

Catalytic Dehydrochlorination of the Solid Poly(vinyl Chloride) in the Presence of Aluminium Chloride (Friedel-Crafts) Catalyst: Studies of the Structure by Spectroscopical Methods

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Synopsis

Catalytic dehydrochlorination (100%) of solid poly(vinyl chloride) (PVC) in the presence of AlCl_3 at 200°C gives a product which has a similar structure to the product of catalytic dehydrochlorination of 1,2-dichloroethane in the presence of AlCl_3 at 60°C . Both products have brown-black color, are completely insoluble, thermally resistant up to more than 400°C , and exhibit conductivities in the range $10^{-6} \text{ S cm}^{-1}$ (after doping with FeCl_3 or I_2 conductivities: $10^{-5} \text{ S cm}^{-1}$). Different spectroscopical methods such as UV/VIS, IR, Raman, ESCA, and ^{13}C -NMR were employed to the structure study of both products, which are crosslinked polyenes with a number of aromatic rings.

INTRODUCTION

Dehydrochlorination of poly(vinyl chloride) (PVC) leads to formation of soluble or not soluble (depending of the method), strongly colored (yellow-orange-brown and even black) products, which have polyene structures similar to polyacetylene.¹⁻⁶ These polyene structures $\text{-(CH}_2\text{=CH}_2\text{)}_n\text{-}$, where $n = 2\text{--}14$,^{1,7-9} have characteristic UV-absorption maxima, some of them amplified by superposition. It has been reported that black product obtained by KOH dehydrochlorination of PVC has identical X-ray diffraction pattern as crystalline polyacetylene.^{4,10} The structure defects in the dehydrochlorination products of PVC differentiate them from polyacetylene and decrease their conductivity. However, doping of these black products with FeCl_3 , BF_3 , or iodine improves to some extent their conductivity.^{6,11-13} Batteries, whose durable anodic electrodes contain dehydrochlorination products obtained from poly(vinyl chloride) or poly(vinyl bromide), have been experimentally designed and tested.^{3,14-18}

Heating of PVC up to 200°C leads only to the partial dehydrochlorination of samples.^{9,13,19} This process is intensified by the addition of ionic catalyzers such as AlCl_3 , FeCl_3 , ZnCl_2 , SnCl_4 , or BF_3 .²⁰⁻²⁶ The degree of dehydrochlorination varies from 10 to 16%, depending of the employed method. In addition

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to the results obtained in this field, we have found that thermal treatment of the solid PVC in the presence of AlCl_3 at 200°C gives a product which is completely 100% dehydrochlorinated. This paper is devoted to the study of the structure of this product by the different available spectroscopical methods.

EXPERIMENTAL

Suspension polymerized poly(vinyl chloride) (PVC) was obtained from Kema-Nord AB (Sweden) in the form of white powder (manufacturer's data: Fikentscher *K* value 66; $\bar{M}_n = 56,000$, $\bar{M}_w = 145,000$, i.e., polydispersity factor 2.59). Chlorine content measured 56.6% (theor. 56.76%).

Aluminium chloride (AlCl_3) (Merck-Schuchardt, East Germany) has been used without further purification. Attempts were made to prevent moisture by storage in a desiccator and by using fresh bottles of AlCl_3 at frequent intervals.

1,2-Dichloroethane (for spectroscopy) (Merck, East Germany) was used without further purification.

In a typical dehydrochlorination experiment of PVC in a solid state, 1 g PVC (0.02 mol) + 2.66 g AlCl_3 (0.02 mol) were carefully mixed in an air and moisture-free dry box, then placed in Alundum thimbles (RA98) and heated in an oven at $200 \pm 1^\circ\text{C}$ in a continuous flow of pure, dried nitrogen (or air) warmed previously up to 200°C . After reaction a black product was extracted with ethanol and subsequently water in a Soxhlet (24 h) and then dried under nitrogen flow. Chlorine and aluminium contents measured in the black powder (obtained in oxygen free atmosphere) were 0.5 and 0.17%, respectively. These results account for a 100% of dehydrochlorination of PVC. Remaining chlorine present in a sample belongs to AlCl_3 , the rest of the catalyst being retained in the product.

In a typical dehydrochlorination experiment of 1,2-dichloroethane, 6.67 g AlCl_3 (0.05 mol) was added to 53.0 g $\text{CH}_2\text{CH}_2\text{Cl}_2$ (0.5 mol) (ratio 1 : 10) and the reaction was carried out at the boiling temperature (60°C) under vigorous stirring in nitrogen atmosphere. The brown-black product was further extracted with ethanol and water in a Soxhlet (24 h) and then dried under nitrogen flow. Chlorine and aluminium contents in this product were 8.8 and 0.79%, respectively. These results show that product contains 6.48% chlorine which does not belong to the AlCl_3 and is chemically bounded to a product.

UV/VIS spectra of dehydrochlorinated PVC film samples were recorded with Perkin-Elmer 575 UV/VIS Spectrometer. Because dehydrochlorinated thin PVC folies are very brittle, PVC film samples were made from the tetrahydrofuran solution directly on the quartz cuvette, and then dehydrochlorinate.

IR spectra were recorded with IR computerized Perkin-Elmer 580B infrared spectrometer in KBr pellets or placed between two NaCl plates. We observed that the black products obtained from dehydrochlorination of PVC or $\text{CH}_2\text{CH}_2\text{Cl}_2$ in nitrogen atmosphere are sensitive to air, especially during the grinding with KBr and oxidized. For that reason preparation of pellets were made in a plastic bag in nitrogen atmosphere.

Laser Raman spectra were recorded with Laser Raman spectrometer type SPEX 1403 using 5145 Å excitation wavelength. The ^{13}C -NMR spectra were measured with a Varian XL200; 50.3 MHz spectrometer (dipol-decoupling), magic angle spinning 2.95 kHz, cross polarization 300 μs , pulse delay 2 s, line broadening 50 Hz, and number of scans \sim 15,000.

ESCA core-level spectra for Cl_{1s} , Cl_{2p} , and O_{1s} were recorded with a VG Scientific LD, ESCA Spectrometer, using $\text{AlK}_{\alpha_{1,2}}$ excitation radiation. Electron microscope pictures were made with Super Mini SEM ISI Microscope.

Electrical conductivity was measured with a four-point measuring cell and Fluke Multimeter 8840A. The FeCl_3 (in dry nitromethane) and I_2 (samples were exposed to I_2 vapor for 24 h at a pressure of about 0.3 mmHg) doping was made according to methods described elsewhere.^{27,28} The amount of Fe was 3.49%, whereas I_2 was 8.70%.

Elemental analyses were performed by Micro Kemi AB, Uppsala, Sweden. Aluminium and iron contents were determined with Atomic Absorption Spectrometer Perkin-Elmer 1100.

