymers (DP = 30): (a) a steric structure of MPD homopolymer without denitrogenation, (b) a steric structure and (c) molecular structures of MPD homopolymer with the characteristics of denitrogenation in MPD unit; (d) steric structure and (e) molecular structure of MPD/EOA (90/10) copolymer with the characteristics of denitrogenation in MPD unit.

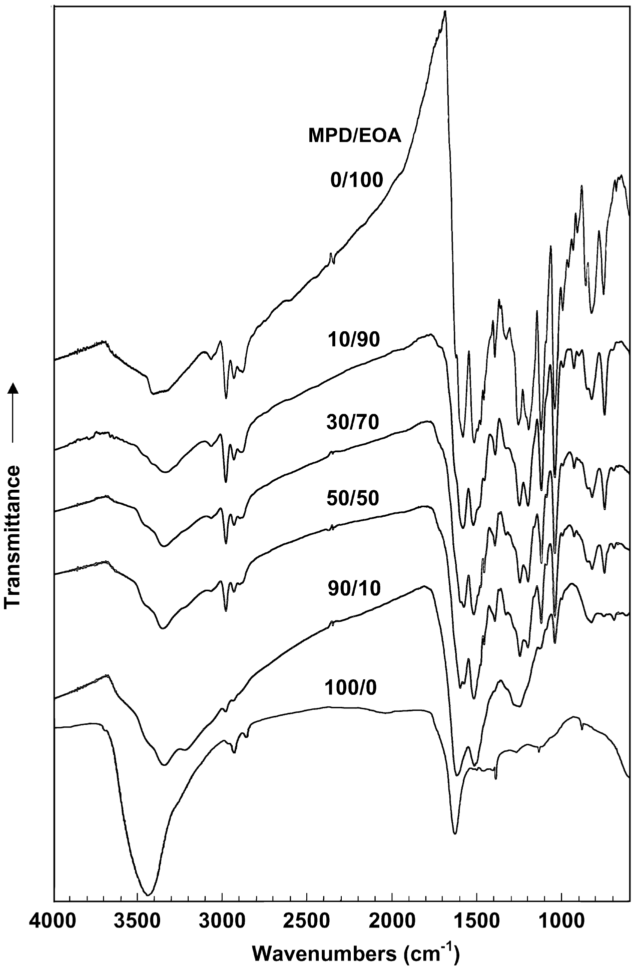
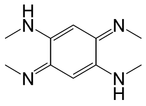


Fig. 3. FT-IR absorption spectra of the copolymers with seven m-phenylenediamine/o-ethoxyaniline molar ratios of 0/100, 10/90, 30/70, 50/50, 70/30, 90/10 and 100/0.

1595–1624 cm^{-1} is assigned to the following quinoid rings:



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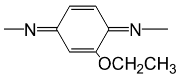
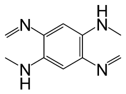
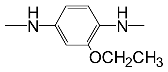


and one at about 1510 cm^{-1} is assigned to the benzenoid rings:



and



The fact that the peak at 1595–1624 cm^{-1} shows the similar peak area as the peak at 1510 cm^{-1} suggests the analogical content of quinoid and benzenoid units in the polymers. But for MPD homopolymer, having a very weak peak at 1510 cm^{-1}, suggests that the ladder structure of MPD homopolymer primarily consists of quinoid rings rather than benzenoid rings [10]. A small and sharp peak at 1384 cm^{-1} could be due to C–N stretching vibration in quinoid imine units and become stronger with adding EOA unit. The peak at 1246–1263 cm^{-1} could be due to C–N stretching vibration in the benzenoid unit and become sharper and stronger with adding EOA unit. The medium peak at 1197 cm^{-1} might be ascribed to the C=N stretching in the quinoid unit. A peak at about 1119 cm^{-1} due to 1,2,4-trisubstituted benzene ring from EOA units in the MPD/EOA polymers is observed and its intensity increases with increasing EOA content. This is quite different from *p*-PD copolymers [22], but similar to *o*-PD copolymer [11]. The intensity of the peaks at 700, 750, 810, 920, and 1040 cm^{-1} increases with increasing EOA content and MPD homopolymer does not exhibit these peaks, suggesting that the peaks are attributed to the EOA unit. Therefore, the IR spectral results confirm the formation of MPD/EOA copolymer.

