ELSEVIER

Polymer 42 (2001) 6095–6103

polymer

www.elsevier.nl/locate/polymer

Synthesis and characterization of pyrrole and anisidine copolymers

Xin-Gui Li[a,*], Lin-Xia Wang[a], Mei-Rong Huang[a], Ya-Qing Lu[a], Mei-Fang Zhu[b], Angelika Menner[c], Jürgen Springer[c]

[a]*Department of Polymer Materials Science and Engineering, College of Materials Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, People's Republic of China*

[b]*State Key Laboratory for Modification of Chemical Fiber and Polymer Materials, Donghua University, Shanghai 200051, People's Republic of China*

[c]*Institute of Technical Chemistry, Macromolecular Chemistry, Technical University of Berlin, D-10623 Berlin, Germany*

Received 2 November 2000; received in revised form 15 January 2001; accepted 23 January 2001

Abstract

A series of copolymers were synthesized by chemically oxidative polymerization of pyrrole (PY) and *o*-anisidine (AS) in acidic aqueous medium. The yield, intrinsic viscosity, and solubility of the copolymers were studied by changing the monomer molar ratio, initial polymerization temperature, oxidant, ratio of monomer over oxidant, acidic medium, and adding dodecylbenzene sulfonate. As prepared PY/AS copolymer powder, was characterized by FT-IR, UV–Vis, ^{1}H NMR, DSC, and TG techniques. The results showed that the oxidative polymerization from PY and *o*-anisidine is exothermic and the resulting copolymers exhibit an enhanced solubility in most of the organic solvents as compared with polypyrrole. The polymer obtained by the oxidative polymerization is a real copolymer containing pyrrole and *o*-anisidine units. The PY molar content calculated based on the ^{1}H NMR spectra is slightly lower than feed PY content when feed PY content is lower than 30 mol%. The thermostability of the PY/AS copolymer increases with increasing PY unit content. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Pyrrole/*o*-anisidine copolymer; Pyrrole-containing copolymer; Oxidative copolymerization

1. Introduction

New aromatic nitrogenous polymers are continuously emerging due to their versatility, easy preparation, and very attractive property–cost performance including much higher gas separation ability than any other polymer [1]. Polypyrrole of aromatic nitrogenous polymers is the more attractive one because of its higher oxygen/nitrogen separation factor up to 8 [2]. However, the polypyrrole membrane used here is usually prepared by electropolymerization or interphase oxidative polymerization, where the membrane area is dependent on the size of the electrode and interphase. Polypyrrole membrane could not be prepared by an easy solvent cast technique because polypyrrole is an insoluble material like most of other conductive polymers. Poly(*o*-anisidine) is a soluble polymer in common organic solvents [3]. Attempts have been made to solubilize pyrrole polymer by copolymerizing pyrrole with other monomers. There are some reports concerning the copolymerization of pyrrole with aniline and thiophene derivatives [4–7], but no report on the chemically oxidative copolymerization of pyrrole with *o*-anisidine is found hitherto. It is known that the oxidation potentials of pyrrole and *o*-anisidine are about 0.8 and 0.89 V, respectively [8–11]. The oxidant with a standard reduction potential higher than 0.8 V appears to be required for the copolymerization of pyrrole and *o*-anisidine [10]. In this article, pyrrole and *o*-anisidine copolymers with different monomer ratios are synthesized for the first time by using four types of oxidants with the standard reduction potential ranging from 0.77 to 2.0 V. The solubility in several organic solvents, macromolecular structure, and thermal behavior of the copolymers are investigated systematically.

2. Experimental

Pyrrole (PY), *o*-anisidine (AS), oxidants, and solvents were commercially obtained and used as received.

2.1. Polymerization

PY/AS copolymers were prepared by an oxidative polymerization through a previously described method [12–15].

---

* Corresponding author. Tel.: +86-21-65799455; fax: +86-21-65982461.

E-mail address: lixingui@citiz.net (X.-G. Li).

PII: S0032-3861(01)00092-1

Table 1
Effect of PY/AS molar ratio on solubility of pyrrole (PY)/*o*-anisidine (AS) copolymers obtained with oxidant $(NH_4)_2S_2O_8$/monomer molar ratio of 1/1 in 1 M HCl aqueous solution

PY/AS molar ratio		Polymerization		Intrinsic viscosity (dl/g)	Solubility[a] and solution color[b]					
Feed	Calculated[c]	Temperature Initial/highest/ΔT (°C)	Yield (%)		NMP (wt%)	DMSO (wt%)	$CHCl_3$	THF	CH_2Cl_2	Benzene
0/100			64	0.18	100(bb)	100	MS(db)	PS(br)	PS(bv)	MS(rv)
10/90	9/91	23.0/31.5/8.5	60	0.19	100(bb)	100(bb)	S(b)	PS(rb)	PS(b)	SS
20/80	17/83	21.2/24.0/2.8	57		78(bb)	88(bb)	MS(bb)	SS	MS(b)	SS
30/70	21/79	22.3/25.3/3.0	55	0.44	65(bb)	40(b)	SS	SS	PS(b)	SS
50/50	25/75	22.2/25.6/3.4	69	0.74	65(bg)	65(bg)	PS(bb)	PS(br)	PS(b)	PS(br)
100/0			50[d]		IS	IS	IS	IS	IS	IS

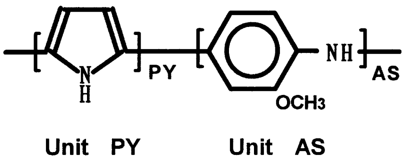
[a] IS = insoluble; MS = mainly soluble; PS = partially soluble; S = soluble; SS = slightly soluble.

[b] The solution color is indicated in the parentheses with the following abbreviations: b = blue; bb = bluish black; bg = bluish green; br = brownish red; bv = bluish violet; db = dark blue; rb = reddish blue.

