

고리에 치환기를 갖는 폴리아닐린의 합성 및 전기전도성

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Synthesis and Electroconductivity of Ring Substituted Polyanilines

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요 약 : 오르토 위치에 치환기를 갖는 몇가지 아닐린을 과황산암모늄을 산화제로 사용하여 염산중에서 중합시켰으며, 얻어진 중합체의 구조적 특성 및 전기전도성을 조사하였다. 치환기(X)는 H, CH₃, OCH₃, Cl, NO₂ 및 C₆H₅이었으며, 니트로기는 중합을 저해하였다. IR 분광분석에 의하면, 모든 중합체는 벤젠형 고리 및 퀴논형 고리구조를 동시에 가지며, 비교적 강한 esr 신호를 보여주어 스핀을 갖고 있음을 알았다. 이같은 스핀의 존재는 ¹H 및 ¹³C-NMR 스펙트럼 분석을 방해하였다. HCl 및 I₂로 도우핑하였을때 이들 중합체의 전기전도도는 크게 증가하였으나, 그 증가도는 치환기의 종류에 복잡한 의존성을 보여주었다. HCl로 도우핑하였을 때는 X=H>OCH₃>CH₃>Cl>C₆H₅ 순으로 전기전도도가 감소하였으나, I₂로 도우핑하였을 때는 X=H>Cl>OCH₃≈CH₃ 순으로 감소하였다. 또한 I₂로 도우핑하였을때는 출발 중합체의 결정성이 파괴되는 것도 알았다.

Abstract : Polyaniline and ring substituted polyanilines were prepared by chemical oxidation and characterized by elemental and IR analyses, esr studies, wide-angle x-ray diffractometry and electroconductivity measurement. IR spectra of the polymers show the coexistence of benzenoid and quinoid structures. Relatively strong esr signals indicate that the polymers have free spins. According to the electroconductivities measured, steric and inductive effects of the substituents play important roles, in a rather complicated manner, in controlling electrical properties of HCl- or I₂-doped polymers. Conductivity decreases in the order of the substituent H>OCH₃>CH₃>Cl>C₆H₅ for HCl-doped compositions and H>Cl>CH₃≈OCH₃ for I₂-doped ones. With the exception of the C₆H₅-substituted polymer, conductivity at room temperature of HCl-doped compositions ranges from 2×10^{-7} to $3 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$ and that of I₂-doped ones from 3×10^{-3} to $4 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$. It also was observed that doping with I₂ drastically destroys the crystallinity of the polymers.

INTRODUCTION

Electroconducting properties of polyconjugated organic polymers is attracting considerable attention because of newly generated scientific concepts as well as of the possible development of new class of materials.¹ Polyacetylene,^{2,3} poly(*p*-phenylene),^{4,5} poly(*p*-phenylenevinylene),^{6,7} polypyrrole,^{8,9} polythiophene^{10,11} and polyaniline^{12,13} are some of the representative compositions which are known to exhibit a wide range of conductivity depending on the nature of the dopant and the degree of doping.

Aniline can be chemically polymerized into black polymeric materials by oxidative polymerization using oxidants such as ammonium persulfate, $\text{CrO}_3\text{-H}_2\text{SO}_4$ etc.. Although the exact structure of the resulting polymers seems to depend on synthetic conditions and are still in controversial to some extent,¹² they are simply called polyaniline as a whole. Polyaniline, an insulator when undoped, becomes a semiconductor when doped, whose conductivity can reach as high as $0.1\text{-}10\ \Omega^{-1}\text{cm}^{-1}$. In this investigation a series of polyanilines with different ring substituents were prepared by chemical oxidation of ring substituted anilines, and their structures and electroconductive properties were studied. The ortho substituents included in the present study are H, CH_3 , OCH_3 , Cl, C_6H_5 , and NO_2 , and ammonium persulfate is the oxidant utilized.