3.2.3. ^{1}H NMR spectra

^{1}H NMR spectra of the MPD/EOA copolymers are characterized by three main signals or groups of signals, corresponding to the aromatic protons and two kinds of ethoxyl protons, as shown in Fig. 4. The broad peak from aromatic protons appears in a wide range from 6.2 to 7.8 ppm and centers at 7.0 ppm that should result from the benzenoid and quinoid protons of the ladder structure of MPD and EOA units. Two strong peaks located in a range from 3.8 to 4.2 ppm and 1 to 1.5 ppm are assigned to protons in $-OCH_2-$ and $-CH_3$ groups, respectively. Two additional strongest peaks at 2.49 and 3.33 ppm are due to DMSO protons and water in DMSO. Additionally, several peaks in 5.7–6.2 ppm could be due to the protons of –NH– and –NH$_2$ groups [10]. Since ^{1}H NMR sprectrum of insoluble MPD homopolymer cannot be obtained until now, it is impossible to compare the NMR spectra of MPD/EOA copolymers with MPD homopolymer. Comparing with the spectra of two homopolymers from *p*-PD and EOA, it is seen that the spectra of two series of polymers have much similarity, implying that the two kinds of the polymers exhibit similar structure to some extent. It appears that the ^{1}H NMR spectra of MPD/EOA copolymers do not change systematically with increasing feed MPD content. These spectra are not much informative on the calculation of sequence distribution of the comonomer units due to the complexity of the copolymer structures. Fortunately, based on a comparison of the area of aromatic proton peak (6.2–7.8 ppm) on MPD and EOA units with ethoxyl proton peak (3.8–4.2 ppm or 1–1.5 ppm) on EOA units, the mole ratio of MPD to EOA units in the copolymers can be calculated and listed in Table 1. The number of aromatic protons on every MPD unit may be calculated through the following equation

