Novel Syntheses of Poly(*o*-aminobenzoic acid) and Copolymers of *o*-Aminobenzoic Acid and Aniline as Potential Candidates for Precursor of Polyaniline

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Poly(*o*-aminobenzoic acid) and copolymers of *o*-aminobenzoic acid and aniline were synthesized as excellent candidates for the precursor of polyaniline. The reaction conditions were optimized with emphasis on the isolated yield. The polymers were characterized by a number of techniques including infrared spectroscopy, ultraviolet-visible spectroscopy, X-ray photoelectron spectroscopy, thermal analyses, and scanning electron microscopy. The yield of poly(*o*-aminobenzoic acid) was remarkably improved by addition of sodium hydroxide (an equivalent mole amount to the monomer) into the reaction system. Spectroscopic results indicate that the polymer has principally an Emeraldine structure. The copolymers were also obtained at high yield by addition of sodium hydroxide (an equivalent mole amount to *o*-aminobenzoic acid). The polymerization mechanism was briefly discussed on the basis of the pH effect upon the yield and easy elimination of the carboxyl group via a ring structure. The copolymer as well as poly(*o*-aminobenzoic acid) were found to be the precursors to produce polyaniline with elimination of carbon dioxide by heat treatment.

Electronically conducting polymers have attracted considerable attention from many scientists since the discovery that the conductivity of polyacetylene could reach the metallic region upon doping with oxidizing or reducing reagents.1) Among the known organic conducting polymers, polyaniline has proved to be particularly interesting because it exhibits excellent environmental stability in the electroconducting form. In addition, the redox chemistry makes it suitable to use polyaniline as a positive electrode in secondary batteries.2—4) Thus, new synthetic methods of polyaniline have been proposed.5,6)

The applications of polyaniline, however, have been limited because of its poor processability,7) which is true for most conducting polymers. The alkyl substitution at phenylene carbon or nitrogen was reported to improve the solubility of conducting polymers in an organic solvent.8—12) For example, the methyl ring derivative, poly(*o*-toluidine), which replaces one hydrogen of each benzene ring with a methyl group, could be dissolved in traditional organic solvents such as toluene or chloroform. The substitution, however, usually decreases the electroconductivity of the polymers.

On the other hand, processable precursor polymers are often used for the preparation of conducting polymers like polyphenylene13) and poly(phenylenevinylene).14) We have recently reported novel preparation of a polyaniline film by heat treatment for the cast film of poly(*o*-aminobenzoic acid) as a precursor polymer as given in Fig. 1a.15)

In addition, poly(*o*-aminobenzoic acid) is of interest as a soluble derivative of polyaniline. Poly(*o*-aminobenzoic acid) is soluble in a polar solvent like *N*-methylpyrrolidone in a neutral state, and soluble even in alcohols and water in a carboxylate ion state.16) Furthermore, poly(*o*-aminobenzoic acid) can have a ring structure due to intramolecular hydrogen bonding, which is similar to the structure of self-doped sulfonated polyaniline.17) However, the conventional synthetic method, previously reported, gave poly(*o*-aminobenzoic acid) at very low yield.15) Chan et al. reported the polymerization of *o*-aminobenzoic acid in an acidic medium, where the yield of the polymer was also very low (8.1%).16)

Here we report some novel syntheses of poly(*o*-aminobenzoic acid), in which the yield was remarkably improved. In this method the copolymers of *o*-aminobenzoic acid and aniline, which are also the potential precursors of polyaniline, were obtained at high yield. Based on the experimental results, such as reaction yields under various conditions, and the proposal of a ring structure as an intermediate for elimination of carboxyl groups, the mechanism of polymerization is briefly discussed.

Experimental

Materials. Aniline was distilled under reduced pressure and kept in the dark under nitrogen prior to use for the polymerization.