EXPERIMENTAL

Synthesis of Polyanilines

Aniline or an ortho substituted aniline (0.50 mol) was dissolved in 500ml of 1M HCl. A solution of ammonium persulfate (171.2g : 0.75mol) dissolved in distilled water (130ml) was added dropwise to the aniline solution under a N_2 atmosphere. The mixture was stirred for 4-5 hours at room temperature. The precipitate was collected on a filter, washed with 1M HCl and dried at 60-70°C in a vacuum oven.

When necessary, the above prepared polyaniline

(40g) was stirred in 500ml of 0.5M KOH for 30-40min. After repeating this neutralization washing 3-4 times, the neutral polyaniline was collected on a filter, washed with 0.5M KOH and then with distilled water. The washed polymer was dried at 60-70°C in a vacuum oven. This neutral form of the polymers was subjected to a Soxhlet extraction with absolute ethanol under a dry N_2 atmosphere. The soluble portion was recovered by evaporating ethanol under a N_2 atmosphere. Soluble and insoluble portions were thoroughly dried in a vacuum oven maintained at 70°C.

Characterization of Polymers

Elemental analyses were performed by the Microanalytical Laboratory of the University of Massachusetts, U.S.A.. IR spectra were obtained on an FT-IR instrument of IBM System 9000. Solution viscosities of the soluble portions were measured at 30°C using a Cannon-Ubbelohde type viscometer on a solution of 0.05-0.1g/dl concentration in *N,N*-dimethylacetamide (DMA). Number average MW of the soluble portion was obtained at 56°C on a Knauer vapor pressure osmometer using 1,1,2,2-tetrachloroethane (TCE) solvent. Benzil was employed as a reference.

Thermal properties were studied on a differential scanning calorimeter (Du Pont 901) and on a Fisher-Johns mp apparatus. Wide angle X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa instrument using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda=1.5418\text{\AA}$). Pressed pellets of about 2mm thick were employed for X-ray studies. Electron spin resonance (esr) spectra were obtained on a Bruker ER-200E instrument at the frequency of 9.44 GHz with the scan speed of 500G/sec. FT-NMR spectra (^1H and ^{13}C) of the solubles were obtained on a Bruker Sy80 machine using dimethylsulfoxide- d_6 as a solvent.

Doping and Conductivity Measurement

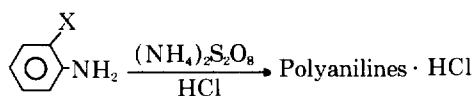
For HCl-doping, powdery polymers were suspended in an aq-HCl solution and stirred for 3 days at room temperature. Degree of doping could be determined quantitatively by analyzing H^+ concentration of the solution before and after doping. This method, however, did not produce

satisfactory results when the concentration change was too low due to either very low degree of doping or very high H^+ concentration of the original dope. For I_2 -doping, the powder samples were placed in an I_2 chamber of $70^\circ C$ under a pressure of 5.0×10^{-1} torr. From weight gain was obtained the degree of doping. Electroconductivity was measured at room temperature on pressed pellets (300 Kg/cm^2) using the four-probe method. Silver paint was utilized for electrical contact. Keithly Model 610C electrometer and Systron Donner digital multimeter(model 7004A) were used in the measurements.

RESULTS AND DISCUSSION

Synthesis and General Characteristics

A series of polyanilines having different substituents were prepared at room temperature by chemical oxidation in aqueous HCl solution of ortho substituted anilines. Ammonium persulfate was utilized as an oxidizing polymerization agent.



As the polymerization proceeded, insoluble, dark precipitate was formed from all of the anilines subjected to the present study, with the sole exception of o-nitroaniline that did not undergo polymerization to the extent of insoluble precipitate formation. The presence of the strongly electron-withdrawing nitro group certainly reduces the compound's tendency toward oxidative polymerization. Since the poly-

anilines thus prepared are in a protonated, that is, in a doped form, they were treated with KOH to obtain neutral forms that are expected to be more soluble and are easier for structural analyses. Even the neutral polymers, however, were not completely soluble. Therefore, they were subjected to ethanol extraction to separate the soluble, low MW fraction from the insoluble high MW fraction. And then, only the insoluble fractions were doped either with HCl or with I_2 for conductivity measurement. It was conjectured that the presence of low MW species in the sample may bring in undesirable artifacts such as moisture sensitivity, terminal group effect, etc..

