Electroconducting Polyaniline Composite Films Prepared by Chemical Oxidative Polymerization at Gas/Liquid Interface

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Synopsis

Electroconducting polyaniline composite films have been prepared by chemical oxidative polymerization at gas/liquid interface between heated aniline vapor and aqueous liquid membrane containing a water-soluble matrix polymer and an oxidizing agent (and proton acid). The formed composite films are green, semitransparent and uniform. Conductivity, transmittance, and visible and IR spectra are investigated with the films prepared under various preparative conditions: aniline vapor exposure time, atmospheric and aniline temperatures, chemical species and concentration of the oxidizing agent, and concentration ratio of the proton acid to the oxidizing agent. The conducting composite films are formed with the liquid membrane containing above 680 mV of oxidation potential and some proton donor. The film conductivity is determined by the absolute amount of the radical cation structure component of polyaniline and the composition ratio of the radical cation component to the quinonediimine component of polyaniline, which is due to the oxidation potential and protonation effect of the liquid membrane. The excess proton acid coexisting with the oxidizing agent contributes to the film transmittance by uniform distribution of polyaniline in the composite film, aside from its contribution to conductivity by increase of the radical cation component at suitable concentration of the oxidizing agent.

INTRODUCTION

Polyaniline has attracted considerable attention because of its unique electrical and optical properties, structural transformation by oxidation and protonation, and good stability in atmosphere. Polyaniline films are studied extensively for a variety of applications, including colored or multicolored electrochromic devices,[1] photoresponsible devices,[2] secondary batteries,[3] and sensors.[4,5] Especially, studies on secondary batteries containing polyaniline films as active electrode materials have progressed most remarkably of all application studies with conducting polymers. A secondary lithium battery containing polyaniline film as a counter-electrode has already been commercialized in 1987 and was the first practical application of conducting polymers. This finding suggests good applicability and stability of polyaniline material.

Polyaniline films are usually prepared by electrochemical oxidative polymerization. This procedure, however, is more or less complicated and is not suitable for large area film production. On the other hand, the polyaniline prepared by conventional chemical oxidative polymerization is generally formed as a bulky powder—so-called "aniline black," which is very difficult to be applied as a material. In order to prepare a conducting polymer with some chemical method in a practical form (e.g., film), a few hybridization methods with the

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other supporting materials are proposed.[6-8] However, these methods thus far have rarely been applied to polyaniline.

This article describes a new preparation method of electroconducting polyaniline composite films by chemical oxidative polymerization at gas/liquid interface between heated aniline vapor and liquid membrane containing a water-soluble matrix polymer and an oxidizing agent. The effects of the preparative conditions on conductivity, transmittance, and chemical structure of the composite films are investigated.

EXPERIMENTAL

Figure 1 shows the preparation apparatus of polyaniline composite films. This apparatus consisted of a desiccator containing an aniline heating bath
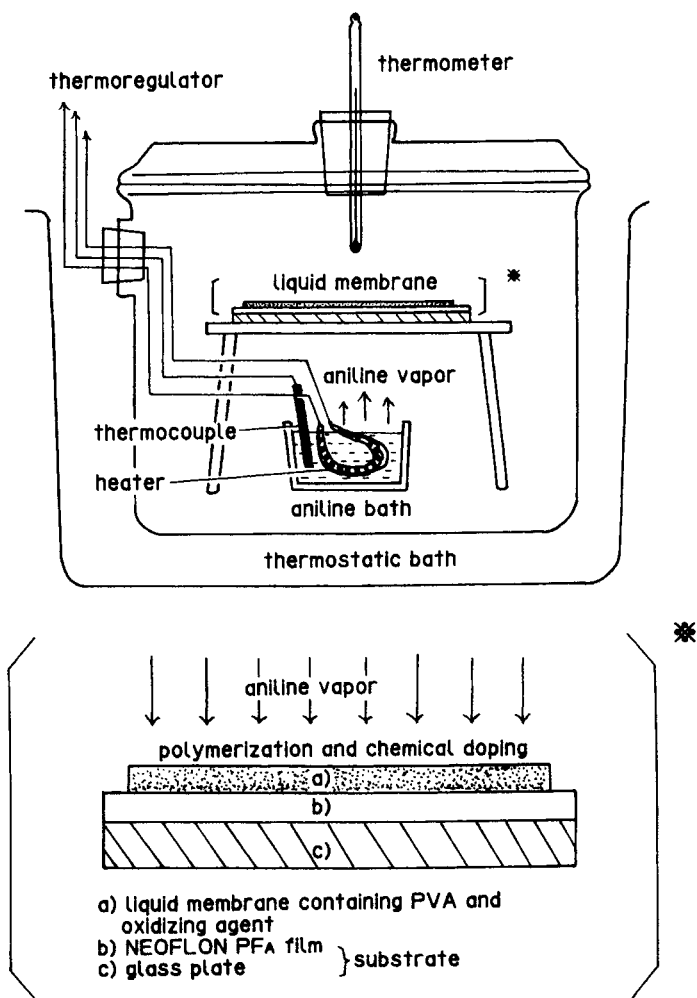