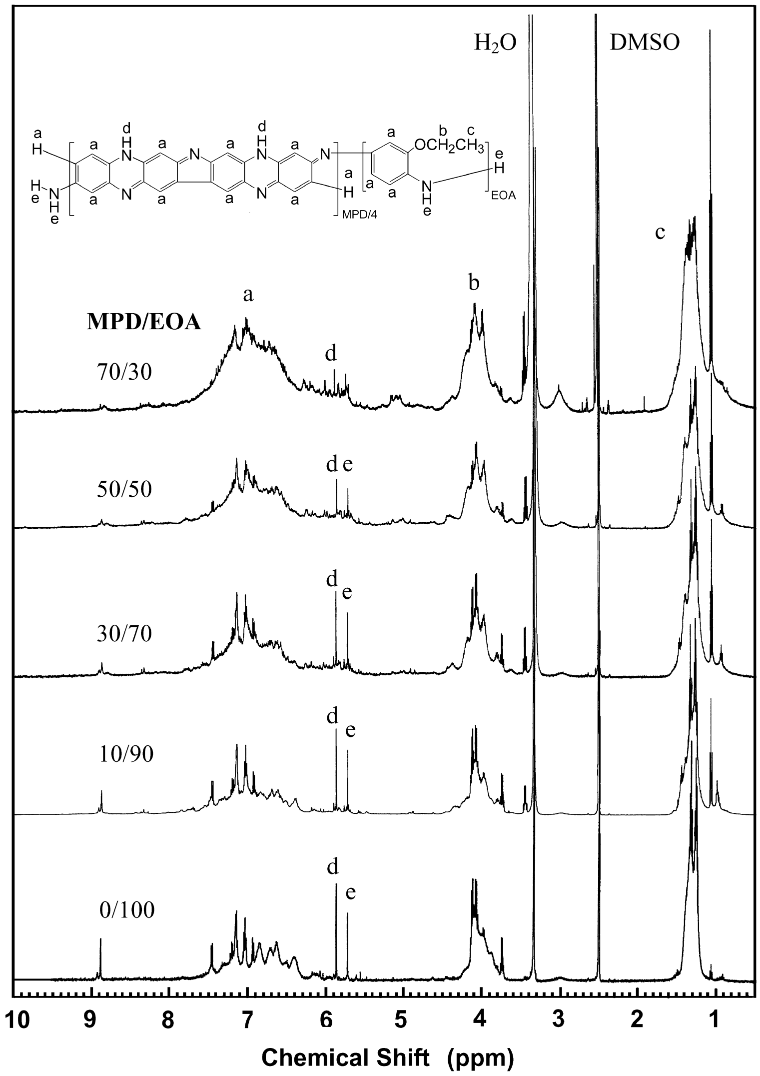


Fig. 4. ^{1}H-NMR spectra of the copolymer solutions with m-phenylenediamine/o-ethoxyaniline molar ratios of 0/100, 10/90, 30/70, 50/50, 70/30 in deuterated dimethylsulfoxide(DMSO-d$_6$) at 500 MHz.

based on the nominal molecular structure in Scheme 1:

MPD proton area

$$= \text{Total aromatic proton area} - \text{Methyl proton area}(-CH_3)$$

Thus

MPD/EOA Molar ratio

$$= (\text{MPD proton area}/2)/(\text{Methyl proton area}/3)$$

It seems that calculated MPD content is higher than feed MPD content for MPD/EOA (30/70) and (50/50) copolymers, which is similar to the copolymerization of *o*-PD with xylidine [11]. However, the calculated MPD content is lower than feed MPD content for MPD/EOA (70/30) copolymers. The deviation from feed ratio is small for MPD/EOA (10/90) and (50/50) copolymers but significantly great for MPD/EOA (30/70) and (70/30) copolymers. Comparing to experiment MPD/EOA ratios calculated by element analysis results, all of the MPD unit contents determined by NMR is higher. This is possibly ascribed to protonation of MPD chains, because the protons doping in MPD ladder structure are difficult to deprotonation. Hydrogens protonated on MPD units should delocalize all over the polymer backbone, leading to a feint of slightly more aromatic MPD protons.

3.2.4. UV–vis spectra

Fig. 5 exhibits the UV–vis spectra of the MPD/EOA copolymers in DMSO. Two strong bands at 258 and 279–283 nm with a low resolution and a shoulder peak at 309–360 nm are observed for five MPD/EOA copolymers together with a weak band centered at 458–470 nm. For EOA homopolymer, two strong bands at 284 and 309 nm and a shoulder peak at 258 nm are observed together with two broad bands at 546 and 614 nm and an additional weak peak around 1070 nm. The absorbance at 258 nm could be