Results of elemental analyses of neutral polyanilines are tabulated in Table 1. We find two intriguing phenomena : experimentally determined content of each element is consistently lower than calculated value, but C/H/N atomic ratio is very close to theoretical prediction. An oxidation catalyst, V_2O_5 , was employed in combustion of the polymers. Other researchers also reported similar observations and the reason is not yet clear.¹²⁻¹⁴

IR spectra of the two different compositions, poly(2-methylaniline) and poly(2-methoxyaniline), are shown in Figures 1 and 2. Absorption bands at 3380 cm^{-1} (N-H stretching), 1590 cm^{-1} (C=C stretching in the quinoid ring) and 1496 cm^{-1} (C=C stretching in benzenoid ring) are clearly observed. The presence of CH_3O -substituent results in splitting the C=C absorption peaks into doublets. The similar effect was observed for poly(2-phenylaniline) ($\text{X} = \text{C}_6\text{H}_5$). Although these spectra demonstrate, without any doubt, coexistence of the quinoid and benzenoid ring structures in the polymer backbone,¹² we are not yet able to quantify

Table 1. Elemental Analysis of Polyanilines.

X	Theoretical value, wt%			Atomic ratio			Experimental value, wt%			Atomic ratio		
	C	H	N	C	H	N	C	H	N	C	H	N
H	79.97	4.48	15.55	6.66	4.44	1.11	75.06	4.90	14.11	6.67	4.65	1.08
OCH ₃	69.98	5.04	11.66	5.83	4.99	0.83	65.54	5.11	10.45	5.85	5.15	0.79
ϕ	86.71	4.86	8.43	7.22	4.81	0.60	77.50	4.82	5.86	7.25	5.05	0.59
CH ₃	80.73	5.82	13.45	6.72	5.76	0.96	74.20	5.66	11.50	6.79	5.74	0.95
Cl	57.86	2.43	11.25	4.82	2.41	0.80	56.01	2.98	10.32	4.90	2.38	0.74

their relative abundance.

Synthetic results and general properties of the obtained polymers are summarized in Table 2. Yields based on the weight of KOH-neutralized form range 66-95%. The C₆H₅-polyaniline was obtained in the lowest yield. The relative amounts of ethanol extractable fractions are very low for

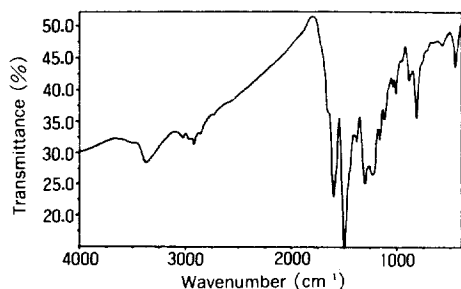


Fig. 1. IR spectrum of polyaniline with X=CH₃.

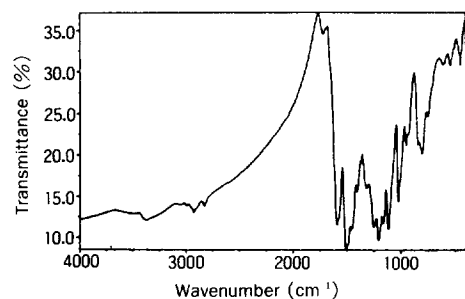


Fig. 2. IR spectrum of polyaniline with X=OCH₃.

polyaniline and poly(2-methylaniline), but they amount about 15% for the rest compositions. Insoluble fractions did not melt before decomposition with the exception of poly(2-phenylaniline), which started to flow between 195-203°C. Soluble fractions, however, started to flow at relatively low temperatures (70-165°C) depending on the structure and probably also on their MW's. The color of the insoluble fractions is either dark brown for polyaniline and poly(2-methylaniline) or black for poly(2-methoxyaniline), poly(2-chloroaniline) and poly(2-phenylaniline).