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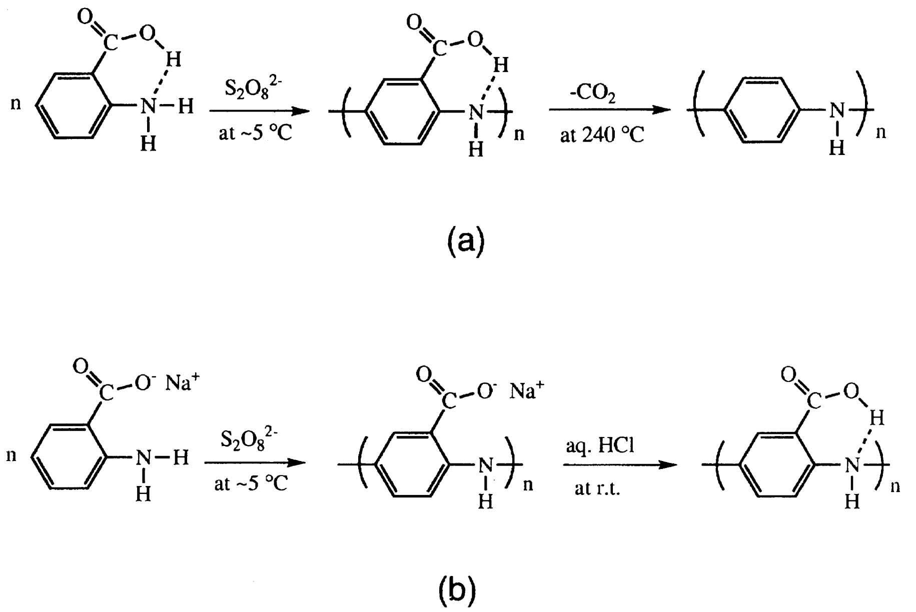


Fig. 1. (a) Poly(*o*-aminobenzoic acid) with a ring structure works as a precursor of polyaniline by heat treatment at 240 °C under nitrogen. (b) Polymerization of *o*-aminobenzoic acid in an aqueous solution of sodium hydroxide.

The other chemicals were used as received.

Preparation of Poly(*o*-aminobenzoic acid). The chemical polymerization of *o*-aminobenzoic acid was performed in the presence or the absence of hydrochloric acid or sodium hydroxide in water. Typically, a solution of ammonium peroxodisulfate was added dropwise over a period of 15 min into a vigorously stirred aqueous solution of *o*-aminobenzoic acid kept at a designed temperature in the presence or the absence of hydrochloric acid or sodium hydroxide. After stirring for a designed reaction time, the produced precipitates were separated by filtration, washed firstly with a 1 mol dm^{-3} hydrochloric acid solution, then distilled water, methanol, and finally acetone. The product was dried at room temperature under reduced pressure overnight.

Preparation of Copolymer of *o*-Aminobenzoic Acid and Aniline. The copolymerization was performed under the optimized conditions for the above reaction at various feed ratios of the comonomers, *o*-aminobenzoic acid and aniline. The produced precipitates were treated with the same procedure as above.

Measurements. FT-IR studies were carried out with a Shimadzu FTIR-4000 spectrometer using a pressed KBr-pellet technique. The electroconductivity was measured for a pressed-pellet type sample of 10 mm in diameter and ca. 1 mm in thickness with a conventional four-probe technique. Scanning electron micrographs of polyaniline, covered with a thin layer of sputtered gold, were measured at 25 kV and recorded on a Hitachi S-520 instrument. UV-vis studies were performed with a Hitachi U-4000 spectrophotometer using *N*-methyl-2-pyrrolidone as the solvent. Thermal analyses were carried out with a Shinku-Riko TGD-7000RH analyzer. Approximately 6 mg of the sample was treated by heat at a temperature-increasing rate of 10 °C min^{-1} under a 120 cm^3 min^{-1} flow of dry nitrogen. X-Ray photoelectron spectroscopic analysis was performed with a Shimadzu ESCA-750 spectrometer using an Al$K\alpha$ radiation source (1487 eV) at a base pressure of 10^{-5} Torr (1 Torr = 133.322 Pa). The molecular weight measurement was performed on a Toso HLC-803D programmable solvent delivery module, equipped with a Toso RI-8000 as a detector, and two TSK-GEL GMHHR-L columns which have a tangent number of 16000 plates per column (3 cm). To perform a gel permeation chromatography (GPC) measurement, ca. 0.01 wt% of *N*-methyl-2-pyrrolidine (NMP) solutions of the polymers were prepared and filtered through a 0.5 μm-filter. The temperature of the GPC column was kept constant at 40 °C. Flow rate was 0.5 ml min^{-1}. GPC molecular weights of the polymers were obtained by comparison of the retention time of sample polymers with the calibration curve obtained by using monodispersed standard polystyrene.

