Electrical Conductivity of Chemically Dehydrochlorinated Poly(vinyl Chloride) Films Doped with Electron Acceptors

HIDEO KISE, MASAHIKO SUGIHARA, and FEI-FENG HE, *Institute of Materials Science, University of Tsukuba, Sakura, Niihari, Ibaraki 305, Japan*

Synopsis

Poly(vinyl chloride) (PVC) films were effectively dehydrochlorinated by the reaction with aqueous sodium hydroxide solutions in the presence of tetrabutylammonium bromide (TBAB) or tetrabutylphosphonium bromide (TBPB). The obtained black films were doped with iodine, ferric chloride, or boron trifluoride. By doping, the electric conductivity markedly increased up to the order of 10^{-3} S cm^{-1}. The activation energy of the conduction was 0.36 eV. The effects of casting solvent, film thickness, and film drawing are described. The change in IR spectrum by doping was discussed in terms of the formation of positively charged polyenes due to electron transfer from the dehydrochlorinated PVC to the dopants.

INTRODUCTION

The formation of conjugated polyenes by thermal degradation of poly(vinyl chloride) (PVC) has been well established. The treatment of PVC solutions with organic or inorganic bases also affords dehydrochlorinated products.[1-9] Recently, the direct treatment of PVC powder or film with aqueous alkaline solutions under phase transfer reaction conditions was reported to give rise to HCl elimination in fairly good conversions.[10] Although the investigation of dehydrochlorinated PVC by IR and UV–VL spectroscopy revealed that the mean number of the conjugated C—C double bond is mostly below 15,[2,3,5-17] the structural resemblance to polyacetylene induced us to examine the electrical conductivity of the dehydrochlorinated PVC.

The polymerization of acetylene with various organometallic catalysts affords cis or trans polyacetylene films with electrical conductivity ranging from 10^{-9} (cis) to 10^{-5} S cm^{-1} (trans).[18] The treatment (doping) of polyacetylene films with electron acceptors such as iodine or arsenic pentafluoride markedly increases the conductivity up to the order of 10^2 S cm^{-1}.[18,19] The large increase in the conductivity has been ascribed to the formation of charged polyenes along the polymer chains by electron transfer from polyacetylene to the acceptors.[20,21]

This paper describes the dehydrochlorination of PVC films by the reaction with aqueous NaOH solutions under phase transfer conditions, and the effects of doping with several electron acceptors on the conductivity of the films. Although the dehydrochlorination of PVC has been extensively studied, only a small number of reports on the electric properties of the products

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have appeared. The reaction products with lithium chloride in DMF[3] or sodium amide in ammonia[4] exhibited semiconductivity. The insolubility of the powder products made it necessary to study the conductivity in the form of compressed pellets. The phase transfer reaction is a simple and versatile method in that PVC films can be dehydrochlorinated by aqueous base solutions eliminating the difficulties of forming pellets or discs from powder products.

EXPERIMENTAL

Materials

PVC samples were kindly provided by Mitsubishi Petrochemical Co. and Asahi Garasu Co. and used without further purification. The chlorine content was 56.72%. PVC films were prepared by casting 7–10% THF solutions onto a glass plate and drying them in a desicator for 2–3 days, followed by further drying under vacuum for 24 h. Some of the films were cast from THF solutions containing tetrabutylphosphonium bromide (TBPB); the molar ratio of vinyl chloride unit to TBPB was 37. The porous films were obtained by casting 8% DMF solutions of PVC onto a glass plate and drying them in air for about 30 min until the films became opaque. Then the films were immersed in water for 1 h and dried under vacuum.[22] The drawing of the films was performed uniaxially using a Shibayama SS-60 instrument at 120°C.

TBAB and TBPB were recrystallized from ethyl acetate. Guaranteed grade of iodine, ferric chloride, and boron trifluoride etherate (47%) were used as purchased.

Dehydrochlorination of PVC Films

In a typical experiment 0.24 g (76 mmol) of TBAB was added to a solution of 5 g (0.22 mol) NaOH in 20 mL water, and the solution was stirred magnetically at 70°C for a few minutes. Then a PVC film (10 × 20 mm) was added, and the mixture was stirred at the same temperature for 24 h. Then the black film was washed thoroughly with water and dried under vacuum. The degree of dehydrochlorination (conversion) was calculated on the basis of the decrease in the weight of the films.