The number average MW (\bar{M}_n) of the soluble portion is the highest (5,600) for unsubstituted polyaniline and it ranges 600-1,800 for others. Since these values are the only average values for the soluble fractions, the corresponding values of the insoluble fractions are expected to be at least several thousands if they could be determined. The \bar{M}_n of the ethanol insoluble fraction of poly(2-phenylaniline) is exceptionally low, only 2,000. Contrary to the other insoluble fractions, the ethanol insoluble fraction of poly(2-phenylaniline) was soluble in such organic solvents as DMA, TCE and DMSO, and, thus, its MW could be determined. According to the \bar{M}_n values of soluble fractions, presence of any substituent appears to hinder propagation reactions. Unfortuna

Table 2. General Properties of Polyanilines.

X	Yield wt. %	Soluble portion ^a wt. %	Color ^b	T _f , °C ^c	m.p., °C ^d	η_{inh} ^e	\bar{M}_n ^f
H	94.7	3.0	blue	137~142	>300	0.30	5,600
OCH ₃	89.2	17.4	red-violet	69~71	>300	0.08	780
CH ₃	88.0	5.7	blue	160~164	>300	0.07	630
Cl	90.0	15.3	violet	91~98	>300	0.13	1,800
Ph	66.2	13.7	dark-violet	71~77	195~203	0.04(sol) 0.26(ins)	760(sol) 2,000(ins)
NO ₂	not polymerized						

^a Soxhlet extraction for 3-5 days with ethanol.

^b Color of soluble portion.

^c Flow temperature measured on a Fisher-John's m.p. apparatus.

^d m.p. of insoluble portion.

^e The solution viscosities were measured on a 0.05 or 0.1g/dl solution in DMAC at 30°C.

^f The average number of molar mass was measured by a vapor pressure osmometer at 56°C.

tely, the mechanism for the oxidative polymerization of aniline is not well understood and it has yet to be established.

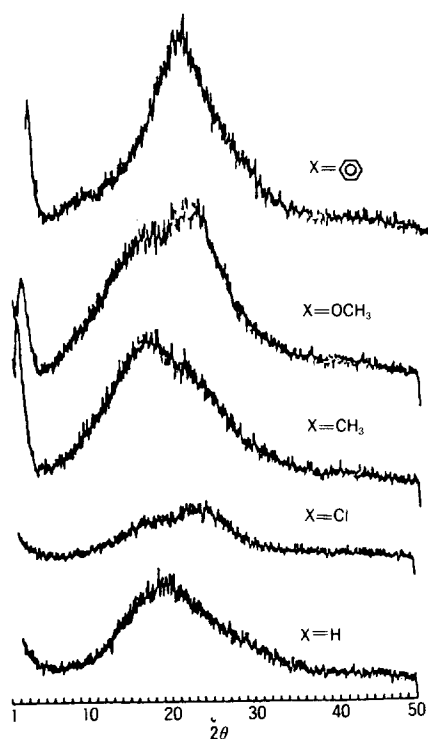


Fig. 3. X-Ray diffractograms of undoped polyanilines.

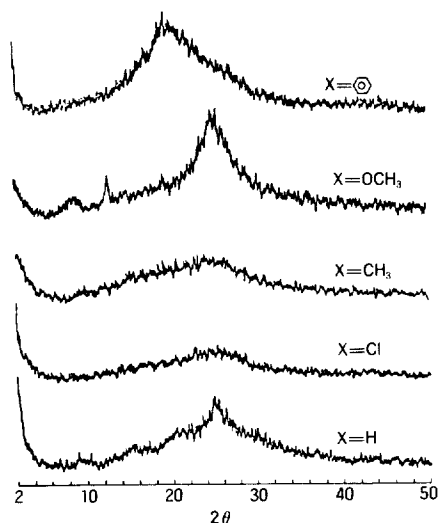


Fig. 4. X-Ray diffractograms of HCl-doped polyanilines.