Results and Discussion

Polymerization of *o*-Aminobenzoic Acid. The polymerizations were performed by the same method as the oxidation of aniline with ammonium peroxodisulfate under comparable conditions. The polymerization conditions were altered so as to maximize the isolated yield. The results are given in Table 1. The polymers, prepared under various conditions, have the same main chain structure according to the IR data. The highest yield of poly(*o*-aminobenzoic acid) (66.4%) is achieved by addition of an equimolar amount of sodium hydroxide to monomer at 5 °C. This results is quite different from the case of polymerization of usual aniline derivatives by a conventional method, since aniline and its derivatives are usually polymerized in an acidic solution,

Table 1. Polymerization of *o*-Aminobenzoic Acid under Various Reaction Conditions[a)]

Run	Acid or Base	Reaction temp/°C	Yield/%
1	HCl (1 mol dm^{-3})	5	2
2	HCl (1 mol dm^{-3})	30	23
3	None	5	26
4	NaOH (equiv mol)[b)]	5	66
5	NaOH (1 mol dm^{-3})[c)]	5	31

a) The reaction was performed using 0.04 mole of monomer for 24 h. b) Equal mole ratio to monomer. c) 2.5 times larger than the amount of monomer.

and not so smoothly done even in a neutral medium. Chan et al.[16] reported the polymerization of *o*-aminobenzoic acid by the conventional method in an acidic medium at a very low yield (8.1%). It could be considered that the steric hindrance and electron-withdrawing effect of the carboxyl group (–COOH) reduce the polymerization activity. Based on our results, however, the reduced steric hindrance and the electron-donating effect of a carboxylato group may remarkably improve the polymerization activity in the case of the sodium salt of carboxylate. The details concerning the effect of neutralization will be discussed later.

Structures of the Polymers. The polymers prepared by the present method were firstly characterized by FT-IR. The IR spectrum of the poly(*o*-aminobenzoic acid), which was produced at the highest yield by addition of an equimolar amount of sodium hydroxide to the monomer (Run 4 in Table 1), has strong peaks at 1692, 1600, and 1490 cm^{-1}. The peak at 1490 cm^{-1} is attributable to C–N bonds of the benzenoid units, and the peak at 1600 cm^{-1} to C=N bonds of the quinonoid units, which are common in polyanilines. In addition, poly(*o*-aminobenzoic acid) has the peak at 1692 cm^{-1} due to C=O bonds of carboxyl groups.

The UV-vis spectrum of the polymer in *N*-methyl-2-pyrrolidone (NMP) shows two absorption bands at 321 and 550 nm. The first absorption band at 321 nm is associated with a π–π^* transition of the conjugated ring systems.[18,19] The second band at 550 nm is assigned to an excitonic transition from a benzenoid to a quinonoid.[20] The intensity of the second band at 550 nm in the spectrum of the poly(*o*-aminobenzoic acid) is much weaker than that of polyaniline, and the position of the band shifts to short wavelength to some extent compared with that of polyaniline (639 nm), indicating that the relative amount of the quinone diimine unit in the former is much less than that of the latter.

Copolymerization of *o*-Aminobenzoic Acid and Aniline. The copolymerization of *o*-aminobenzoic acid and aniline was examined in the present system. The results are shown in Table 2. The structure of the copolymer was confirmed by spectroscopic techniques. The FT-IR spectra of the copolymers, shown in Fig. 2, have peaks at 1692, 1600, and 1490 cm^{-1}, similar to those of the homopolymer of *o*-aminobenzoic acid. However, the peaks at 1692 cm^{-1} due to C=O bonds are much weaker than that of the homopolymer. These results indicate that the copolymers involve both *o*-aminobenzoic acid and aniline units.

