Novel Synthesis of Polyaniline Using Iron(III) Catalyst and Ozone

Naoki Toshima*, Hu Yan, Masashi Kajita, Yasuyuki Honda, and Naonori Ohno
Department of Materials Science and Engineering, Science University of Tokyo in Yamaguchi, Onoda, Yamaguchi 756-0884

(Received October 10, 2000; CL-000917)

Polymerization of aniline using iron(III) and ozone as a catalyst and an oxidant, respectively, provided polyaniline with an emeraldine form based on IR and UV–vis spectroscopic data, although influence of the reaction temperature upon the molecular weight of the polyaniline was different from the case of ammonium peroxodisulfate. Preliminary results of experiments have revealed that polyaniline is produced catalytically in terms of iron(III). Morphology of polyaniline produced significantly influenced electrical conductivity of the polyaniline pellet.

Polyaniline is one of the most attractive electrically conducting polymers because of its good environmental stability[1] and electronic properties easily-tunable by changing the oxidation state and the degree of protonation,[2,3] as well as relatively good processability.[4] Its applications have already been studied for electronic devices such as, polymer-LED,[5] tantalum solid electrolyte capacitors,[6] secondary polymer batteries,[7] antistatic and electromagnetic shielding materials,[8] and potential thermoelectric materials.[9,10]

Preparation methods of polyaniline from aniline can be divided into two categories, i.e. an electrochemical[11] and a chemical method.[12] The chemical method is considered to be more useful than the electrochemical method from the viewpoint of mass production of polyaniline.[13] There are many researches on polymerization of aniline by a chemical method, especially by using ammonium peroxodisulfate[14] and $Ce(SO_4)_2$[15] as oxidants. In these reactions the oxidant is consumed stoichiometrically. Thus, the reaction requires a large amount of chemicals for the mass production, resulting in difficult separation of polyaniline from the reaction mixtures and troublesome treatment of the acidic by-products of oxidants. This is evidently a disadvantage from the viewpoint of environmental protection and production cost.

Recently, H_2O_2 and iron(II)[16] or horseradish peroxidase (HRP)[17] were used for the polymerization of aniline, in which iron(II) or HRP is a catalyst, H_2O_2 is an oxidant consumed stoichiometrically, and the main by-product is water. This is environmentally friendly synthesis of polyaniline. H_2O_2, however, is produced by a considerably complicated process and is provided as a quite inconvenient aqueous solution to be used.

Previously we have suggested syntheses of conducting polymers by using atmosphereic oxygen,[13] and reported that polyaniline[18] and polypyrrole derivative[19] can be obtained at high yield from the corresponding simple monomers under oxygen atmosphere by using small amount of metal salts as "real" catalysts. These reactions proceed catalytically in terms of the metal ion while molecular oxygen is used as an oxidant. In the reactions, the main by-product is water and the oxidant is plentiful oxygen. The polyaniline produced by this method, however, exhibits low electrical conductivity because some branched structures induced by low oxidation potential of copper(II) (0.16 V vs NHE). Although iron(III) (0.77 V vs NHE) has high oxidation potential for the polymerization of aniline,[20] molecular oxygen (0.40 V vs NHE) has too low oxidation potential to convert iron(II) to iron(III). In contrast, ozone (2.1 V vs NHE), which is easily convertible by an electrochemical method from oxygen in air, has enough high oxidation potential to convert iron(II) to iron(III). Here we present novel synthesis of polyaniline using iron(III) and ozone as a catalyst and an oxidant, respectively.

Typical polymerization was carried out as follows: aniline and iron(III) (5/1, mole ratio) were added in 1 mol dm^{-3} HCl aqueous solution. An ozone gas, which was directly converted from oxygen with ozone generator, was blown into the aniline-containing solution at 3.0×10^{-2} mol h^{-1} for 3 h at 60 °C. The polymers were separated from the mixtures and treated with an aqueous solution of ammonia. The products were characterized by infrared (IR) and ultraviolet-visible (UV–vis) spectroscopies. Molecular weights of the products were determined by gel permeation chromatography. The polymerization was carried out under various reaction conditions. Effect of concentration of aniline, reaction temperature, and other conditions on the percentage yield, electrical conductivity and molecular weight, as well as details of the characterization, will be reported elsewhere.