When the reactions were followed by the change in UV–VL spectra, the films were reacted at 60°C using 16% NaOH solution and 15 mM TBPB as a catalyst, and the absorbance at 400–430 nm was measured at intervals.

Doping and Conductivity Measurement

The conductivity of dehydrochlorinated PVC films was measured on 6 × 10 mm samples by two-probe d.c. technique in a glass vessel saturated with iodine vapor. The four-probe technique gives more reliable values, but in the present study the differences between the conductivities measured by two- and four-probe methods were within the experimental error. The platinum wire (0.3 mm diam) were used as electrodes which were attached to the films with Electrodag 502. The temperature of the vessel was regulated

with a thermostated water bath. The resistivity across the electrodes was measured at intervals with a Takeda Riken Digital Multimeter TR 6856. Some of the measurements were made with an additional piece of polymer film without electrodes in order to measure the weight increase of the film by doping. Temperature dependence of resistivity was determined by doping a film by the above method for a given time and then transfering it to another glass vessel to measure the resistivity.

In the case of $FeCl_3$ doping, a dehydrochlorinated PVC film was immersed in a nitromethane solution of $FeCl_3$ at room temperature for a given time. The range of $FeCl_3$ concentration was 0.25–1.5M. The film was dried under vacuum and the resistivity was measured by the above method. BF_3 doping was conducted by placing a dehydrochlorinated PVC film about 10 mm above the surface of a BF_3 etherate solution at 30°C.

RESULTS AND DISCUSSION

Dehydrochlorination of PVC Film

Thermal and radiolytic degradation of PVC have been the subjects of extensive studies in view of the improvement of the stability of the polymer. The initial process is the elimination of HCl to form polyene structure. The UV–VL analyses of low conversion products revealed that the number of conjugated C—C double bond has a distribution ranging from 2 to 15.[13–17]

In the case of chemical degradation of PVC in solutions by organic or inorganic bases, such as DMF or potassium t-butoxide, the polyene distribution was similar to that found in thermally or radiolytically degraded PVC.[5–9,11,12] Since the solubility of highly degraded PVC is very low, the UV–VL analyses have been limited to the low conversion products.

When a PVC film was treated with an aqueous NaOH solution in the presence of TBAB or TBPB, color development was observed in the polymer in a few minutes. The absorption spectra of the reacted films had broad bands with maxima at 400–430 nm without fine structure. The maximum wave length was almost independent of the degree of the reaction, implying that the distribution of the conjugated polyene length is almost constant during the reaction. The lack of the fine structure in the spectra was also reported for the dehydrochlorination products by sodium amide in ammonia[23] and by DMF.[7] The distribution of the individual sequence of conjugated polyenes could not be calculated, but the absorption maxima around 400–430 nm indicates that the mean number of conjugated double bond is 9–10.[3,6,11,13–16] The reaction conditions, such as temperature, base, and catalyst concentration, had little effects on the polyene distribution.

Although studies on the mechanism of the basic dehydrochlorination of PVC are very few and the present study is not intended to obtain evidence for a specific mechanism, the above result seems to support the "zipping" mechanism in which the α-position relative to a double bond is activated leading to a kind of chain reaction rather than stepwise mechanism.

The structural defects in the original PVC polymer, such as branching and head to head structure, may be responsible for the short polyene length, since the propagation of the polyene structure would be inhibited by these

defects. However, recent studies on the structural defects in PVC revealed that the average number of these defects is very small; the total of branches is less than 5 per 1000 carbons,[24,25] and the content of internal head to head structure is less than 2 per 1000 monomer units.[26]

A more likely reason for lowering the polyene conjugation is the initiation of the reaction at more than one site in a polymer chain. For a simplified reaction scheme two growing polyenes would have equal opportunity to form a conjugated or nonconjugated polyene sequence at the growing ends. Thus random initiation along a polymer chain would lower the average number of double bonds in conjugation. As the allylic activation of the dehydrochlorination becomes smaller, the longer and the more stabilized by resonance the adjacent polyene sequence is.[15] This would lead to the termination of the "zipping" reaction enhancing the random initiation and therefore causing the lowering of the polyene length.

