Makromol. Chem. **193**, *1723–1728 (1992)*

Preparation of polyaniline by oxidation of aniline using H_2O_2 in the presence of an iron(II) catalyst

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(Date of receipt: November 21, 1991)[a]

SUMMARY:

Oxidative polymerization of aniline using the H_2O_2-$FeSO_4$ system gave polyaniline under mild conditions. The prepared powdery emeraldine base, a form of polyaniline, is blue black and shows high solubility in organic solvents (e. g., ca. 200 mg/mL in *N*-methylpyrrolidone). The number-average molecular weight ($\overline{M}_n$) of the polymer obtained was $1{,}3-1{,}7 \cdot 10^4$ (via gel permeation chromatography vs. polystyrene) and $\overline{M}_w/\overline{M}_n = 1{,}6-2{,}2$. Poly(2-ethylaniline) and poly(2-propylaniline) with high molecular weights were also synthesized by this procedure in high yield.

Introduction

Polyaniline has attracted growing attention as a material used in electrochromic devices and for electrodes of batteries[1]. Chemical oxidation of aniline with peroxodisulfate salts is a useful method to prepare polyaniline in large scale[2], and polyaniline thus prepared for industrial purposes has been developed[2c, d]. Control of molecular weight and polydispersity of polyaniline is considered to be a significant subject, since the physical properties of the polymer are influenced by the molecular weight[3]. However, polyanilines prepared by the above oxidation procedure as well as by electrochemical oxidation of aniline show complicated gel permeation chromatograms[2b, 4]. Hence, we have investigated new methods, which allow to prepare polyaniline by using industrially more common chemicals and to control the molecular weight of polyaniline.

Recently we have observed that fully reduced polyaniline $\left(NH{-}C_6H_4{-}NH{-}C_6H_4\right)_n$ (leucoemeraldine base, abbreviated as PLM) reacts with relatively weak oxidizing agents, such as H_2O_2, in the presence of $FeCl_3$ or $FeCl_2$, to give 50% dehydrogenated polyaniline $\left[\left(C_6H_4{-}NH{-}C_6H_4{-}NH\right)/\left(C_6H_4{-}N{=}C_6H_4{=}N\right)\right]_n$ (emeraldine base, abbreviated as PEM)[5]. The oxidation proceeds smoothly at room temperature presumably through redox reactions[5, 6] and does not cause further oxidation of the resulting PEM to give the fully oxidized polymer $\left(C_6H_4{-}N{=}C_6H_4{=}N\right)_n$.

Since PLM undergoes oxidation involving abstraction of the NH hydrogen, treatment of aniline with H_2O_2 and Fe-catalyst is expected to cause formation of PEM, which can be turned into electrically conducting material by acidification.

Here we report on the oxidation of aniline under the conditions given above as well as on the characterization of the obtained polyaniline.

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[a] Revised manuscript of January 28, 1992.

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CCC 0025-116X/92/$05.00

Experimental part

Materials

Aniline, iron(II) sulfate and iron(III) chloride were purchased from Koso Chemical Co. Ltd., whereas 2-alkylanilines (2-ethylaniline and 2-propylaniline) and H_2O_2 (31% aq.) were purchased from Tokyo Kasei Kogyo Co. Ltd. and Mitsubishi Gas Chemical Co. Inc., respectively. All of the reagents were reagent grade and used without further purification.

Polymerization experiments

Aniline (4,6 mL; 50 mmol) was dissolved in 100 mL of aqueous H_2SO_4 (0,50 mol · L^{-1}) and the mixture was kept at 30 °C. Powdery $FeSO_4 \cdot 7H_2O$ (139 mg; 0,49 mmol) was added to the solution with vigorous stirring. After stirring for 10 min, 25 mmol of 31% H_2O_2 was slowly added to the solution with vigorous stirring over a period of 2 h. After the addition, the reaction mixture was agitated continuously for another 5 h under air at 30 °C to cause formation of a precipitated blue-black powder, which was collected on a glass filter and washed with ice water and ethanol. It was neutralized by treatment with 28% aqueous ammonia and washed with ethanol. Finally it was dried with dynamic vacuum at room temperature. Polymerization of 2-ethylaniline and 2-propylaniline was carried out analogously.