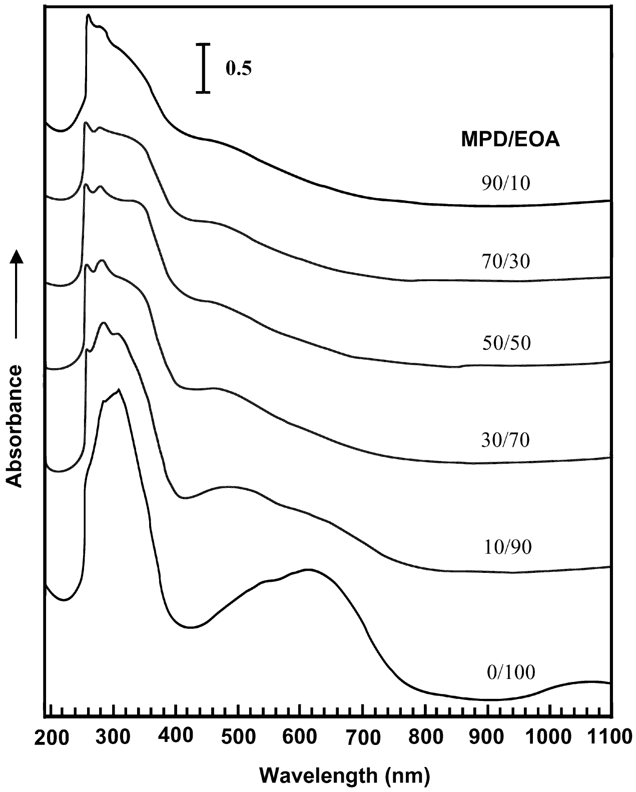


Fig. 5. UV-vis absorption spectra of copolymers with m-phenylenediamine/o-ethoxyaniline molar ratios of 0/100, 10/90, 30/70, 50/50, 70/30, 90/10.

ascribed to the quinonediimine-like units [12]. Shorter wavelength for MPD/EOA polymers than PAN (330 nm) indicates a larger breakdown of the conjugation between repeat units [10,11]. The absorption bands at 458–615 nm seem to suggest quinoneimine structure according to the UV–vis spectra of emeraldine PAN (637 nm) [10,23]. Note that a shorter wavelength for the MPD/EOA copolymers should be due to lack of π electron conjugation with adjacent monomer units.

Comparing six UV–vis curves in Fig. 5 and characteristics of the absorption peaks in Table 8, it is found that with increasing EOA content each peak changes continuously and regularly. The strongest peak at 258 nm of MPD/EOA (90/10) copolymer gradually becomes weaker but does not shift in wavelength. The peak at 279 nm becomes stronger and steadily shifts to 284.4 nm with increasing EOA content. Apparently, the peak could be attributed to quinonediimine structure in emeraldine EOA unit rather than phenazine (ladder) structure in MPD unit by a comparison of UV–vis spectra of PAN [10,23] with Fig. 5. The longer wavelength of the peak than that of fully oxidative PAN-pernigraniline (at 273 nm) is due to the influence of $-OC_2H_5$ with electron-supply effect so that π electron conjugation with adjacent monomer units increases. However, with increasing EOA content, a long ladder structure consisting of phenazine units is broken by EOA units with quinonediimine structure, so the conjugation π electron in the polymer chains becomes less. This could explain the blue shift of the peak with increasing EOA content. A transition at 309–338 nm could be due to $\pi \rightarrow \pi^*$ transition between adjacent conjugated benzenoid rings and it should be also ascribed to EOA unit since with increasing EOA content the peak becomes stronger and shifts to shorter wavelength irregularly. Very similarly, the peak at 458 nm of MPD/EOA copolymers becomes stronger and shifts to a longer wavelength with an increase in EOA content, indicating that the peak at 458–615 nm is attributed to quinoneimine structure of EOA unit. In summary, the strong bands at 279–284 nm and weak bands centered at 458–615 nm may correspond to $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transition in neutral form of EOA unit, respectively. The EOA homopolymer and MPD/EOA (10/90) copolymer have a peak at 614 and 615, respectively, [9], but the peak disappears at the EOA content of up to 30 mol%, because EOA unit becomes fully oxidized with increasing MPD unit and phenazine structure predominates in polymer chains. Particularly, only EOA homopolymer exhibits a broad and weak peak around 1070 nm, suggesting a presence of small amount of highly conjugated structure. The continuous variation of wavelength and intensity of UV–vis bands of the soluble part of the MPD/EOA copolymers in DMSO may result from copolymerization effect of MPD with EOA. In other words, the polymer formed by oxidative polymerization of MPD with EOA is the copolymer of two monomers rather than the mixture of two homopolymers.