Another possibility is the inter- or intramolecular cyclization due to the Diels–Alder mechanism. This has been suggested for the crosslinking of polyacetylene,[27] but no evidence for this process was obtained in the present dehydrochlorination of PVC.

The rate of dehydrochlorination reaction of PVC films prepared under different conditions was estimated by following the change in the absorbance. The reaction without catalyst is very slow (Fig. 1), while the reactions of THF- or TBPB-containing films were faster than neat film. Under phase transfer conditions THF in the film may be replaced by aqueous NaOH solution giving a porous film and therefore larger surface area to be reacted than dry films.

The catalytic activities of TBAB and TBPB were comparable. Since the stability of TBAB in alkaline solutions is higher than TBPB, most of the reactions were carried out using TBAB. The degree of dehydrochlorination (conversion) was estimated by weight decrease of the film and controlled by reaction time, and conversion up to 90% was obtained for 20 μm thick film.
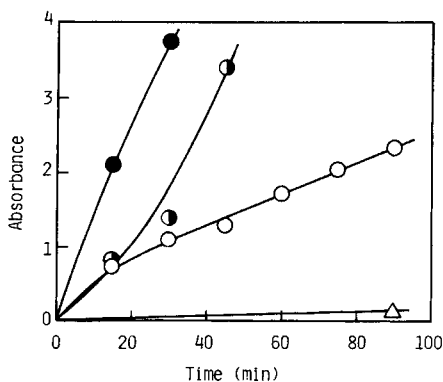

Fig. 1.   Change of absorbance of PVC films during dehydrochlorination under phase transfer conditions (400–430 nm). 16% NaOH, TBPB 15 mM, 60°C: (△) without catalyst; (○), dry film; (◑) THF-containing film; (●) TBPB-containing film.

Iodine Doping

When a dehydrochlorinated PVC film was exposed to iodine vapor, a marked increase in conductivity was observed. Some typical examples of time-conductivity curves are shown in Figure 2. Conductivity levels off within 6 h, and stays constant for the following 15 h. The conductivity is independent of the degree of dehydrochlorination, but rather depends largely on the thickness of the film. Thinner films exhibit higher conductivity (Table I) since the films were not fully reacted as revealed by the IR spectra which show unreacted C—Cl bands around 620 and 690 cm^{-1} (Fig. 4). The conductive portion is limited to near the surface of the thick films.

The degree of polymerization had little effect on the conductivity as manifested by the comparison between the samples of $\overline{P}$ = 700 and 1300, and a film which was cast from a DMF solution exhibited comparable conductivity to a THF-cast film. Moreover, a porous film, which was prepared by casting a DMF solution of PVC followed by leaching in water, absorbed more than twice as much iodine by weight as the film, but the conductivity showed only a small increase compared to the nonporous and low iodine content films. Table II lists the results for the conductivity measurement on drawn PVC films. The thickness of films is not constant, but there is a tendency that drawing increases conductivity, though not as much as expected, along the drawing axis.

The effect of temperature on conductivity is shown in Figure 3. The temperature range of the linear relationship between $1/T$ and log σ is too
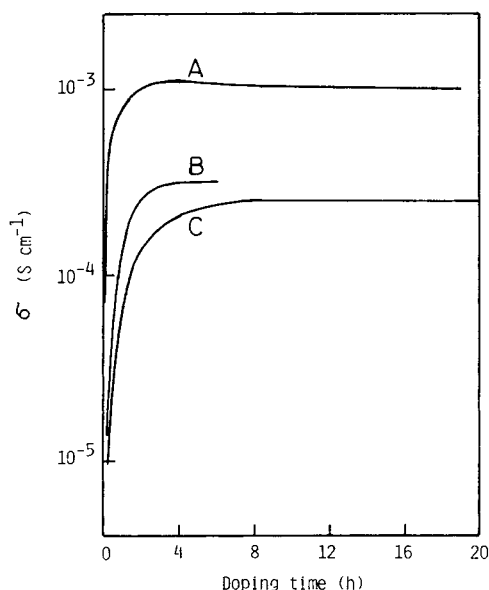

Fig. 2.   Conductivity of I$_2$-doped films. Dehydrochlorinated by 20% NaOH and 38 mM TBAB at 70°C. Film thickness (μm) and reaction time (h) are: (A) 36, 24; (B) 41, 5; (C) 46, 48.

