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Catalytic Polymerization of Aniline and Its Derivatives by Using Copper(II) Salts and Oxygen. New Type of Polyaniline with Branched Structure

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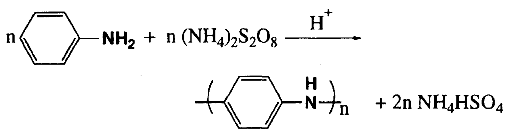
The catalytic polymerization of aniline and its derivatives was performed by stirring the solution of the corresponding monomer and copper(II) salts (50/5, mmol/mmol) in acetonitrile and water (1/1, v/v) under oxygen at room temperature for 24 h. Among copper salts, $CuBr_2$ and $CuCl_2$ are more active than the others. In each case the copper salts do not work as a stoichiometrical oxidant but work as a catalyst, which can be proved on the basis of turn-over-frequency. The polymers isolated were characteristic of polyaniline with an Emeraldine structure, although a small amount of branched structures were by-produced by an addition reaction at *ortho*-position. Thus, heat treatment of the polymer at 284 °C results in partial decomposition to produce the stable polymer and aniline. Although the resulting polymer had an Emeraldine type structure, a strong doping effect on its electroconductivity was not observed, probably because of the amorphous morphology. The UV-vis spectra of the reaction solution have suggested that the catalytic polymerization of aniline proceeds through the formation of the copper(II) complex of aniline.

Polyaniline is one of the most attractive electroconducting polymers. It has already been used, for example, as an electrode of secondary lithium battery.[1] Thus, mass production of polyaniline is of practical interest.

Preparation of polyaniline from aniline can be divided into two methods, i.e., an electrochemical and a chemical method. The chemical method is considered to be more useful than the electrochemical method from the viewpoint of mass production of polyaniline. There are many researches on polymerization of aniline by a chemical method, especially by using ammonium peroxodisulfate as an oxidant. The reaction schemes are shown in Eqs. 1 and 2, where the oxidant is consumed stoichiometrically.[2—8] Thus, the reaction requires a large amount of chemicals for the mass production. Recently we have reported that poly(1,4-phenylene), polytoluene and polypyrrole can be obtained at high yield from the corresponding simple monomers under oxygen atmosphere by using a small amount of metal salts as a "real" catalyst.[9—12] These reactions proceed as shown in Eqs. 3 and 4, where moleculer oxygen is used as an oxidant.



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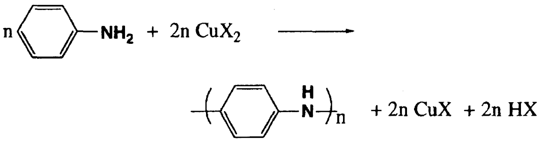

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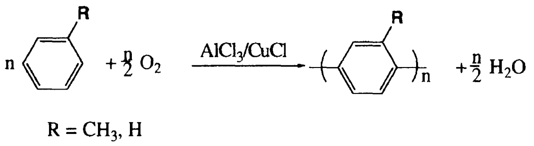

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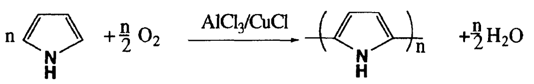


(4)

Here, we report the catalytic synthesis and the characterization of polyaniline and its derivatives. At the first stage, we wanted, but failed, to apply the same catalytic system, $AlCl_3$–$CuCl$–O_2, as that for polyphenylene and polypyrrole to the polymerization of aniline. We have thus selected a copper salt and moleculer oxygen as a catalyst and an oxidant, respectively. To search the optimum preparation conditions, the effects of various copper(II) salts and solvents as well as the effect of reaction temperature are examined. On the basis of the FT-IR, UV-vis, ^1H NMR, and thermal analyses, the structure of the resulting polymers and the polymerization mechanism are discussed.

Experimental

Materials. Aniline and acetonitrile were distilled under reduced pressure prior to use. The other chemicals were used as received.