RESULTS AND DISCUSSION

Poly(vinyl chloride) (PVC) thermally degraded in nitrogen at 200°C (1 h) gives orange-brown, partially crosslinked product (noted here as a product I). The color formed is a result of the formation of polyene structures by the dehydrochlorination of PVC. Polyene structures are not regularly distributed, and they are not only present as linear structures, but occasionally also in the form of unsaturated cyclic (aromatic) structures.^{9,29} The degree of dehydrochlorination changes with the time of heating, temperature and thermal treatment program. Product I, flash heated at 200°C for 1 h in nitrogen atmosphere, has been dehydrochlorinated less than 0.2%.

Poly(vinyl chloride) (PVC) powder mixed with AlCl_3 (1 : 1 mol) and stored at room temperature after a few days became gray-black and slow dehydrochlorination of PVC less than 1% occurred. This reaction is accelerated with increasing temperature. After a heating of PVC powder with AlCl_3 (1 : 1 mol) for 1 h at 100°C dehydrochlorination occurs from 56.6% Cl to 36.5% Cl content, whereas at 200°C dehydrochlorination is almost 100% (0.5% Cl content). It is impossible to measure the kinetics of the dehydrochlorination of PVC- AlCl_3 mixtures at higher temperatures, because a part of AlCl_3 sublimates and is transported simultaneously with HCl. All products obtained by AlCl_3 -catalyzed dehydrochlorination (in nitrogen or air) are black, completely insoluble, infusible and do not decompose up to 400°C (the limit of our range covered by our equipment). Because 100% dehydrochlorination occurs already at 190–200°C, most of the samples were prepared in that temperature range. The black product (noted here as product II) obtained at 200°C contains only 0.5% Cl and 0.17% Al. This small amounts of chlorine belongs to AlCl_3 (retained in the product II), rather than being chemically bonded.

Electron microscope pictures of the product II [Fig. 1(C)] show that the surface is very porous (cauliflower morphology) and differs from product I [Fig. 1(B)], which has a smooth surface (powder grains were melted at 200°C) (globular morphology). Cauliflower morphology is a result of extensive dehy-

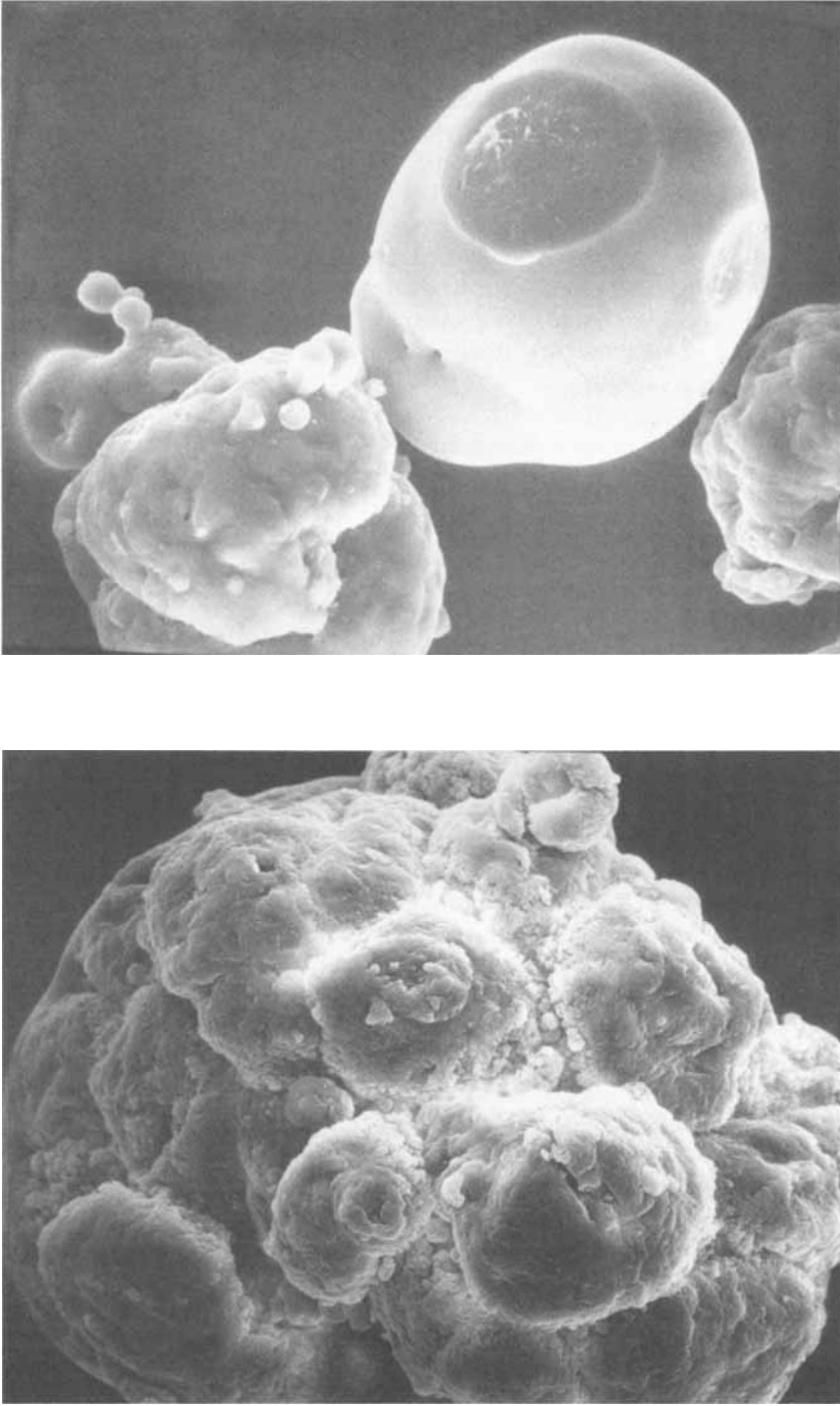
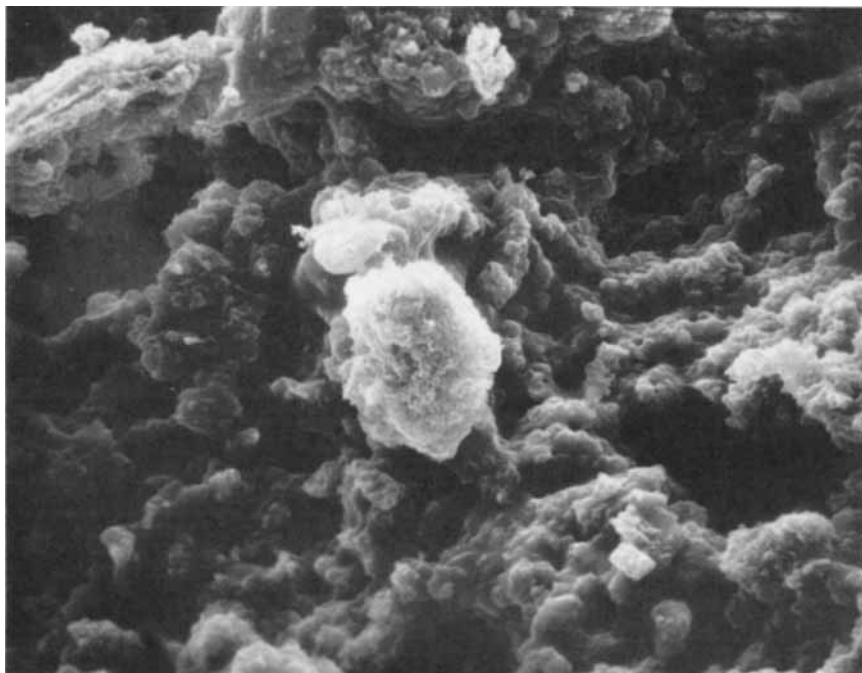
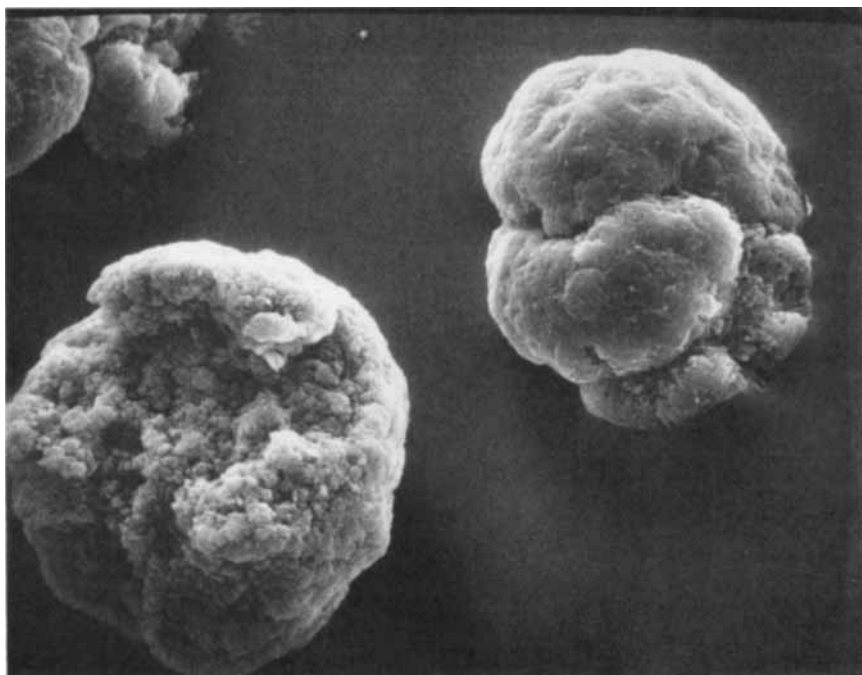
**A****B**

