Soluble copolymers via oxidative polymerization of pyrimidylamine and anisidine

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Abstract

A series of copolymers was synthesized by oxidative polymerization of 2-pyrimidylamine (MA) and \textit{o}-anisidine (AS) with five monomer ratios using ammonium persulfate as an oxidant in 1 M HCl aqueous solution at room temperature. The yield, intrinsic viscosity, and solubility of the MA/AS copolymers were studied in detail. The copolymers were characterized by \textsuperscript{1}H NMR, FT-IR, wide-angle X-ray diffraction, and thermogravimetry. Based on \textsuperscript{1}H NMR spectra of the copolymers, the actual MA/AS molar ratio in the copolymers was compared with their feed ratio. The results showed that the MA/AS copolymers are amorphous and their polymerization yield, intrinsic viscosity, solubility in common organic solvent, thermostability, as well as activation energy of thermal degradation all increase with increasing AS content, but their char yield at 700°C in nitrogen decreases. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: 2-Pyrimidylamine-containing copolymer; Poly(o-anisidine); \textsuperscript{1}H NMR spectrum

1. Introduction

Multifunctional polymers have attracted attention recently because they can be used as advanced gas separation membranes, electroconductive materials, macromolecular drugs, antitumor agents, and macromolecular catalysts. Pyrimidylamine polymer is one of the multifunctional polymers because of its high electroconductivity up to 5.4 S/cm [1], anticancer characteristics [2], and potential high oxygen/nitrogen separation capability [3,4]. However, the solubility, air stability, and thermostability of poly(pyrimidylamine) are all not good enough. The purpose of the present study is to synthesize a soluble copolymer of 2-pyrimidylamine (MA) with \textit{o}-anisidine (AS) in common organic solvents including chloroform, ethylene chloride, benzene, and absolute ethanol by introducing a methoxyl group-containing anisidine unit on the poly(pyrimidylamine) main chain, and to describe the variations in yield, intrinsic viscosity, macromolecular structure, crystallinity, thermostability, and degradation kinetics with comonomer ratio. This topic may be of importance in elaborating the structural and property improvement induced by copolymerization of MA and AS. No report about the above-mentioned MA/AS copolymer has been found hitherto.

2. Experimental

2.1. Reagents

MA, AS, ammonium persulfate, and all solvents were commercially obtained and used without further purification.

2.2. Polymerization

MA/AS copolymers were prepared through oxidative polymerization by using a previously described method [5]. A typical procedure for the preparation of the copolymer with MA/AS molar ratio of 30:70 is as follows: to 40 ml of 1 M HCl solution was added 1.426 g (0.015 mol) MA and 4.004 ml (0.035 mol) AS in a 100-ml two-neck glass flask. 11.4 g (0.05 mol) ammonium persulfate (\((\text{NH}_4)_2\text{S}_2\text{O}_8\)) was dissolved separately in 35 ml 1 M HCl to prepare an oxidant solution. Both the solutions were stirred vigorously and separately for half an hour at ambient temperature. The monomer solution was stirred and simultaneously treated with the oxidant solution added drop-wise at a rate of less...
than 1 ml/min at 18°C in ca. 2 h (the total molar ratio, monomer/oxidant = 1:1). Immediately after the first twenty drops, the reaction solution turned blue-violet. The reaction mixture was stirred for 10 h in a water bath at 18°C. 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 oligomer. The hydrochloride salt was subsequently neutralized in 100 ml 0.2 M ammonium hydroxide for 24 h to obtain the base form of the MA/AS copolymer. The copolymer base was washed with excess water. A dark green powder was left to dry in ambient air for one week. The copolymer (3.4 g) was obtained with the yield of 59%. The MA/AS copolymer exhibits the structure shown in Scheme 1.