Preparation of Polyaniline and Its Derivatives. The catalytic polymerizations of aniline and its derivatives were performed by stirring the mixed solution of the corresponding monomer and copper(II) salt (50 and 5 mmol, respectively) in acetonitrile and water (1/1, v/v) under an atmospheric pressure of oxygen at room temperature for 24 h. The typical reaction procedure is as follows: 5.0 g (0.05 mol) of aniline was added into a 20 cm^3 acetonitrile/water (1/1, v/v) solution of Cu(II) salts (0.7g, 0.005 mol) under nitrogen. After the atmosphere was changed to oxygen, the reaction mixtures were stirred at 30 °C for 24 h under 1 at-

Table 1. Polymerization of Aniline with Oxygen Catalyzed by Transition Metal[a)]

Run	Transitional metal	Yields%		TOF/% d^{-1} [b)]
		Isolated	Calcd from O_2 consumed	
1	$Cu(BF_4)_2$	12	17	240
2	$Cu(BF_4)_2$[c)]	48	120	316
3	$Cu(CH_3COO)_2$	14	17	280
4	$Cu(NO_3)_2$	16	18	320
5	CuI	5	11	100
6	$CuBr_2$	34	33	680
7	CuBr	22	30	440
8	$CuCl_2$	26	29	520
9	CuCl	20	23	400
10	$CuSO_4$	0[d)]	0	0

a) Reaction of 50 mmol of aniline with O_2 in the presence of 5 mmol of transition metal in 20 cm^3 of acetonitrile/water (1/1, v/v) at 30 °C for 24 h. b) Turn over frequency of the transition metal catalyst for the isolated yield of the polymer per day. c) Reaction for 73 h. d) White precipitates were obtained instead of aniline polymer.

mosphere of oxygen. The absorption of oxygen was followed with a gas buret every hour. The resulting black precipitates were filtered and washed repeatedly with methanol, a 1 $mol\,dm^{-3}$ HCl solution, and then pure water. The products were dried under vacuum at 50 °C overnight.

Measurements. FT-IR studies were carried out with a Shimadzu FT-IR-4000 spectrometer using a pressed KBr pellet technique. UV-vis studies were recorded with a Shimadzu UV-356 spectrophotometer under designed conditions. ^1H NMR spectra were measured in DMSO-d_6 with a JEOL GX400 FT-NMR system. Thermal analyses were carried out with a Shinku-Riko TGD-7000RH analyzer. Approximately 6 mg of the sample was heated at rate of 10 $°C\,min^{-1}$ under 120 $cm^3\,min^{-1}$ flow of dry nitrogen. Electroconductivity was measured for a pressed-pellet type sample of 10 mm in diameter and 1 mm in thickness with a conventional four-probe technique.

Results and Discussion

Effect of the Copper(II) Salts as Catalyst for Polymerization of Aniline. Aniline is known to polymerize in the presence of Cu(II). In fact the 50 cm^3 solution of 0.2 $mol\,dm^{-3}$ aniline and 0.2 $mol\,dm^{-3}$ $CuCl_2$ in acetonitrile/water (1/1, v/v) gave 0.22 g of polyaniline under nitrogen. The yield of polyaniline was 22% of the charged aniline and 44% of the charged $CuCl_2$ reacted with aniline. In other words, the turn-over-number, based on the amount of $CuCl_2$ used, is 44%. Thus, the $CuCl_2$ can not work as a catalyst, but can work only as an oxidant.

In contrast with the above result under nitrogen, the yield and the turn-over-number can be improved when the reaction is carried out under oxygen. The yield of polyaniline and that calculated from the amount of oxygen consumed are listed in Table 1 for the reaction using various Cu(II) salts. Among them, $CuBr_2$ and $CuCl_2$ are more active than the other Cu(II) salts examined from the viewpoint of the yield of polyaniline. In all cases the Cu(II) salts are not the stoichiometrical oxidant but work as the catalysts, which can be proved on the basis of the turn-over-number. In the case of $CuSO_4$, however, a water-insoluble yellow precipitate was obtained instead of polymeric products. This could be the sulfate salt of 'Cu(II)–aniline complex'. It is probably because the sulfate salt is much less soluble in acetonitrile/water than other salts. Thus, the stable

Table 2. Influence of the Solvent and Its Composition on the Polymerization of Aniline with Oxygen Catalyzed by $CuCl_2$[a)]

Run	Solvent	Volume ratio of acetonitrile/water	TOF/% d^{-1} [b)]
1	Acetonitrile/water	1 : 0	160
2	Acetonitrile/water	3 : 1	240
3	Acetonitrile/water	1 : 1	520
4	Acetonitrile/water	1 : 3	280
5	Acetonitrile/water	0 : 1	360
6	Ethanol	—	160
7	Methanol	—	320
8	Benzonitrile	—	80

a) Aniline=50 mmol, $CuCl_2$=5 mmol, solvent=20 cm^3, 30 °C for 24 h. b) Turn over frequency of $CuCl_2$ for the isolated yield of the polymer per day.