Fig. 1. Preparation apparatus of the polyaniline composite films.

with a heater and a thermocouple connected to a thermoregulator. The desiccator was immersed in a thermostatic bath. In the desiccator, atmospheric temperature and aniline vapor pressure was controlled by adjusting temperatures of the thermostatic bath and aniline bath.

In a usual procedure, polyaniline composite films were prepared as follows: a liquid membrane was prepared on a substrate by hand casting with a given interval slit from an aqueous solution containing a water-soluble matrix polymer and an oxidizing agent (and proton acid). Neoflon PF_A film (tetrafluoroethylene–perfluoroalkylvinylether copolymer, Daikin Industries, Ltd.) pasted on a glass plate was used as the substrate. The aqueous liquid membrane was retained on this substrate without repulsion. The liquid membrane on the substrate was put into the desiccator and exposed to the aniline vapor. Aniline was polymerized by chemical oxidative polymerization at gas/liquid interface between the liquid membrane and the aniline vapor. The formed polyaniline was simultaneously doped with anion produced from the oxidizing agent (and the coexisting proton acid). After the reaction, the liquid membrane on the substrate was taken out of the desiccator and dried, resulting in formation of polyaniline-matrix polymer composite film. The formed composite film was finally stripped off from the substrate. In this work, poly(vinyl alcohol) (PVA; Nippon Gosei Kagaku N-300, M_n = 67000) was used as a matrix polymer. The liquid membrane was prepared at 0.05 cm of thickness in 6 × 6 cm^2 with 5% PVA aqueous solution containing various oxidizing agents (and HCl as a proton acid). The liquid membrane was exposed to the aniline vapor for a given time at given atmospheric and aniline temperature, and then dried at 30°C for 16 h to be a sample of the polyaniline-PVA composite film.

The film conductivity was measured using the standard 4-probes technique under 10^{-3} Torr at 40°C for elimination of absorbants and moisture from the film surface. The transmittance was measured with a Shimadzu UV-240 spectrophotometer at the wave length 540 nm. The absorbance at the other wave length was measured with the same spectrophotometer and standardized to a value per 1 μm of the film thickness. The surface structure of the film was investigated by observation of ATR spectrum with a Nicolet 5DX FT-IR spectrophotometer. The oxidation potential (O.R.P.) of the liquid membrane was measured at 25°C with a Orion Research 701A ionanalyzer using a reference of Ag/AgCl. Chemicals used in this work were all of special reagent grade and used without further purifications, except for aniline and PVA. Special reagent grade aniline was further purified by distillation before use. PVA was purified by reprecipitation from water.

RESULTS AND DISCUSSION

The polyaniline-PVA composite films prepared by this method are green, semitransparent and uniform. Figure 2 shows the effect of the aniline vapor exposure time on the conductivity and the transmittance of the composite film. These evaluated films have been prepared with the liquid membrane containing 3% ferric chloride ($FeCl_3$) as an oxidizing agent under the condition, 0°C of the atmosphere and 30°C of the aniline. "Aniline side" and "substrate side" represent the film side which has been exposed to the aniline vapor and the
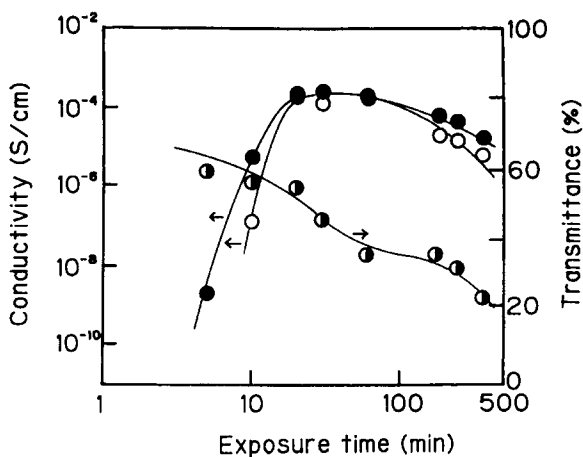
Fig. 2.   Effect of the aniline vapor exposure time on the conductivity and the transmittancᵥ of the composite films. (○) aniline side; (●) substrate side.

