Synthesis, Structure, and Properties of Conjugated Polyene Films by Dehydrochlorination of PVC Films

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INTRODUCTION

It is well known that poly(vinyl chloride) is easily transformed into conjugated polyenes by dehydrochlorination.[1-3] The dehydrochlorination also takes place only by heating.[4] However, the dehydrochlorination by the chemical method using catalysts is necessary to get highly conjugated polyenes. Tsuchida et al.[1] obtained a completely dehydrochlorinated polyene material by treating PVC with sodium amide in liquid ammonia. Soga et al.[2] obtained a polyene material having electrical conductivity of 10^{-8} S/cm by treating PVC with 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), which is the strongest organic base so far known. Yamamoto et al.[3] tried a surface dehydrochlorination of PVC films.

In this study we are interested in the dehydrochlorination of solid PVC. As is well known, polyene has no good solvents to make the solution without any noticeable degradation, and also it does not melt before it is decomposed thermally. These properties of polyene make the casting and molding difficult. If we can dehydrochlorinate solid PVC, without dissolving it into the solvent, what we must do is only to prepare the PVC specimens with suitable shape and size and also with the most suitable fine structure as the precursor of polyenes. Molecular orientation and the crystallinity may be important factors controlled in PVC specimens. In this work our attention is concerned with the general features of the dehydrochlorination using DBU, with particular interest in (1) the effect of solvent to swell PVC film during the reaction and (2) the fine structure of dehydrochlorinated specimens.

EXPERIMENTAL

Sample and Reagents. PVC films about 10 μm thick were cast from THF (1–3 wt %) solutions of a commercial PVC ($\overline{\mathrm{DP}} = 1100$, Mitsubishi Kasei Co.). Strips 15 mm wide and 35 mm long were cut from the film, and some of them were drawn six times with a manually operated device. Dimethylformamide (DMF), cyclohexanone (CHN), tetrahydrofuran (THF), methyl ethyl ketone (MEK), and o-dichlorobenzene (ODB) were used as swelling solvents, and methanol (MeOH) was used as a nonsolvent. DBU

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was used as a reagent for the dehydrochlorination. They were all purified by distillation and stored under nitrogen.

Dehydrochlorination. Schlenk flask techniques, inert atmosphere, and vacuum line techniques were applied throughout this work.

In a typical reaction, 15 mg of PVC film (2.4×10^{-4} mol) was placed in 100 mL of DMF–MeOH mixture (2:3) in a Schlenk flask. After the film became sufficiently swollen in the mixture, 5 mL of DBU (3.4×10^{-2} mol) was added to the mixture. The system under N_2 atmosphere was then shaken at 50°C for about 36 h. This is called the first-step treatment. For the second-step treatment, the solvent was replaced by pure DMF and the same amount of DBU as in the first-step treatment. The second-step treatment proceeded for 24 h under the same conditions as the first-step treatment. Then, specimen films were washed several times with MeOH and dried *in vacuo*. The DBU concentration in the DMF–MeOH solvent and the reaction time were varied in the first-step treatment. In order to improve the dehydrochlorination, some specimens were heat-treated at 80–180°C after the first-step treatment. For comparison, *trans*-polyacetylene (tr-PA) films were prepared by the method of Ito et al.[5]

Iodine doping was carried out by exposing the dehydrochlorinated PVC films and tr-PA films to iodine vapor of a known pressure at room temperature *in vacuo* or in a nitrogen atmosphere.

Measurement. Infrared spectra were measured with a Hitachi EPI-G3 Spectrometer under a nitrogen atmosphere in order to prevent the oxidation of films. The degree of dehydrochlorination was estimated from the elemental analysis data. Visible and near IR spectra were measured with a Hitachi EPI-3T Spectrometer. Electron spin resonance was measured on a JEOL ESR-3BX. X-ray measurements were carried out using Ni-filtered CuKα radiation. Electrical conductivity was measured by a four-probe technique in the same way as in previous paper.[6]

RESULTS AND DISCUSSION

The First-Step Treatment

During the first-step treatment, the transparent PVC film becomes yellow to red and finally slightly shiny black. Figure 1 shows the infrared spectra of dehydrochlorinated PVC films with various degrees of dehydrochlorination and of original PVC and tr-PA films. For the dehydrochlorinated films, the intensities of the characteristic absorption bands of PVC (ν_{C-Cl},600–700 cm^{-1}) are decreased by dehydrochlorination and new bands appear at 1010 and 3015 cm^{-1}, which are assigned to the C—H out-of-plane deformation of conjugated trans double bonds and the C—H stretching in unsaturated carbon, respectively, by comparison with the assigned absorption spectrum of tr-PA.[7]