Wide angle X-ray diffractograms of the neutral, and the maximum HCl- and I_2 -doped polymers are compared in Figures 3~5. According to the diffractograms shown in Figure 3, all of the neutral polymers are semicrystalline or simply of partially aligned molecular chains. The molecular order, however, is significantly reduced, as shown in Figure 4, when they are doped with HCl. HCl-doped poly(2-methylaniline) and poly(2-chloroaniline) are almost amorphous. When doped with I_2 all of them become amorphous, see Figure 5. Intercalation of large dopant species between the chains certainly destroys the original molecular order. It is rather well established that when polyconjugated polymers are doped with I_2 , I_3^- and, in a less amount, I_5^- are the primary chemical species being formed.^{15,16} These ionic species are fairly large and must be able to hinder the polymers from achieving a three or lower dimensional order. Poly(2-phenylaniline) is peculiar in that, when doped with I_2 , it becomes a hygroscopic semisolid. Therefore, we did not measure the electroconductivity of the I_2 -doped polymer.

1H - and ^{13}C -NMR spectra of the soluble fractions were obtained in DMSO for structural analysis. However, surprisingly enough, all of the spectra provided very little information of structural details. As an example, Figure 6a and 6b show 1H - and ^{13}C -NMR spectra of poly(2-chloroaniline). In Figure 6a one can see the resonance peaks at δ 1.2 and 3.7 from residual ethanol and a peak at δ 2.5 from the solvent. The broad and poorly

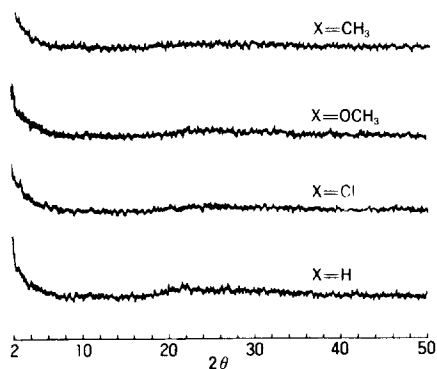


Fig. 5. X-Ray diffractograms of I_2 -doped polyanilines.

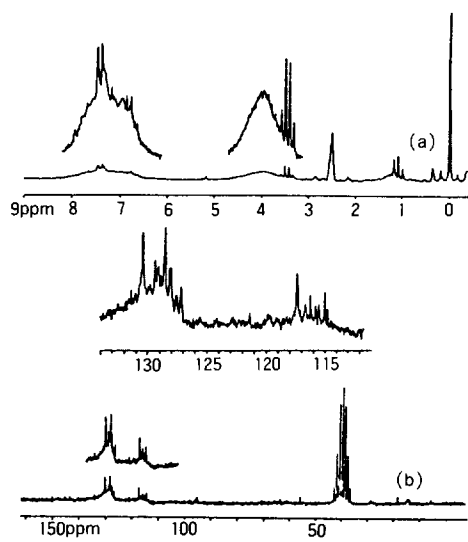


Fig. 6. ^1H (a) and ^{13}C -NMR spectra (b) of polyaniline with $\text{X}=\text{Cl}$.

resolved, weak peaks for benzenoid and quinoid protons appear between δ 6.5 and 8. A broad peak around δ 4 suggests the presence of exchangeable protons, probably imino protons. Nuclear quadrupole broadening by the imino nitrogen atom may be one of the reasons for the peak broadening.¹⁷ Proton-decoupled ^{13}C -NMR spectrum (Figure 6b) also exhibits rather poorly resolved peaks. One group of peaks centers around δ 117 and the other around δ 129. The former probably arises from the carbons in quinoid rings and the latter from those in benzenoid rings. Both of the expanded peaks reveal at least close to a dozen identifiable peaks, respectively, suggesting much more complicated structure was formed compared with many idealized structures previously proposed.^{12,13} The peaks at δ 40 are from the solvent, $\text{DMSO}-d_6$.