Table 3. Influence of the Reaction Temperature on the Polymerization of Aniline with Oxygen Catalyzed by $CuCl_2$[a)]

Run	Reaction temp/°C	TOF/% d^{-1} [b)]
1	10	160
2	30	520
3	50	280

a) Aniline=50 mmol, $CuCl_2$=5 mmol, solvent=20 cm^3, 30 °C for 24 h. b) Turn over frequency of $CuCl_2$ for the isolated yield of the polymer per day.

Table 4. Polymerization of Xylidies with Oxygen Catalyzed by Copper(II) Chloride[a)]

Run	Starting monomer	Product	Isolated yield/%	O_2 comsumed/%	TOF/%d^{-1} [c)]
1	Aniline	Polymer	26	29	520
2	2,6-Xylidine	Polymer	18	19	385
3	3,5-Xylidine	Copper complex	43[b)]	—	—
4	3,4-Xylidine	Azobenzene derivative	38	26	—

a) Reaction of 50 mmol of aniline or xylidine with oxygen in the presence of 5 mmol of copper(II) chloride in 20 cm^3 of acetonitrile/water (1/1, v/v) at room temperature for 24 h. b) The yield based on the charged copper salt. c) Turn over frequency of $CuCl_2$ for the isolated yield of the polymer per day.

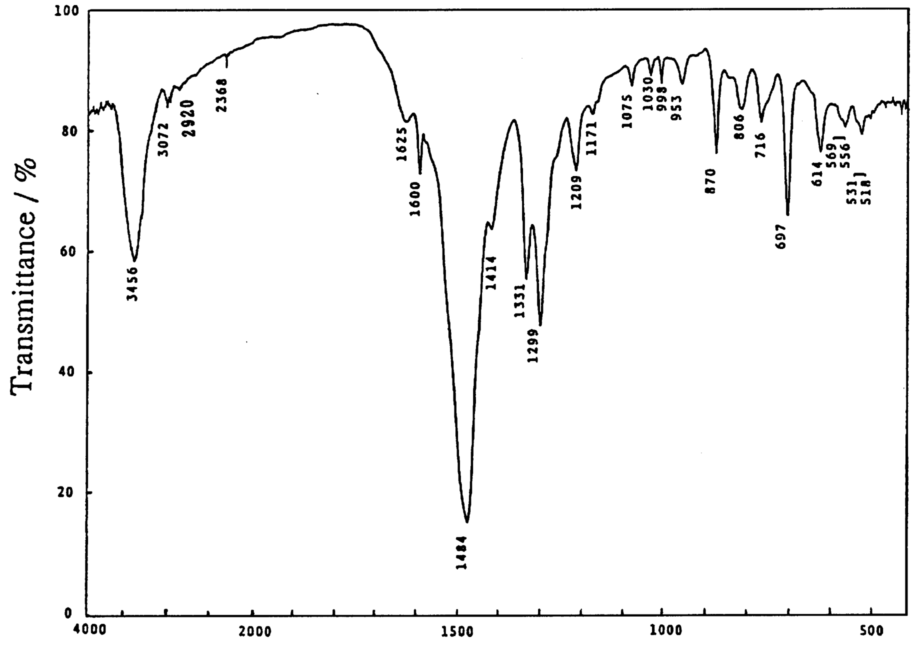


Fig. 1. FT-IR spectrum of the polyaniline in KBr pellet.

precipitates could strongly hinder the polymerization of the aniline coordinating to the copper.