The C—H out-of-plane bands remain at 1010 cm^{-1} independently the degree of dehydrochlorination. This implies that the conjugated double bonds are formed through a zipper mechanism, as reported previously.[1,7]
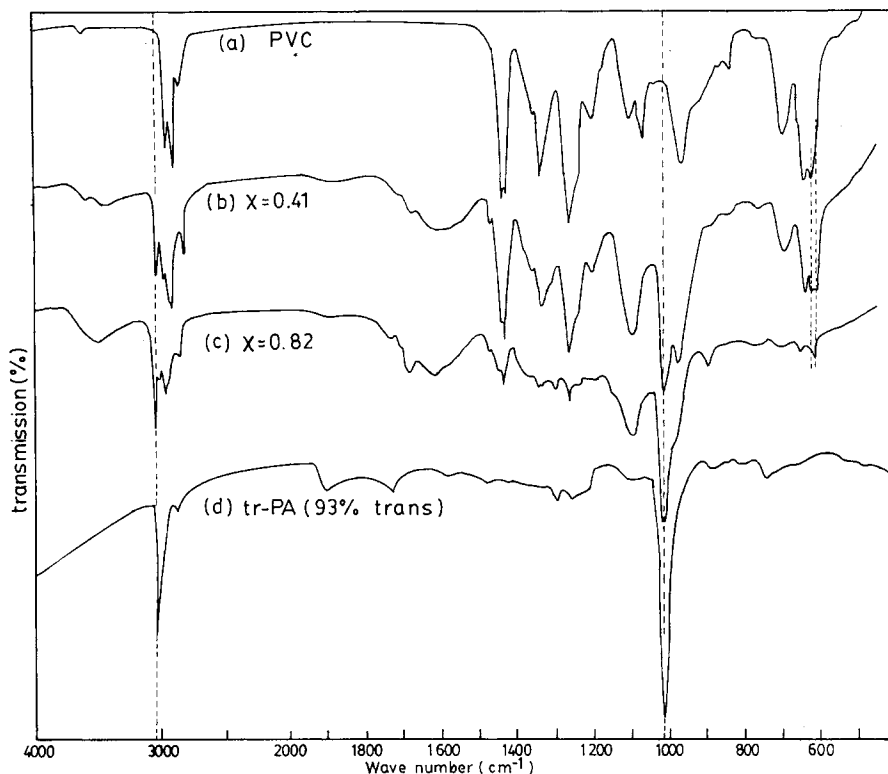
Fig. 1. IR spectra of (a) original PVC, (b) dehydrochlorinated PVC films (χ = 0.41), (c) dehydrochlorinated PVC film (χ = 0.82), and (d) tr-PA.

The calculation of the normal vibrations[8] indicates the formation of conjugated chain with the number of conjugation greater than 5.

Figure 2(a) shows the degree of dehydrochlorination as a function of DBU concentration in DMF–MeOH at a fixed (DBU)/(vinyl chloride monomer unit) molar ratio of 4 and reaction time of 72 h. The conversion increases with DBU concentration. When the concentration of DBU is higher than 0.2 v/v, films are dissolved into the solution. Figure 2(b) shows the conversion as a function of reaction time at the DBU concentration of 0.05 v/v and DBU/Cl molar ratio of 4. The degree of dehydrochlorination increases with increasing time until 40 h and then reaches the saturated value of 0.8 under these conditions.