2.3. Measurements

The intrinsic viscosity for the MA/AS copolymers in NMP was measured with an Ubbelodhe viscosimeter at 25°C. The solubility of the polymers is evaluated using the following method: a polymer powder sample of 5 mg was added into the solvent of 0.5 ml and dispersed thoroughly. After the mixture was shaken continuously for 24 h at room temperature, the solubility of the polymers was characterized semi-quantitatively. IR spectra were recorded on a Nicolet FT-IR 5DXC Spectrometer made in USA at 2 cm⁻¹ resolution on KBr pellets. A ¹H NMR spectrum was obtained in deuterated trifluoroacetic acid using a Bruker MSL-300 spectrometer operated at 300.13 MHz. Wide-angle X-ray diffractograms were recorded using Rigaku RAX-10 diffractometry with monochromatized CuKα (λ = 0.1541 nm) radiation operated at 30 kV and 20 mA in a reflection mode. The scanning rate is 8°/min. The precision for the measurement of the Bragg angle is 0.01°. Thermogravimetry (TG) measurement was carried out at a heating rate of 10°C/min in nitrogen (10 ml/min) and in static air with a sample size of 0.9–1.0 mg using NETZSCH TG 209 Geratebau GmbH Thermal analyzer.

3. Results and discussion

3.1. Synthesis of 2-pyrimidylamine and o-anisidine copolymers

Five polymers with five MA/AS molar ratios were prepared by oxidative copolymerization with ammonium persulfate as an oxidant in 1 M HCl aqueous solution at 18°C for 10 h. It was found that the yield and intrinsic viscosity of the MA/AS copolymer both increased from 13 to 74% and 0.16 to 0.21 dl/g, respectively, with increasing AS content from 30 to 90 mol%, as shown in Fig. 1. When the AS content increased continuously to 100 mol%, both decreased slightly. That is to say, the yield and intrinsic viscosity of the MA/AS copolymers are dependent on the MA/AS monomer ratio, which might be due to the copolymerization effect between both the monomers, indicating that the polymers obtained are indeed copolymers consisting of both the monomer units. The fact that the MA/AS (70:30) copolymer containing the largest MA unit content exhibits the lowest yield and lowest intrinsic viscosity suggests that the MA monomer has much less polymerizing reactivity than the AS monomer during the oxidative polymerization. Similar results have been observed for the MA and o-toluidine or aniline copolymerization [6]. One possible reason is that there are two nitrogen atoms with greater electronegativity on the pyrimidyl ring, resulting in lowering of electron density of the 5-position carbon atoms on the MA monomer, and furthermore leading to lower reactivity of electrophilic aromatic substitution polymerization than aniline and aniline derivatives such as AS. The fact that MA could not homopolymerize oxidatively under the same conditions has been confirmed in our laboratory. When MA and AS monomers coexist in the polymerization systems, the polymerization reactivity of the MA monomer is catalyzed by the AS monomer with higher reactivity. Furthermore, the catalyzing effect becomes more obvious with increasing AS concentration in the system. The possible polymerization mechanism is shown in Scheme 2 [7]. Perhaps the chain initiation is attributed to the AS monomer, but the chain propagation and termination are attributed to both AS and MA monomers.

3.2. Solubility of 2-pyrimidylamine and o-anisidine copolymers

It can be seen from Table 1 that the MA/AS copolymers were completely soluble in NMP, DMSO, and trifluoroacetic acid.
acid (TFA) when the concentration of copolymers is ca. 1 g/100 ml solvent. These copolymers are partially soluble in chloroform (CHCl₃), ethylene chloride, benzene, absolute ethanol, tetrahydrofuran (THF), and acetone but only slightly soluble in glacial acetic acid and tetrachloromethane (CCl₄). Note that the enhanced solubility in TFA, chloroform, ethylene chloride, benzene, and absolute ethanol was observed with increasing AS unit content. Obviously, a better solubility of the copolymers results from the presence of a large number of methoxyl substituents on the AS ring, which increases the distance between the macromolecular chains and then significantly reduces the interaction between the copolymer chains. After a comparison of Fig. 1 with Table 1, it is seen that the MA/AS (10:90) copolymer with the highest intrinsic viscosity shows the higher solubility in TFA, chloroform, benzene, and ethanol than the MA/AS (30:70), (50:50), and (70:30) copolymers with relatively low intrinsic viscosity. The MA/AS (70:30) copolymer having the lowest intrinsic viscosity exhibits the poorest solubility in TFA and ethanol. This is contrary to expectation, i.e. generally, the polymer with lower intrinsic viscosity should show better solubility than a similar polymer with higher intrinsic viscosity. This result suggests that the solubility may be primarily determined by molecular structure rather than intrinsic viscosity of the polymers [8].