[c] PY/AS molar ratio calculated based on the ^1H NMR spectra shown in Fig. 3.

[d] The oxidant used for polymerization is $FeCl_3$ and polymerization medium is pure water [16].

A representative procedure for the preparation of the PY/AS (10/90) copolymer is as follows: to 20 ml of a 1 M HCl solution was added 0.09 ml (1.3 mmol) PY and 1.32 ml (11.7 mmol) *o*-anisidine in a 100 ml glass flask in water bath and stirred vigorously for half an hour. Ammonium persulfate $[(NH_4)_2S_2O_8]$, 2.964 g (13 mmol), was dissolved separately in 10 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 23.4°C in ca. 45 min (the total molar ratio is monomer/oxidant = 1/1). Immediately, after the first few drops, the reaction solution turned bluish-violet. The reaction mixture was stirred for 24 h at ambient temperature. The copolymer hydrochloride salt was isolated from the reaction mixture by filtration and washed with an excess of distilled water to remove the oxidant and oligomers. The hydrochloride salt was subsequently neutralized in 200 ml of 0.2 M ammonium hydroxide and stirred for 24 h to obtain the base form of PY/AS copolymer. The copolymer base was washed with excess water. A bluish-black solid powder was left to dry in ambient air for one week. The copolymer of 0.907 g was obtained with a yield of 60%. The PY/AS copolymers exhibit the following nominal structure:



2.2. Measurements

The intrinsic viscosity for the copolymers of pyrrole with *o*-anisidine 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 5 mg was added into the solvent of 0.5 ml and dispersed thoroughly. After the mixture was swayed continuously for 24 h at room temperature, the solubility of the polymers was characterized. IR spectra were recorded on a Spectrum One Spectrometer at 4 cm^{-1} resolution for DBS-free copolymer and on a Nicolet Magna FT-IR 550 Spectrometer made in USA at 2 cm^{-1} resolution for DBS-containing copolymer on KBr pellets. UV–Vis spectra were measured on a Kontron Uvikon 860 in a range of 200–800 nm with a homogeneous solution of the copolymers in DMSO. ^1H NMR spectra were obtained in deuterated dimethylsulfoxide using a Bruker AC200 spectrometer operating at 200 MHz and a Bruker MSL-300 spectrometer operating at 300.13 MHz. DSC measurement was performed at a heating rate of 10°C/min with a sample size of 6–7 mg using a Perkin–Elmer 7 Pyris Thermal Analyzer. Thermogravimetry (TG) measurements were performed at a heating rate of 10°C/min in a flowing rate of 10 ml/min with a sample size of 4.1–4.3 mg by using a NETZSCH TG 209 Geratebau GmbH thermal analyzer. The degradation temperature, T_d, was determined by extrapolation of the initial decomposition portion of the TG curve. T_{dm} is the temperature at the maximum weight-loss rate obtained by derivative thermogravimetry (DTG) curves.

3. Results and discussion

3.1. Synthesis of the copolymers of pyrrole and o-anisidine

The copolymerization of pyrrole and *o*-anisidine with ammonium persulfate as an oxidant in 30 ml 1 M HCl aqueous solution afforded bluish-black precipitates as products after the oxidative polymerization of 24 h. The progress in copolymerization reaction was followed by

Table 2
The effect of polymerization temperature on solubility of pyrrole (PY)/*o*-anisidine (AS) (30/70) copolymers with monomer/$(NH_4)_2S_2O_8$/dodecylbenzene sulfonate (DBS) ratio 5/1/1 in 1 M HCl aqueous solution

Polymerization		Intrinsic viscosity (dl/g)	Solubility[a] (solution color)[b]					
Temperature (°C)	Yield (%)		NMP (wt%)	DMSO (wt%)	$CHCl_3$	THF	CH_2Cl_2	Benzene
−12	18	1.01	41(br)	25(br)	SS	SS	SS	SS
0	19	0.36	47(g)	16(br)	SS	SS	SS	SS
12	19	0.96	52(g)	42(br)	SS	PS(b)	SS	SS
26	24	0.47	80(g)	31(g)	PS(bb)	MS(bb)	PS(bb)	SS

[a] MS = mainly soluble; PS = partially soluble; SS = slightly soluble.
[b] The solution color is indicated in the parentheses: bb = bluish black; br = brownish red; g = gray.

measuring the solution temperature. It was found that with dropping oxidant solution slowly and regularly, the polymerization solution temperature increases and exhibits two or three peaks and finally reaches a nearly constant temperature. PY/AS(10/90) copolymerization exhibits the strongest exothermic capability among the four copolymerization systems. The enhancement of the solution temperature is 8.5° for the PY/AS(10/90) system, as listed in Table 1. On the contrary, PY/AS (20/80) copolymerization exhibits the lowest exothermic effect with an enhancement of the solution temperature of 2.8°. These results may be due to the highest initial polymerization temperature for PY/AS(10/90) and the lowest initial temperature for PY/AS(20/80). That is to say, the exothermic capacity from the PY/AS copolymerization is dependent on the initial temperature of reaction solution. In other words, initial solution temperature appears important for the oxidative copolymerization of PY with AS.