TABLE I
Conductivity of Dehydrochlorinated PVC with Iodine[a]

$\bar{P}$	Casting soln	Reaction time (h)	Thickness (μm)	I_2/polymer (wt/wt)	$\sigma \times 10^3$ (S cm^{-1})
700	THF	24	138	—	3×10^{-3}
700	THF	24	138	0.20	0.131
700	THF	48	46	0.32	0.264
700	THF	5	41	0.08	0.338
700	THF	24	36	0.41	1.15
1300	THF	24	60	—	0.15
1300	THF	24	25	—	1.25
700	DMF	24	123	0.05	0.124
700	DMF—H$_2$O[b]	24	85	2.45	0.315

[a] Dehydrochlorinated with 20% NaOH and 31–38 mM TBAB at 70°C for 24 h, and doped with iodine at 30°C.
[b] Porous film.

narrow to give a reliable activation energy of conduction, but the approximate value was calculated to be 0.36 eV. The value is much smaller than that for PVC (glass state, 18 kcal mol^{-1}),[28] and comparable to those of undoped polyacetylene[29] or high temperature decomposed polyacrylonitrile.[30] The reason of the leveling off of the conductivity at higher temperatures is not clear, but it is most likely due to the irreversible addition of iodine to the C—C double bonds.

Figure 4 shows a dramatic change in the IR spectra of dehydrochlorinated PVC films before and after iodine doping. The characteristic bands of conjugated C—C double bonds (1580 and 1000 cm^{-1}) largely diminished and new bands appeared at 1440, 1090, and 980 cm^{-1}. Polyacetylene films prepared by Shirakawa's method are semiconductive, but by doping with electron acceptors, such as iodine and arsenic pentafluoride, the conductivity increases over 7 orders of magnitude. Harada et al. investigated the change in the molecular structure of polyacetylene by doping using β-carotene as a model compound.[31] They reported that by addition of iodine to β-carotene new broad bands appeared at 1464, 1122, and 972 cm^{-1} [Fig. 4(D)]. Considering the observation of Raman scattering by anionic species such as $(I_3^-)_x$ and I_5^-, these bands were assigned to the molecular vibration of the cationic portions formed by electron transfer from β-carotene to iodine.[31] The frequency and relative intensity of the bands of iodine-doped dehy-

TABLE II
Effect of Drawing on Conductivity[a]

$\bar{P}$	Casting soln	Drawing ratio	Thickness (μm)	$\sigma \times 10^3$ (S cm^{-1})
1300	THF	1	60	0.150
1300	THF	4	82	0.427
1300	THF	7	109	0.688

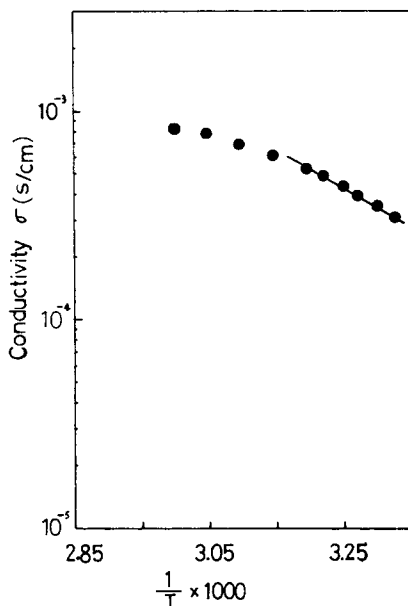[a] Reaction and doping conditions are the same as Table I.

Fig. 3. Effect of temperature on conductivity of I_2-doped film (25 μm). Dehydrochlorinated by 20% NaOH and 31 mM TBAB at 70°C for 24 h.

drochlorinated PVC are very similar to those of iodine-doped β-carotene. Charge transfer from dehydrochlorinated PVC to iodine is responsible for the large increase in conductivity of the film. The mean length of conjugated polyene sequence in the dehydrochlorinated PVC is close to that of β-carotene (9 conjugated transpolyene with terminal ionone groups) as deduced from the absorption wave length described above.