It has been known that the conjugated double bonds are introduced when PVC is dehydrochlorinated by heat treatment.[4] Thus, samples prepared by the first-step treatment were heat-treated at 80°C, 130°C, or 180°C for 4 h *in vacuo*. Figure 3 shows the effect of heat treatment on the conversion. The film became somewhat brittle when treated at 180°C. Points on the left margin in Figure 3 represent the conversion before heat treatment. The degree of dehydrochlorination is increased remarkably by heat treatment at 130°C and 180°C, while no increase in the conversion is observed at 80°C. However, the effect of heat treatment is small on the samples already highly
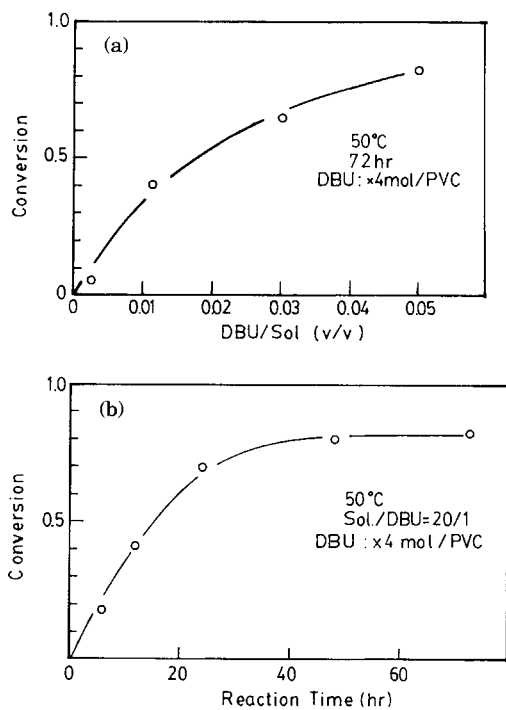
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Fig. 2. (a) Conversion as a function of DBU concentration in DMF–MeOH solution. (b) Conversion as a function of reaction time.
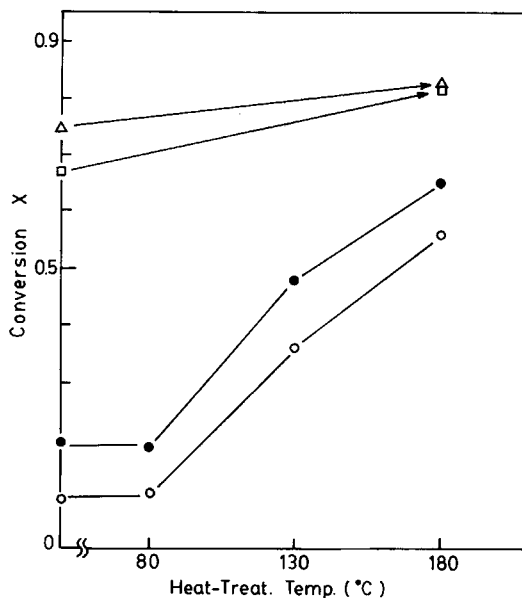

Fig. 3. Conversion as a function of heat-treatment temperature.

dehydrochlorinated by the prior chemical treatments. Figure 4 shows the IR spectra of the dehydrochlorinated films before and after the heat treatment. In the spectra of the heat-treated samples, a band at 605 cm^{-1} is clearly observed. This band has been observed for the highly dehydrochlorinated sample ($\chi = 0.82$) as seen in Figure 1, but not observed for the original untreated PVC film, which shows a band at 615 cm^{-1}. The band at 605 cm^{-1} is assigned to C—Cl stretching of crystalline PVC, while the band at 615 cm^{-1} is assigned to that of amorphous PVC.[9] These results imply that the amorphous phase is predominantly dehydrochlorinated and that the crystalline region remains unchanged after the first-step treatment and the heat treatment. Thus, we supposed that the maximum conversion of 0.8 achieved by the first-step treatment and the subsequent heat treatment would be related to the fact that the reaction took place only in the amorphous region. The crystallinity of PVC is not so high as usual crystalline polymers such as nylons and polyolefines. PVC is, however, still crystalline and the fraction of 0.2 resistant to the dehydrochlorination may be related to the crystalline region. DMF is a very strong solvent for PVC, and therefore a nonsolvent, MeOH, was added to DMF to control the solvent power. In the second-step treatment, pure DMF was used without nonsolvent as a swelling agent. It made the sole use of DMF possible that after the first-step treatment films were swollen but not soluble in any good solvent for PVC. We expected that in the second-step treatment the PVC crystals would be dissolved and chains thus dissolved would participate in the dehydrochlorination reaction.

The conversion increased up to 0.95 by the second-step treatment, as expected. Figure 5 shows the IR spectra for the specimen films before and after the second-step treatment. The band at 605 cm^{-1} almost vanishes,
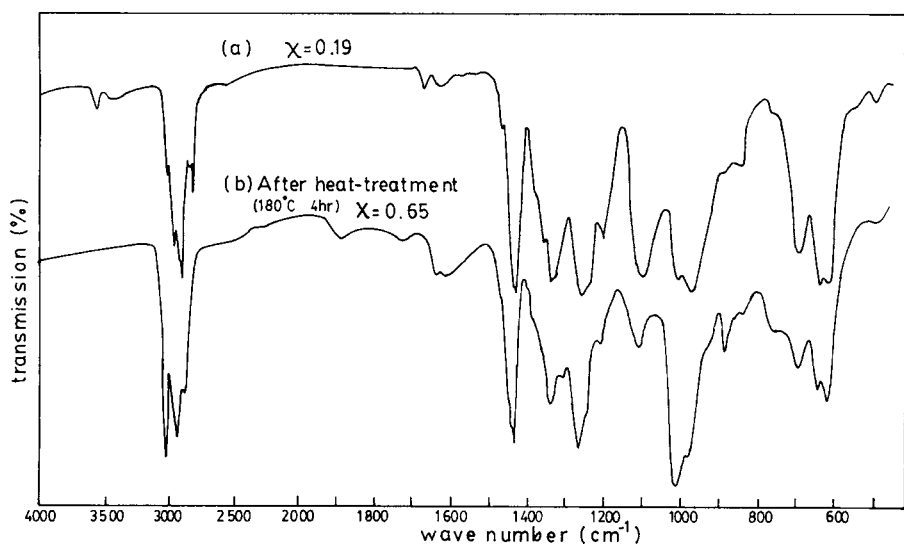