It was found that the copolymerization yield of pyrrole and *o*-anisidine was dependent on the monomer ratio as shown in Table 1. The yield decreased with an increase in feed PY content from zero to 30 mol% but increased with a further increase in feed PY content from 30 to 50 mol%. The PY/AS copolymerization shows the minimal yield at the feed PY content of ca. 30 mol% but the highest yield at the feed PY content of 50 mol%. The highest yield 69% is higher than that of polypyrrole when $FeCl_3$ was used as an oxidant and the oxidant/PY ratio is 1/1 [16]. A different relationship between the intrinsic viscosity and comonomer ratio (Table 1) is observed. The intrinsic viscosity of the PY/AS copolymers increased slightly with increasing feed pyrrole content from 0 to 10 mol% and almost linearly with increasing feed pyrrole content from 10 to 50 mol% and reached the highest value of 0.74 dl/g at the pyrrole content of 50 mol%. The enhancement of the intrinsic viscosity may be responsible for the enhancement of the molecular weight of the copolymers and also of the rigidity of the copolymer chains. Note that almost no report on the intrinsic viscosity of polypyrrole is found because polypyrrole is insoluble in most of the organic solvents. Therefore, it is impossible for us to compare the intrinsic viscosities of PY/AS copolymers with polypyrrole. It can be concluded that the yield and intrinsic viscosity of the copolymer of pyrrole with *o*-anisidine was significantly influenced by the monomer ratio. The copolymer with the PY/AS ratio of 50/50 exhibits both the largest yield and the highest intrinsic viscosity. An introduction of less than 30 mol% pyrrole monomer might retard the polymerization of *o*-anisidine and result in difficulty in the formation of high molecular weight copolymer.

As shown in Table 2, by increasing the polymerization temperature from −12°C to 26°C, the polymerization yield increased but the intrinsic viscosity of the copolymers obtained exhibited two maxima. It appears that −12°C is the most suitable for the preparation of high molecular weight PY/AS(30/70) copolymer possibly due to lower

Table 3
The effect of $(NH_4)_2S_2O_8$ content on solubility of pyrrole(PY)/*o*-anisidine (AS) (30/70) copolymers containing dodecylbenzene sulfonate (DBS) at polymerization temperature 15–19°C in 1 M HCl aqueous solution and polymerization time 24 h

Monomer/oxidant/DBS	Yield %	Intrinsic viscosity (dl/g)	Solubility in solvents[a] (%) and solution color[b]					
Feed molar ratio			NMP (wt%)	DMSO (wt%)	$CHCl_3$	THF	CH_2Cl_2	Benzene
10/2/1	19	0.92	62(bb)	57(bb)	PS(bb)	PS(bb)	PS(bb)	SS
10/5/1	43	0.41	81(bb)	76(bb)	MS(bb)	PS(bb)	PS(bb)	SS
10/10/1	98	0.36	99(bg)	92(bg)	MS(bb)	PS(bg)	MS(bb)	SS

[a] MS = mainly soluble; PS = partially soluble; SS = slightly soluble.
[b] The solution color is indicated in the parentheses: bb = bluish black; bg = bluish green.

Table 4
Influence of oxidant and its standard reduction potential on copolymerization of pyrrole (PY)/*o*-anisidine (AS)(30/70) with oxidant/monomer/dodecylbenzenesulfonate (DBS) molar ratio = 10/10/1 in 1 M HCl aqueous solution

Oxidant	Standard reduction potential (V)	Polymerization		Intrinsic viscosity (dl/g)	Solubility[a] (solution color)[b]					
		Temperature (°C)	Yield (%)		NMP (wt%)	DMSO (wt%)	$CHCl_3$	THF	CH_2Cl_2	Benzene
$(NH_4)_2S_2O_8$	2.0	18.7	98	0.36	99(bg)	92(bg)	MS(bb)	PS(bg)	MS(bb)	SS
$(NH_4)_2S_2O_8$[c]					S	S	IS			
$K_2S_2O_8$	2.0	17.1	96	0.52	83(bb)	85(bb)	MS(bb)	MS(bg)	MS(bb)	SS
$K_2Cr_2O_7$	1.0	17.0	99	0.96	78(br)	83(br)	MS(br)	MS(br)	MS(br)	PS(br)
$FeCl_3$	0.77	15.5	31	0.93	41(bb)	40(bb)	PS(bb)	PS(bb)	PS(bb)	SS

[a] About 0.3 g bluish black polymer powder was added into the NMP or DMSO of 100 ml. IS = insoluble; MS = mainly soluble; PS = partially soluble; S = soluble; SS = slightly soluble.

[b] The solution colour is indicated in the parentheses: bb = bluish black; bg = bluish green; br = brownish red.

[c] For polypyrrole from Ref. [17].

chain terminating velocity of oxidative polymerization from AS monomer at lower temperature; 12°C is also suitable to the preparation of higher molecular weight copolymer mainly owing to lower chain terminating rate of oxidative polymerization from PY monomer.

The effect of monomer/oxidant(ammonium persulfate) molar ratio on the copolymerization of pyrrole/*o*-anisidine (30/70) in 1 M HCl aqueous solution in a temperature range from 15 to 18°C was studied. It can be seen from Table 3 that with increasing molar ratio of monomer over oxidant the copolymerization yield decreases significantly but the intrinsic viscosity of the copolymer obtained increases. When less oxidant was added, the oxidant will be consumed fast and some monomer can not be further oxidized to polymerize, leading to low polymerization yield. Higher intrinsic viscosity of the copolymer at low oxidant concentration might be due to priority of chain propagation from monomer as compared with chain initiation because the probability of chain propagation is larger than that of chain termination.

Influence of oxidant and its standard reduction potential on polymer yield and intrinsic viscosity of the PY/AS (30/70) copolymers obtained is listed in Table 4. It seems that $K_2Cr_2O_7$ is the best oxidant to prepare the highest molecular weight copolymer with the highest yield. When $FeCl_3$ with the lowest standard reduction potential was used as an oxidant, the copolymer with the second highest intrinsic viscosity can be obtained at the lowest yield. Perhaps only pyrrole could be oxidized at low applied potential to initiate the polymerization at a slow rate. High yields of copolymerization are observed when $(NH_4)_2S_2O_8$ and $K_2S_2O_8$ are employed as oxidants because their standard reduction potentials are high enough to achieve a fast rate of copolymerization of pyrrole and *o*-anisidine. It should be noted that the copolymers obtained might undergo degradation reaction at the high applied potential, leading to low intrinsic viscosity and good solubility, as listed in Table 4. By the way, it can be seen from Table 4 that the PY/AS(30/70) copolymer exhibits better solubility in chloroform than polypyrrole [17].