FeCl₃ and BF₃ Doping

When a dehydrochlorinated PVC film was treated with a nitromethane solution of $FeCl_3$, rapid increase in conductivity was observed. However, prolonged treatment with the solution caused a large decrease in conductivity giving a maximum in the time-conductivity curve as shown in Figure 5. The maximum conductivity was obtained at around 15 min for 0.5M solution. With a constant doping time, conductivity increased with increasing $FeCl_3$ concentration up to 1.5M (Fig. 6). The decrease in the conductivity by excess doping was also reported for polyacetylene.[32] The Mössbauer spectroscopic study made by Sakai et al.[33] indicated the formation of $FeCl_2 \cdot nH_2O$ ($n = 1$ and/or 2) and $FeCl_4^-$ presumably by the electron transfer and hydration by the water in the solvent:

$$FeCl_3 + e^- \rightarrow FeCl_2 + Cl^-$$

$$FeCl_3 + Cl^- \rightarrow FeCl_4^-$$
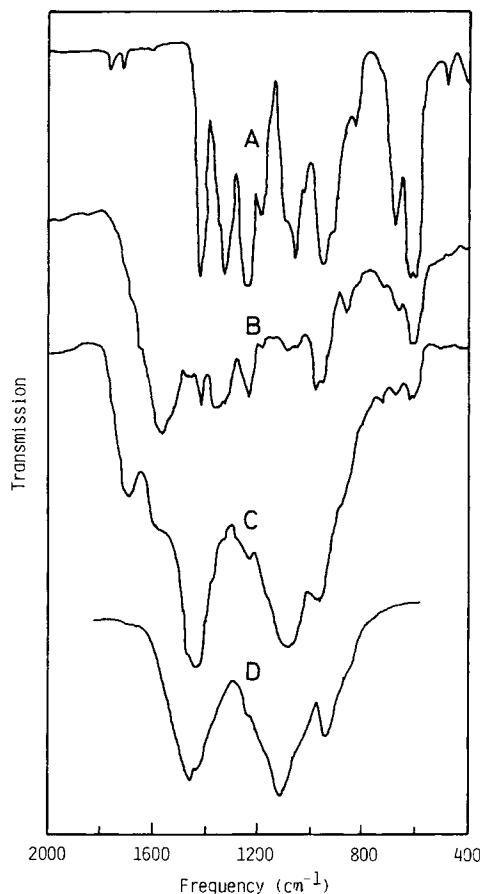
$$FeCl_2 + nH_2O \rightarrow FeCl_2 \cdot nH_2O$$
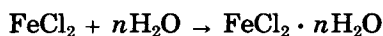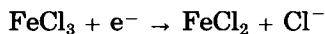
Fig. 4. IR spectra of films: (A) intact PVC; (B) dehydrochlorinated PVC (conversion 84%); (C) after doping B with iodine; (D) iodine doped β-carotene.[31]

The FeCl$_3$-doped dehydrochlorinated PVC exhibited a very similar IR spectrum to that of I$_2$-doped one (Fig. 7). New bands appeared at 1450, 1110, and 980 cm^{-1} at the expense of the bands at 1580 and 1000 cm^{-1}. This implies the formation of almost identical charged polyene structure by doping with I$_2$ and FeCl$_3$.

The decrease in the conductivity in higher doping with FeCl$_3$ is due to the addition reaction of chlorine to C—C double bonds. The change in the C—Cl stretching bands is not clear; but the band at 1450 cm^{-1} diminished, and the intensity of the bands at 1500–1600 cm^{-1} increased by prolonged doping with FeCl$_3$ (Fig. 7). The decrease in the polyene length is due to some chemical reactions such as chlorine addition.