other side which has been contacted with the substrate, respectively. The conductivity of both sides rapidly increases to a saturated value within 30 min, passes through a plateau, and then decreases gradually as the exposure time increases. The conductivity of the substrate side increases a little faster before it reaches the plateau, and decreases after the plateau a little slower than that of the aniline side. Both conductivities, however, are not different from each other on the plateau. On the other hand, the film transmittance decreases uniformly with an increase of the exposure time. Figures 3 and 4 show the ATR spectrum changes by the aniline exposure time on the aniline side and on the substrate side, respectively, of the composite films used in Figure 1. The ATR spectra are shown with regard to the two regions from 650 to 900 cm^{-1} and from 1400 to 1800 cm^{-1}, which are assigned to polyaniline structure. The ATR spectra are standardized by the spectrum of the matrix film (PVA). As shown in Figure 3, the peak strength at 1504 and 1600 cm^{-1} assigned to the in-plane skeletal vibration of benzene ring increases uniformly with an increase of the aniline exposure time. However, the peak at 820 cm^{-1} assigned to the out-of-plane deformation vibration of p-di-substituted benzene ring, which means formation of polyaniline, increases within 30 min of the exposure time, keeps a constant strength for a few hours, then decreases gradually. This peak change at 820 cm^{-1} represents a similar trend with the conductivity change (see Fig. 2), whereas the peaks at 690 and 745 cm^{-1} assigned to the out-of-plane deformation vibration of monosubstituted benzene ring increase gradually as the exposure time increases. These peaks suggest formation of some oxidative decomposition products of polyaniline and/or byproducts from the oxidized aniline which has not been polymerized. The peak at about 1650 cm^{-1}, which is assigned to aromatic nitro compounds or acid amides, appears at a longer exposure time. As mentioned above, it is considered that the formation and decomposition of polyaniline are in competition with each other. Hence, the decrease of the film conductivity at prolonged exposure time is due to decomposition of polyaniline and/or increase of byproduct formation. The ATR spectrum change on the substrate side is similar to that on the aniline side, except the initial increase
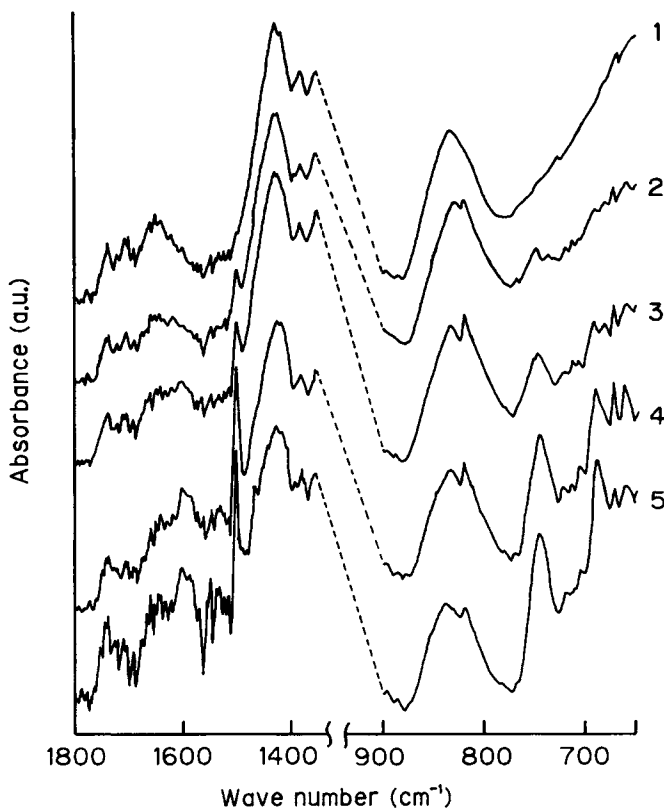
Fig. 3. FT-IR spectra (ATR) of the aniline side at various exposure times (min). (1) 0, (2) 10, (3) 30, (4) 180, (5) 360.

of the peak at 820 cm^{-1} (formation of polyaniline) is a little faster, and the subsequent decrease of the peak at longer exposure time (decomposition of polyaniline) is a little slower. However, the ATR spectra of both sides are not different from each other when the peak at 820 cm^{-1} keeps a constant strength. This finding suggests uniform distribution of polyaniline in the composite film.