Table 5 lists the dependence of the copolymerization yield, intrinsic viscosity, and solubility of PY/AS(30/70) copolymer on the acidic medium. When HNO_3 was employed, the highest yield and best solubility in NMP were observed. The highest intrinsic viscosity of the copolymer and the

Table 5
Influence of polymerization medium on the copolymerization of pyrrole (PY)/*o*-anisidine (AS)(30/70) at oxidant [$(NH_4)_2S_2O_8$]/monomer molar ratio of 1/1 in 1 M acidic aqueous solution

Polymerization			Intrinsic viscosity (dl/g)	Solubility[a] (solution color)[b]					
Medium	Temperature (°C)	Yield (%)		NMP (wt%)	DMSO (wt%)	$CHCl_3$	THF	CH_2Cl_2	Benzene
HNO_3	25–27	63.1	0.45	81(bb)	58(bb)	MS(bb)	PS(bv)	PS(b)	PS(bv)
HCl	23–25	54.5	0.44	65(bb)	40(b)	SS	SS	PS(b)	SS
HNO_3 + HCl	26–27	53.2	0.49	59(bb)	69(bb)	MS(bb)	PS(bb)	PS(b)	PS(br)
$HNO_3 + H_2SO_4$	25–26	52.3	0.83	78(bb)	60(bb)	PS(bb)	PS(bv)	PS(b)	MS(bb)
H_2SO_4[c]	25–26	49.6	0.14	74(br)	75(gb)	PS(br)	PS(bv)	PS(bv)	PS(br)
H_2SO_4 + HCl	26–27	43.3	0.36	67(bb)	68(bb)	PS(bb)	PS(bv)	PS(b)	MS(bb)

[a] About 0.3 g bluish black polymer powder was added into the NMP or DMSO of 100 ml. MS = mainly soluble; PS = partially soluble; SS = slightly soluble.

[b] The solution colour is indicated in the parentheses: b = blue, bb = bluish black; bg = bluish green; br = brownish red, bv = blackish violet, gb = grey black.

second best solubility in NMP were obtained if a mixture of $HNO_3 + H_2SO_4$ was used as a polymerization medium. Generally, the copolymer obtained in 1 M HNO_3- and/or HCl-containing medium exhibits both higher yield and intrinsic viscosity, since the oxidant exhibits higher reduction potential in HNO_3- and/or HCl-containing medium possessing larger pH value than in 0.5 M H_2SO_4 medium possessing smaller pH value. However, the highest solubility in DMSO observed in Table 5 should be due to the lowest intrinsic viscosity of the corresponding copolymer. A systematic investigation on the solubility of the PY/AS copolymers was discussed in Section 3.2.

3.2. Solubility of the copolymers of pyrrole and o-anisidine

It can be seen from Tables 1–5 that the solubility of PY/AS copolymers is strongly influenced by PY/AS molar ratio, polymerization temperature, monomer/oxidant/DBS molar ratio, oxidant type. As compared with polypyrrole, all PY/AS copolymers exhibit much better solubility in the six solvents (Table 1). With increasing feed AS content, the PY/AS copolymer exhibits an enhanced solubility in NMP and DMSO. Finally, PY/AS (0/100) and (10/90) polymers were soluble in NMP and DMSO, and mainly soluble in chloroform, ethylene chloride, and benzene. Although the intrinsic viscosity of the PY/AS copolymers decreased with increasing feed AS content (Table 1), the PY/AS (50/50) copolymer with the lowest feed AS content but the highest intrinsic viscosity exhibits better solubility than PY/AS(30/70) copolymer. Thus, it could be speculated that the improvement of the copolymer solubility with increasing AS content may be due to the change of molecular structure rather than the change of intrinsic viscosity of the copolymers [3]. Possibly, the incorporation of anisidine unit into polypyrrole backbone can decrease the structural regularity and rigidity of the chains of polypyrrole as well as the interaction between polypyrrole chains to some extent. In addition, improved solubility with inducing PY unit into AS polymer is an evidence that the polymerization product is indeed copolymer containing PY and AS units rather than a simple mixture of two homopolymers. With increasing polymerization temperature from −12 to 26°C, the PY/AS(30/70) copolymer exhibits an increased solubility in NMP and THF (Table 2). As listed in Table 3, with increasing oxidant content in the polymerization system, the solubility of PY/AS(30/70) copolymer in NMP, DMSO, $CHCl_3$, and CH_2Cl_2 gets better continuously. The solubility of PY/AS(30/70) copolymer in NMP, DMSO, $CHCl_3$, and CH_2Cl_2 increases with the variation of the oxidant from $FeCl_3$, $K_2Cr_2O_7$, $K_2S_2O_8$ to $(NH_4)_2S_2O_8$ (Table 4). Above mentioned improvement of solubility is attributed to the decrease of the molecular weight of the copolymer obtained.

3.3. FT-IR spectra of the copolymers of pyrrole and o-anisidine

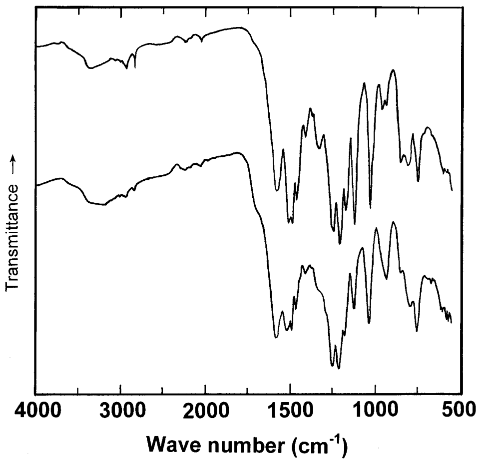
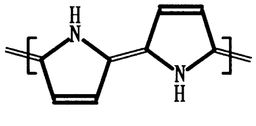


Fig. 1. FT-IR absorption spectra of the copolymer bases with PY/AS molar ratios of 10/90 (upper) and 50/50 (lower).

