

Partially Dehydrochlorinated PVC.

II. Reactions With Dienophiles and Hydroxylating Agents

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Synopsis

Samples of poly(vinylchloride) containing polyene sequences were made by partial dehydrochlorination by alkali in tetrahydrofuran solution, by alkali in dioxane, and thermally in dimethylformamide. The reactions of polyene PVC were followed by UV spectrophotometry. Dienophiles were found to have relative reactivities similar to those found in reactions with low molecular-weight dienes. The reaction with maleic anhydride yielded polymers which after hydrolysis contained carboxyl groups. Hydroxylation was made with osmium tetroxide and performic acid. With the latter reagent the reactions proceeded to complete disappearance of the UV-absorption peaks from trienes and higher polyenes. Gel permeation chromatography analysis showed that hydroxylation could be made with only minor changes in molecular-weight distribution. The formation of gel upon thermal dehydrochlorination in DMF was shown to be due to physical cross linking probably arising by crystallization of polyene segments. The adhesion of the hydroxylated and carboxylated polymers to glass and stainless-steel surfaces was investigated. Films adhered stronger as the degree of dehydrochlorination of the polyene PVC used to make the derivative increased. Samples with long sequences adhered much stronger than those containing short sequences of corresponding degrees of total substitution.

INTRODUCTION

When poly(vinylchloride) (PVC) is dehydrochlorinated under the influence of heat or alkali, sequences of conjugated double bonds are formed as the primary reaction product.¹ Under carefully controlled conditions and at low degrees of dehydrochlorination (below about 10%) it was possible to suppress secondary reactions and to obtain products with only slightly changed molecular-weight distributions compared to the original PVC.² In the absence of oxygen and ultraviolet radiation the polyene sequence containing PVC (polyene PVC) could be isolated and stored for long periods without secondary reactions. The structure of the polyene PVC varied with the method of synthesis. When alcoholic KOH acted on PVC beads swollen by dioxane or on solutions of PVC in tetrahydrofuran (THF) short polyene sequences were introduced at random. They interspersed segments of PVC with an average degree of polymerization of about 70. Thermal degradation in dimethyl formamide (DMF) gave rise to fewer and longer polyene segments which interspersed PVC segments of an average degree of polymerization of about 220.²

Polyenes in general are very reactive and capable of undergoing numerous

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different reactions. Low molecular-weight polyenes have been studied intensely particularly by Karrer and co-workers.³ On the other hand, only a few publications have appeared dealing with the reactions of polyene sequences in dehydrohalogenated PVC. Loan⁴ in studies of the mechanism of stabilizer action made model experiments with dienophiles. Their reactivities were of the same order as for low molecular-weight dienes. Epoxides have been made by reaction of polyene PVC with organic peracids.^{5,9} Daniels and Rees⁶ studied the mechanism of bleaching of polyene PVC by α -hydroperoxytetrahydrofuran. The grafting of several vinyl monomers onto polyene PVC has been reported in the patent literature.^{7,8}

By reacting polyene PVC with various reagents it should be possible to prepare derivatives with unique structures not available by other techniques. They can be considered as block copolymers of the type ABABAB . . . , with A being PVC blocks and B being short or long segments of derivatives of polyenes. In the present paper we shall report on the reaction of polyene PVC with dienophiles and its hydroxylation.

EXPERIMENTAL

Dehydrochlorination. The PVC used was a suspension polymerized material (Pevikon S, KemaNord AB). The dehydrochlorinations were made by three procedures: (1) by reaction of alcoholic KOH with a solution of PVC in tetrahydrofuran (THF); (2) by reacting alcoholic KOH with beads of PVC swollen in 1,4-dioxane; and (3) by heating to 130°C or refluxing (153°C) a solution of PVC in dimethyl formamide. The details of the methods were described in a previous paper.²

Diels-Alder Reactions. Polyene PVC in solution in peroxide-free THF was reacted with the dienophiles at 25°C unless otherwise stated. A cover of oxygen-free nitrogen was maintained except in the experiments of Figure 1 (a) and the reaction flask was kept in the dark during the reaction.