Additionally, a certain dependence of solubility of the polymers in TFA, chloroform, ethylene chloride, benzene, and ethanol, on the MA/AS ratio, is an evidence that the polymerization products are indeed copolymers containing the two monomers rather than a simple mixture of two homopolymers [9]. Moreover, without the existence of the AS monomer, no MA homopolymer could be obtained under the same polymerization conditions.

Table 1

<table>
<thead>
<tr>
<th>MA/AS</th>
<th>NMP</th>
<th>DMSO</th>
<th>TFA</th>
<th>CHCl₃</th>
<th>Ethylene chloride</th>
<th>Benzene</th>
<th>Ethanol</th>
<th>THF</th>
<th>Acetone</th>
<th>Acetic acid</th>
<th>CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:100</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>MS(DB)</td>
<td>MS(DB)</td>
<td>MS(RV)</td>
<td>MS(RB)</td>
<td>PS(RB)</td>
<td>PS(DR)</td>
<td>PS(B)</td>
</tr>
<tr>
<td>10:90</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>MS(DB)</td>
<td>PS(DB)</td>
<td>MS(RV)</td>
<td>MS(RB)</td>
<td>PS(B)</td>
<td>PS(Br)</td>
<td>SS</td>
</tr>
<tr>
<td>30:70</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S(B)</td>
<td>PS(V)</td>
<td>PS(DR)</td>
<td>PS(DR)</td>
<td>PS(DR)</td>
<td>PS(RV)</td>
<td>PS(R)</td>
<td>SS</td>
</tr>
<tr>
<td>50:50</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>PS(R)</td>
<td>PS(R)</td>
<td>PS(BV)</td>
<td>PS(RV)</td>
<td>PS(R)</td>
<td>PS(R)</td>
<td>SS</td>
</tr>
<tr>
<td>70:30</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>MS(BB)</td>
<td>PS(DR)</td>
<td>PS(DR)</td>
<td>PS(R)</td>
<td>SS(R)</td>
<td>PS(R)</td>
<td>SS(DR)</td>
<td>IS</td>
</tr>
</tbody>
</table>
3.3. $^1$H NMR spectrum of 2-pyrimidylamine and o-anisidine copolymers

$^1$H NMR spectra of MA/AS copolymers are characterized by three main signals, which exactly correspond to the three types of protons on the copolymer chains, as shown in Figs. 2 and 3. It is seen from Fig. 2 that the $^1$H NMR spectrum of the MA/AS (70:30) copolymer exhibits the strongest and sharpest peak at 3.454, 3.648, 3.662, 3.762, 3.779, 3.826, and 4.008 ppm owing to methoxyl groups; a medium doublet centered at 6.934 and 7.191 ppm owing to aromatic protons on the methoxyl phenylene unit and the pyrimidylene unit, respectively; and a very weak broad peak centered at 5.92 ppm owing to $-\text{NH}^-$ linkages. The MA/AS (30:70) copolymer shows a similar $^1$H NMR spectrum with the strongest and sharpest peak at 3.430, 3.603, 3.617, 3.631, 3.708, 3.780, and 3.952 ppm owing to methoxyl groups; a medium doublet centered at 6.801 and 7.101 ppm owing to aromatic protons on the methoxyl-phenylene unit and the pyrimidylene unit, respectively; and a very weak broad peak centered from 5.2 to 5.88 ppm owing to $-\text{NH}^-$ linkages (Fig. 3). For the same proton, the chemical shift seems to increase slightly with decreasing AS unit content. In addition, the top of medium peaks from phenyl protons was observed at 6.801 and 6.934 ppm owing to the protons of $p$-disubstituted anisidine. This suggests a linear structure of the MA/AS copolymer synthesized by oxidative copolymerization.