Table 2. Copolymerization of *o*-Aminobenzoic Acid and Aniline[a)]

Run	Molar ratio[b)]	Reaction time/h	Yield/%	GPC MW[c)]
1	3 : 1	24	44	2.1×10^4
2	1 : 1	24	68	1.3×10^5
3	1 : 2	24	80	3.1×10^5
4	1 : 3	24	82	5.0×10^5
5	1 : 1	48	69	—

a) Reaction in the presence of aqueous NaOH solution (equimolar amount to *o*-aminobenzoic acid) at 5 °C. b) Molar ratio of *o*-aminobenzoic acid to aniline. c) Molecular weight obtained directly based on the standard polystyrene calibration.

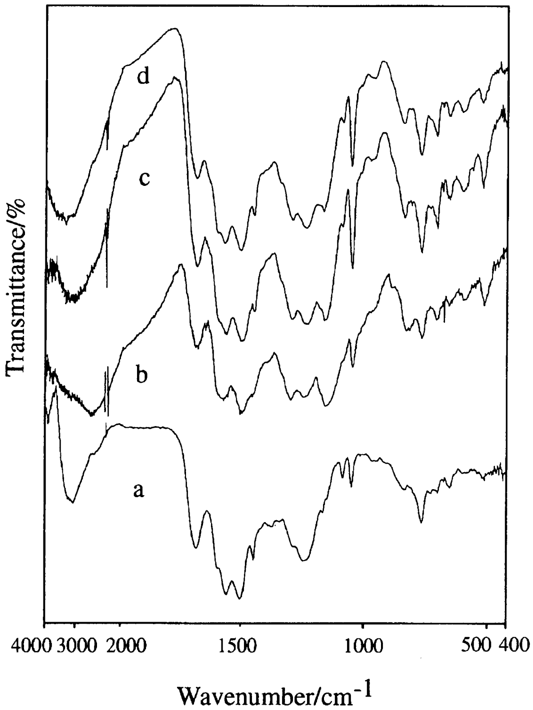


Fig. 2. FT-IR spectra of copolymers, prepared in the comonomer feed ratio of *o*-aminobenzoic acid/aniline (mol/mol) of (a) 3 : 1, (b) 1 : 1, (c) 1 : 2, and (d) 1 : 3.

The UV-vis spectra of copolymers, given in Fig. 3, consist of two major absorption bands. The band at 312—321 nm is stronger, while the band at 639 nm is weaker, than the corresponding band of polyaniline. It could be considered that the degree of π-conjugation in the main chain of the copolymers is less extended than the homopolymer of aniline[6)] because of the steric effect of the carboxyl groups. The band at 639

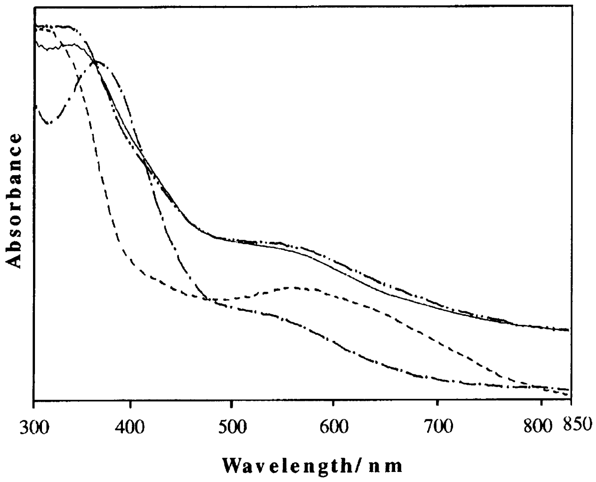


Fig. 3. UV-vis spectra of copolymers, prepared in the comonomer feed ratio of *o*-aminobenzoic acid/aniline (mol/mol) of 3 : 1 (–·–), 1 : 1 (- - -), 1 : 2 (–··–), and 1 : 3 (—).

nm decreases in intensity and shifts to a shorter wavelength with an increase in the proportion of *o*-aminobenzoic acid in the comonomer feed.