3.2.5. CD spectra

The circular dichroism spectra of the copolymers with MPD feed content from 0 to 90 mol% are shown in Fig. 6,

Table 8
Variation of the wavelength (nanometers) of UV–vis spectral bands of *m*-phenylenediamine (MPD) and *o*-ethoxyaniline(EOA) copolymers in DMSO with feed monomer ratios

MPD/EOA feed molar ratio	Wavelength (nm)	
	Strong band	Weak band
90/10	258.0(strongest), 279.0, 338.4	458.2
70/30	258.0(strongest), 279.0, 358.0	460.0
50/50	258.0(strongest), 281.0, 358.0	461.0
30/70	258.0, 283.0(strongest), 360.0	470.0
10/90	258.0, 283.0(strongest), 309.3	495.0, 615.0
0/100	258.0, 284.4, 309.3(strongest)	546.1, 614.3, 1070

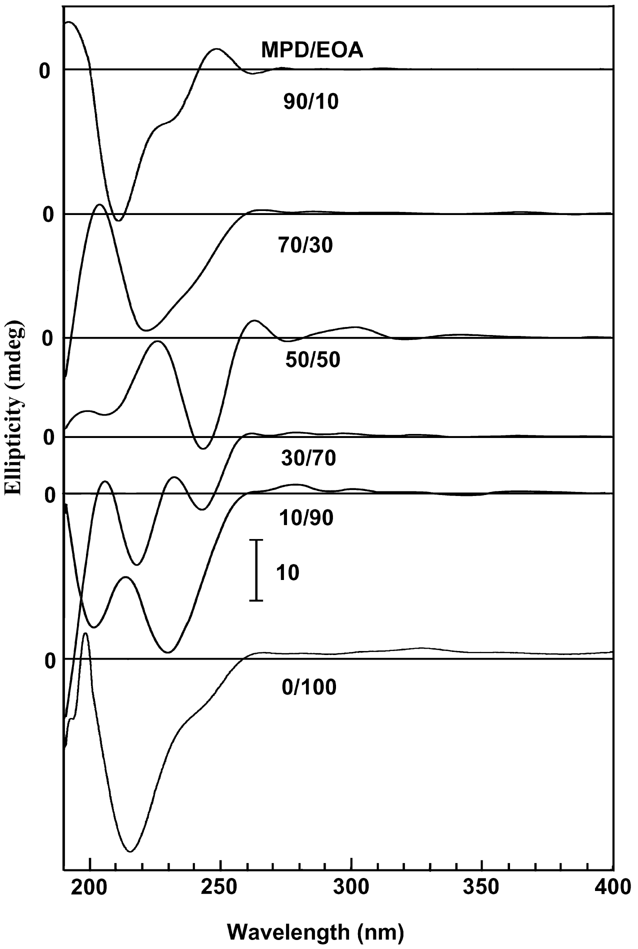


Fig. 6. Circular dichroic spectra of copolymers with *m*-phenylenediamine/*o*-ethoxyaniline molar ratios of 0/100, 10/90, 30/70, 50/50, 70/30, 90/10.

which confirmed that they are chiroptically active. EOA homopolymer exhibits a positive peak at ca. 200 nm, a negative peak at 215 nm and some weak peaks between 255 and 400 nm, while the MPD/EOA copolymers exhibit remarkably different spectra. In addition, the spectra of five copolymers are also different from each other, implying various conformations. The change in conformation of the polymer backbone is presumably due to the incorporation of MPD ladder structure into EOA homopolymer backbone through increasing the rigidity of the polymer chains, thereby causing the polymer backbone to deviate from original arrangement. With increasing MPD content, the CD spectra change irregularly, suggesting no clear relationship between chiroptical properties and copolymer composition. These results indicate a random incorporation of MPD unit into EOA homopolymer through a random copolymerization effect of MPD with EOA. That is to say, the results confirm again that the polymer formed by oxidative polymerization of MPD with EOA is a copolymer.