Effects of the Solvent and Temperature. The solvent used for the present reaction has a big effect on the reaction yield, as shown in Table 2. The mixed solvent acetonitrile/water (1/1, v/v) results in the highest isolated yield of the polymer among those examined after 24 h reaction. The 1 : 1 mixed solvent gives the best result when the volume ratio of acetonitrile to water is varied. When the reaction temperature is varied, the highest isolated yield of the polyaniline is obtained at 30 °C as listed in Table 3. In the case of polymerization of aniline using $FeCl_3$ as an oxidant, the similar result was obtained by T. Shimidzu et al.[13)] It could be considered that the polymerization process competes with the degradation process. Thus, the rate of polymerization is higher than that of degradation at low temperature, while the rate of degradation becomes higher than that of polymerization at high temperature.

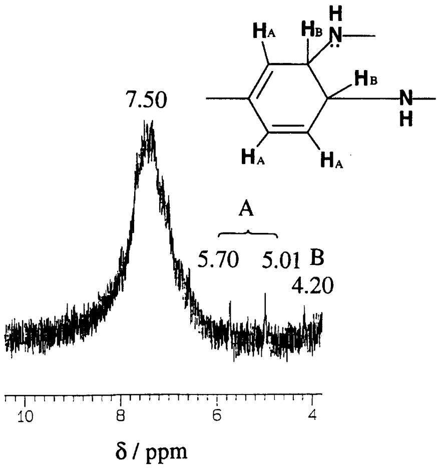


Fig. 2. ^1H NMR spectrum of the polyaniline in DMSO-d_6.

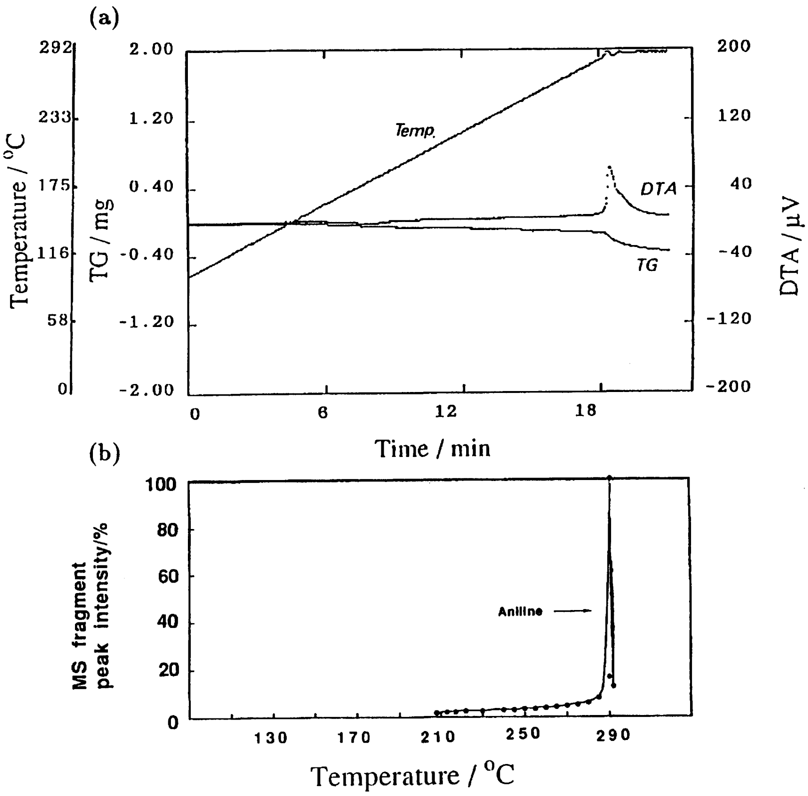


Fig. 3. Thermal analysis of polyaniline under helium.