Fig. 1. SEM pictures ($400\times$) of: (A) starting pure PVC grain particles; (B) thermally treated PVC at 200°C , 1 h (Product I). Grain particles are melted (globular morphology); (C) Dehydrochlorinated PVC in the presence of AlCl_3 at 200°C , 1 h (Product II). Grain particles are very porous (cauliflower morphology); (D) Product III obtained from dehydrochlorination of 1,2-dichloroethane in the presence of AlCl_3 at 60°C (4 h). Product is composed from very small particles which are irregularly linked to each other.



D



C

Fig. 1. (Continued from the previous page.)

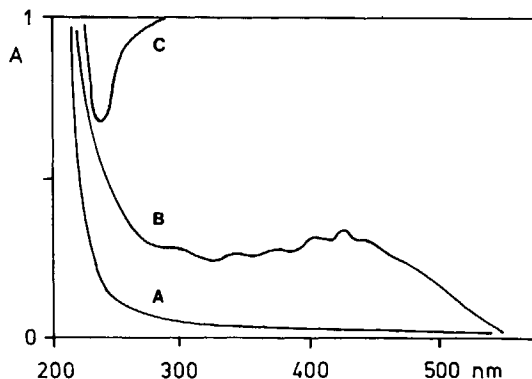


Fig. 2. UV/VIS absorption spectra of: (A) starting pure PVC; (B) thermally treated PVC at 200°C, 1 h (Product I); (C) dehydrochlorinated PVC in the presence of AlCl_3 at 200°C, 1 h (Product II).

drochlorination, during which HCl diffuses out of PVC powder grains, making the surface structure very porous.

Products I and II differ structurally from the starting PVC samples. The UV/VIS spectra of thin PVC films cast on quartz cuvettes and further dehydrochlorinated in the presence of AlCl_3 (product II) [Fig. 2(C)] show very high absorption in all spectral ranges and do not exhibit characteristic UV/VIS absorption maxima for thermally dehydrochlorinated PVC (product I) [Fig. 2(B)]. The very strong absorption of the product II is a result of a superposition of absorption peaks of high content polyene structures.

The IR spectra of both product I and II obtained in nitrogen or air differ, because of oxidation processes which accompanies dehydrochlorination. Samples obtained in air show the presence of very high amount of HO/OOH (at 3440 cm^{-1}) and CO (ketoallylic) (at 1680 cm^{-1}) (Fig. 3). The products obtained in nitrogen are free of these absorption bands, however, during the grinding with KBr in air are easily oxidized.

Product II contains much higher content of $\text{C}=\text{C}$ groups (1630 cm^{-1}) than product I does. This stretching band for $\text{C}=\text{C}$ is shifted in comparison to that reported in the literature (1667 cm^{-1}) for PVC dehydrochlorinated catalytically in the presence of other ionic catalysts.³⁰

Aluminium chloride gives adducts with water ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) and methanol ($\text{AlCl}_3 \cdot \text{CH}_3\text{OH}$ and $\text{AlCl}_3 \cdot 2\text{H}_2\text{O}$).³¹ IR spectra of these adducts are shown in Figure 4 and exhibit a strong broad absorption band at 1630 cm^{-1} . After dehydrochlorination at 200°C product II was extracted with ethanol and further with water in order to remove all excess AlCl_3 . Analysis for aluminium in product II show that very small amount of AlCl_3 (0.17% calculated for the Al content) has been retained and could not be removed, even by prolonged washing with water (3 days). In a PVC sample mixed with AlCl_3 (0.2%), the absorption peak at 1630 cm^{-1} was negligible. From these results we can assume that the band 1630 cm^{-1} can be attributed to the stretching band for $\text{C}=\text{C}$, rather than to the presence of traces of AlCl_3 water or alcohol adducts.