3.2.6. Partial ladder structure

On the basis of the C/H/N ratio and structural characteristics revealed by elemental analysis and IR spectrum, respectively, it is generally recommended that the MPD homopolymer exhibits a rigid-rod like ladder structure sometimes with a zig-zag characteristics (Fig. 2a–c) containing phenazine rings because the both amino groups of MPD monomer are oxidized during the oxidation polymerization [10]. The steric structures shown in Fig. 2a, b and d are simulated by the CS Chem3D Pro developed by CambridgeSoft, 1999. The EOA homopolymer should be a flexible linear chain. However, the mechanism of the oxidative polymerization of the both monomers has not so far been perfectly expatiated due to their complexity. It was proposed that a two-electron oxidation leads to an insoluble ladder MPD homopolymer [10], whereas the oxidative polymerization of the EOA monomer should follow one electron-oxidation mechanism to a linear polymer. So the generalized mechanism of oxidation copolymerization of MPD and EOA for the formation of the partial ladder structure could be shown in Scheme 1. According to the above-mentioned structural characteristics and the formula of the copolymers listed in Scheme 1, the steric structure of MPD/EOA (90/10) copolymer is shown in Fig. 2d. It can be seen that molecular chains do distort at the position of EOA unit, and the ladder degree of the copolymers may be monitored by controlling MPD/EOA ratio, which suggests that adding EOA unit really interrupts the ladder structure of MPD units and hence decreases the chain rigidity. Because of the relatively higher polymerizing reactivity of EOA monomer than MPD monomer revealed by the higher experimental EOA content than feed EOA content listed in Tables 1 and 8, the feed MPD monomer content of more than 50 mol% is statistically required for the maintenance of the partial ladder structure of the copolymers. Therefore, the copolymerization of MPD with EOA monomers is chosen to take advantage of the combination of good solubility of EOA homopolymer with the novel ladder-like structure of MPD homopolymer. This can obviously enhance solubility of the insoluble wholly ladder MPD homopolymer in common solvents, as discussed below.

3.3. Properties of the MPD/EOA polymers

3.3.1. Solubility

It can be seen from Tables 1–6 that the solubility of MPD/EOA copolymers is influenced by MPD/EOA ratio, temperature, monomer/oxidant ratio, oxidant, and acid concentration, but not by the polymerization time. As compared with MPD homopolymer, all the MPD/EOA copolymers exhibit much better solubility in the chosen solvents. With increasing EOA content, the MPD/EOA copolymers exhibit an enhanced solubility in the solvents (Table 1). When EOA content is up to 30 mol%, the copolymers are soluble in NMP, DMSO, DMF, formic acid, H_2SO_4 and *m*-cresol with higher boiling point, larger solubility parameter (23–27 $J^{1/2}/cm^{3/2}$), and higher polarity index (6.4–7.4), indicating that the polymerization product is indeed a copolymer containing MPD and EOA units rather than a simple mixture of two homopolymers because MPD homopolymer is insoluble. The solubility of polymers in $CHCl_3$, THF, toluene, and xylene having lower boiling point, lower solubility parameter (18–20 $J^{1/2}/cm^{3/2}$), and lower polarity index (2.4–4.1), clearly exhibits a gradually improving tendency from insoluble to slightly soluble, partially soluble, and up to mainly soluble with increasing feed EOA content from 0 to 100 mol%. The variation of solubility of the copolymers with comonomer ratios is simply a reflection of macromolecular structure variation. The gently enhanced solubility of the copolymers results from the increase of a large number of ethoxyl substituents on the aniline ring and amorphous supramolecular structure, which increase the distance between the macromolecular chains and significantly reduce interactions between the chains. Particularly, the incorporation of EOA unit into MPD backbone can decrease the structural regularity and chain rigidity as well as break the ladder structure of MPD homopolymer to some extent. Thus, it could be speculated that the improvement of the copolymer solubility with increasing EOA content is due to the change of molecular structure rather than that of molecular weight (I.V.). The copolymers with MPD feed content from 10 to 90 mol% are completely soluble in formic acid(Table 1), indicating the copolymers do not contain insoluble MPD homopolymer. On the contrary, the copolymers with EOA feed content from 10 to 70 mol% are slightly soluble or even insoluble in toluene and xylene (Table 1), indicating the copolymers do not contain EOA homopolymer because of its partial solubility. Soluble MPD/EOA (10/90) copolymer in $CHCl_3$ should not contain EOA homopolymer because of only major solubility of the homopolymer. That is to say, all five copolymers obtained here do not contain MPD or EOA homopolymer. Additionally, the MPD/EOA binary copolymer exhibits a better improvement of solubility than the MPD/anisidine/xylidine terpolymers [15]. It appears that one ethoxy group may be more effective for the solubility improvement than two neighboring methyl groups.