Fig. 4.   IR spectra of dehydrochlorinated PVC films (a) before heat treatment ($\chi = 0.19$) and (b) after heat treatment of (a) ($\chi = 0.95$).

indicating that the crystalline region is dehydrochlorinated in the second-step treatment. This reaction could occur because of the swelling of crystalline region by pure DMF. From this result we can conclude that highly dehydrochlorinated polyene films ($\chi = 0.95$) are obtained from PVC films by two-step treatment: The amorphous region is reacted in the first-step treatment, and the crystalline region is dehydrochlorinated in the second-step treatment.

Effect of Solvent

Figure 5 shows that the highly dehydrochlorinated polyene films have three absorption bands at 1665, 1720, and 3450 cm^{-1}. The bands at 1665 cm^{-1} and at 1720 cm^{-1} are carbonyl bands as reported by Shirakawa and Ikeda.[8] These are assigned to α,β-unsaturated ketone and isolated ketone chromophores, respectively. The absorption band at 3450 cm^{-1} corresponds to a hydroperoxy group (—OOH) and/or a hydroxy moiety.[10] As described above, the reactions are carried out in an inert atmosphere or *in vacuo*, and, therefore, the resultant oxygen bands were supposed to be caused by DMF, which was used as the swelling solvent. Thus the solvent effect on the reaction was studied with CHN, MEK, THF, and ODB. The procedure of the reaction was the same as in the case with DMF except for the mixing ratio of solvents to MeOH in the first-step treatment. The mixing ratios used were 0.39, 0.67, 0.50, and 1.27 for CHN, MEK, THF, and ODB, respectively, as determined from the reprecipitation experiments. Figure 6 shows the IR spectra for the highly dehydrochlorinated polyene films obtained in various solvent systems. The reaction rate in ODB–MeOH was very small even under the more severe conditions, and the second-step treatment was not tried. Since the characteristic absorption bands of PVC
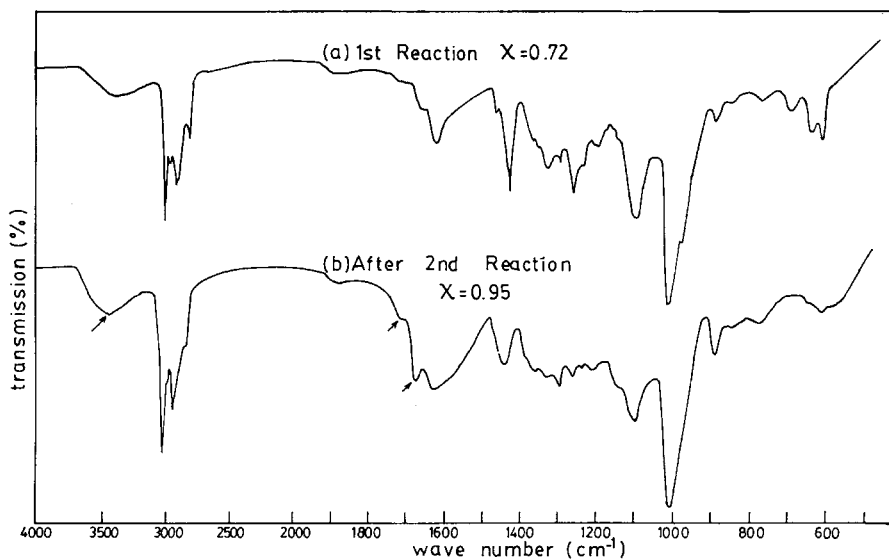