The prepared polymers were reduced by excess hydrazine monohydrate to prepare polyaniline leucoemeraldine by modifying the method of Green and Woodhead⁷⁾.

Measurements

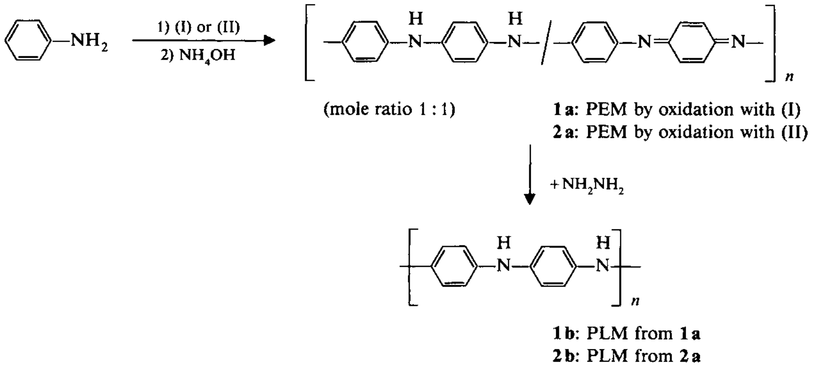
Gel permeation chromatograms (GPC) were recorded on a Toso HLC-810 apparatus at 25 °C using 0,01 mol/L LiBr/*N,N*-dimethylformamide as eluent. From the GPC results, the number-average ($\overline{M}_n$) and weight-average ($\overline{M}_w$) molecular weights were determined by standard procedures using polystyene standards. The intrinsic viscosity was measured in *N*-methylpyrrolidone (NMP) with an Ubbelohde viscometer at 30 °C. IR spectra were recorded using as Jasco-810 spectrometer with KBr pellets. UV/VIS spectra were recorded on a Hitachi 200-20 spectrophotometer at room temperature. The thermal properties of the polymers were measured on Shimadzu TG-30 under nitrogen at a constant heating rate of 10 °C/min. Free standing PEM (polyaniline emeraldine base) films were prepared by vacuum drying of PEM/NMP solutions in a glass vessel. Conductivity measurements were made by a two-probe method using an Advantest R8340A Ultra high resistance meter. X-ray measurements were carried out at room temperature with a Rigaku-Denki diffractometer by the symmetrical reflection method using Cu-K_α radiation.

Results and discussion

The reaction of aniline with aqueous H_2O_2 in the presence of $FeSO_4$ in an acidic medium proceeds smoothly to give blue-black polyaniline in protonated form which is converted into PEM (**1a**) by treatment with NH_4OH (Eq. (1)). Reduction of the polymer with NH_2NH_2 gives PLM (**1b**). For comparison, PLM and PEM were also prepared by the reported method²ᵇ⁾ with $(NH_4)_2S_2O_8$ and assigned to **2a** and **2b**, respectively.

The powdery polyaniline emeraldine base (**1a**) is blue black, and showed much higher solubility in *N,N*-dimethylformamide (DMF) (ca. 100 mg/mL), dimethyl sulfoxide (DMSO) and *N*-methylpyrrolidone (NMP) (ca. 200 mg/mL) than **2a** which shows medium solubility in NMP (ca. 20 mg/mL) and low solubility in DMF and DMSO. The lower solubility of **2a** may be attributed to a very-high-molecular-weight

Scheme 1:



(1)

(mole ratio 1 : 1)

1a: PEM by oxidation with (I)
2a: PEM by oxidation with (II)

(2)

1b: PLM from **1a**
2b: PLM from **2a**

(I): H_2O_2 and Fe^{2+}, at 30 °C in an aqueous H_2SO_4 solution
(II): $(NH_4)_2S_2O_8$ as oxidizing reagent in an aqueous H_2SO_4-HCl solution[2)]

fraction[2b,4)]. Tab. 1 summarizes the results of the preparation of **1a** under various conditions.