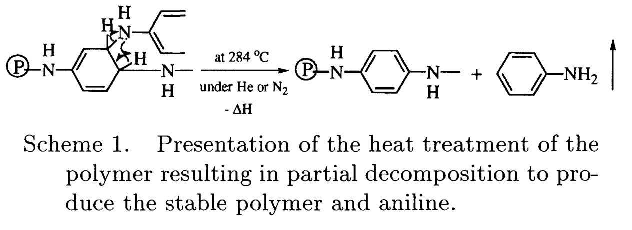
Structure of the Polyaniline. The polyaniline, prepared by the present method, was characterized by FT-IR and ^{1}H NMR spectra. The IR spectrum of the polyaniline, which has been reported to be characteristic of polyaniline as shown in Fig. 1, has the peak at 1299 cm^{-1}, attributed to C–N stretching of the benzenoid units, and the weak peak at 1625 cm^{-1}, attributed to C=N stretching of the quinonoid units. In addition, a weak peak at 2920 cm^{-1}, which is associated with an aliphatic carbon, is observed in the present spectrum of the polyaniline.

The ^{1}H NMR spectrum of the polyaniline in DMSO-d_6, shown in Fig. 2, gives a strong broad peak at δ=7.50. The peak at δ=7.50 is due to the aromatic proton of the polymer. In addition, weak peaks are observed at δ=5.70, 5.01, and 4.20, which could be associated with the adduct structure contained in the polymer. The peaks at δ=5.70 and 5.01 could be corresponding to the vinyl protons, whereas the peak at δ=4.20 could be due to aliphatic protons in the adduct structure.

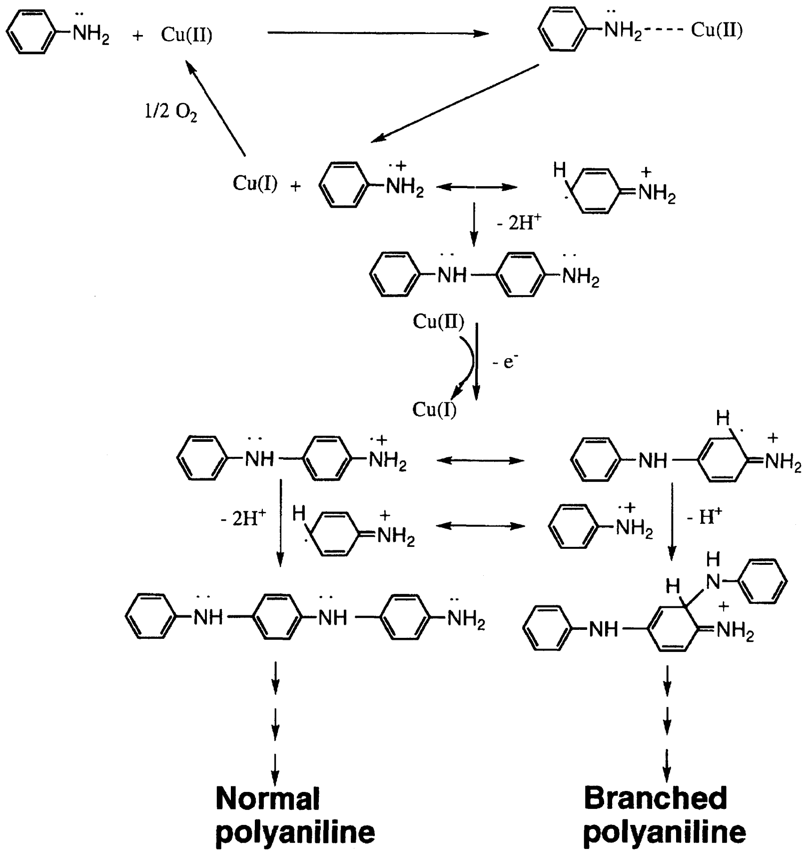
These results suggest that the polymer has a polymeric chain structure, although it contains a small amount of branched structures produced by addition of aniline at *ortho*-position. The low electroconductivity (7.4×10^{-4} S cm^{-1}) of the polymeric product could be due to presence of the adduct structures.

Thermal analyses of the present polyaniline were carried out under helium. The results, shown in Fig. 3-(a), are quite different from those of usual polyaniline prepared by a conventional method. At 284 °C, the polymer starts to decompose resulting in the decrease in weight in TG and in the sharp positive peak in DTA, which should be attributed to the exothermic decomposition of the polymer. The gaseous products, produced by the decomposition, were analyzed to be molecular aniline by mass spectroscopy. Production of the aniline has a sharp maxinum at 284 °C, as shown in Fig. 3-(b). These results indicate that the polymer partially decomposes at 284 °C to produce aniline and a stable polymer. Thus, the reaction process shown in Scheme 1 can be proposed for the thermal decomposition of the polymer based on the structural analyses and the thermal analyses. Although the polymer produced by thermal decomposition is proposed to have an Emeraldine-type structure, a strong doping effect on the electroconductivity was not observed. It is estimated that the amorphous morphology is still maintained, although the molecular structure of the polymer changes to the non-branched polyaniline by the heat treatment.