Fig. 5.   IR spectra of dehydrochlorinated PVC films (a) after first-step treatment ($\chi = 0.72$) and (b) after second-step treatment ($\chi = 0.95$).
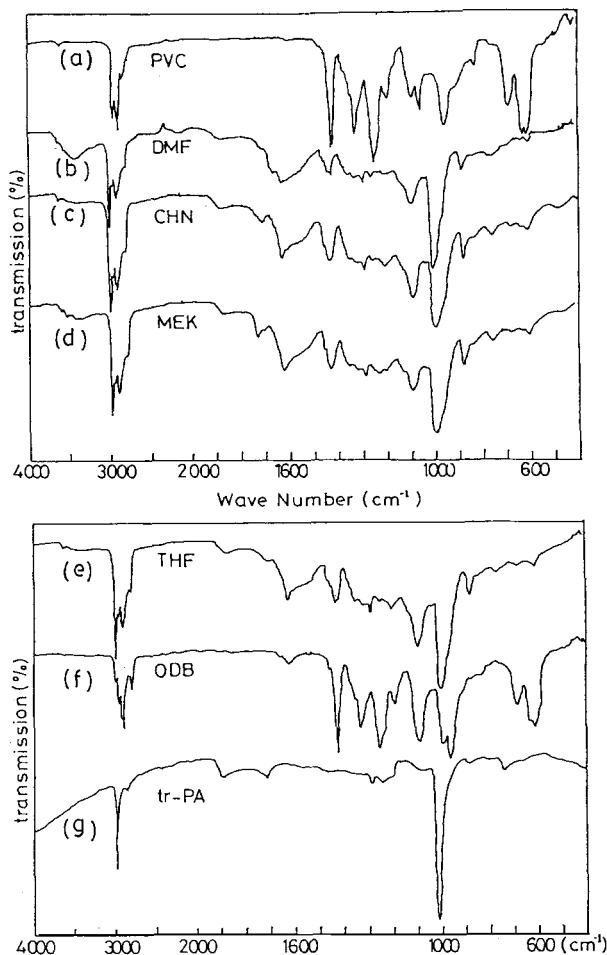
Fig. 6.   IR spectra of (a) original PVC film and dehydrochlorinated PVC films obtained in (b) DMF, (c) CHN, (d) MEK, (e) THF, (f) ODB, and (g) tr-PA. (The spectrum for ODB is that after the first-step treatment. See text.)

($\nu_{\text{C--Cl}}$) almost vanish and the bands assigned to the conjugated trans bonds (3015 cm^{-1} and 1010 cm^{-1}) appear strongly in the spectra, the dehydrochlorination reaction proceeds effectively, and the conjugated polyene sequences are formed in any solvent studied, except ODB.

It is noted that the bands related to the oxidation are not observed or very weak for the samples dehydrochlorinated in CHN, MEK, and THF, as compared with the sample in DMF. This suggest that the oxidation occurs in DMF because DMF is a strong dipolar solvent.

Dehydrochlorination of Oriented PVC Film

For dehydrochlorination of the oriented PVC film, drawn PVC films were fixed to stainless-steel holders to prevent shrinkage during the reaction. The reaction was performed under the same conditions as in the case of the undrawn films. The conversion of the drawn sample after the second-

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step treatment was 0.92, similar to that of the unoriented sample. The same solvent effect as discussed above was also noticed from the IR spectra. Figure 7 shows X-ray diffraction photographs of original PVC, polyene films obtained in DMF and CHN solvents and tr-PA. In the photographs for the two polyene films, the diffraction from PVC crystallite vanishes completely, and a very broad diffraction appears on the equator instead. This indicates that the polyene molecules are still oriented uniaxially to some extent after the dehydrochlorination, although the degree of orientation is not as high as the original PVC film. Figure 8 shows the equatorial X-ray diffraction intensity curves of PVC, the polyene film obtained in CHN and tr-PA. For the polyene film, a weak and broad peak at $2\theta = 22°$ (spacing 4 Å) is observed, while a peak at $2\theta = 19°$ is seen for the original PVC. The tr-PA has a strong and sharp peak at 22.4° assigned to the doublet of (110) and (200).[11] The peak of the polyene from PVC film is about five times broader than that of tr-PA. These results on the X-ray intensity suggest that the polyene obtained by dehydrochlorination of PVC is completely amorphous. It is well known that the PA obtained by polymerization of gaseous acetylene

PVC (λ=6)
(a)

PVC deHCl (DMF)
(λ=6)
(b)

Draw Direction

PVC deHCl (CHN)
(λ=6)
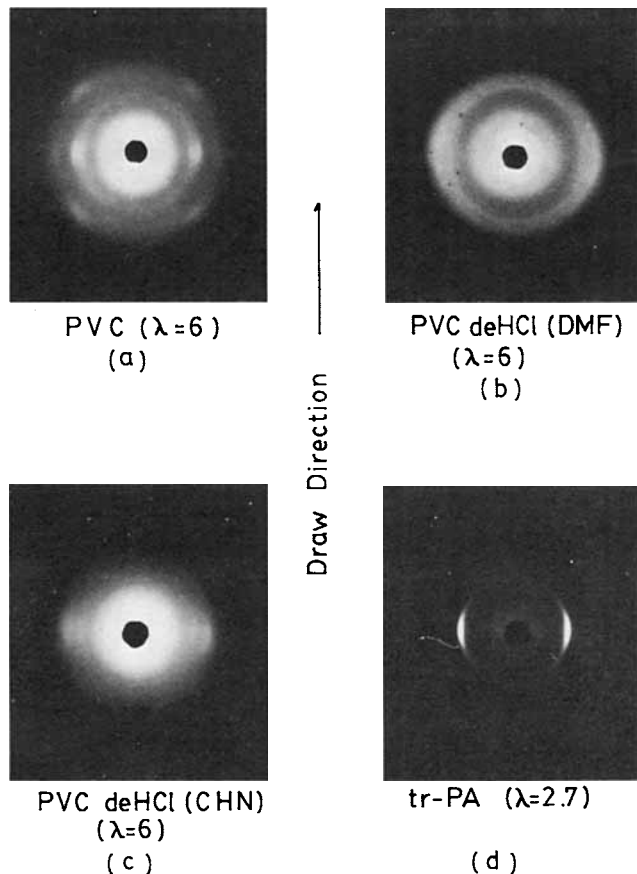(c)