In the XPS core level spectra for C 1s, O 1s, and N 1s of the copolymers, the corresponding binding energy values were in agreement with those previously reported.[16] Among them, the C 1s spectrum showed that the peak of the carboxyl group at 287.6 eV decreased with an decrease in the proportion of fed *o*-aminobenzoic acid. These results are consistent with those from IR.

Thermogravimetric analyses (TGA) of the two samples showed three stages of weight losses: at around 100, 200, and 470 °C under nitrogen, as shown in Fig. 4. The weight loss at around 100 °C has been assigned mainly to the loss of water.[21] The weight loss at around 200 °C is mainly due to low-molecular-weight chlorine compounds, such as hydrogen chloride, which are contained in the polymer as a dopant.[22] The weight loss at around 470 °C could be attributed to the polymer decomposition. The curves of all samples are essentially the same except for the weight loss at ca. 100 °C, which is much less in the copolymers than that of polyaniline. This means that the copolymers are less doped by hydrogen chloride, and thus, contain fewer binding water molecules than polyaniline.[21]

The comonomer feed ratio and the reaction time have some effects on the yield of the produced polymers in the present reaction. As for the comonomer feed, comparing the results in Runs 1—4 of Table 2, the highest isolated yield of the copolymer is achieved at the feed ratio of 1 : 3. The influence, however, is not so strong. Thus, in all the cases the copolymers are obtained at rather high yields compared with the homopolymer of *o*-aminobenzoic acid.[15] It could be considered that the formation of sodium salt of carboxylic acid remarkably decreases the electron-withdrawing effect and steric hindrance effect upon the electrophilic substitution during the polymerization. In the case of the acidic medium,[15] however, the yields of the homopolymers were very low, and the yields of copolymers greatly decrease with an increase in the proportion of *o*-aminobenzoic acid in the comonomer feed. The electron-withdrawing carboxyl group decreases the reactivity of *o*-aminobenzoic acid, in addition to its steric effect, and retards the participation of *o*-aminobenzoic acid in the copolymerization. Thus, these considerations allow us to conclude that the present copolymers are block copolymers rather than random copolymers.

GPC measurements were carried out on the copolymers. The gel permeation chromatogram of the copolymer (Run 2, in Table 2) in *N*-methyl-2-pyrrolidone (NMP), as shown in Fig. 5, exhibits one broad peak with GPC molecular weight of ca. 130000 based on the monodispersed-polystyrene calibration. The molecular weights of the other samples are summarized in Table 2.

As for the effect of reaction time, the long reaction time (Run 5, in Table 2) gave the polymer at a little higher isolated yield than the short one (Run 2), but the effect is not so evident. This fact suggests that the salt formation of carboxylic acid makes the *o*-aminobenzoic acid highly active, resulting in the completion of polymerization even in a short reaction time. The detailed mechanism of the polymerization

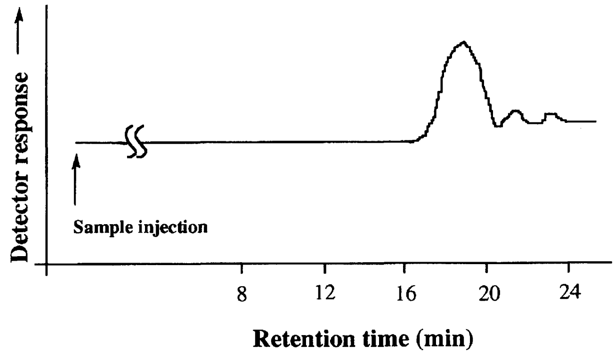


Fig. 5. Gel permeation chromatogram of copolymer (comonomer feed mole ratio: 1/1). Solvent: *N*-methyl-2-pyrrolidone, flow rate: 0.5 cm^3 min^{-1}.