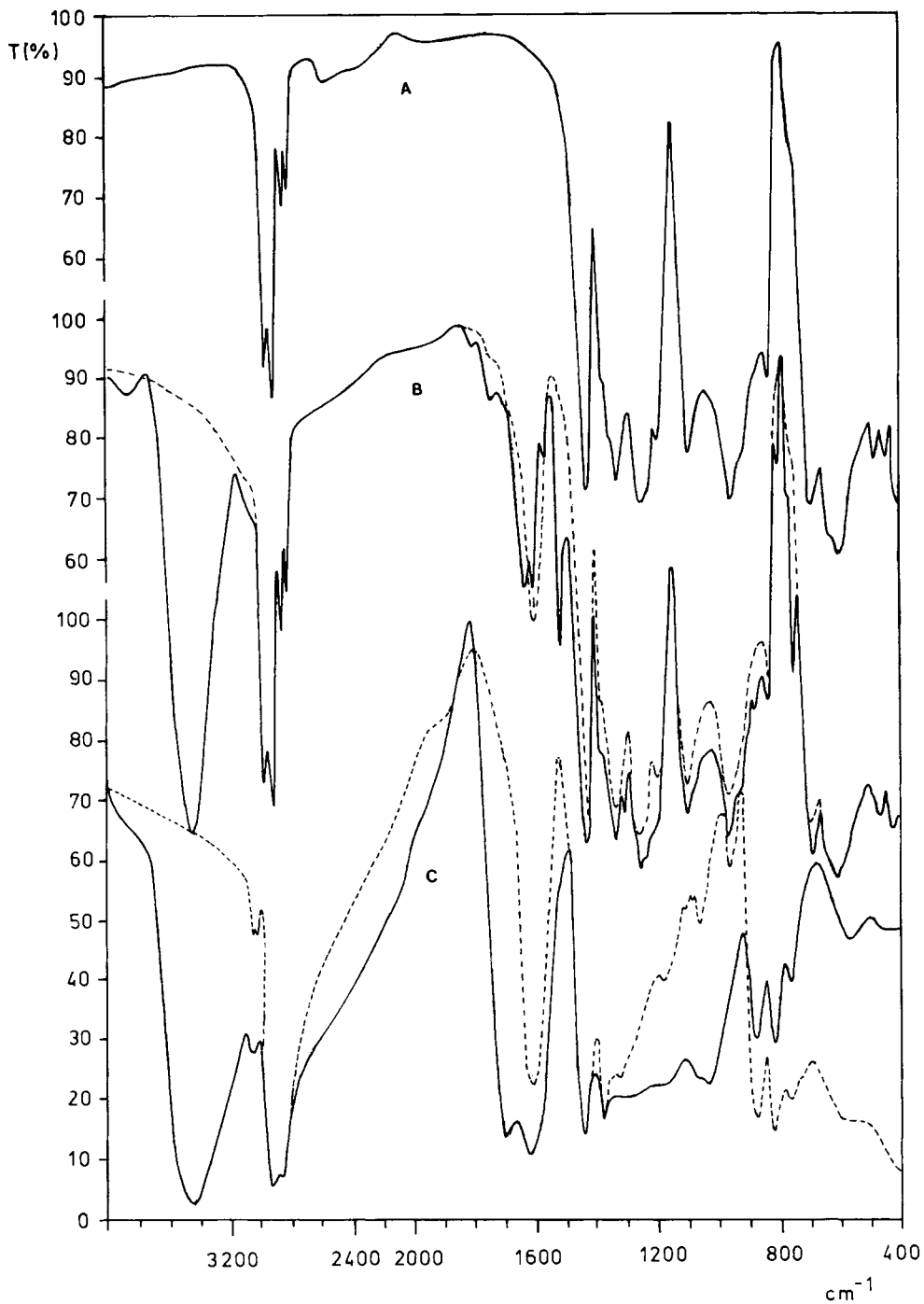


Fig. 3. IR absorption spectra of: (A) starting pure PVC; (B) thermally treated PVC at 200°C, 1 h; (C) dehydrochlorinated PVC in the presence of AlCl_3 at 200°C, 1 h (Product II); (---) samples prepared in nitrogen; (—) samples prepared in air.

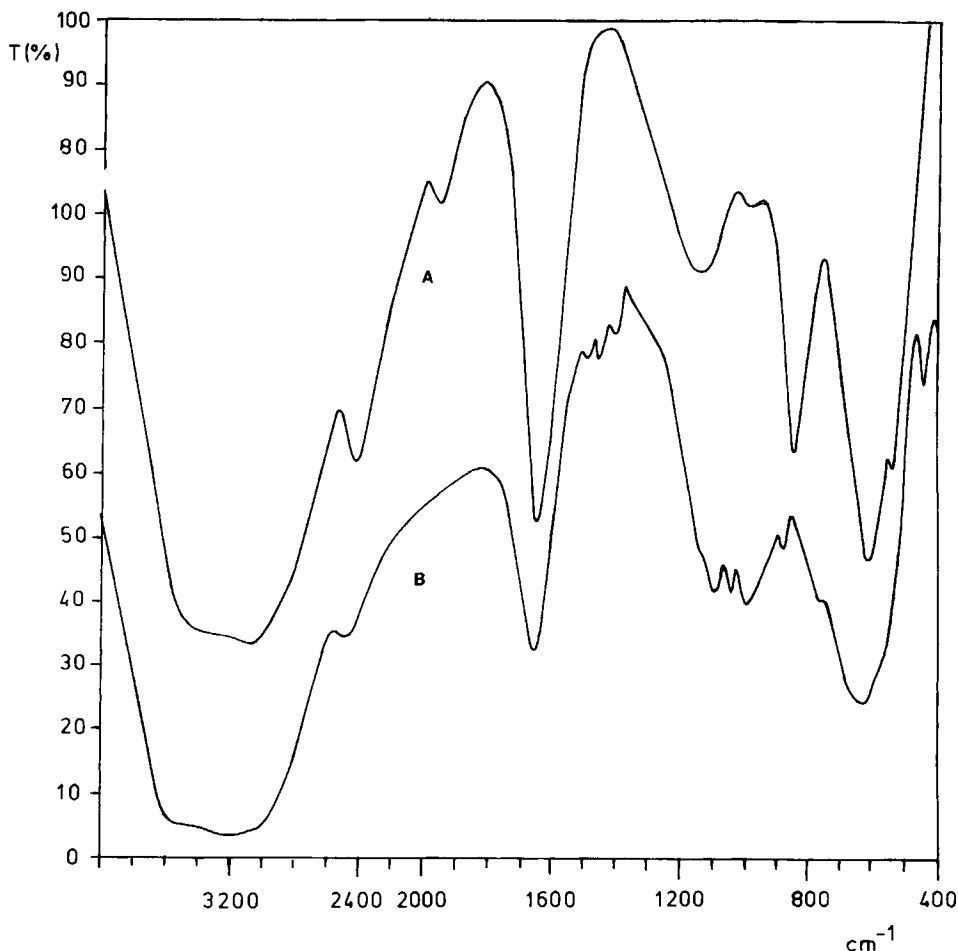
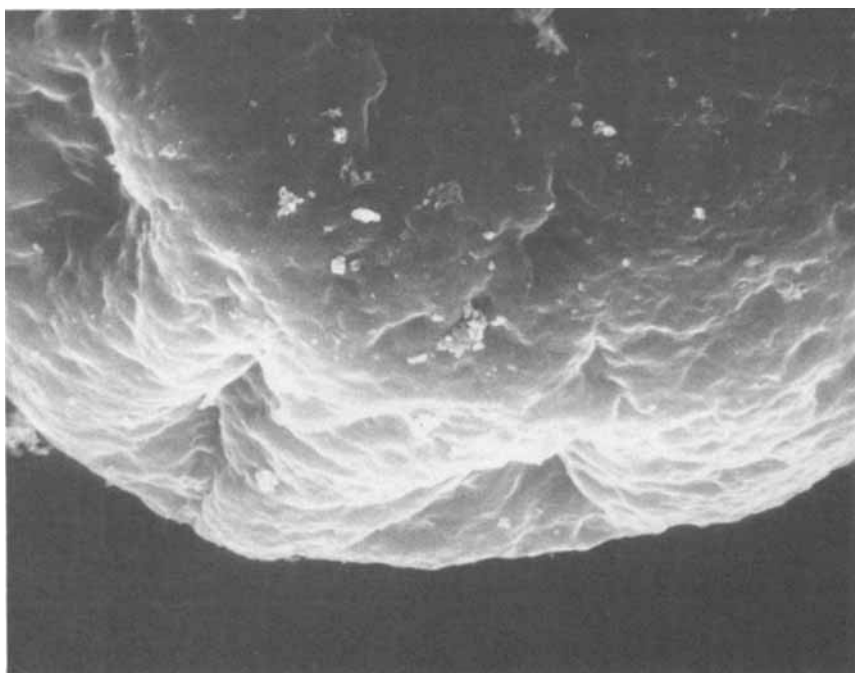