tr-PA (λ=2.7)

(d)

Fig. 7. WAXS photographs of (a) original PVC ($\lambda = 6$), dehydrochlorinated PVC films obtained in (b) DMF ($\lambda = 6$), and in (c) CHN ($\lambda = 6$), and (d) tr-PA ($\lambda = 2.7$).
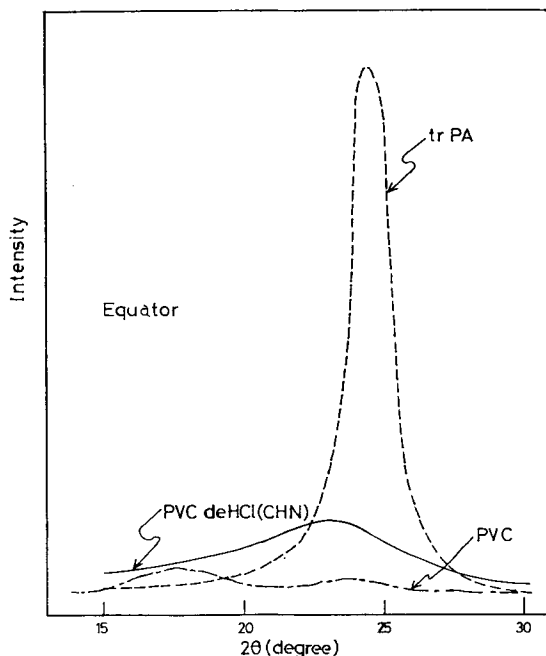
Fig. 8. WAXS intensity curves for PVC (— · —), dehydrochlorinated PVC film (— —), and tr-PA (———).

is the highest crystalline polymer ever known.[11] This poor crystallinity of the polyene from PVC may be due to the structural irregularities of original PVC such as in tacticity, branching, head to head linkage of vinyl chloride monomer units, as well as the imperfection of the dehydrochlorination.

VL-NIR Spectroscopy

A very thin film less than 1 μm thick was prepared on a slide glass by a spin casting method to measure the visible light and near infrared spectra of the dehydrochlorinated specimens. The film was dehydrochlorinated on the slide glass. Figure 9 compares a VL-NIR spectrum for a thin polyene film obtained in the two-step treatment in CHN with those of a thermally degraded PVC film and the original PVC film. The thermally degraded PVC film was obtained by the hot press molding at 180°C. The polyene shows a strong absorption in the region from 340 to ca. 500 nm and becomes transparent gradually as the wave length increases. The absorbance, normalized with thickness, of the polyene film in this region is surprisingly higher than those of the thermally degraded PVC film and the original PVC film. This is due to the formation of conjugated double bond sequences. For the thermally degraded PVC film, some fine structure are observed at shorter wave lengths. These fine structure has been assigned to the polyene sequences of different lengths by previous workers.[4] However, no significant fine structure is observed for the polyene film, as reported by Tsuchida et al. for the completely dehydrochlorinated PVC powder.[12] They supposed that the absence of the fine structure is due to the very wide distribution
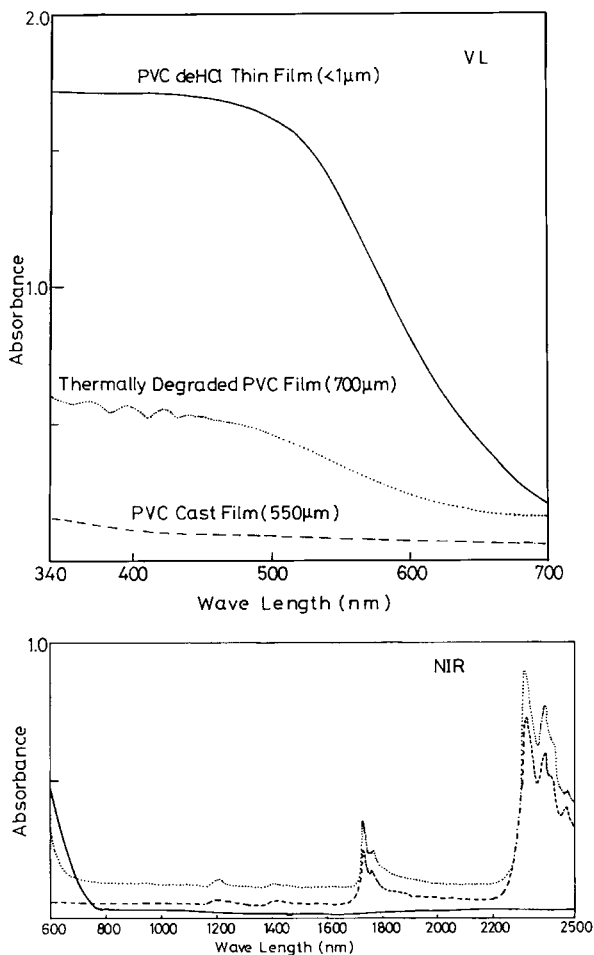
Fig. 9.   VL-NIR spectra of dehydrochlorinated PVC film (< 1 μm) (— —), thermally degraded PVC film ($\simeq$700 μm) ($\cdots$), and original PVC film ($\simeq$550 μm) (———).