Mechanism of the Catalytic Polymerization of Aniline. In the UV-vis spectra of the reaction mixture shown in Fig. 4, main absorptions are observed at



Scheme 1. Presentation of the heat treatment of the polymer resulting in partial decomposition to produce the stable polymer and aniline.



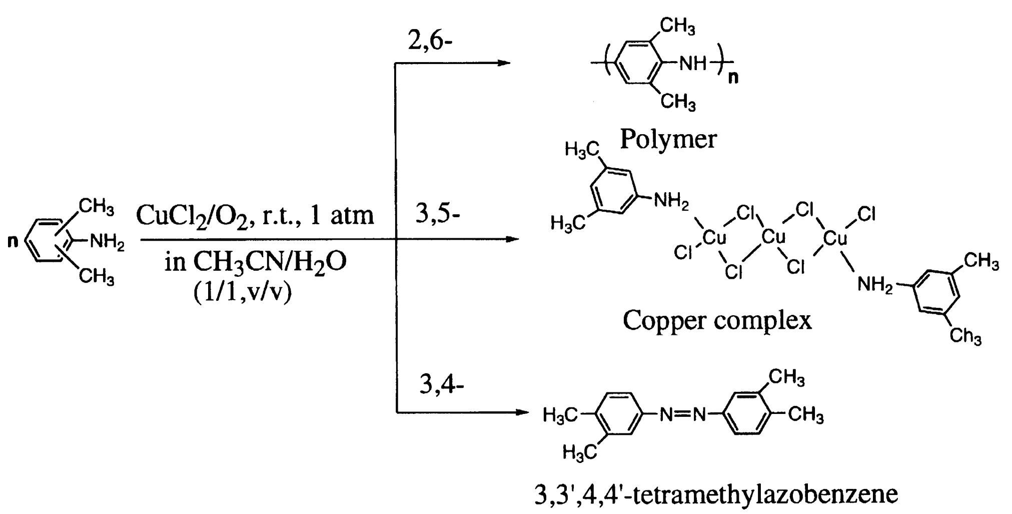
Scheme 2. Suggested mechenism of the polymerization of aniline.

380 and 520 nm. When the molar ratio of aniline to copper(II) is varied, the peak at 520 nm increases in comparison with the peak at 380 nm, with increasing the ratio of aniline to Cu(II)Cl$_2$ from 1 : 3 to 20 : 3. The peak at 520 nm increases in comparison with the peak at 380 nm again, with increasing the reaction time till 48 h as shown in Fig. 5. The spectra were compared with that of polyaniline and the copper(II) complex of 3,5-xylidine, which can be isolated and estimated to be a potential model of the intermediate in the polymerization of aniline and its derivatives (cf. Fig. 6). Thus, we can considered that the peak at 380 nm is due to the copper(II) complex of aniline, whereas the peak at 520 nm is due to the oligomer of aniline.

On the basis of the results of the UV-vis spectra, a possible mechanism is illustrated in Scheme 2. At the beginning of the polymerization, the copper(II) complex of aniline could be produced. Then, the copper(II) could extract one electron from the aniline in the complex, resulting in the radical cation of aniline and copper(I) ions. The copper(I) ions, thus produced, can be oxidized by molecular oxygen to produce copper(II) ions. By this way copper ions work as a catalyst and molecular oxygen works as an oxidant. The polymerization process after the formation of the radical cation is considered to be quite similar to that suggested by E. M. Genies et al.[14] for the production of polyaniline by an electrochemical method. After the formation of the radical cation of dimer, however, the reaction process can be divided into two. One produces the normal linear polymer, and the other produces the branched polymer by the coupling of two radicals.