The effects of aniline and atmospheric temperatures on the film conductivity and transmittance, and on the formation and decomposition rates of polyaniline are shown in Figures 5, 6, 7, and 8. These figures show results on the composite films prepared with 3% FeCl$_3$ at various aniline and atmospheric temperatures. Figures 5 and 6 show the saturated conductivity and transmittance at saturation of the conductivity, respectively. The saturated conductivity does not depend largely on aniline temperature at any atmospheric temperatures. The transmittance decreases remarkably with an increase of aniline temperature. At any aniline temperature, the film containing both maximum conductivity and transmittance is prepared at 0°C for all atmospheric temperatures. Figures 7 and 8 show the time required to saturate the film conductivity (t_s) and the time required to decrease the conductivity until $\frac{1}{10}$ of the saturated conductivity (t_d), respectively. The former indicates the formation rate of polyaniline, and the latter indicates its decomposition. From Figures 7 and 8, the changes in conductivity and transmittance in Figures 5 and 6 are interpreted as follows: at
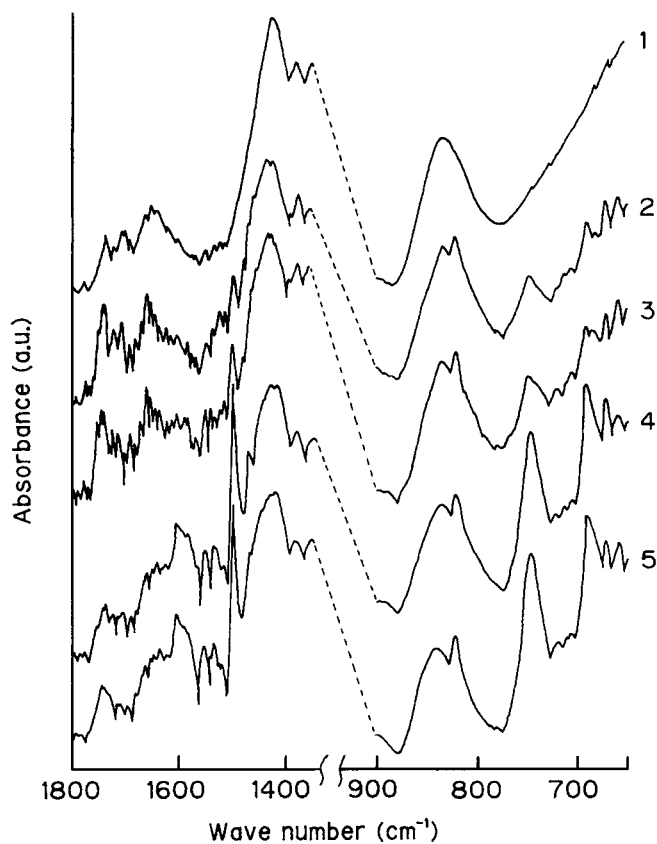
Fig. 4.   FT-IR spectra (ATR) of the substrate side at various exposure times (min). (1) 0, (2) 10, (3) 30, (4) 180, (5) 360.
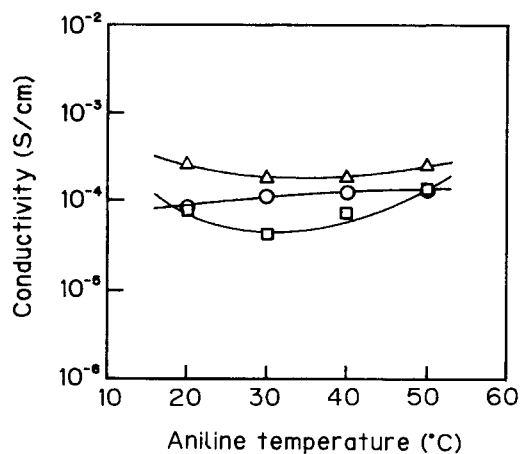

Fig. 5.   The saturated conductivity of the composite films as a function of aniline temperature at various atmospheric temperatures (°C). (O) 5, (△) 0, (□) −10.
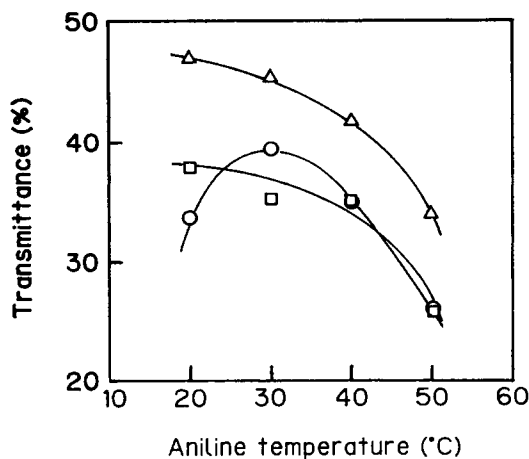
Fig. 6.   The transmittance of the composite films with the saturated conductivity as a function of aniline temperature at various atmospheric temperatures (°C). (○) 5, (△) 0, (□) −10.

lower atmospheric temperature, aniline vapor pressure is higher because the boiling point of aniline (183°C) is much higher than that of water (100°C), while both formation and decomposition rates of polyaniline are lower. On the other hand, at higher atmospheric temperature, both formation and decomposition rates are higher, while aniline vapor pressure is lower. As a result both conductivity and transmittance are the highest at 0°C, the middle atmospheric temperature. As aniline temperature increases, both aniline vapor pressure and formation rate of polyaniline increase. However, the decomposition rate of polyaniline and byproduct formation also increase. Hence, the conductivity does not largely change at any aniline temperature, while the transmittance is lower at higher aniline temperature.