Polyaniline and poly(2-methylaniline) did not show any ^{13}C -resonance peak when scanned up to δ 160 ppm. Poly(2-methoxyaniline) and poly(2-phenylaniline) showed only the ^1H - and ^{13}C -resonance peaks for the respective substituents, but the peaks for the atoms of the main chain did not appear or they were extremely broad and weak.

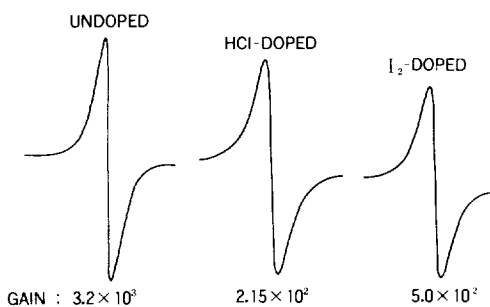


Fig. 7. ESR spectra of polyaniline with $\text{X}=\text{Cl}$.

After observing that only rather poor quality NMR spectra could be recorded, the possibility for the polymers to bear free electron spins was scrutinized. As shown in the representative ESR spectrum of poly(2-chloroaniline) in Figure 7, all of the undoped, neutral and doped polymers revealed strong ESR signals. Absence of hyperfine structure of the observed spectra indicates mobile nature of the spins. It is believed that the presence of free spins in the polymers causes shortened relaxation times for ^1H and ^{13}C nuclear spins, which, in turn, result in fouled spectra. In addition, it was noted qualitatively that doping increased spin densities.

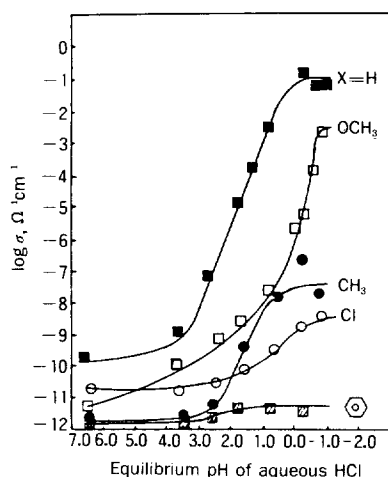
Electroconductivity

All of the polymers in the undoped, neutral form are insulators, whose conductivities are in the range of $10^{-12} - 10^{-10} \Omega^{-1}\text{cm}^{-1}$. When they are doped with HCl , their conductivity increases and the extent of increase is dependant on the nature of the ring substituent and also on the degree of doping. Table 3 and Figure 8 show how each polymer's conductivity changes with HCl -doping. When $\text{X}=\text{H}$, conductivity starts to increase rapidly at the equilibrium pH of about 3 reaching the maximum attainable value of approximately $1 \times 10^{-1} \Omega^{-1}\text{cm}^{-1}$.

The electron-donating groups, CH_3 , and OCH_3 , on the ring exhibited an unexpected, negative effect. For example, the HCl -doped poly(2-methoxyaniline)'s maximum conductivity is only in the order of $10^{-3} \Omega^{-1}\text{cm}^{-1}$, about one hundredth of the unsubstituted polyaniline's. When the ring

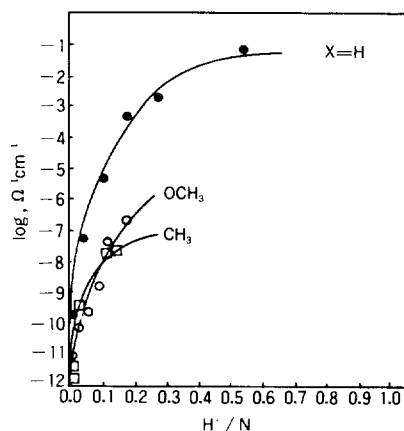
Table 3. Conductivity of HCl-Doped Polyanilines.