Polymerization of Aniline Derivatives. The polymerization of xylidines was examined by using the present catalytic system. The results are shown in Table 4. The IR spectrum of the poly(2,6-xylidine) is quite similar to that of an Emeraldine polymer.[15] On the other hand, the reaction of 3,5-xylidine gave a copper(II) complex, instead of polymeric products, this complex was characterized with elemental analysis (Found: C, 29.7; H, 3.4; N, 4.3%. Calcd for $C_{16}H_{22}N_2Cu$: C, 29.6; H, 3.6; N, 4.2%.), whereas the reaction of 3,4-xylidine gave an azobenzene derivative, which was characterized by the ^{1}H NMR spectrum ($\delta=7.50$, 5.70, 5.01, and 4.20). Scheme 3 summarizes these results.

Various transition metal compounds, specially Cu(II) complexes, were shown to function as intiators for polymerization of pyrrole by Bjorklund[16] and Myers.[17] Bjorklund proposed a mechanism in which the rate-determining step is the oxidation of pyrrole to form a radical cation through an activated complex. The present experimental results about the aniline derivatives are quite consistent with the mechanism proposed by Bjorklund, i.e., 2,6-xylidine is easily converted into the corresponding polymer through the activated complex 'Cu(II)–aniline complex' by head-to-tail combina-



Scheme 3. Steric effect of methyl groups on the polymerization of xylidines.

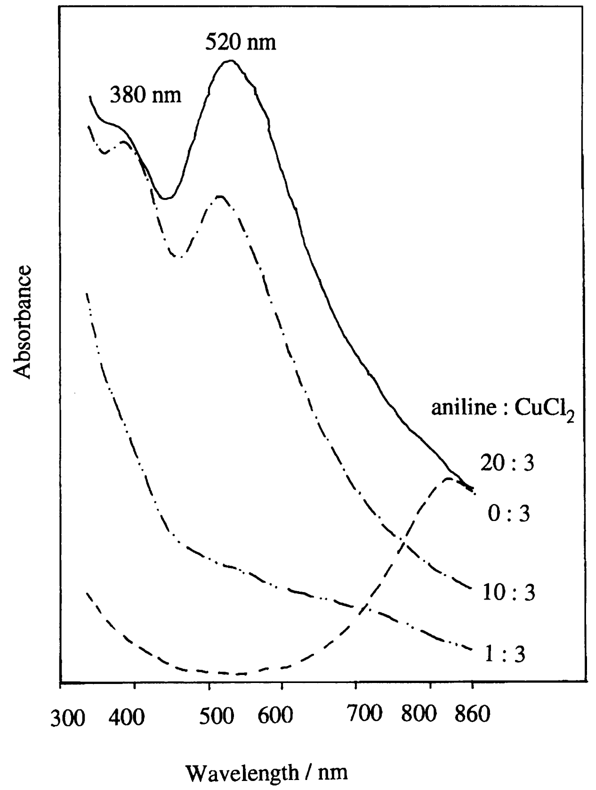


Fig. 4. UV spectra of the reaction mixtures at various molar ratios of aniline to Cu(II) in CH_3CN/H_2O under nitrogen.

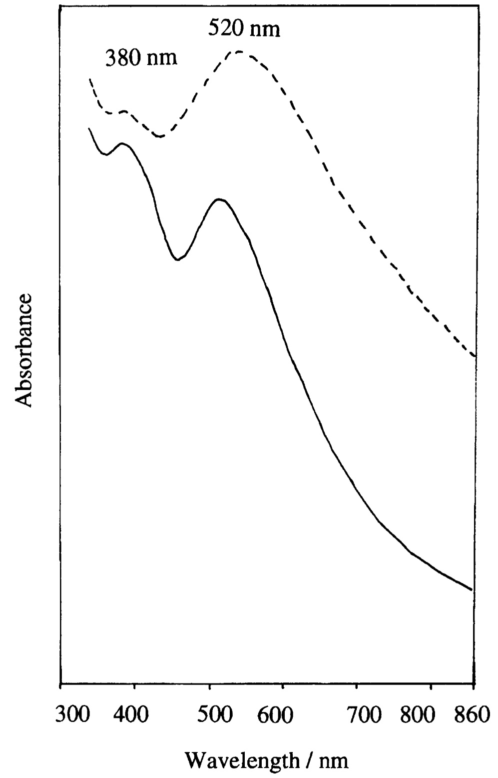


Fig. 5. UV spectra of the reaction mixtures (aniline/Cu(II) = 10/3) under oxygen, initial stage (—) and after 48 h (- - -).