Fig. 4. IR absorption spectra of: (A) aluminium chloride adduct with water ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$); (B) aluminium adduct with methanol (mixture of $\text{AlCl}_3 \cdot \text{CH}_3\text{OH}$ and $\text{AlCl}_3 \cdot 2\text{CH}_3\text{OH}$).

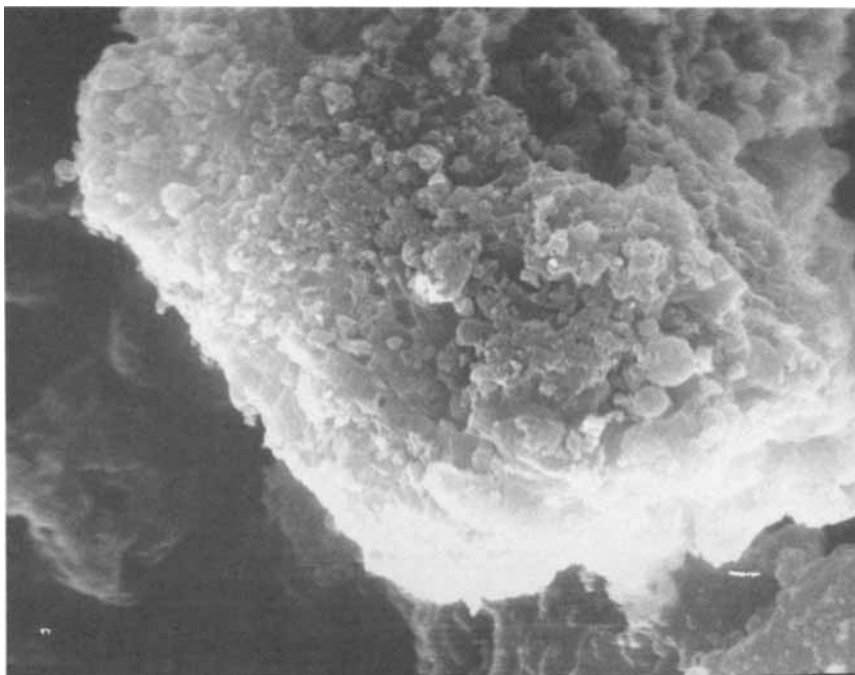
The IR absorption bands in the region $1500\text{--}1800\text{ cm}^{-1}$ differ very much for product II, depending on preparation in nitrogen or air, and also differ from product I [Figs. 3(B), (C)]. The difference of IR spectra in the above region might be the result of the formation of an oxidized product. Ethers (C—O—C) and peroxy (C—O—O—C) linkages, which exhibit characteristic stretching bands in this region, exhibit variation in the frequency of absorption, depending upon the nature of the carbon atom substitution.³³

The IR spectra of product II display an absorption at 1015 cm^{-1} characteristic of a linear conjugation of *trans* $\text{C}=\text{C}$ double bonds³²; however, in the same region $1000\text{--}1200\text{ cm}^{-1}$, there appears an absorption from in-plane motions of the aromatic ring, including in-plane bending of the hydrogen atoms on the ring. Two other bands at $835\text{--}890\text{ cm}^{-1}$ are characteristic for the isolated hydrogen atom in 1,3,5-trisubstituted aromatics.

The bands at 2860 cm^{-1} (asymmetric CH stretch), 2840 cm^{-1} (in-phase CH stretch), 1425 cm^{-1} (deformation vibrations) and 740 cm^{-1} (in-phase rocking) are very characteristic for the CH_2 groups in PVC.^{9,30}



A



B

Fig. 5. SEM pictures ($2000\times$) of: (A) dehydrochlorinated PVC in the presence of AlCl_3 at 200°C , 1 h (Product II); (B) product III obtained from dehydrochlorination of 1,2-dichloroethane in the presence of AlCl_3 at 60°C (4 h).