Representative FT-IR spectra for the copolymers with PY/AS molar ratios of 10/90 and 50/50 were shown in Fig. 1. It is reported that poly(*o*-anisidine) exhibits –NH– stretching vibration at 3395 cm^{-1} [3] and polypyrrole hardly ever exhibits –NH– vibration peak [16,18]. A broad and weak band centered at 3349–3264 cm^{-1} due to the characteristic N–H stretching vibration suggests the presence of –NH– groups in AS and PY units. The broad band becomes weaker and broader and shifts to lower wave number with an increase in PY feed content from 0 to 100 mol%. Two weak peaks at 2936 and 2835 cm^{-1} should be due to aromatic and aliphatic C–H stretching vibrations, respectively. With increasing feed PY content, these two peaks both become weaker because PY unit contains less aromatic C–H bond and does not contain aliphatic C–H bond. Thus the characteristics of IR absorption spectra of PY/AS copolymers above 2000 cm^{-1} are dominated by the AS unit. However, the IR absorption below 2000 cm^{-1} is influenced by the PY units. A comparison of the spectra of polyanisidine [3], polypyrrole [16,18] and PY/AS copolymer shown in Fig. 1 reveals some differences in the relative absorbance and wave number. With increasing feed PY content, the relative absorption intensity at 1578–1579, 1244–1246, and 929–933 cm^{-1} gets stronger significantly. This should be attributable to PY unit to some extent because the bands at about 1540, 1170, and 900 cm^{-1} are characteristic of polypyrrole. The absorption at 1578–1579 cm^{-1} increases significantly with increasing feed PY content, suggesting that the PY unit in the polymer chains seems to exist mainly in the following quinoid form [19].



The difference of wave number might result from the copolymerization effect of pyrrole with *o*-anisidine.

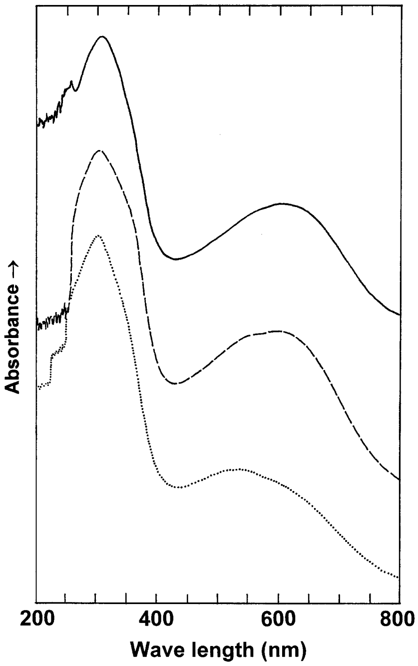


Fig. 2. UV–Vis absorption spectra of the copolymer base solutions with PY/AS molar ratios of 20/80 (—) 30/70 (– – –), and 50/50 (·····) in dimethylsulfoxide.

3.4. UV–Vis spectra of the copolymers of pyrrole and o-anisidine

Fig. 2 shows the UV–Vis absorption spectra of three copolymer solutions with PY/AS ratios of 20/80, 30/70, 50/50 in dimethylsulfoxide. A strong band and a broad and weak band are observed. These UV–Vis spectra look like those of poly(*o*-anisidine) [20]. The strong band at 295–313 nm and weak band centered at 536–620 nm may correspond to $\pi \rightarrow \pi *$ transition and $n \rightarrow \pi *$ transition in the neutral form, respectively [20,21]. It can be seen from Table 6 that the wavelength of the both bands shifts to lower value continuously with increasing feed PY content. Additionally, the relative intensity of the weak band gets weaker further with increasing PY content. The continuous variation of wavelength and intensity of UV–Vis bands may result from copolymerization effect of pyrrole with *o*-anisidine. In other words, the polymer formed by oxidative polymerization of pyrrole with *o*-anisidine is the copolymer of two monomers rather than the mixture of two homopolymers. Furthermore, pure polypyrrole is hardly soluble in dimethylsulfoxide.

3.5. ^{1}H NMR spectra of the copolymers of pyrrole and o-anisidine

^{1}H NMR spectra of the copolymers of pyrrole and *o*-anisidine are characterized by two signals, a weak broad peak and a strong broad peak, which are exactly corresponding to the aromatic protons and methoxyl protons, as shown in Fig. 3. The weak peak from aromatic protons appears in a wide range from 6.4 to 7.3 ppm which might result from two aromatic protons on PY and AS units, but the strong peak locates in a range between 3.7 and 3.9 ppm. Two strongest peaks at 2.49 and 3.33 ppm are due to protons of DMSO and water in DMSO. It appears that the ^{1}H NMR spectra of PY/AS copolymers do not change systematically with increasing feed PY content. These spectra are not much informative on the calculation of sequence distribution of the comonomer units. Fortunately, based on a comparison of the area of aromatic proton peak (6.4–7.3 ppm) on PY and AS units with methoxyl proton peak (3.7–3.9 ppm) on AS unit, the ratio of PY to AS units on the copolymers can be calculated and listed in Table 1. Because there are the same numbers of aromatic protons as those of methoxyl protons on every AS unit in the polymer chains, the number of aromatic protons on PY units may be calculated through the following equation:

PY proton area = Total aromatic proton area − Methoxyl proton area

Therefore,

Molar ratio of PY over AS = (PY proton area/2) ÷ (Methoxyl proton area/3)

It seems that the actual PY content is slightly lower than feed PY content for PY/AS (10/90) and (20/80) copolymers. Especially, the actual PY content is significantly lower than

Table 6

The variations of UV–Vis spectra of PY/AS copolymers in DMSO and their thermal degradation parameters in nitrogen at 10°C/min with PY/AS molar ratio obtained at oxidant [$(NH_4)_2S_2O_8$]/monomer molar ratio of 1/1 in 1 M HCl aqueous solution

Feed PY/AS	Wavelength (nm)		$T_d/T_{dm1}/T_{dm2}$ (°C)	$(d\alpha/dt)_{m1}/(d\alpha/dt)_{m2}$ (%/min)	Char yield at 700°C (wt%)
Molar ratio	Strong band	Weak band			
0/100[a]	313	620	407/390/537	2.1/3.8	0
10/90	310	615	367/395/537	2.1/2.9	5.6
20/80	308	609	387/390/585	1.6/2.6	12.2
30/70	304	597	378/400/585	1.6/2.5	12.1
50/50	295	536	380/380/625	1.5/2.3	18.1
100/0		525[b]	393/293/620[c]	1.3/2.2[c]	21.0[c]

[a] Undoped poly(*o*-anisidine) solution in NMP [20].