X = H		X = OCH ₃		X = CH ₃		X = Cl		X = ϕ	
pH	$\sigma, \Omega^{-1} \text{cm}^{-1}$	pH	$\sigma, \Omega^{-1} \text{cm}^{-1}$	pH	$\sigma, \Omega^{-1} \text{cm}^{-1}$	pH	$\sigma, \Omega^{-1} \text{cm}^{-1}$	pH	$\sigma, \Omega^{-1} \text{cm}^{-1}$
6.5	2.0×10^{10}	6.5	7.9×10^{12}	6.5	1.7×10^{12}	6.5	5.7×10^{11}	6.5	2.5×10^{12}
3.5	1.5×10^9	3.5	9.1×10^{11}	3.5	2.7×10^{12}	3.5	3.6×10^{11}	3.5	1.1×10^{12}
2.8	6.4×10^8	2.4	6.1×10^{10}	2.5	5.5×10^{12}	2.3	4.5×10^{11}	2.8	2.3×10^{12}
1.9	1.4×10^5	1.9	1.2×10^9	1.6	3.0×10^{10}	1.7	6.6×10^{11}	1.9	6.5×10^{12}
1.2	3.9×10^4	0.8	4.1×10^8	0.9	1.8×10^8	0.8	3.4×10^{10}	1.0	5.1×10^{12}
0.9	2.1×10^3	0.9	2.4×10^6	0.0	2.2×10^7	0.0	1.1×10^9	-0.5	3.1×10^{12}
0.0	2.3×10^1	-0.1	7.8×10^5	-0.5	2.6×10^8	-0.5	4.4×10^9		
-0.3	1.1×10^2	-0.5	6.8×10^4						
-0.6	1.0×10^2	-0.7	2.4×10^3						

**Fig. 8.** Conductivity of HCl-doped polyanilines.

substituent is CH₃ group, maximum conductivity is even far less, in the order of $10^{-8} \Omega^{-1} \text{cm}^{-1}$. When the substituent is the electron-attracting chlorine, the conductivity enhancement on HCl-doping is less than when it is CH₃. Moreover, phenyl substituent appears to practically inhibit conductivity increase (Table 3 and Figure 8) on HCl-doping.

Figure 9 compares the conductivities of three polymers as a function of the degree of doping, i.e., number of H⁺ per repeating unit. We assumed the polymer chains consist of alternating sequence of benzenoid and quinoid structures as proposed earlier by others for polyaniline.^{12,13} The figure clearly demonstrates that even at the same degree of doping, conductivity decreases in the order

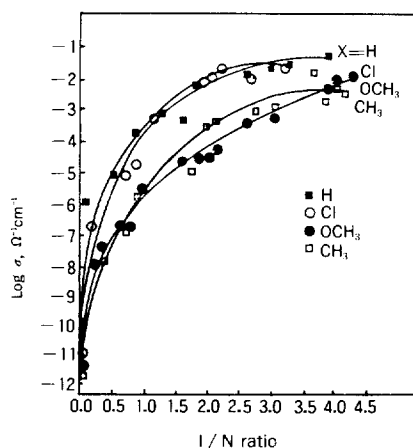
**Fig. 9.** Conductivity of HCl-doped polyanilines vs. doping level per repeating unit.

of $X=\text{H} > \text{OCH}_3 > \text{CH}_3$. Another important point to be noted is that polyaniline($X=\text{H}$) reaches the maximum conductivity at the doping level of 0.5 proton per repeating unit. The degree of protonation was calculated from H⁺ concentration change of HCl solution after treatment of each polymer. The similar quantitative determination for other polymers and compositions could not be made, because H⁺ concentration changes were too low to make a reliable analysis.

Our observations strongly imply that a ring substituent exerts more than electronic effect on the conductivity of HCl-doped polyanilines. Similar phenomena were observed earlier for substituted polyacetylenes²¹ and polyheterocycles.²² Structural and electronic perturbations of the original structures

Table 4. Conductivity of I₂-Doped Polyanilines.