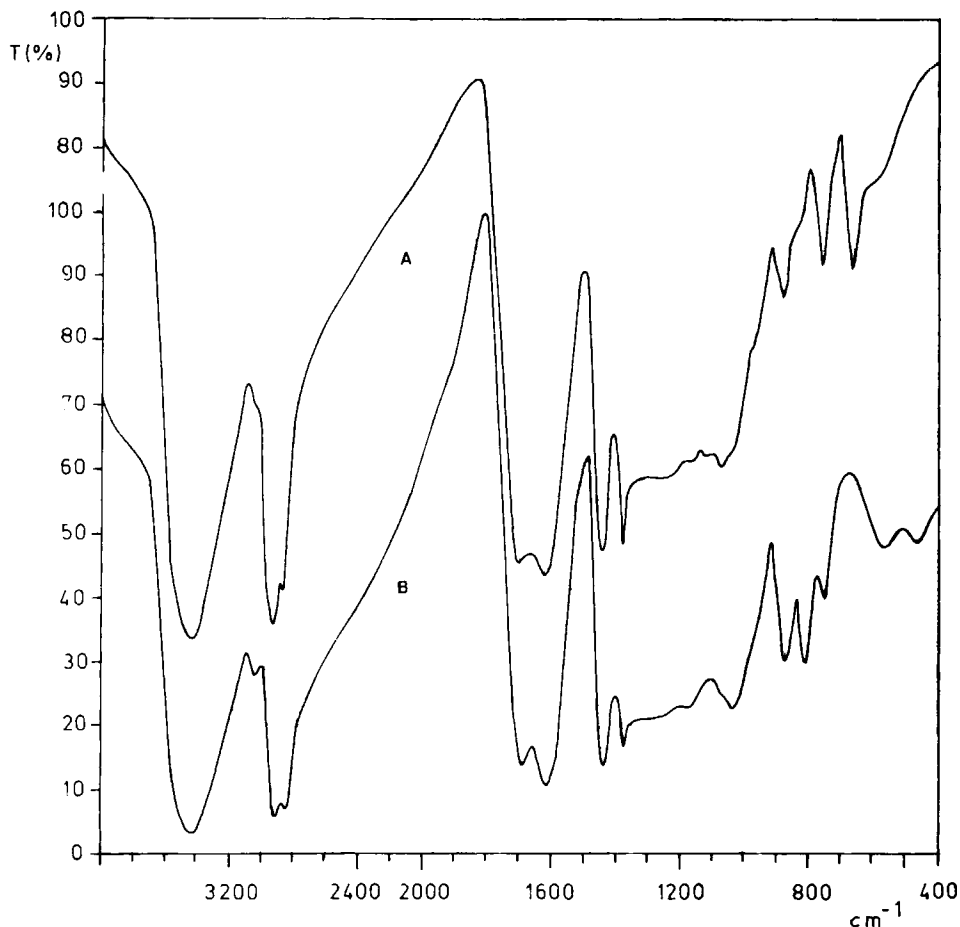


Fig. 6. IR absorption spectra of: (A) product III obtained from dehydrochlorination of 1,2-dichloroethane in the presence of AlCl_3 at 60°C (4 h) in air; (B) product II, dehydrochlorinated PVC in the presence of AlCl_3 at 200°C , 1 h in air.

The bands at 692, 634, and 610 cm^{-1} [Fig. 3(A)], present in the starting PVC material and also present in product I [Fig. 3(B)] arising from the C—Cl stretching modes, disappear completely in product II [Fig. 3(C)]. This is relevant with respect to the complete dehydrochlorination of PVC in the AlCl_3 catalyzed reaction.

During the heating of 1,2-dichloroethane with AlCl_3 at 60°C an insoluble brown-black powder (noted here as product III) precipitates, which is composed from very small particles which are irregularly linked to each other [Fig. 1(D)]. It is better seen at SEM picture at 2000 enlargement (Fig. 5). The chlorine content in the product III is 6.48%, which does not belong to the retained AlCl_3 and is chemically bound to a product.

The IR spectra of both products II and III are almost identical (Fig. 6). Product III gives a band at 610 cm^{-1} (C—Cl) which does not exist in the product II. In addition, product III contains a much higher amount of ethers (C—O—C) and/or peroxy (C—O—O—C) linkages (bands at 1100–1200

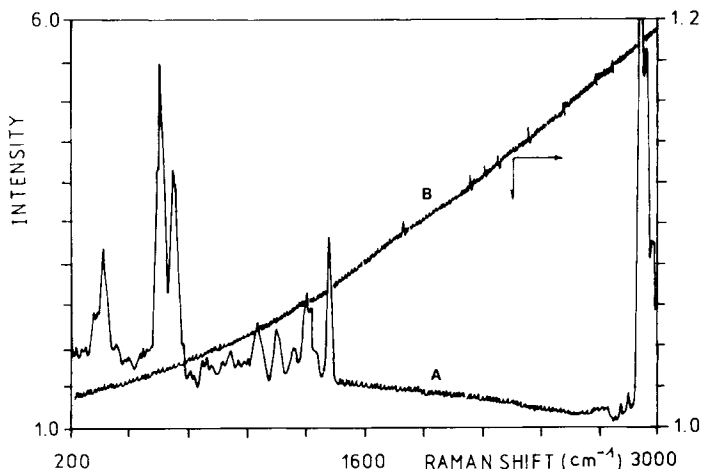


Fig. 7. Raman spectrum of pure PVC (A) and strong fluorescence background from product II (similar from product III).

cm^{-1}) than product II. There is also slight shift in the stretching band for $\text{C}=\text{C}$ (1600 cm^{-1}) in product III in comparison with product II. The stretching band for $\text{C}=\text{C}$ can lie in the very broad region of absorption from $1400 \text{ up to } 1800 \text{ cm}^{-1}$.

The well-developed Raman spectrum for pure PVC completely disappears in products II and III [Figs. 7(A),(B)]. The intensity of the fluorescent background increases with the time of laser irradiation. It was impossible to decrease the fluorescence background even by changing excitation wavelengths of laser radiation, using defluorescent agent (KBr in the mixture with the products II or III) and removing the fluorescent groups by "burning out." However, using the available Raman spectrometer, we could not make low temperature Raman scattering experiments which are essential for the determination *cis/trans* $(\text{CH})_x$ groups in polyacetylene.^{34,35}

The ^{13}C -NMR spectra of product II obtained in nitrogen or air and product III in air (Fig. 8) show broad peaks, which are characteristic of very irregular structures. The peak at $50\text{--}70 \text{ ppm}$ attributed to $-\text{CHCl}-$ disappears in products II and III. This is consistent with the dehydrochlorination process. At the same time a new peak at $120\text{--}160 \text{ ppm}$ attributed to $\text{C}=\text{C}$ (both polyene and/or aromatic structures) appears. The peak with strong intensity at $10\text{--}15 \text{ ppm}$ indicates the presence of aliphatic carbon structures. Because all products are insoluble in all available solvents, it was not possible to make ^1H -NMR spectra.

The ESCA spectra show that the Cl_{2p} peak characteristic for pure PVC [Fig. 9(A)] completely disappears in product II [Fig. 9(B)], but exists as a small intensity peak in product III [Fig. 9(C)]. ESCA spectra of products II and III obtained in air contain characteristic O_{1s} core level peaks, which do not exist in the samples obtained in nitrogen. The C_{1s} core level ESCA spectra of pure PVC (Fig. 10) consists of a peak characteristic of two components separated approximately by their linewidth.³⁶ There is a remarkable shift of C_{1s} peak in product II (Fig. 10) and Cl_{2p} peak in product III (Fig. 11) in comparison to the C_{1s} and Cl_{2p} peaks in pure PVC. The C_{1s} core level shift

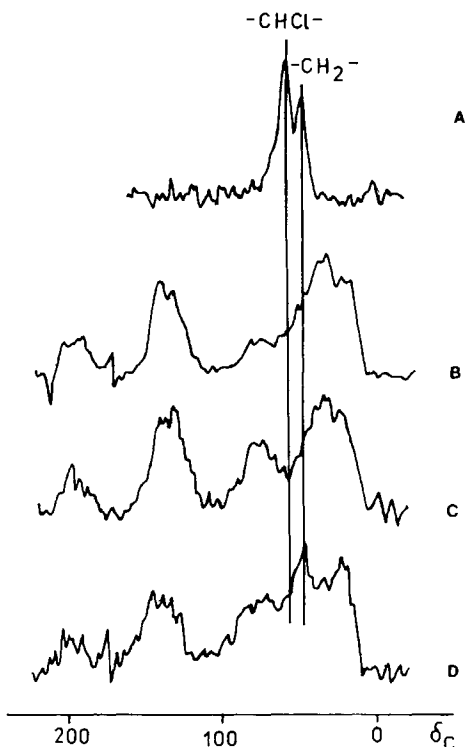
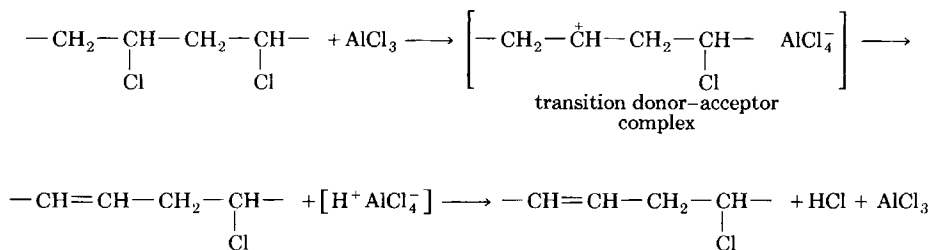