[b] The sample used is a reduced polypyrrole film obtained by electropolymerization [21].

[c] From Ref. [22].

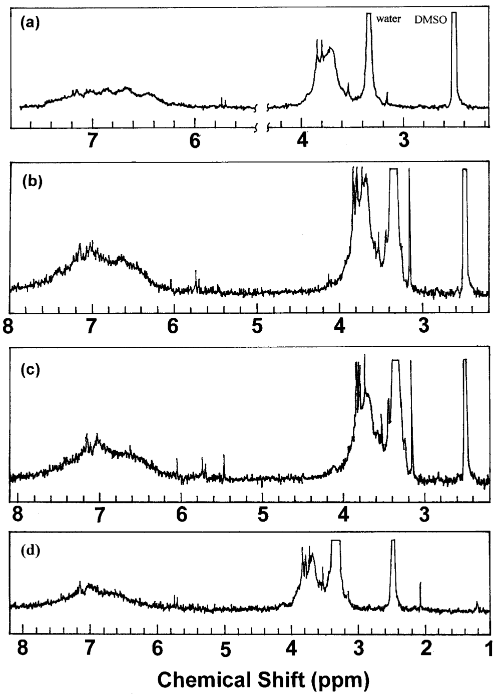


Fig. 3. ^{1}H NMR spectra of the copolymers with PY/AS molar ratios of (a)10/90, (b) 20/80, (c) 30/70, and (d) 50/50 in deuterated dimethylsulfoxide (DMSO-d_6) at 200 MHz.

feed PY content for PY/AS (30/70) and (50/50) copolymers. This difference of PY content should be due to the lower solubility of the both copolymers in DMSO as listed in Table 1 because the higher PY content, the lower the solubility of the copolymer in DMSO is. It should be noted that the ^{1}H NMR spectra of the PY/AS copolymers in $CDCl_3$ (Fig. 4) are quite different from those in DMSO-d_6 (Fig. 3), because of much lower solubility of the copolymers in $CDCl_3$. A weak methoxyl proton peak and a very weak aromatic proton peak are observed, indicating that the solubility of both PY/AS copolymers in $CDCl_3$ is not good enough. As shown in Fig. 4, the peaks at 1.6 and 7.2 ppm are ascribed to water in the measuring solution and chloroform, respectively. The water protons in chloroform exhibit smaller chemical shift than those in DMSO because there is a stronger interaction between water and polar DMSO. Additionally, two resonance peaks from NH_2 protons at 5.71 and 5.75 ppm shown in Fig. 3 are very weak, indicating the PY/AS copolymers should have high molecular weight, which is substantially coincident with the intrinsic viscosity result shown in Table 1.

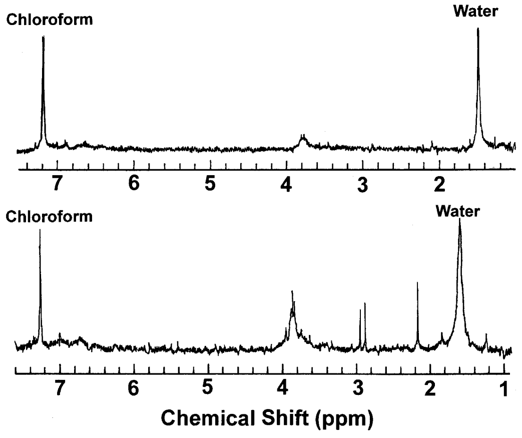


Fig. 4. ^{1}H NMR spectra of the copolymers with PY/AS molar ratios of 30/70 (upper) and 50/50 (lower) in deuterated chloroform at 200 MHz.

3.6. *The effect of dodecylbenzene sulfonate on pyrrole and o-anisidine copolymerization*

The PY/AS (30/70) copolymer synthesized by adding sodium dodecylbenzene sulfonate (DBS) exhibits different solubility and FT-IR spectra, as shown in Tables 1–4 and Fig. 5. The solubility of the copolymer containing DBS as an additive of copolymerization is lower than that of corresponding DBS-free copolymer. The FT-IR spectra of DBS-containing copolymer powder are similar to the IR spectra shown in Fig. 1 for DBS-free copolymer, except that there is an increased absorption of C–H vibration at 2850–2970 cm^{-1} due to dodecyl group. ^{1}H NMR spectrum of the soluble part of the DBS-containing copolymer in DMSO-d_6 exhibits three strong aliphatic proton peak at 0.75–1.53 ppm(where the second strongest peak centered at 0.82 ppm is due to end methyl group on dodecyl side chain, the strongest peak centered at 1.17 ppm and medium broad peak centered at 1.51 ppm due to methylene group on dodecyl side chain, and the weak peak at 2.34 ppm (next to the DMSO proton peak) due to the methylene directly connected on benzene ring), medium and sharp aromatic