X=H		X=OCH ₃		X=CH ₃		X=Cl	
I/N	$\sigma, \Omega^{-1}\text{cm}^{-1}$	I/N	$\sigma, \Omega^{-1}\text{cm}^{-1}$	I/N	$\sigma, \Omega^{-1}\text{cm}^{-1}$	I/N	$\sigma, \Omega^{-1}\text{cm}^{-1}$
0.00	2.0×10^{-10}	0.00	7.9×10^{-12}	0.00	1.7×10^{-12}	0.00	5.7×10^{-11}
0.28	1.5×10^{-6}	0.27	1.3×10^{-8}	0.48	6.3×10^{-6}	0.26	1.3×10^{-6}
0.57	7.1×10^{-6}	0.64	2.0×10^{-7}	0.72	4.2×10^{-6}	0.70	1.9×10^{-6}
0.87	1.9×10^{-4}	0.98	3.5×10^{-6}	1.19	5.5×10^{-5}	0.87	1.3×10^{-6}
1.41	4.6×10^{-4}	1.55	1.5×10^{-5}	1.80	2.2×10^{-4}	1.24	5.9×10^{-4}
1.59	2.3×10^{-4}	1.89	2.0×10^{-5}	2.25	7.9×10^{-4}	1.50	2.5×10^{-3}
1.82	2.8×10^{-3}	2.13	3.1×10^{-4}	2.74	6.8×10^{-4}	1.91	5.9×10^{-3}
2.17	6.4×10^{-4}	2.61	2.9×10^{-4}	3.15	3.6×10^{-4}	1.99	6.5×10^{-3}
2.52	2.3×10^{-3}	3.14	8.0×10^{-4}	3.67	4.4×10^{-3}	2.37	1.0×10^{-2}
2.99	1.5×10^{-3}	3.95	2.9×10^{-3}	3.94	6.2×10^{-4}	2.75	7.2×10^{-3}
3.27	6.8×10^{-3}	4.24	2.1×10^{-3}	4.14	8.3×10^{-4}	3.35	9.4×10^{-3}
3.93	4.0×10^{-2}	4.40	3.2×10^{-3}	4.24	5.7×10^{-4}		


 Fig. 10. Conductivity of I₂-doped polyanilines.

tend to diminish conductivity. Probably, maintenance of coplanar, linear polyconjugated structure is the most important in attaining high electrical conductivity after doping. Doping with I₂ of the same polymers provided us with complete different results, which are summarized in Table 4 and Figure 10. All of the polymers, regardless of the nature of the ring substituent, reveals smooth increase in conductivity with I₂-doping. In general, conductivity reaches the maximum at the doping level of slightly higher than 3 iodine atoms per repeating unit. This agrees with other reports that I⁻-doping generate I₃⁻ and, to a lesser extent,

I₅⁻.^{15,16} Polyanilines with X=H and Cl exhibit comparable conductivity at the same level of doping with the maximum value being about $1 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$. When the substituent is either OCH₃ or CH₃, slightly lower maximum conductivity is obtained. The conductivity decreases in the order of X=H>Cl>OCH₃≈CH₃. It is well known that HCl-doping of polyaniline results in protonation of imino nitrogens and that I₂-doping causes electron transfer from the polymer backbone to iodine. We, however, are not sure why such different doping mechanisms should exhibit dissimilar substituent effect as observed in this study.

CONCLUSION

The following conclusions can be drawn from the present investigation :

- 1) Polymerization of anilines by chemical oxidation using ammonium persulfate is sensitive to the nature of the ring substituent : strongly electron-attracting nitro group hinders polymerization.
- 2) Polyaniline backbones consist of benzenoid and quinoid structures as deduced from IR spectral analysis. Polyanilines prepared bear free spins as observed by esr spectra and, therefore, do not provide satisfactory NMR spectra.
- 3) Doping, in general, reduces the molecular order of the original polymers. I₂-doping completely

destroys the molecular order.

4) Electroconductivity of doped polymers exhibits a complicated dependence on the ring substituent. Conductivity of HCl-doped polymers decreases in the order of the ortho substituent $X=H>OCH_3>CH_3>Cl>C_6H_5$, while that of I_2 -doped ones decreases in the order of $X=H>Cl>OCH_3\approx CH_3$.

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