of the conjugated chain length. Their interpretation may be true if the polyene sequence are formed through a zipper mechanism.

In the NIR region, the polyene film is completely transparent, while the thermally degraded PVC film and the original PVC film show absorptions at ca. 1700 nm and 2300 nm, which are assigned to the overtone and/or the combination bands of —CH_2—.[13]

ESR Measurement

Electron spin resonance (ESR) was measured at room temperature using the x-band. The sample was sealed into an ESR quartz tube *in vacuo*. DPPH was used as a standard in the estimate of the g-factor and the spin concentration. The estimated g-factor, spin concentration, and ΔH_{msl}, the half-width value, are summarized in Table I for the highly dehydrochlorinated polyene film treated in CHN and PAs. The data for the *cis*-PA by Shirakawa et al.[14] are quoted in Table I for comparison. A singlet signal without any

TABLE I
Results of the ESR Measurements for the Dehydrochlorinated PVC Film and PAs

	g-Factor	spin concn (spins/g)	ΔH_{msl} (gauss)
PVC deHCl film (CHN)	2.0032	5.66×10^{18}	10.25
tr-PA (93%)	2.0033	3.22×10^{19}	1.53
cis-PA (93%)[a]	2.0026	2.2×10^{18}	6.6

[a] Data by Shirakawa et al.[14]

fine structure is observed for both the polyene and tr-PA samples, while no significant signal can be observed for the original PVC film. The g-factor of the polyene film is very close to that of tr-PA. The spin concentration of the polyene film is about 1/6 of that of tr-PA but is about twice as that of cis-PA. It has been reported that most of the spins in the tr-PA are generated during the cis–trans thermal isomerization.[15] However, when the polyene is formed by dehydrochlorination of PVC, trans double bonds are created directly. The difference in the spin concentration between the polyene and tr-PA is due to the difference in the mechanism of the formation of trans double bonds. The ΔH_{msl} for the polyene film is much wider than that for PAs. This implies that the unpaired electrons in this conjugated polyene are much more located than in PAs. The conjugated chain length of the polyene may be shorter than that of PA because of the imperfection of dehydrochlorination and the structural irregularity of PVC; then the motional narrowing is difficult to occur. Furthermore, the exchange narrowing cannot result in the polyene because of its poor crystallinity.[16] Thus, the absence of both modes of narrowing may make the line width broad.

Electrical Conductivity of Polyene

The electrical conductivities of the polyene film and tr-PA were measured at room temperature in vacuo (see Table II). The last column in Table II shows the conductivities in the direction of the molecular orientation, i.e., the direction of draw for the uniaxially oriented samples. Others are the data for the unoriented samples. The conductivity of the original PVC film was measured with a vibrational reed type pico ammeter. The conductivity of the polyene film is 4–6 orders of magnitude higher than that of the original PVC. It is, of course, due to the formation of the conjugated polyene