The IR spectra of the products have peaks at 1500, 1600, and 830 cm^{-1} attributed to benzenoid units, quinonoid units, and *para*-disubstituted phenyl rings, respectively. The UV–vis spectra have two absorption bands at 330 and 620 nm, assigned to π–π^* of phenyl rings and exciton transition from benzenoid units to quinonoid units, respectively. These data are well consistent with those of the well-defined emeraldine structure of polyaniline.[14] The polyaniline, obtained in 87% yield in the typical polymerization, has the electrical conductivity of 0.4 S cm^{-1} and weight-average molecular weight M_w of 2×10^4 Da after dedoping with aqueous ammonia.

The isolated yield and the molecular weight are significantly influenced by reaction temperature, as shown in Figure 1. The yield increases with increase of the reaction temperature, which is quite similar to the case of polymerization using ammonium peroxodisulfate.[14] The reason for the slight decrease of the isolated yield after 60 °C, however, is not clear yet. On the other hand, the M_w unpredictably increases with increase of the temperature, which is clearly different from the case of ammonium peroxodisulfate.[21] The results indicate that the present polymerization of aniline proceeds by the mechanism different from the case of ammonium peroxodisulfate. The electrical conductivities, measured on pellets by a four-probe technique, and the M_ws of the polyaniline were much lower than those polymerized by ammonium peroxodisulfate. At a glance the lower M_ws were considered to result in lower electrical conductivities. It is, however, easily postulated that morphology of polyaniline powders could significantly influence the electrical conductivity of pellets according to the conduction mechanism of polyaniline.[22]

To probe the correlation between the M_w and the electrical conductivity a cast film was prepared from *m*-cresol solution of

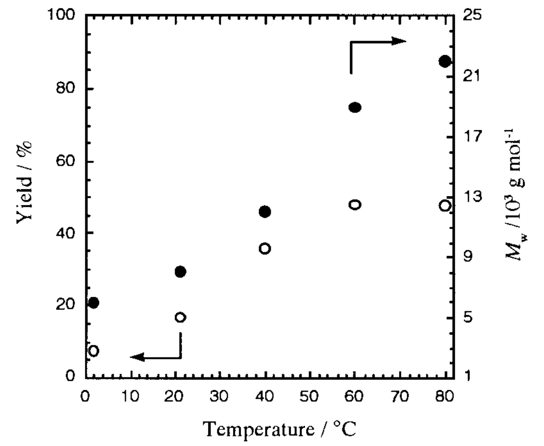


Figure 1. Effect of the polymerization temperature upon yield (left) and weight-averaged molecular weight (right) of the polyaniline.

(±)-10-camphorsulfonic acid (CSA)-doped polyaniline, as previously reported.[23] The results are compared with the case of ammonium peroxodisulfate (Table 1). The electrical conductivity of the present polyaniline pellet, prepared at 60 °C which is optimum in terms of the isolated yield, is much lower than that of ammonium peroxodisulfate. The M_w of the present polyaniline is also much lower than that of ammonium peroxodisulfate. The electrical conductivity of the cast film, however, is not so different from that of ammonium peroxodisulfate. These results indicate that the M_w of polyaniline does not significantly influence the electrical conductivity of polyaniline. On the basis of the results it is postulated that the morphology of produced polyaniline powders could considerably influence the electrical conductivity of pellets. Interestingly the low M_w of the polyaniline results in higher percentage of soluble fraction of polyaniline than that prepared by ammonium peroxodisulfate. The good solubility of polyaniline gives an advantage for wide applications through solution-processing.

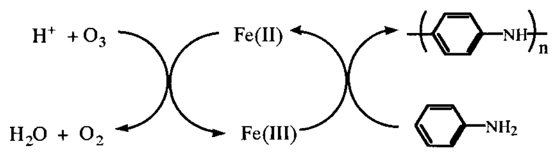
As mentioned above, the present polymerization proceeds in the way different from that in the case of ammonium peroxodisulfate in terms of molecular weight. To investigate the mechanism the following experiments were carried out: When only iron(III) was added in an acidic solution of aniline without ozone, polyaniline was obtained as previously reported.[20] As expected, polyaniline was not obtained when iron(II) was added in the solution without ozone. Polyaniline was not obtained as well when only ozone was blown into the solution without iron(II). However, polyaniline was obtained when the ozone-blown solution of iron(II) was added in the solution of aniline.

On the basis of these results, the present polymerization proceeds catalytically in terms of iron(III), as shown in Scheme 1. At the beginning of polymerization, the iron(III) ions could oxidize aniline and convert themself into iron(II) ions. The produced radical cations of aniline react with aniline to form dimers, oligomers and finally polyaniline through multi-steps reactions. On the other hand, the iron(II) ions produced could be oxidized into iron(III) ions by ozone. By this way iron ions work as catalysts and ozone works as an oxidant. The oxidation of iron(II) ions by ozone is postulated to be a rate-determining step in the present polymerization. The reaction could be quite slow at low temperature. Thus, enough amount of radical cations of aniline could not participate in the propagation step of polymerization, resulting in polyaniline with low molecular weight. Thus, the reaction temperature could influence not only the yield but also the molecular weight of polyaniline. The mechanism including kinetics is under investigation.