The two spectra shown in Figs. 2 and 3 are not very informative on the calculation of sequence distribution of the comonomer units. However, the actual MA/AS ratio in the copolymers can be roughly calculated based on the area ratio of the MA aromatic proton peak to the AS aromatic proton peak. The actual MA/AS molar ratio calculated by this method is 62:38 for the MA/AS (70:30) copolymer and 39:61 for the MA/AS (30:70) copolymer. It can be seen that there is a small difference between the feed molar ratio and actual molar ratio.

3.4. FT-IR spectra of 2-pyrimidylamine and o-anisidine copolymers

Representative FT-IR spectra for the copolymers with MA/AS molar ratios of 70:30 and 0:100 are shown in Fig. 4. A broad band centered at 3402 cm$^{-1}$ for the MA/AS (70:30) copolymer and at 3395 cm$^{-1}$ for the MA/AS (0:100) polymer owing to the characteristic free N–H stretching vibration suggests the presence of $-\text{NH}_2$
and secondary amino groups (\(-\text{NH}\)-) and becomes weaker with an increase in AS unit content from 30 to 100 mol\%, indicating that the molecular weight becomes higher. This is the same as the intrinsic viscosity result shown in Fig. 1. A small shoulder band at 3261 cm\(^{-1}\) corresponds to the hydrogen-bonded N–H vibration. The peaks at about 3071 and 3064 cm\(^{-1}\) might be due to C–H stretching on the pyrimidylene and phenylene rings, respectively. The two peaks at 2938 and 2832 cm\(^{-1}\) are attributed to the C–H stretching vibration in methoxyl groups and get stronger with increasing AS unit content from 30 to 100 mol\%. The IR absorptions in 1454–1581 cm\(^{-1}\) are associated with aromatic ring stretching. The peak at 1581 cm\(^{-1}\) is assigned to the following quinoid ring and gets weaker with increasing AS unit content, suggesting that this peak results mainly from the MA unit.

\[
\text{N} = \text{N} \quad \text{and} \quad \text{N} = \text{N} \quad \text{OCH}_3
\]

The peak at 1518 cm\(^{-1}\) is due to the following benzenoid ring and remains almost constant with the variation in the MA/AS molar ratio.

\[
\text{N} \quad \text{NH}^- \quad \text{and} \quad \text{N} \quad \text{NH}^- \quad \text{OCH}_3
\]

A shoulder peak at 1454–1461 cm\(^{-1}\) should be attributed to the stretching of the benzene ring because its intensity gets stronger with increasing AS unit content. For the MA/AS (70:30) copolymer, nearly the same peak area of 1581 cm\(^{-1}\) as that of 1518 and 1461 cm\(^{-1}\) was observed, but the fact that the peak at 1581 cm\(^{-1}\) for the MA/AS (0:100) polymer has a lower intensity than the peaks at 1518 and 1454 cm\(^{-1}\) suggests less quinoid units in the polymer. This result is verified by the above-mentioned \(^1\)H NMR study. Two clear peaks of methoxyl groups on the AS unit were observed in Fig. 3 and the left weaker peak at 3.964 ppm could correspond to the resonance of methoxyl groups on quinoid segments. A weak shoulder peak at 1401–1408 cm\(^{-1}\) is attributable to the C–N stretching vibration in quinoid imine units. A weak peak at 1321 and 1342 cm\(^{-1}\) is due to the C–N stretching vibration in triad segments of quinoid–benzenoid–quinoid and quinoid–benzenoid–benzenoid. A strong peak at 1250 cm\(^{-1}\) is ascribed to the C–N stretching in the

![Fig. 4. FT-IR absorption spectra of the copolymers with the MA/AS molar ratios of 0:100 (—) and 70:30 (･･･).](image1)

![Fig. 5. Wide-angle X-ray diffraction diagrams of the as-polymerized copolymer powders with MA/AS molar ratios of 0:100 (upper), 30:70(medium), and 70:30 (lower).](image2)
benzenoid–benzenoid–benzenoid triads. This indicates that there are more benzenoid–benzenoid–benzenoid triad sequences, which is also confirmed by the $^1$H NMR spectra. Two sharp peaks at 1215 and 1018–1032 cm$^{-1}$, which get stronger significantly with increasing AS unit content, confirm the existence of methyl phenylene ether. On the other hand, two peaks at 1110 and 955 cm$^{-1}$ owing to C–H in-plane bending of the 1,2,4-trisubstitued benzene ring as well as two peaks at 835 and 758 cm$^{-1}$ owing to C–H out-of-plane bending of the 1,4- and 1,2-benzene rings, respectively, all get stronger with an increase in AS unit content, indicating that these four peaks are all from the AS unit. The presence of these disubstituted and trisubstituted AS units and secondary amino groups suggests the formation of polymers.