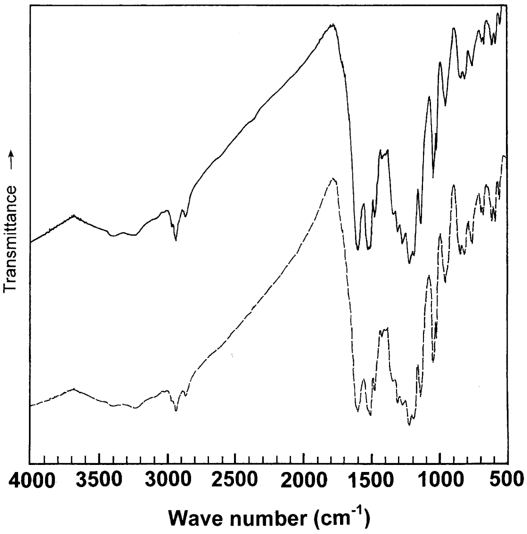


Fig. 5. FT-IR absorption spectra of PY/AS(30/70) copolymer base powders. The copolymers were prepared at the monomer/ammonium persulfate/sodium dodecylbenzene sulfonate molar ratios of 10/10/1(—) and 10/2/2 (– – –) in 1 M HCl and the copolymer hydrochloride salt was subsequently neutralized in 180 ml 0.2 M ammonium hydroxide, stirred for 24 h, and washed with excess water to obtain the base form of PY/AS(30/70) copolymers.

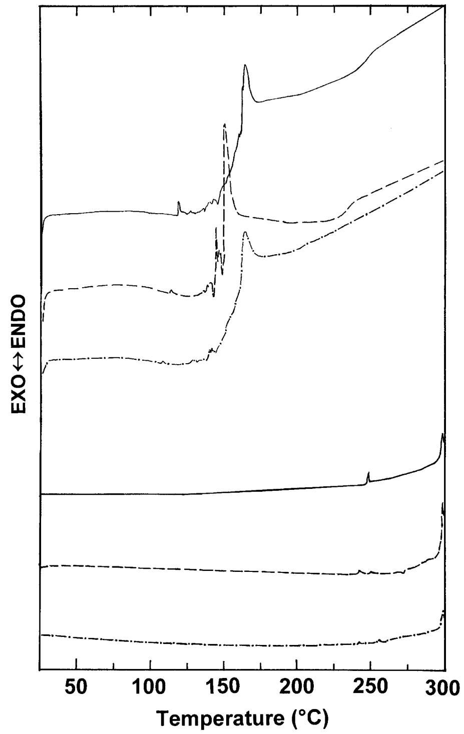


Fig. 6. Differential scanning calorimetry thermograms of the as-polymerized copolymer powders with PY/AS molar ratios of 20/80 (—), 30/70 (– – –), and 50/50 (–·–·–·). The upper three lines are heating curves, and the lower three lines are cooling curves.

proton peak at 6.0–7.5 ppm, weak methoxyl proton peak on AS unit at about 3.8 ppm, weak $-NH_2$ peak at 4.73 ppm, and very weak –NH– peak on PY ring at 10.85–10.98 ppm. The NMR spectrum of DBS-containing copolymer exhibits much higher resolution than those in Fig. 3. The NMR results reveal that soluble part of the DBS-containing copolymer in DMSO is low molecular weight oligomer which consists of the DBS and a small number of *o*-anisidine and pyrrole units. Thus, there is an obvious influence of (DBS) on the oxidative copolymerization of pyrrole and *o*-anisidine.

3.7. Thermal behavior of the copolymers of pyrrole and o-anisidine

The DSC scans of the PY/AS copolymers with three PY/AS ratios of 20/80, 30/70 and 50/50 are shown in Fig. 6. Three scans all show a small and sharp endothermic peak at 164, 150, and 163°C for PY/AS (20/80), (30/70), and (50/50) copolymers respectively. The respective endotherms are 45, 61, and 82 J/g. This endotherm should be due to the dedoping process of the copolymers. This speculation is further supported by the fact that in the cooling scan after the sample was allowed to maintain at 300°C for about half an hour. The cooling curves seem featureless except for very weak endothermic and exothermic peaks. Therefore the PY/AS copolymers do not appear to melt at the temperature below 300°C. It should be noted that PY/AS (20/80) and (30/70) copolymers exhibit an apparent glass transition at 249 and 234°C respectively. This glass transition should be attributed to the AS units in the polymer chains because it was reported that glass transition temperature of poly(*o*-anisidine) in its undoped state is 240°C [20]. There is neither exothermic peak due to oxidative degradation nor endothermic peak due to thermal degradation at the temperature lower than 300°C, implying that the PY/AS copolymers are thermally stable, as discussed below.

Representative TG and DTG curves of the PY/AS copolymers with three PY/AS ratios of 10/90, 20/80, and 50/50 are shown in Figs. 7 and 8, from which a series of thermal degradation parameters are obtained and listed in Table 6. The copolymers lose weight gradually with increasing temperature from 100 to 300°C and more rapidly from 300 to 790°C. With increasing PY content from 0 to 100 mol%, the temperature at the second maximum weight-loss rate (T_{dm2}) and char yield at 700°C increase, suggesting that the char yield at elevated temperature could be attributed to PY unit in the copolymer. Two maximum weight-loss rates ($(d\alpha/dt)_{m1}$ and $(d\alpha/dt)_{m2}$) both decrease with decreasing AS content from 100 to 0 mol%, implying that the maximum weight-loss rate might be controlled by the AS unit. These results show that the

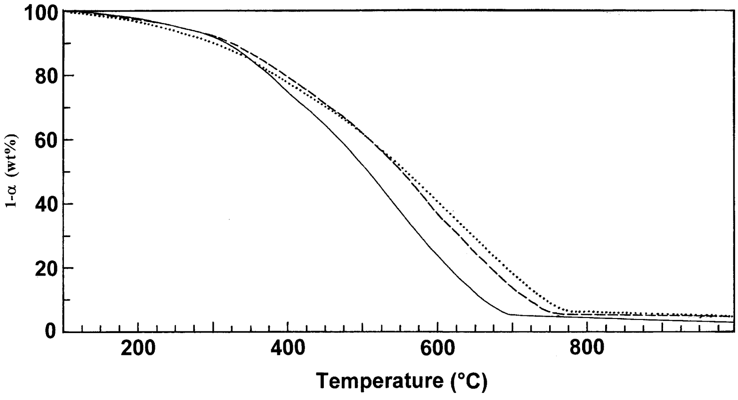


Fig. 7. TG thermograms of the as-polymerized copolymer powders with PY/AS molar ratios of 10/90(—), 20/80 (– – –), and 50/50 (····) at a heating rate of 10°C/min in a flowing nitrogen.