tion of 2,6-xylidine, in which the two methyl groups give no steric hindrance to the 4-position of the monomer. However, 3,5-xylidine provides a 'Cu(II)–aniline complex' instead of the corresponding polymer. The two methyl groups probably give strong steric hindrance to the 4-position of the monomer. Thus, the strong steric hindrance could strongly inhibit the formation of the corresponding polymer. On the other hand, 3,4-xylidine provides neither the corresponding polymer nor the 'Cu(II)–aniline complex', but an azobenzene derivative. Park et al.[18] studied the electrochemical polymerization of aniline and concluded that the growing process of polyaniline competes with the degradation process. The present results suggest that the polymerization also competes with the reaction forming azobenzene in addition to the degradation, when the *para*-position of aniline is substituted by an alkyl group. Thus, the steric hindrance by the substituent can give a great effect on the competition.

If the polymerization can proceed via *para*-position

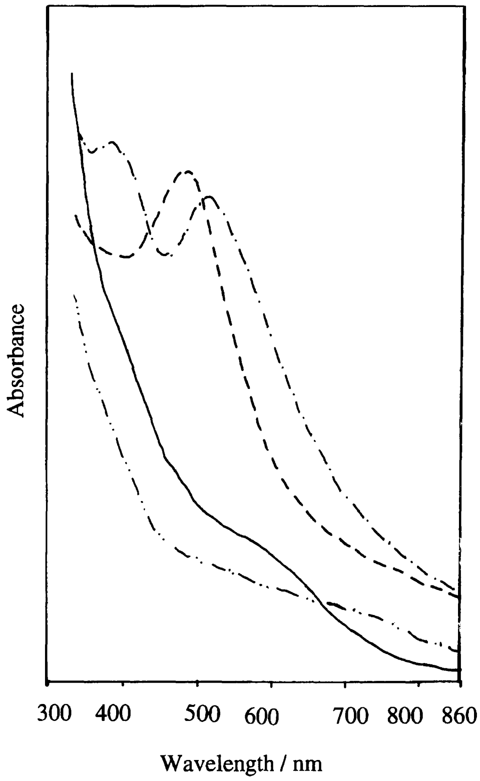


Fig. 6. UV spectra of polyaniline (- - -), copper complex of xylidine (——), and the reaction mixtures at the initial stage at the ratio of aniline/Cu(II)=1/3 (-··-) and 10/3 (-·-).

of aniline, 2,6- and 3,5-xylidines can produce the same polymer. In fact, 2,6-xylidine can produce the polyaniline derivative, while 3,5-xylidine does form the complex with Cu(II) ions. This fact suggests that the reactivity of the intermediate having a radical at the *para*-position of aniline should play an important role in the polymerization.

Conclusion

Polymerization of aniline and 2,6-xylidine can take place by using the Cu(II) salts and molecular oxygen as a catalyst and an oxidant, respectively. However, this is not true for 3,5- and 3,4-xylidines. In the polymerization reaction, the monomer is proposed to be oxidized by the Cu(II) ions to produce the polymer through the Cu(II) complex of the monomer. The Cu(I) ion, the reductive product of the Cu(II) ion, is oxidized by molecular oxygen to return back to the Cu(II) ion. The polymers were characteristic of polyaniline, although they contain a small amount of branched structures. The spectroscopic experiments have suggested that the polymerization of aniline proceeds through the Cu(II) complex of aniline. The present catalytic system can produce a large amount of polymeric products by using a small amount of metal salt as a catalyst and enough amount of oxygen as an oxidant. The system provides an effective method for the mass production of the polyaniline and its derivatives. Although the polyaniline thus produced does not have high enough electroconductivity to be used as a secondary lithium battery, it is semiconductive, and the conductivity is expected to be improved by doping after the mass production. The comparison of the reactivity of xylidines as well as the spectroscopic measurements provides information on the reaction mechanism.

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