The polyaniline-PVA composite films prepared with $FeCl_3$ have a definite absorption at about 800 nm, although absorption below 500 nm is not clear
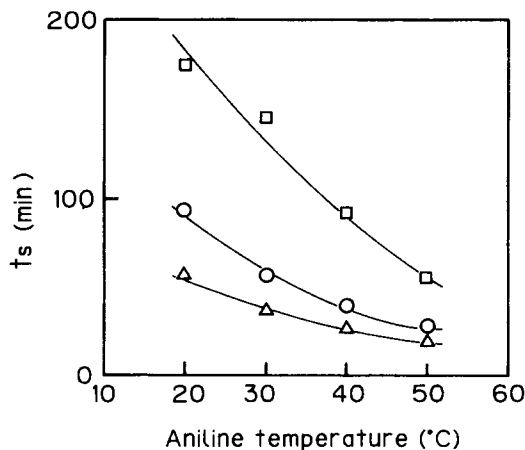

Fig. 7.   The time required to saturate the film conductivity (t_s) as a function of aniline temperature at various atmospheric temperatures (°C). (○) 5, (△) 0, (□) −10.
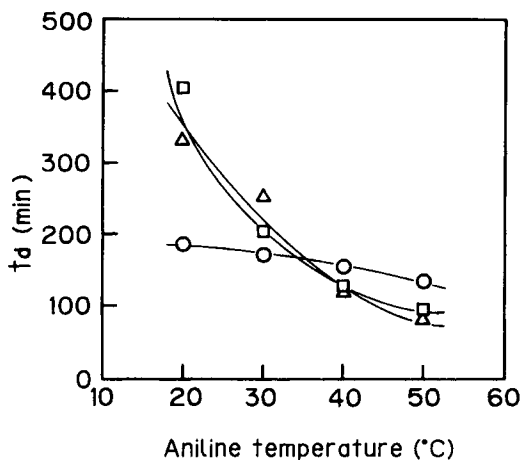
Fig. 8. The time required to decrease the film conductivity until 1/10 of the saturated conductivity (t_d) as a function of aniline temperature at various atmospheric temperatures (°C). (○) 5, (△) 0, (□) −10.

because of overlap with $FeCl_3$ absorption. The relationship between this absorbance at 800 nm and the film conductivity is shown in Figure 9. Their correlation is given a straight line in regard to both aniline and substrate sides. The evaluated films are prepared with the liquid membranes containing 3% $FeCl_3$ for various aniline exposure times at various aniline and atmospheric temperatures. Further, the data after saturation of the conductivity are rejected in order to eliminate the influence of oxidative decomposition of polyaniline. McManus et al.[9] have reported that polyaniline prepared by electrochemical oxidative polymerization has had three limiting structures based on oxidation level as follows: (1) aromatic amine (reduced-insulating) structure with an absorption band at 320 nm; (2) radical cation (conductive) structure with three
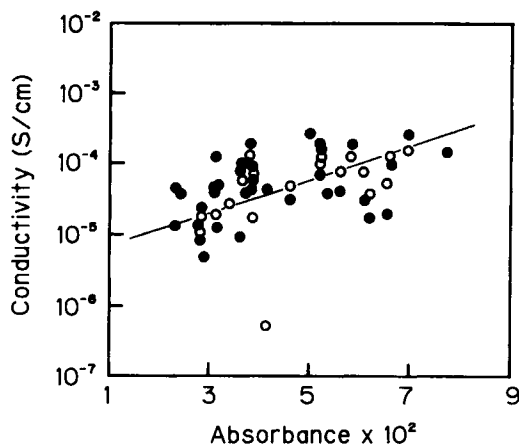

Fig. 9. The relationship between the film conductivity and the absorbance at 800 nm. (○) aniline side, (●) substrate side.

absorption bands at 320, 420, and 800 nm; and (3) quinonediimine (oxidized-insulating) structure with two absorption bands at 320 and 580 nm. They have also reported that the band at 800 nm of the intermediate oxidation state (2) has been characteristic of a radical cation, and that the absorbance at 800 nm has been correlative with the conductivity, which corresponds with the results in Figure 9. Therefore, increase of the radical cation structure component of polyaniline contributes to the conductivity on this chemical oxidative preparation of the polyaniline composite films.