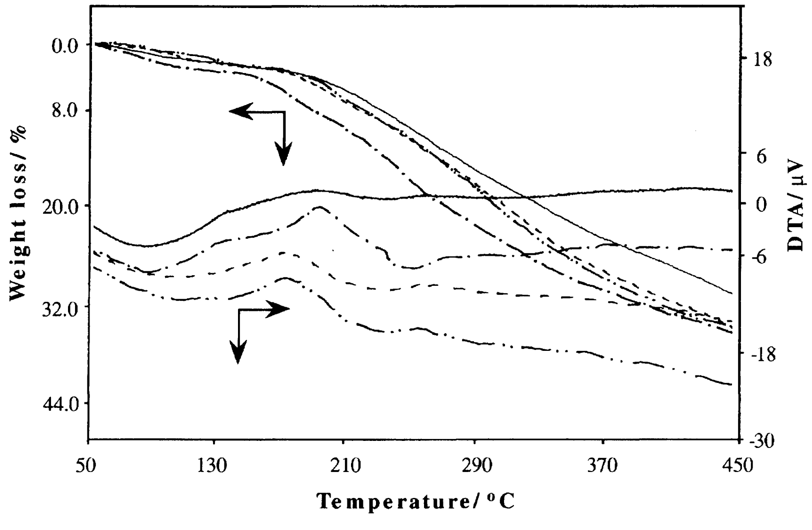
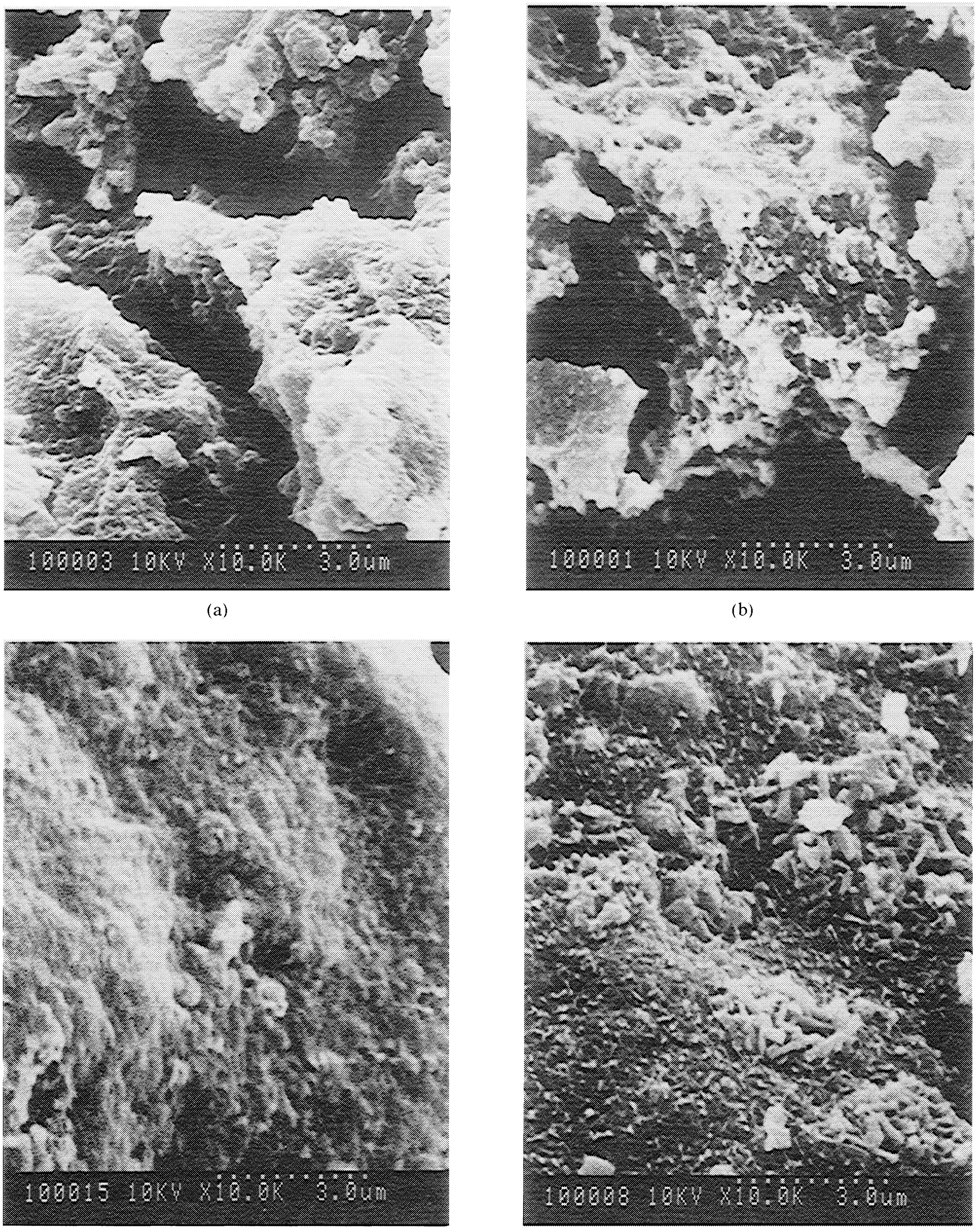