3.5. Wide-angle X-ray diffractogram of 2-pyrimidylamine and o-anisidine copolymers

Wide-angle X-ray diffractograms of as-prepared copolymer powders with three MA/AS molar ratios are shown in Fig. 5. The three copolymers all exhibit a broad strong peak at $2\theta = 23.5–24^\circ$ and a medium shoulder peak at $2\theta = 18^\circ$. It appears that the broad shoulder peak becomes stronger with increasing AS unit content from 30 to 100 mol%, suggesting that this peak might be mainly ascribed to the AS unit. The broad peaks are characteristic of the diffraction by an amorphous polymer. These results indicate that the introduction of methoxyl groups on the AS unit increases intermolecular chain spacing and amorphousness.

Fig. 6. Thermogravimetry (TG, upper) and derivative thermogravimetry (DTG, lower) traces of the copolymer powders with MA/AS molar ratios of 0:100 (—), 30:70 (- - -), and 70:30 (···) at a heating rate of 10°C/min in flowing nitrogen.

Fig. 7. Thermogravimetry (TG, upper) and derivative thermogravimetry (DTG, lower) of the copolymer powders with MA/AS molar ratios of 0:100 (—), 30:70 (- - -), and 70:30 (···) at a heating rate of 10°C/min in static air.
Amorphous structure is required for gas separation membranes having high permeating performance.

3.6. Thermogravimetric diagrams of 2-pyrimidylamine and α-anisidine copolymers

Figs. 6 and 7 show the TG and derivative thermogravimetry (DTG) curves of the as-polymerized copolymer powders with three MA/AS molar ratios in flowing nitrogen and static air. The MA/AS (0:100) and (30:70) polymers exhibit four-stage decomposition in both atmospheres. Note that the MA/AS (30:70) and (70:30) copolymers show a very gradual degradation in the temperature range from 25 to 900°C and larger char yield at 900°C of 29 wt%.

The first weight loss of 3–4% at ca. 60°C resulted from water evaporation in the polymer powders. Two weight-loss processes at 200–360°C might be due to the exclusion of the methoxyl groups on the AS units. The largest weight loss in the range 540–720°C is attributable to the thermal degradation and thermal oxidative degradation of polymer main chains in nitrogen and air, respectively.

Table 2 shows the stable and kinetic parameters of the thermal degradation of the MA/AS copolymers. With increasing AS unit content, decomposition temperature \( T_d \) in both atmospheres increases, but char yield at 700°C decreases. However, the MA/AS (30:70) copolymer exhibits the highest temperature \( T_{dm} \) at the maximum weight-loss rate and smallest maximum weight-loss rate \( (\text{da}/\text{dt})_{\text{max}} \). This suggests that the MA/AS (30:70) copolymer is the most thermostable among the three MA/AS polymers. The lower thermal stability of the MA/AS (0:100) polymer than the MA/AS (30:70) copolymer results from more methoxyl groups, which is easily excluded thermally from the macromolecular chains at an elevated temperature such as 500°C. For the same MA/AS polymers, higher thermostability was observed in nitrogen than in air, because the polymers exhibit higher decomposition temperatures (\( T_d \) and \( T_{dm} \)), lower maximum decomposition rate \( (\text{da}/\text{dt})_{\text{max}} \), and much larger char yield at 700°C. This results from the thermo-oxidative decomposition that occurred following the thermal decomposition in air.