Table 1. Comparison of properties of the present polyaniline with that prepared by a previous method

Synthetic method	M_w / g mol^{-1}	Soluble fraction [a] / wt%	σ / S cm^{-1} Pellet[b]	σ / S cm^{-1} Film[c]
Previous method[d]	5 x 10^4	1.4	2	47
Present method	2 x 10^4	3.4	0.4	28

[a]Weight percentage of CSA-doped polyaniline in *m*-cresol. [b]By a four-probe method on HCl-doped polyaniline pellets. [c]By four-point method on CSA-doped polyaniline films. [d]Ref. 14.



Scheme 1. The proposed catalytic cycles of the polymerization.

In conclusion we have succeeded in an environmentally friendly synthesis of polyaniline using iron(III) ion and ozone as a catalyst and an oxidant, respectively. The polymerization of aniline proceeds catalytically in terms of iron(III) ions. The cast films of the polyaniline showed high electrical conductivity in comparison with the low electrical conductivity of powdered polyaniline. This indicates that morphology has significant effect on the electrical conductivity of polyaniline pellets. However, the low M_w of the polyaniline did not significantly influence the electrical conductivity of cast films. This is a considerable advantage for wide applications of polyaniline through solution-processing.

References

1 A. G. MacDiarmid, J. C. Chiang, A. F. Richter, and A. J. Epstein, *Synth. Met.*, **18**, 285 (1987).
2 J. G. Masters, Y. Sun, A. G. MacDiarmid, and A. J. Epstein, *Synth. Met.*, **41**, 715 (1991).
3 J. C. Chiang and A. G. MacDiarmid, *Synth. Met.*, **13**, 193 (1986).
4 G. L. Baker, *Adv. Chem. Ser.*, **218**, 271 (1988).
5 B. P. Jelle and G. Hagen, *J. Electrochem. Soc.*, **140**, 3560 (1993).
6 K. Amano, H. Ishikawa, A. Kobayashi, M. Ston, and E. Hasegawa, *Synth. Met.*, **62**, 229 (1994).
7 E. M. Genies, P. Hany, and C. J. Santier, *J. Appl. Electrochem.*, **18**, 285 (1988).
8 A. S. Wood, *Mod. Plast.*, **8**, 47 (1991).
9 H. Yan and N. Toshima, *Chem. Lett.*, **1999**,1217.
10 H. Yan, N. Ohno, and N. Toshima, *Chem. Lett.*, **2000**, 392.
11 A. F. Diaz and J. A. Logan, *J. Electroanal. Chem.*, **111**, 111 (1980).
12 W. W. Focke, G. E. Wnek, and Y. Wei, *J. Phys. Chem.*, **91**, 5813 (1987).
13 N. Toshima, *Macromol. Chem., Macromol. Symp.*, **59**, 123 (1992).
14 A. G. MacDiarmid, L. S. Yan, W. S. Huang, and B. P. Humphrey., *Synth. Met.*, **18**, 393 (1987).
15 N. Toshima and H. Yan, *Bull. Chem. Soc. Jpn.*, **68**, 1056 (1995).
16 Z. -C. Sun, Y. -H. Geng, J. Li, X. -H. Wang, X. -B. Jing, and F. -S. Wang, *J. Appl. Polym. Sci.*, **72** 1077 (1999).
17 W. Liu, J. Kumar, S. Tripathy, K. J. Senecal, and L. Samuelson, *J. Am. Chem. Soc.*, **121**, 71 (1999).
18 N. Toshima, H. Yan, and M. Ishiwatari, *Bull. Chem. Soc. Jpn.*, **67**, 1947 (1994).
19 N. Ohno and N. Toshima, *Chem. Lett.*, **1999**, 435.
20 A. Yasuda and T. Shimidzu, *Polym. J.*, **25**, 329 (1993).
21 P. N. Adams, P. J. Laughlin, and A. P. Monkman, *Polymer*, **37**, 3411 (1996).
22 F. Zhou, M. Angelopoulos, A. G. MacDiarmid, and A. J. Epstein, *Phys. Rev. B*, **36,** 3475 (1987).
23 Y. Cao, P. Smith, and A. J. Heeger, *Synth. Met.*, **55-57**, 3514 (1993).