As shown in Table 2, with prolongating polymerization time from 5 to 24 h, the MPD/EOA (50/50) copolymers obtained exhibit a similar solubility in NMP, DMSO, DMF, *m*-cresol, formic acid, H_2SO_4, $CHCl_3$, and THF. However, in toluene, xylene, toluene/DMSO and xylene/*n*-butanol, their solubility changes irregularly with polymerization time. MPD/EOA (50/50) copolymers for 20–24 h with higher I.V. show better solubility than those for 10–15 h with lower I.V., indicating a structure variation of the copolymers with polymerization time. In addition, it also suggests that the change of copolymer solubility with polymerization time might be due to the change of their molecular chain structure rather than that of their I.V.

With elevating polymerization temperature from −18 to 30 °C, the MPD/EOA (50/50) copolymers also exhibit a similar solubility in most of the solvents (Table 3), which have no definite relation with I.V. As listed in Table 4, with lowering oxidant content in the polymerization system, the solubility of MPD/EOA (50/50) copolymers in DMSO, DMF, and *m*-cresol increases, possibly due to a decrease in their I.V. despite the independence of the copolymer solubility in NMP, formic acid, and H_2SO_4. In addition, all above-mentioned polymers are substantially insoluble in xylene and toluene, but slightly or partly soluble in toluene/DMSO (90/10) and xylene/*n*-butanol (90/10) due to cooperating effect of two solvents. In summary, all improvement of solubility in Tables 1–4 and 6 is mostly attributed to the decrease of the molecular weight of the copolymers obtained, although softening of the rigid polymer chain plays some role. Furthermore, the MPD/EOA copolymer solutions in NMP exhibit good film-forming ability and the films obtained thus look homogeneous and exhibit smooth surface. These are not achieved for the MPD homopolymer.

3.3.2. Thermal behavior

The DSC scans of the MPD/EOA copolymers with MPD feed content from 10 to 100 mol% are shown in Fig. 7. All curves show a strong endothermic peak centered at 80–115 °C due to the evaporation of water trapped inside the copolymers, and also to the dedoping process of HCl. The

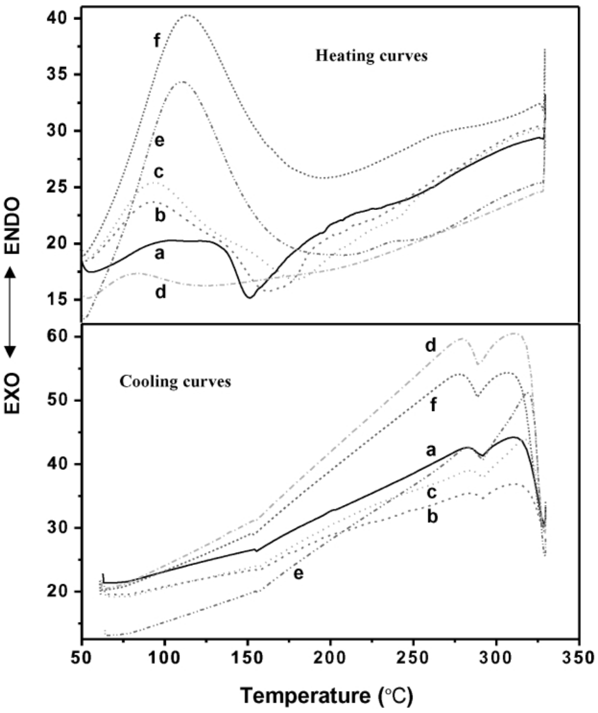


Fig. 7. DSC thermograms of the as polymerized copolymer powders with the MPD/EOA molar ratios of 10/90(a), 30/70(b), 50/50(c), 70/30(d), 90/10(e), and 100/0(f) at the sample size of ca. 5.0 mg. The upper five lines are heating curves, and the lower five lines are cooling curves. The heating and cooling 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.