The kinetic parameters of the thermal degradation for the MA/AS copolymers are calculated [10–13] through Fig. 8 using the Friedman method by Eq. (1)

\[
\ln(\text{da}/\text{dt}) = \ln Z + n \ln(1 - \alpha) - E/RT
\]

where \( \alpha \) is the weight loss, \( \text{da}/\text{dt} \) the weight-loss rate, \( R \) the gas constant (8.3136), and \( T \) the absolute temperature. It can be seen from Table 2 that the activation energy \( E \) and frequency factor \( \ln Z \) values are both larger but the decomposition order \( n \) is smaller in air than in nitrogen. Three kinetic parameter values of thermal degradation in both atmospheres increase with increasing feed AS content. The regular variation of thermostability and degradation

Table 2
Thermally stable and kinetic parameters of the copolymers of 2-pyrimidylamine (MA) and α-anisidine (AS) calculated by Friedman technique

<table>
<thead>
<tr>
<th>Feed Sample size (mg)</th>
<th>( T_d ) (°C)</th>
<th>( T_{dm} ) (°C)</th>
<th>( (\text{da}/\text{dt})_{\text{max}} ) (%/min)</th>
<th>Char yield at 700°C (wt%)</th>
<th>( E ) (kJ/mol)</th>
<th>( n )</th>
<th>( \ln Z ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA/AS (mol%)</td>
<td>Atmosphere</td>
<td>0:100</td>
<td>0.91 411 600 3.7</td>
<td>6 34</td>
<td>0.7</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>0:100</td>
<td>Nitrogen</td>
<td>0.91 411 600 3.7</td>
<td>6 34</td>
<td>0.7</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0:100</td>
<td>Nitrogen</td>
<td>4.90 405 550 3.8</td>
<td>0 26</td>
<td>0.4</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0:100</td>
<td>Air</td>
<td>0.96 337 530 4.1</td>
<td>0 35</td>
<td>0.6</td>
<td>2.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30:70</td>
<td>Nitrogen</td>
<td>0.97 386 656 1.2</td>
<td>37 15</td>
<td>0.7</td>
<td>−1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30:70</td>
<td>Nitrogen</td>
<td>0.98 325 580 2.7</td>
<td>3 24</td>
<td>0.5</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70:30</td>
<td>Nitrogen</td>
<td>0.99 259 569 1.3</td>
<td>42 8</td>
<td>0.5</td>
<td>−2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70:30</td>
<td>Air</td>
<td>0.94 267 539 3.2</td>
<td>0 18</td>
<td>0.3</td>
<td>−0.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8. Friedman method (plot of \( \text{da}/\text{dt} \) vs. \( 1/T \)) for the calculation of the activation energy of the thermal degradation of the copolymer powders with MA/AS molar ratios of 0:100 (○) in nitrogen at the sample size 1 mg, 0:100 (△) in nitrogen at the sample size 4.9 mg, 0:100 (□) in air, 30:70 (●) in nitrogen, 30:70 (○) in air, 70:30 (△) in nitrogen, and 70:30 (□) in air.
kinetics with the MA/AS ratio might be another evidence that the polymer indeed consists of MA and AS monomer units.

The influence of sample size on the thermal stability of the AS homopolymer in nitrogen was simply investigated. It is found from Table 2 that $T_d$ and $(d\alpha/dt)_m$ remain substantially constant but $T_{dm}$, char yield at 700°C, and three kinetic parameters decrease with an increase in sample weight from 0.9 to 4.9 mg for the TG measurement.

Predicted isothermal TG curves at 623 K using Eq. (2) are shown in Figs. 9 and 10 [13–17].

Heating time $= [1 - (1 - \alpha)^{1-n}] \exp(E/RT)/[Z(1 - n)]$

$(n \neq 1)$

4. Conclusions

A series of soluble copolymers of 2-pyrimidylamine (MA) and $o$-anisidine (AS) has been synthesized by oxidative polymerization in acidic media at 18°C for the first time. The actual MA/AS molar ratio in the copolymers is slightly different from the feeding molar ratio. The polymers obtained are confirmed to be real copolymers consisting of two monomer units by FTIR, NMR, and wide-angle X-ray diffraction studies rather than the mixture of two homopolymers. The MA/AS copolymers are amorphous and their polymerization yield, intrinsic viscosity, solubility in common organic solvent, thermostability, and activation energy of thermal degradation all increase with increasing AS unit content, but their char yield at 700°C in nitrogen decreases.

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