Table I shows oxidation potential (O.R.P.) of the liquid membranes containing various oxidizing agents and the conductivity of the composite films prepared with these liquid membranes. The evaluated films have been prepared fixing the aniline exposure time to 1 h at 0°C of the atmosphere and 30°C of the aniline. Table II shows redox system and standard oxidation potential of various oxidizing agents. In the case of Fe^{3+} salts, proton acid is produced by their hydrolysis. The redox systems of $S_2O_8^{2-}$, ClO_3^-, BrO_3^-, and IO_3^- salts and their oxidation potentials in the presence of proton acid are different from those in the absence of it. As shown in the tables, conducting polyaniline composite films whose conductivity is above 10^{-5} S/cm are formed under the condition that the liquid membrane has more than 680 mV of O.R.P. and some proton donor. Anion species of the oxidizing agents are much more influential on the film conductivity than cation species. Hence, some anion dopants from the oxidizing agent anions contribute to the film conductivity, besides HCl doping.

Effects of the concentration of the oxidizing agent and proton acid on conductivity and transmittance and absorption bands of the polyaniline composite films are shown in Figures 10, 11, 12, 13, 14, and 15. The evaluated films have

TABLE I
The Conductivity of the Polyaniline–PVA Composite Films Prepared
with Various Oxidizing Agents

Oxidizing agent	Conc. (M/L)	HCl conc. (M/L)	O.R.P.* (mV)	Conductivity (S/cm)
$FeCl_3$	0.12	0	686	1.9×10^{-4}
$Fe_2(SO_4)_3$	0.12	0	693	1.6×10^{-5}
$Fe(NO_3)_3$	0.12	0	732	5.5×10^{-5}
$CuCl_2$	0.12	0	507	$< 10^{-11}$
$K_2S_2O_8$	0.02	0	799	$< 10^{-11}$
$KClO_3$	0.02	0	414	$< 10^{-11}$
$KBrO_3$	0.02	0	470	$< 10^{-11}$
KIO_3	0.02	0	393	$< 10^{-11}$
$K_2S_2O_8$	0.02	0.2	845	8.8×10^{-4}
$KClO_3$	0.02	0.2	672	9.5×10^{-8}
$KBrO_3$	0.02	0.2	504	2.5×10^{-8}
KIO_3	0.02	0.2	787	5.6×10^{-2}
$NaIO_3$	0.02	0.2	790	9.4×10^{-2}
$LiIO_3$	0.02	0.2	789	8.2×10^{-2}
HIO_3	0.02	0.2	790	7.6×10^{-2}

* Vs. Ag/AgCl, 25°C.

TABLE II
Redox Systems and Standard Oxidation Potentials of Various Oxidizing Agents Used in Table I

Redox system	Standard oxidation potential* (mV)
$Fe^{3+} + e = Fe^{2+}$	771
$Cu^{2+} + e = Cu^+$	153
$S_2O_8^{2-} + 2e = 2SO_4^{2-}$	2010
$S_2O_8^{2-} + 2H^+ + 2e = 2HSO_4^-$	2123
$ClO_3^- + H_2O + 2e = ClO_2^- + 2OH^-$	330
$ClO_3^- + 6H^+ + 6e = Cl^- + 3H_2O$	1450
$ClO_3^- + 3H^+ + 2e = HClO_2 + H_2O$	1210
$BrO_3^- + 3H_2O + 6e = Br^- + 6OH^-$	610
$BrO_3^- + 6H^+ + 5e = 1/2Br_2 + 3H_2O$	1520
$IO_3^- + 3H_2O + 6e = I^- + 6OH^-$	260
$IO_3^- + 6H^+ + 5e = 1/2I_2 + 3H_2O$	1195

* Vs. NHE, 25°C.

been prepared with various concentrations of KIO_3 as an oxidizing agent and HCl as a proton acid at 0°C of the atmosphere and 30°C of the aniline, fixing the exposure time to 1 h. Figure 10 shows the film conductivity as a function of KIO_3 concentration at various HCl/KIO_3 ratios. The film conductivity increases to a saturated value, and then decreases with an increase of KIO_3 concentration. The conductivity increases and starts to decrease with lower KIO_3 concentration at higher HCl/KIO_3 ratio. Figure 11 shows O.R.P. of the liquid membranes as a function of KIO_3 concentration at various HCl/KIO_3 ratios. The O.R.P. increases to saturation with an increase of KIO_3 concentration at