The reaction was completed in about 5 h. The polymerization did not proceed in the absence of Fe^{2+} (nos. 6 and 7). The intrinsic viscosity $[\eta]$ of the polymer was 0,86 dL/g in NMP at 30 °C. The number-average molecular weight of **1a** was $1{,}3-1{,}7\cdot 10^4$ (GPC, vs. polystyrene) regardless of the reaction conditions. The molecular weight

Tab. 1. Polymerization of aniline with H_2O_2 catalyzed by iron(II) sulfate

No.	$[H_2O_2]$ [a)] / $\text{mol}\cdot L^{-1}$	Temp.[b)] in °C	Time[c)] in h	Yield in %	$\bar{M}_n$[d)] $\cdot 10^{-4}$	$\bar{M}_w/\bar{M}_n$[d)]	$[\eta]$ [e)] / $\text{dL}\cdot g^{-1}$
1	0,15	30	5	28	1,62	1,99	
2	0,25	30	5	41	1,70	1,57	0,86
3	0,50	30	4	65	1,31	2,18	
4	0,25	30	24	41	1,50	2,04	
5	0,25	15	24	23	1,59	1,92	
6[f)]	0,50	30	24	0			
7[g)]	0,50	30	24	0			
$(NH_4)_2S_2O_8$[h)]		5–25			1,40	9,3	0,5

[a)] Reactions were carried out using H_2O_2 (31%; 0,5 mol/mol of aniline) in the presence of 4,9 $\text{mmol}\cdot L^{-1}$ $FeSO_4$ (1 mol-% per aniline except for nos. 6 and 7) in an aqueous H_2SO_4 solution.
[b)] Polymerization temperature.
[c)] Polymerization time.
[d)] Molecular weights were evaluated by GPC.
[e)] Intrinsic viscosity measured in NMP at 30 °C.
[f)] Without $FeSO_4$.
[g)] Without $FeSO_4$ in an aqueous HCl solution.
[h)] From ref.[2b)]

distribution of polyaniline synthesized in this system shows a single peak in the GPC curve and is rather narrow ($\overline{M}_w/\overline{M}_n$ = 1,6–2,2, see Tab. 1), in contrast to the complex GPC pattern and the large $\overline{M}_w/\overline{M}_n$ ratio of **2a**[4]. The [η] and $\overline{M}_n$ values of **1a** are comparable to those of **1b**, suggesting that deposition of polyaniline from acidic aqueous solutions, at least partly, determined the molecular weight. Formation of PEM from aniline requires 1,25 mol of H_2O_2 per mol of aniline, and the yield higher than 40% observed for nos. 2–4, which were carried out in the presence of 0,5 mol of H_2O_2 per mol of aniline, suggests participation of Fe-catalyzed oxidation of aniline or initially formed PLM by O_2[5]. Use of a higher amount of H_2O_2 (2 mol/mol of aniline) gave a higher yield (75%).

Fig. 1 shows IR spectra of **1a** and **1b**, which are essentially identical with those of **2a** and **2b**. Tang et al. have assigned the peaks at about 1590 cm^{-1} and 1500 cm^{-1} to quinoid and benzenoid ring deformations, respectively; the band at 1160 cm^{-1} is characteristic of polyaniline emeraldine base[8]. Polymer **1b** exhibits a very weak peak at 1590 cm^{-1} of the quinoid structure and no absorption at 1160 cm^{-1}.

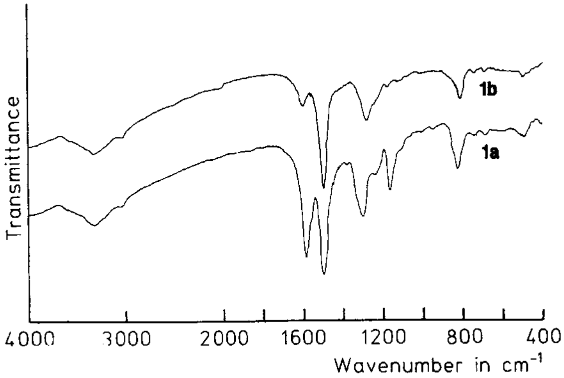


Fig. 1. IR spectra (KBr) of **1a** and **1b**

UV-VIS spectra of **1a** and **1b** in NMP were also essentially identical to those of previously prepared **2a** and **2b**[5,9]. The powder X-ray diffraction patterns show a broad peak at $2\theta \approx 19{,}5°$ (Cu-K_α) characteristic of amorphous polyaniline[3]. All these data indicate that **1a** and **1b** have normal PEM and PLM structures, respectively.