Fig. 4. TG/DTA curves of copolymers, prepared in the comonomer feed ratio of *o*-aminobenzoic acid/aniline (mol/mol) of 3 : 1 (– • –), 1 : 1 (- - -), 1 : 2 (– •• –), and 1 : 3 (—).



(a) (b)

(c) (d)

Fig. 6. Scanning electron microscopic (SEM) photographs of copolymers, prepared in the comonomer feed ratio of *o*-aminobenzoic acid/aniline (mol/mol) of (a) 3 : 1, (b) 1 : 1, (c) 1 : 2, and (d) 1 : 3.

is discussed in the next section.

Proposed Mechanisms of the Polymerization. The steric hindrance and electronic effect of the –COOH group in an acidic medium can make the polymerization activity of *o*-aminobenzoic acid lower than that of aniline. It could be considered that the monomer forms a chelate ring structure, as shown in Fig. 1a, which remarkably hinders the initiation and propagation of the polymerization. In order to evaluate this concept, the polymerization of methyl ester of *o*-aminobenzoic acid has been performed. In this case, the monomer cannot easily form the chelate ring structure, which would make the concerned polymerization easy by providing the corresponding polymer at very high yield (68% under the same reaction conditions as the case of *o*-aminobenzoic acid at 26% yield).

The addition of sodium hydroxide, described in the previous section, has produced a similar effect (cf. Fig. 1b). Thus, the polymerization activity of *o*-aminobenzoic acid is evidently improved by the addition of sodium hydroxide. This is probably because sodium hydroxide efficiently hinders the formation of chelate ring structure since the carboxylic acid group is converted to a carboxylato group. This difficult formation of the chelate ring structure makes the polymerization easier, thus resulting in the high yield of polymers (66%). Therefore, prolonging the reaction time has no effect on the reaction yield, as mentioned in the previous section.

Morphologies of the Polymers. Polyaniline prepared by the conventional chemical method usually provides an amorphous morphology, while poly(*o*-aminobenzoic acid) provides some crystalline morphology, probably due to inter- and intra-molecular hydrogen bonds.[16] All the copolymers at various feed ratios were partially crystalline. However, some difference in the morphology was observed among the copolymers by the present method. The polymer prepared in rather high feed ratio of *o*-aminobenzoic acid had similar morphology to the homopolymer of *o*-aminobenzoic acid. However, in the case of rather low feed ratio of *o*-aminobenzoic acid, the polymer was divided into two parts in morphology. One part, which is soluble in aqueous sodium hydroxide, provides some crystalline morphology. Another part, which is insoluble, is amorphous like polyaniline. The scanning electron micrographs are shown in Fig. 6.