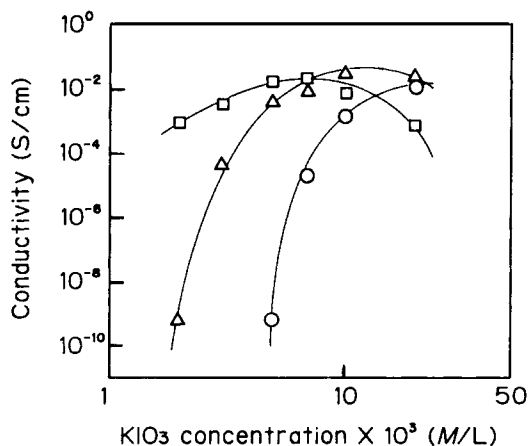Fig. 10. The film conductivity as a function of KIO_3 concentration at various HCl/KIO_3 ratios. (○) 6, (△) 20, (□) 50.
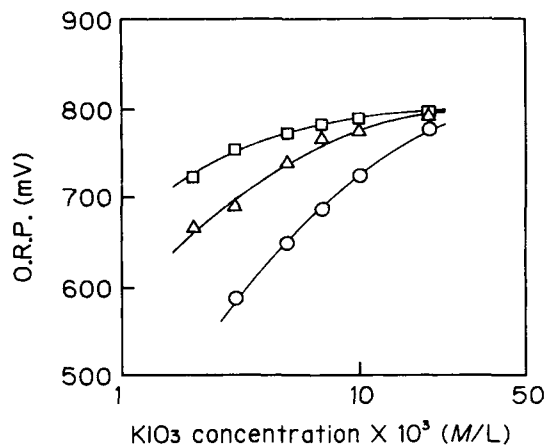
Fig. 11. The O.R.P. of the liquid membrane as a function of KIO_3 concentration at various HCl/KIO_3 ratios. (O) 6, (△) 20, (□) 50.

any HCl/KIO_3 ratio. And the O.R.P. increases with lower KIO_3 concentration at higher HCl/KIO_3 ratio. As shown in Figures 10 and 11, the film conductivity increases over 650 mV of O.R.P. and starts to decrease when the O.R.P. is raised over about 790 mV. The spectrum of the composite films prepared with KIO_3 and HCl have two absorption bands (800 and 420 nm), which is clearly below 500 nm and different from that of the films prepared with $FeCl_3$. Figure 12 shows the film absorbance at 800 nm as a function of KIO_3 concentration at various HCl/KIO_3 ratios. The absorbance increases with lower KIO_3 concentration at higher HCl/KIO_3 ratio, which means an increase in the amount of conductive radical cation component of polyaniline as mentioned before. The increasing rate of the absorbance is accelerated by protonation with the excess HCl. However, it starts to decrease with lower concentration of KIO_3 at higher HCl/KIO_3 ratio. An especially remarkable decrease of the absorbance
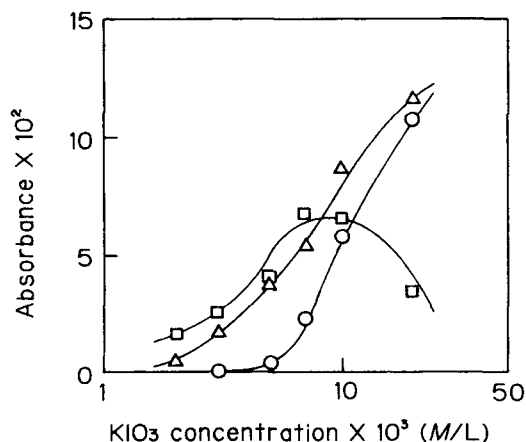

Fig. 12. The absorbance at 800 nm of the composite films as a function of KIO_3 concentration at various HCl/KIO_3 ratios. (O) 6, (△) 20, (□) 50.

is shown at 50 of the ratio. In order to make clear the spectral change of polyaniline under different preparative conditions, Figure 13 shows the ratio of the absorbance at 800 nm to the absorbance at 580 nm as a function of KIO_3 concentration at various HCl/KIO_3 ratios. The absorbance at 580 nm indicates the quinonediimine (oxidized-insulating) structure amount of polyaniline, as mentioned before. Hence, the absorbance ratio reflects the composition ratio of the radical cation component to the quinonediimine component. As shown in Figures 10 and 13, the film conductivity is correlative with the absorbance ratio. Consequently, the film conductivity is determined by the absolute amount of the radical cation component of polyaniline and the composition ratio of the radical cation component to the quinonediimine component. These two values are due to the O.R.P. and the protonation effect of the liquid membrane, which depend on the KIO_3 concentration and the HCl/KIO_3 ratio. At higher $HCl/$ KIO_3 ratio, the film conductivity increases with lower concentration of KIO_3 in correspondence to the increase of the two values. However, the O.R.P. of the liquid membrane also increases with lower concentration of KIO_3 and the relative amount of the insulating-quinonediimine component increases. Especially, when the O.R.P. is raised over 790 mV, the quinonediimine component increases remarkably. As a result the film conductivity turns to decrease.