Fig. 8. ^{13}C -NMR spectra: (A) starting pure PVC; (B) dehydrochlorinated PVC in the presence of AlCl_3 at 200°C , 1 h in air (product II); (C) dehydrochlorinated PVC in the presence of AlCl_3 at 200°C , 1 h in nitrogen; (D) product III obtained from dehydrochlorination of 1,2-dichloroethane in the presence of AlCl_3 at 60°C (4 h) in nitrogen.

probably results from photoionization of the C_{1s} level for the aromatic rings coupled to polyene structures which are strongly crosslinked. The Cl_{2p} core level shift in product III (Fig. 11) is a consequence of its binding to the π system of polyene and/or aromatic structures.

The results obtained from IR, NMR, and ESCA spectra suggest that structure of insoluble products II and III can be presented as is shown in Figure 12. This image contains some structural elements which are randomly distributed in the very crosslinked net.

It is generally accepted that catalytic dehydrochlorination of PVC in the presence of AlCl_3 (Friedel-Crafts catalysts) occurs by an ionic mechanism^{20, 21, 25, 26, 37}:



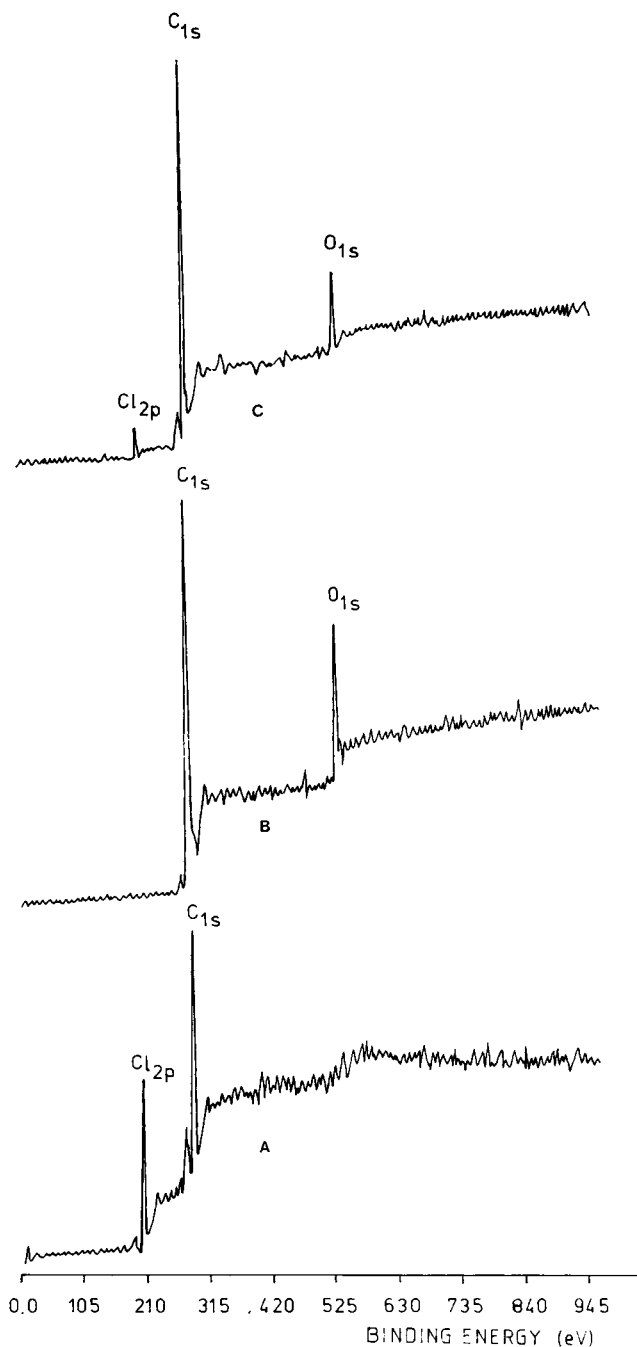


Fig. 9. ESCA spectra of: (A) starting pure PVC dehydrochlorinated PVC in the presence of AlCl_3 at 200°C , 1 h in air (product II); (C) product III obtained from dehydrochlorination of 1,2-dichloroethane in the presence of AlCl_3 at 60°C (4 h) in air. Products II and III obtained in nitrogen do not show O_{1s} core level peak.

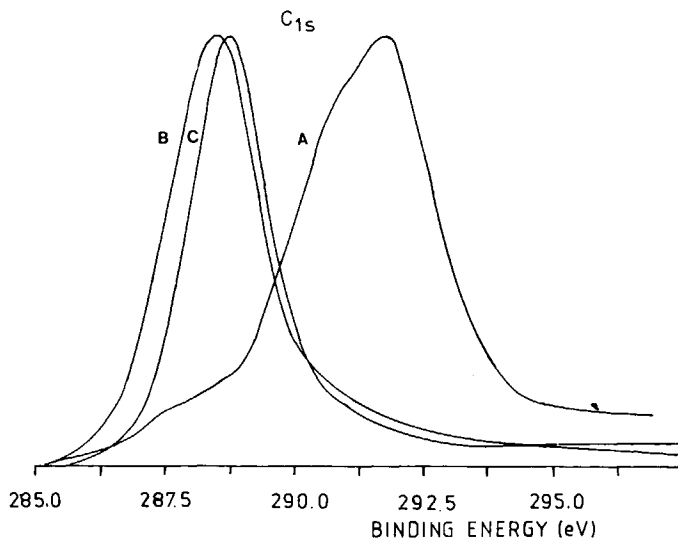


Fig. 10. ESCA C_{1s} spectra of: (A) starting pure PVC; (B) dehydrochlorinated PVC in the presence of $AlCl_3$ at 200°C, 1 h in nitrogen (product II); (C) product III obtained from dehydrochlorination of 1,2-dichloroethane in the presence of $AlCl_3$ at 60°C (4 h) in nitrogen.