A different kind of reaction between the dehydrochlorinated PVC and FeCl$_3$ is also possible which involves the abstraction of unreacted chlorine in the polymer by FeCl$_3$ to form a positively charged polymer and FeCl$_4^-$. If the chlorine is on the α-position to C—C double bond, especially between two separated ones, the reaction would largely contribute to conductivity because of the elongation of conjugation by the formed carbonium ion:
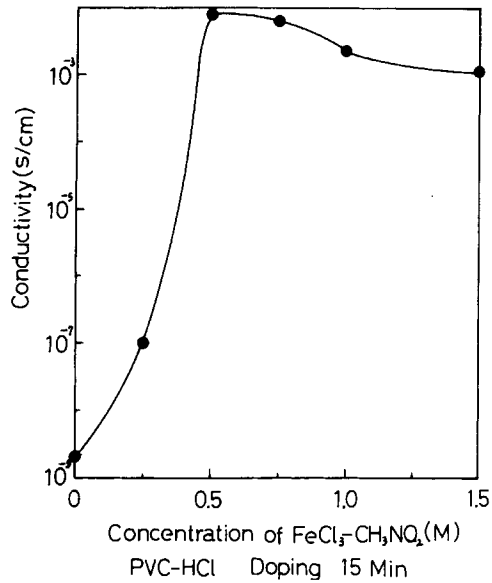
Fig. 5. Effect of $FeCl_3$ doping time. Films (28–35 μm) were dehydrochlorinated by 20% NaOH and 31 mM TBAB at 70°C for 24 h.

$$ -CH=CH-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH=CH- \; + \; FeCl_3 \longrightarrow -CH=CH-\overset{+}{CH}-CH=CH- \; \overset{+}{} + FeCl_4^- $$

$$ \updownarrow $$

$$ -CH=CH-CH=CH-\overset{+}{CH}- \quad etc. $$

Since Berets and Smith[34] reported that the exposure of polyacetylene to BF_3 appreciably increased its conductivity, the doping of dehydrochlorinated PVC with BF_3 was examined. The effect on conductivity was comparable to I_2 or $FeCl_3$ (Table III). BF_3 has a vacant p orbital and forms 1:1 complexes with various electron donors. Although no further study on the reaction mechanism of polyenes with BF_3 was made, it is probable that a charge-transfer complex was formed between the dehydrochlorinated PVC and BF_3. Chlorine abstraction mentioned above is also possible for BF_3.

Fig. 6. Effect of FeCl$_3$ concentration. Reaction conditions are the same as for Figure 5.

In general the doping of dehydrochlorinated PVC films with some kinds of electron acceptors markedly increases the electric conductivity. The use of phase transfer catalyst reaction and doping by the above method enable us to produce semiconductive films of desired size and thickness from PVC.
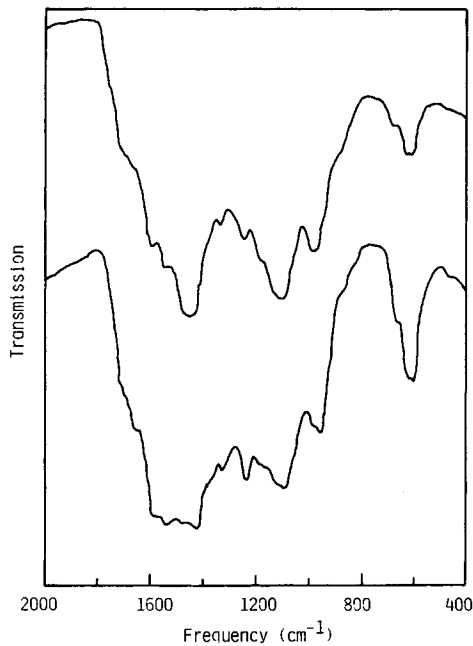

Fig. 7. IR spectra of FeCl$_3$(0.5M)-doped films. Conversion (%) and doping time (min) are 90, 15 (upper) and 83, 30 (lower).

TABLE III
Conductivity of Dehydrochlorinated PVC Doped with $FeCl_3$ or BF_3OEt_2[a]

$\bar{P}$	Conversion (%)	Dopant	Doping time (min)	Thickness (μm)	$\sigma \times 10^3$ (S cm^{-1})
700	37	$FeCl_3$[b]	15	65	1.16
700	37	$FeCl_3$	60	65	0.58
1300	60	$FeCl_3$	15	30	1.13
1300	92	$FeCl_3$	15	30	3.70
1300	73	BF_3OEt_2	240	30	1.03

[a] Dehydrochlorinated with 20% NaOH and 30 mM TBAB at 70°C for 24 h.
[b] 1.5M $FeCl_3$ in nitromethane.

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