TABLE II
Conductivity of the Dehydrochlorinated PVC Film, tr-PA, and PVC

	Conductivity (S/cm)	
	Undrawn	Drawn
PVC deHCl film (CHN)	4.4×10^{-12}	8.9×10^{-12} ($\lambda = 6$)
PVC deHCl film (DMF)	5.7×10^{-10}	4.2×10^{-9} ($\lambda = 5$)
tr-PA (93%)	5.0×10^{-6}	2.2×10^{-5} ($\lambda = 2.3$)
PVC	4×10^{-16}	—

sequences. However, this value is about 6 orders lower than that of tr-PA because of the less delocalization of the unpaired electrons and the poor crystallinity. The conductivities of the oriented polyene films are higher than those of the unoriented ones. The molecular orientation, although being low as shown by the X-ray analysis, shows a significant effect on the conductivity. The polyene film treated in DMF has a higher conductivity than that treated in CHN. This suggests that the slight oxidation caused by DMF increases the conductivity as in the case of oxygen doping to PA.[10]

Iodine Doping

The iodine content of the doped samples was determined from the weight uptake. In Table III, the iodine contents of tr-PA and the polyene film highly dehydrochlorinated in DMF are summarized. The left column in Table III shows the approximate equilibrium content achieved after 1 week doping in a nitrogen atmosphere at room temperature, and the residual amounts of iodine after evacuating for given periods at room temperature are shown on the right. The equilibrium content of the polyene film is very close to that of tr-PA; however, the residual amount after evacuation is much less than in tr-PA even after a shorter evacuation period. In the previous work, we found that iodine penetrates into the crystals of tr-PA to form "iodine–PA" cells when the iodine vapor pressure is higher than a threshold value of about 0.08 Torr at room temperature, and that the iodine atoms in the crystals are not removed by evacuation.[6] Thus, the small amount of the residual iodine for the polyene film is explained in terms of the poor crystallinity of the polyene film.

Finally, the change of the electrical conductivity in the iodine doping is shown in Figure 10 as a function of time. Iodine doping was carried out at 25°C with iodine of 0.28 Torr. The conductivity increases over several orders of magnitude even at the earliest stage of the doping and reaches to the ultimate value in the order of 10^{-4} S/cm after about 1 h. This behavior is in good agreement with the result obtained by Deits et al. for the completely dehydrochlorinated PVC powder prepared by treating with sodium amide in liquid ammonia.[17] The ultimate value is independent of the conductivity measured before doping. When tr-PA is doped under the same conditions, a similar behavior is observed, but its ultimate value is at the order of 10^2 S/cm. The difference in conductivities between doped polyene films and doped tr-PA is due to the structure of materials, such as regularities of conjugation and crystallinity.

TABLE III
Iodine Contents of the Dehydrochlorinated PVC Film and tr-PA

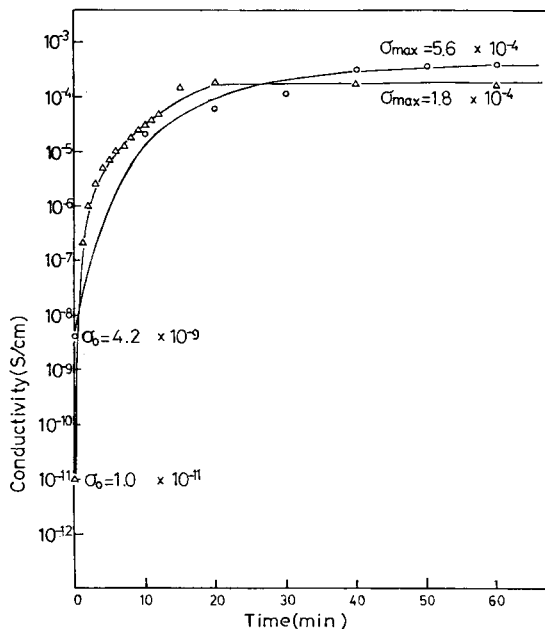|	y in —(—CHI$_y$—)—	
	Doped for 1 week in N_2	After evacuation
PVC deHCl film ($\chi = 0.95$)	0.28	0.06 (18 h)
tr-PA (93%)	0.33	0.20 (several days)

Fig. 10.Conductivity changes in PVC deHCl as a function of iodine doping time: (○) polyene film obtained in DMF ($\lambda = 5$); (△) polyene film obtained in CHN.

CONCLUSIONS

1. A film of conjugated polyene system can be obtained by dehydrochlorination of poly(vinyl chloride) by treating with DBU in polar solvents, such as DMF, CHN, THF, and MEK, under the two step treatment, and a molecularly oriented polyene film is also obtained by the treatment of the drawn PVC film.

2. The polyene film has a considerably long conjugated sequence, but the length of the conjugated chain is very widely distributed.

3. The polyene film is an amorphous material.

4. DMF is not a good solvent for this treatment because of the oxidation, although it has a high rate of reaction.

5. The electrical conductivity of the polyene film is in the orders of 10^{-12}–10^{-9} S/cm, and the molecular orientation shows a significant effect on the conductivity.

The conductivity of the iodine doped polyene film is in the order of 10^{-4} S/cm.

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