Figure 14 shows the transmittance of the composite films as a function of KIO_3 concentration at various HCl/KIO_3 ratios. The transmittance decreases with an increase of KIO_3 concentration at any HCl/KIO_3 ratio. With regard to the KIO_3 concentration region where conducting film is formed, the transmittance vs. the conductivity is higher at higher HCl/KIO_3 ratio. Particularly, the formed polyaniline tends to be agglomerated partially in the composite film when HCl concentration is deficient. Therefore, the excess proton acid contributes to the film transmittance by uniform distribution of polyaniline in the composite film, aside from its contribution to the conductivity by increase of the radical cation component at the suitable concentration of the oxidizing agent, does not significantly raise the O.R.P.
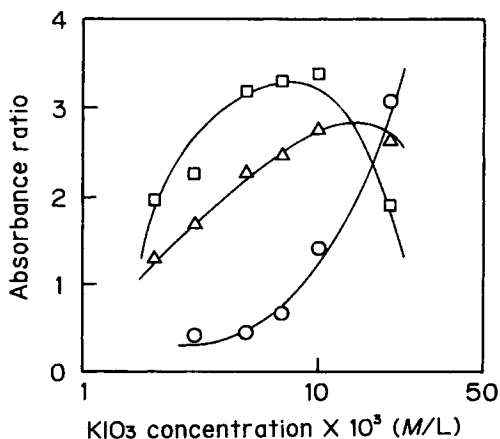

Fig. 13.   The absorbance ratio (= absorbance at 800 nm/absorbance at 580 nm) of the composite films as a function of KIO_3 concentration at various HCl/KIO_3 ratios. (○) 6, (△) 20, (□) 50.

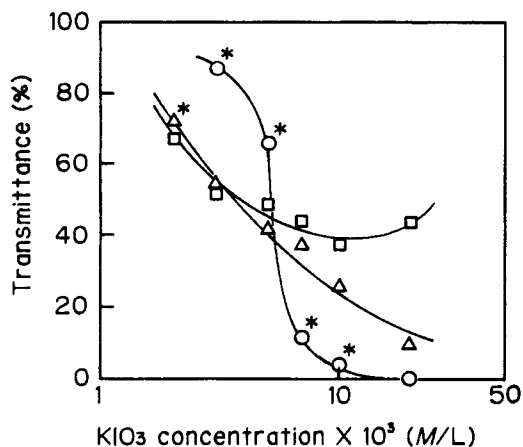Fig. 14. The transmittance of the composite films as a function of KIO_3 concentration at various HCl/KIO_3 ratios. (O) 6, (△) 20, (□) 50. The superscript (*) represents a partial agglomeration of polyaniline in the composite film.

CONCLUSION

Electroconducting polyaniline–water-soluble matrix polymer composite films are prepared by chemical oxidative polymerization at gas/liquid interface. The conductivity and transmittance of the composite films depend on the aniline exposure time, atmospheric and aniline temperatures, chemical species of the oxidizing agent, and concentration of the coexisting proton acid. When the composite film is prepared with a constant concentration of oxidizing agent and proton acid (with a constant concentration of $FeCl_3$) under the other conditions changed, the film conductivity is correlated with the absorbance at 800 nm (formation of the radical cation structure of polyaniline). On the other hand, when the film is prepared with various concentrations of the oxidizing agent at different proton acid/oxidizing agent ratios (with various concentration of KIO_3 at various HCl/KIO_3 ratios) under the other conditions constant, the film conductivity depends on the O.R.P. and proton acid concentration of the liquid membrane. The conductivity increases to saturation, and then turns to decrease with lower concentration of the oxidizing agent at higher proton acid/oxidizing agent ratio in this system. Because the film conductivity is determined by the absolute amount of the radical cation component of polyaniline and the composition ratio of the radical cation component to the quinonediimine component, the amount and ratio depend on the concentration of oxidizing agent and proton acid in the liquid membrane. Moreover, film transmittance vs. conductivity is higher at higher proton acid/oxidizing agent ratio. The excess proton acid, therefore, contributes to the film transmittance aside from its contribution to conductivity.

As mentioned above, the composite film with both high conductivity and transparency is obtained by optimizing the preparative conditions. Transparency of conducting material is an important factor for construction of optoelectronic devices. Furthermore, in terms of industrial production, the conducting film by this chemical method can be prepared in large scale in comparison with

electrochemical process. The film has high mechanical strength and flexibility because it is a composite with a strong and flexible matrix polymer. We hope this preparative method will be useful for practical applications with polyaniline.

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