endothermic peak was found to be the strongest for the two copolymers with the highest MPD contents, indicating their strongest affinity to water and HCl. On the contrary, an exothermic peak at 134, 141, and 151 °C was observed only for MPD/EOA (10/90), (30/70) and (50/50) copolymers, respectively, but not for MPD/EOA (70/30), (90/10) and (100/0) polymers. The endothermic peaks should be attributed to a series of complex chemical reactions, involving bond scissoring (such as the exclusion of ethoxyl groups), followed immediately by new bond formation and crosslinking [24]. It is suggested that the reaction is primarily related with EOA units since when the EOA content decreases to 30 mol% there is not any measurable peak from 130 to 200 °C. This means that the EOA units-containing polymers are chemically instable upon heat treatment. It should be noted that all six polymers do not seem to melt at the temperature below 325 °C, but a comparatively clear glass transition was found. The glass transition shifts to low temperature and becomes indistinct with increasing EOA content. Apparently, the glass transition could be attributed to the MPD segments in the polymer chains because only MPD homopolymer and MPD/EOA (90/10) polymer exhibit an obvious glass transition at 280 and 245 °C, respectively. It also suggests that adding EOA unit really changes the ladder structure of MPD homopolymer, i. e. the polymers prepared must be real partial ladder copolymers containing both monomer units. The cooling curves seem featureless except for two small exothermic peaks at 289 and 155 °C. After the sample was allowed to maintain at 65 °C for 30 min, with rising temperature from 65 to 325 °C again the second heating curves of the dried copolymers do not exhibit any peak (the figures are not shown), which is similar to the DSC of *p*-PD/EOA copolymer. It is seen from the DSC traces that neither exothermic peak due to oxidative degradation nor endothermic peak due to thermal degradation is observed, implying that the MPD/EOA copolymers are thermally stable below 325 °C. By the way, the conductivity of the copolymers exhibits an apparently increasing trend from 10^{-11} to 10^{-3} S/cm with increasing EOA content from 0 to 100%, something like MPD/aniline copolymer [10].

4. Conclusions

A series of new MPD/EOA copolymers with partly ladder-like structure have been successfully synthesized by an oxidative polymerization. The ladder degree of the copolymers may be monitored by controlling MPD/EOA ratio. The copolymers exhibit an obvious dependency of polymerization yield, I.V., solubility, and thermal properties on the MPD/EOA ratio. The polymerization yield and I.V. of the MPD/EOA copolymers were reversely influenced by the comonomer ratio, polymerization time, or the nature of acidic medium. The optimal polymerization temperature and monomer/oxidant(ammonium persulfate) molar ratio are 0 °C and 4/8, respectively, for the preparation of MPD/EOA (50/50) copolymer with both high yield and I.V. A systematic investigation on the molecular structure suggests that the polymers obtained are actual random copolymers consisting of two monomer units. The MPD/EOA ratios calculated by ^{1}H NMR are close to the feed ratio for MPD/EOA (10/90) and (50/50) polymers, which differ from the MPD/EOA ratios calculated by element analysis. Element analysis shows that observed MPD content is lower than feed content and denitrogenation takes place in MPD units during the polymerization. The MPD/EOA copolymers exhibit much better solubility than completely insoluble MPD homopolymer, suggesting that the insolubility of the MPD homopolymer can be overcome by copolymerizing MPD with EOA. However, its infusibility cannot be overcome by the copolymerization, due to a weak interior plasticization from short ethoxy group. Comonomers with longer side group should be required for a significant improvement of its fusibility.

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