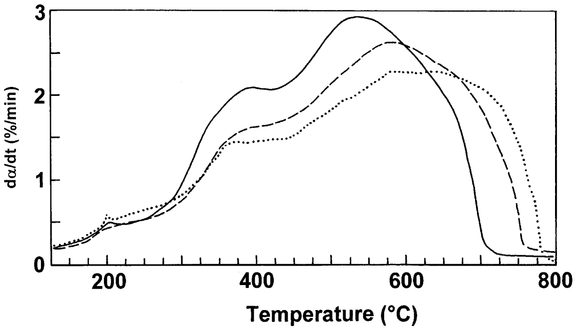


Fig. 8. DTG thermograms of the as-polymerized copolymer powders with PY/AS molar ratios of 10/90 (—), 20/80 (– – –), and 50/50 (····) at a heating rate of 10°C/min in a flowing nitrogen.

thermostability of the PY/AS copolymer increases with increasing PY unit content because PY unit has higher aromatics than AS unit and also methoxyl group on the AS unit is easily excluded from the polymer chain at an elevated temperature. Note that no regular relation between T_d or T_{dm1} and PY/AS molar ratio was found.

4. Conclusions

A series of copolymers from pyrrole and *o*-anisidine were synthesized by oxidative polymerization in HCl aqueous medium at a temperature range from −12°C to 26°C. The oxidative polymerization of pyrrole with *o*-anisidine is highly exothermic. The copolymers exhibit an obvious dependency of polymerization yield, intrinsic viscosity, and solubility on copolymer monomer PY/AS ratio, oxidant/monomer/dodecylbenzene sulfonate molar ratio, oxidant type, polymerization temperature, and acidic medium. Available highest yield and intrinsic viscosity are 69% and 0.74 dl/g for PY/AS (50/50) copolymer. The insolubility of polypyrrole can be overcome by copolymerizing pyrrole with *o*-anisidine. Therefore its solution processability should be better. The FT-IR, UV–Vis spectra and ^{1}H NMR suggest that the polymers obtained are real copolymers consisting of two monomer units. DSC measurement indicates that the copolymers do not melt at the temperature below 300°C. The temperature at the second maximum weight-loss rate, the maximum weight-loss rate, and char yield at elevated temperature are significantly relative to the PY/AS molar ratio. The thermostability of the PY/AS copolymer increases with increasing PY unit content.

Acknowledgements

The project is supported by (1) the National Natural Science Fund of China (29804008), (2) the Fund for the University Key Teacher of the Chinese Ministry of Education (GG-430-10247-1186), (3) the State Key Laboratory for Modification of Chemical Fiber and Polymer Materials at Donghua University, Shanghai, China.

References

[1] Li X-G, Huang M-R. J Appl Polym Sci 1997;66:2139.
[2] Martin CR, Liang W, Menon V, Parthasarathy R, Parthasarathy A. Synth Met 1993;55–57:3766.
[3] Li X-G, Huang M-R, Jin Y, Yang Y-L. Polymer 2001;42:3427.
[4] Yamamoto R, Bun T. JP06-329766, 1994.
[5] Sato M, Amano K, Ishikawa H. JP07-118371, 1995.
[6] Wei Y, Tian J, Hsueh KF. Polym Mater Sci Engng 1994;71:586.
[7] Czerwinski W, Wrzeszcz G, Kania K, Rabek JF, Linden LA. J Mater Sci 2000;35:2305.
[8] Bhattacharya A, De A. J Macromol Sci, Rev Macromol Chem Phys 1999;C39:17.
[9] Karakisla M, Sacak M. J Polym Sci, Part A Polym Chem 2000;38:51.
[10] Wei Y, Jang GW, Chan CC, Hsueh KF, Hariharan R, Patel SA, Whitecar CK. J Phys Chem 1990;94:7716.
[11] Kilmartin PA, Wright GA. Synth Met 1999;104:145.
[12] Li X-G, Huang M-R, Li F, Cai W-J, Jin Z, Yang Y-L. J Polym Sci, Part A Polym Chem 2000;38:4407.
[13] Li X-G, Huang M-R, Yang Y-L. Polym J 2000;32:348.
[14] Li X-G, Huang M-R, Yang Y-L. Polymer 2001;42:4099.
[15] Huang M-R, Li X-G, Yang Y-L. Polym Degrad Stab 2000;71:31.
[16] Sak-Bosbar M, Budimir MV, Kovac S, Kukulj D, Duic L. J Polym Sci, Part A Polym Chem 1992;30:1609.
[17] Song KT, Lee JY, Kim Hd, Kim DY, Kim SY, Kim CY. Synth Met 2000;110:57.
[18] Kang ET, Neoh KG, Tan TC, Ong YK. J Macromol Sci, Chem 1987;A24:631.
[19] Kurosu H, kikuchi M, Ando I. J Polym Sci, Part B Polym Phys 1995;33:769.
[20] Pandey SS, Annapoorni S, Malhotra BD. Macromolecules 1993;26:3190.
[21] Peters EM, Van Dyke JD. J Polym Sci, Part A Polym Chem 1992;30:1891.
[22] Kalaycioglu E, Akbulut U, Toppare L. J Appl Polym Sci 1996;61:1067.