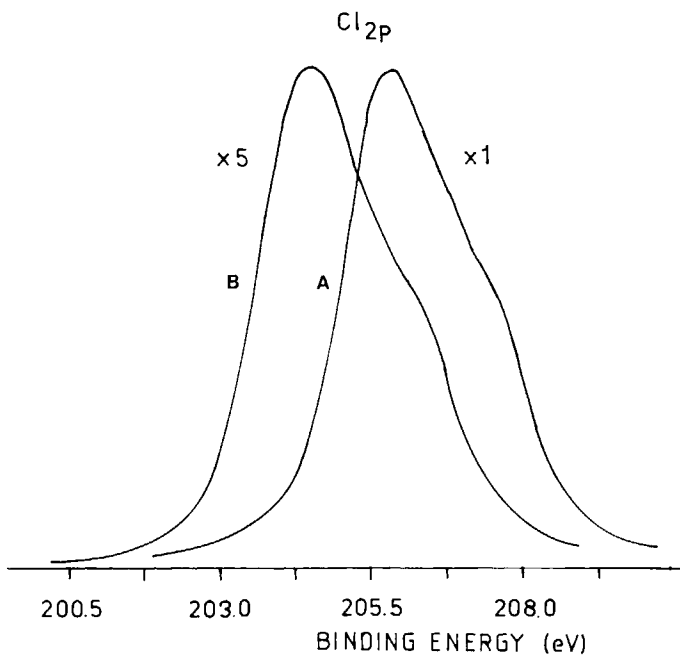


Fig. 11. ESCA Cl_{2p} spectra of: (A) starting pure PVC; (B) product III obtained from dehydrochlorination of 1,2-dichloroethane in the presence of $AlCl_3$ at 60°C (4 h) in nitrogen.

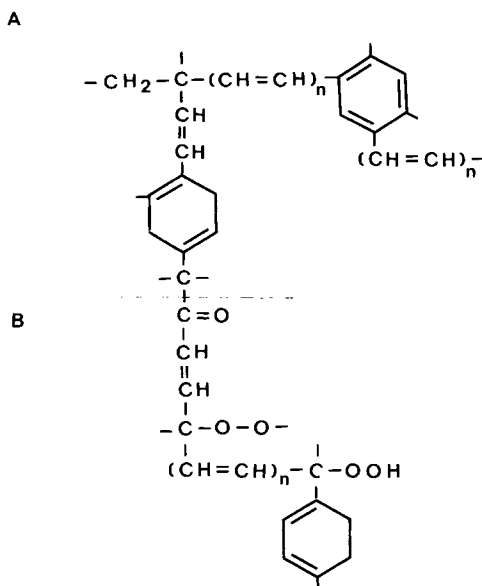


Fig. 12. Hypothetical structure of products II and III obtained: (A) in nitrogen and (B) in oxygen atmosphere.

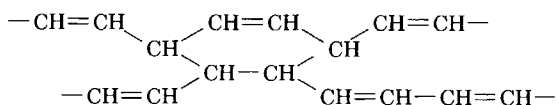
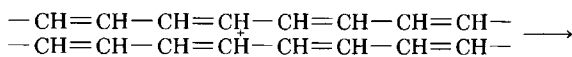
A cross-dehydrochlorination mechanism is probably responsible for the formation of the crosslinked structures.²⁶ A prerequisite for this reaction is the presence of highly activated chlorine atoms, such as those to β to random unsaturation. However, such structures initially show a higher tendency to form polyene sequences. The activation energy for the "zipper reaction" is believed to pass through a minimum with increasing length to polyene sequences. The crosslinking reaction, which will terminate the growing polyene chain, is therefore favored. A complete dehydrochlorination of PVC in the presence of AlCl_3 at higher temperatures (200°C), followed by a crosslinked reaction, may be due to the higher activation for energy for this reaction. At higher temperatures a larger number of initiation sites may be activated as well.

The AlCl_3 catalytic dehydrochlorination of PVC at higher temperatures is accompanied by the simultaneous thermal dehydrochlorination of PVC, which may occur by a free radical mechanism.^{29,38}

Dehydrochlorination of PVC in air gives rise to the oxidation reactions during which hydroxy/hydroperoxy (OH/OOH), carbonyl (CO), ethers (C—O—C), and peroxy (C—O—O—C) groups are formed. These groups are probably formed in reactions of oxygen with free radicals produced in the thermal dehydrochlorination reactions. Alkoxy and peroxy radicals formed may react with each other and form internal and/or cross-chain ethers and peroxy linkages.

The aromatic structures, mainly benzene rings and/or polycyclic (not well identified) rings, can be formed by the Diels–Adler cyclo addition between

polyenes³⁹⁻⁴²:

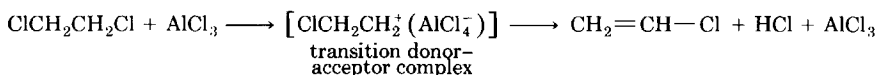


However, neither IR- nor ¹³C-NMR spectra give an indication of what type of aromatic structures are formed.

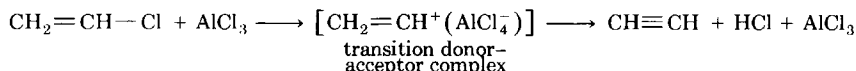
Product III obtained by the reaction of 1,2-dichloroethane with AlCl₃ at 60°C has an almost identical structure to that produced by the catalytic dehydrochlorination of PVC in the presence of AlCl₃ (product II).

The product III is probably formed by the following reaction:

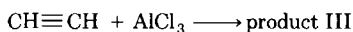
1. Dehydrochlorination of 1,2-dichloroethane to vinyl chloride:



2. Vinyl chloride cannot be polymerized to PVC in the presence of AlCl₃ as catalyst; however, it is easily dehydrochlorinated to acetylene⁴³⁻⁴⁵:



3. Acetylene can be further polymerized to the product III:



Products II and III exhibit conductivities in the range 10⁻⁶ S cm⁻¹ which are comparable to conductivities of cis or trans polyacetylene film with electrical conductivities ranging from 10⁻⁹ S cm⁻¹ (cis) to 10⁻⁵ S cm⁻¹ (trans). Because of the products II and III are strongly crosslinked, their grains cannot be pressed into pills even under 30 tons pressure. For that reason electrodes in a measuring cell do not achieve good contact with porous particles of product II and III. Conductivity between electrodes and measured materials may depend on the differences in the charges resulting from microstructural and morphological properties of the products. Doping of product II with FeCl₃ (4.49% Fe) or iodine (8.70% I) does not improve the conductivity significantly (~ 10⁻⁵ S cm⁻¹). Samples doped with FeCl₃ show two new low intensity bands at 1370 and 940 cm⁻¹, whereas for those doped with I₂ a band characteristic for halogens appears at 690 cm⁻¹. Doping with FeCl₃ or I₂ is probably ineffective because products II and III are strongly crosslinked and diffusion of dopants into grains is limited.

In conclusion, it is worth noting that catalytic dehydrochlorination of solid PVC (powder and eventually films) can give products, which can have practical application in the construction of electrochemical devices; however, their conductivity must be improved by avoiding crosslinking and formation of structural defects.

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