Fig. 2 shows the thermogravimetric analysis curve of **1a**. The curve indicates that **1a** has a thermal stability similar to that of **1b** and the major weight loss occurs at about 400 °C[10].

A film of **1a** affords an electrical conductivity of 1 S · cm^{-1} when treated with HCl. Use of $FeCl_3$ or Cu(II) compounds ($CuSO_4$ and $CuCl_2$) as the catalyst affords polyaniline in low yield (20% and 8% in the cases of $FeCl_3$ and $CuSO_4$, respectively, and 0% in the case of $CuCl_2$).

The present polymerization is also applicable to substituted anilines. Poly(2-ethylaniline) was prepared under the same conditions. Use of $FeSO_4$ (0,49 mmol/L) as the catalyst in 1 M aqueous H_2SO_4 at 30 °C and with 0,025 or 0,5 M H_2O_2 afforded poly(2-ethylaniline) in about 50% yield. The color of the polymer is similar to that of

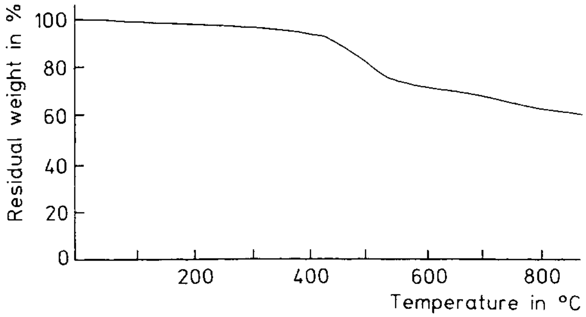


Fig. 2. Thermogravimetric analysis curve of **1a** under nitrogen at a heating rate of 10 °C/min

polyaniline. It shows the same UV-VIS spectrum (λ_{max} = 620 nm and 310 nm, in DMF) as the previously prepared poly(2-ethylaniline)[11]. It further shows an $\overline{M}_w/\overline{M}_n$ ratio of 1,57 and a higher molecular weight ($\overline{M}_n$ = 8000) than the poly-(2-ethylaniline) obtained using $(NH_4)_2S_2O_8$ ($\overline{M}_n$ = 5000)[11]. Poly(2-propylaniline) with high molecular weight ($\overline{M}_n$ = 8500) and $\overline{M}_w/\overline{M}_n$ = 2,33 was obtained analogously in 60% yield, whereas use of $(NH_4)_2S_2O_8$ as the oxidizing reagent afforded the polymer in only 2% yield[11]. Gel permeation chromatograms of the polymers are shown in Fig. 3.

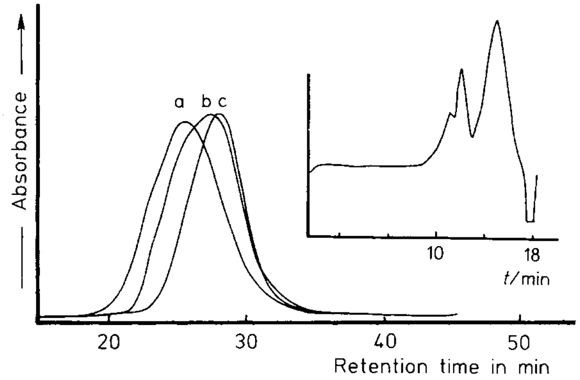


Fig. 3. Gel permeation chromatograms of the polymers. (a) Polyaniline (**1a**); (b) poly(2-propylaniline); (c) poly(2-ethylaniline); eluent: DMF. Insert: Polyaniline (**2a**); from ref.[3b]; eluent: NMP

In conclusion, use of H_2O_2, a simple and industrially favorable chemical reagent, in combination with Fe^{2+} affords polyaniline and polymers of aniline derivatives in high yields. Polyaniline thus obtained has a high solubility in organic solvents. On the other hand it shows similar chemical, physical and spectral properties as previously prepared polyaniline using $(NH_4)_2S_2O_8$.

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