Potential Application to a Precursor of Polyaniline Films. Poly(*o*-aminobenzoic acid), prepared by oxidative polymerization of *o*-aminobenzoic acid with ammonium peroxodisulfate,[19] reveals high solubility in an aqueous solution of sodium hydroxide or *N*-methyl-2-pyrrolidone (NMP). Casting of the NMP solution forms a smooth film of poly(*o*-aminobenzoic acid). Heat treatment of the cast film at ca. 240 °C produces a polyaniline film while eliminating carbon dioxide, which can provide a new method of preparation of the polyaniline film from the precursor film.[15] Aromatic carboxylic acid does not easily lose carbon dioxide from the hydroxycarbonyl group. The thermal decarboxylation, however, occurs more easily through sodium salts or cyclic processes in which the intramolecular hydrogen bonding plays an important role.[23]

The copolymers prepared by the present method also have good solubility in polar organic solvents. Thus, the present copolymers of *o*-aminobenzoic acid and aniline are considered to be potential precursors to prepare polyaniline film by a similar method. The film could be prepared by casting the NMP solution of the soluble copolymers and treating by heat at 240 °C. In the IR spectrum of the copolymer after heat treatment at 240 °C, the peak due to C=O almost disappeared, while the peaks due to C–N and C=N remained clearly, as shown in Fig. 7. Such results reveal that the decarboxylation of the copolymer occurs almost completely, resulting in polyaniline. I has been suggested that the copolymers could be the promising precursors of polyaniline. Since the copolymer has fewer carboxylic groups and evolves less carbon dioxide per unit weight than the homopolymer of *o*-aminobenzoic acid, it is expected that the copolymer will be a better precursor for polyaniline formation than poly(*o*-aminobenzoic acid) in the sense of molding of polyaniline products in precise forms.

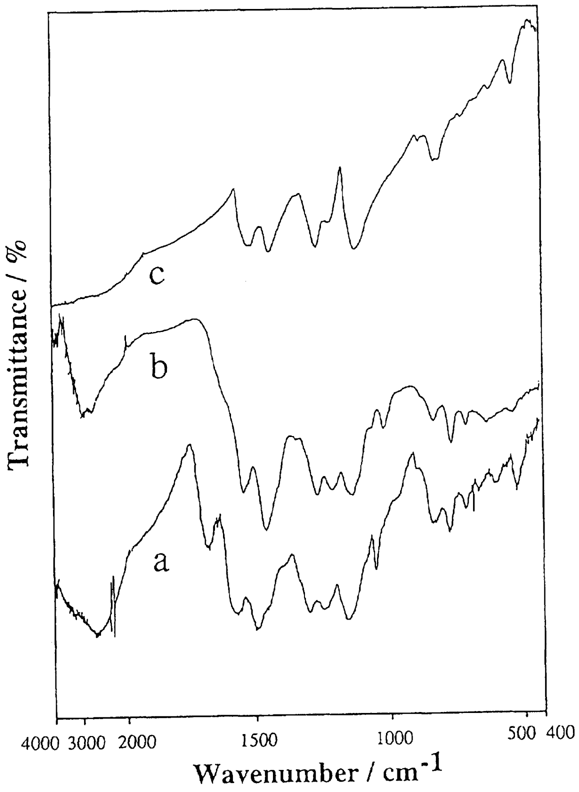


Fig. 7. FT-IR spectra of copolymer of *o*-aminobenzoic acid and aniline (a) before and (b) after heat treatment at 240 °C under nitrogen flow, and of (c) polyaniline prepared by using ammonium peroxodisulfate.

Conclusion

The poly(*o*-aminobenzoic acid) and the copolymers of *o*-aminobenzoic acid and aniline were successfully prepared at high yields by addition of sodium hydroxide (equimolar amount to *o*-aminobenzoic acid). The results indicate that *o*-aminobenzoic acid could form a chelate ring structure in an acidic medium, which remarkably decreases the polymerization activity. In contrast, the addition of sodium hydroxide could hinder the formation of the ring structure and weaken the electron-withdrawing effect of carboxyl group, thus evidently improving the reactivity of *o*-aminobenzoic acid. A similar ring structure has been considered in the case of transferring poly(*o*-aminobenzoic acid) to polyaniline by heat treatment. The homo- and co-polymers could be promising precursors of polyaniline.

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