Hydroxylation. The reactions with osmium tetroxide were performed in solution in THF at room temperature. The osmiate esters were hydrolyzed by addition of a few drops of aqueous HCl. The product was recovered by precipitation in dilute HCl. Hydroxylation by performic acid was made in solution in THF or in suspensions of polyene PVC swollen in chloroform or benzene. The performic acid was formed in situ by mixing formic acid with 30% hydrogen peroxide.

Ultraviolet Spectrophotometry. A Beckman DK-2A double-beam spectrophotometer was used. Freshly distilled THF was used as solvent and reference. Normally absorption from 260 nm upwards was used for the analysis. Some dienophiles absorbed in this region and the solutions could only be analyzed at wavelengths from 360 nm upwards. All operations were carried out under a nitrogen blanket.

Gel Permeation Chromatography. Experimental conditions and procedures were given in a previous paper.²

Adhesion. Films of PVC and derivatives were cast on defatted glass and stainless-steel plates from THF solutions. Residual solvent was removed *in vacuo* for 18 hr. A tensile tester was used to measure the force required to separate the film from the plate according to the Jacquet test.²⁰

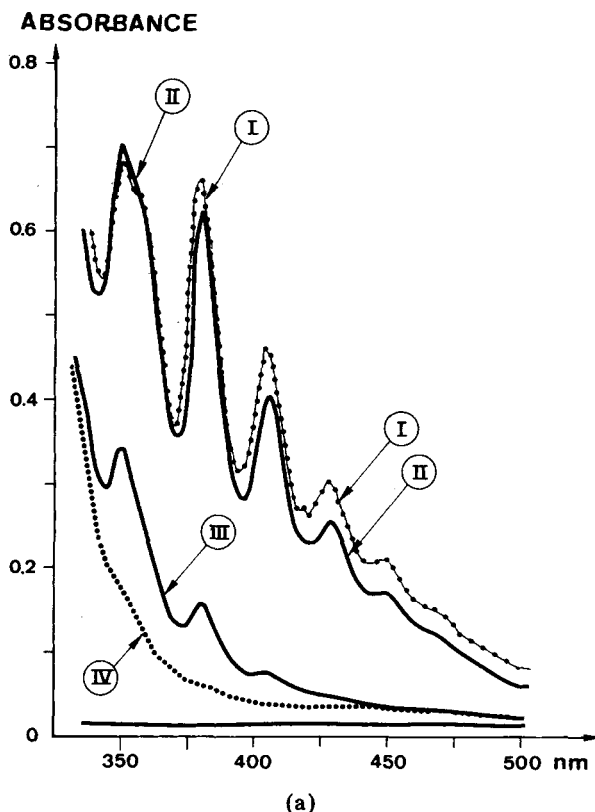


Fig. 1. Ultraviolet spectra of samples taken from reactions of polyene PVC with varying amounts of maleic anhydride in THF at 25°C. Samples were taken after 48 hr (a) and 41 hr (b). (a) 0.182 g/l polyene PVC (D_{tot} 7.8 mole %), made by reaction with alcoholic KOH in THF, with: I: Maleic anhydride 0; II: Maleic anhydride 0.0200 g/l (0.204 mmole/l); III: Maleic anhydride 0.520 g/l (5.31 mmole/l); IV: Maleic anhydride 4.34 g/l (44.2 mmole/l). (b) 0.212 g/l of polyene PVC, made by refluxing (153°C) for 26 min in DMF, with maleic anhydride in THF (25°C). I: Maleic anhydride 0; II: Maleic anhydride 0.020 g/l (0.204 mmole/l); III: Maleic anhydride 0.441 g/l (4.50 mmole/l); IV: Maleic anhydride 3.53 g/l (36.0 mmole/l).

RESULTS AND DISCUSSION

Reactions with Dienophiles

Preliminary experiments showed that polyene PVC was bleached by maleic anhydride in THF solution at room temperature. In order to evaluate the influence of some variables a number of experiments were made in which the course of the reactions were followed by UV spectrophotometry. Since the dienophiles used absorbed in the UV region only the polyenes with more than five double bonds could be analyzed for. Using the procedure of Shindo and Hirai¹⁶ to calculate the number of double bonds in polyenes with 6–10 double bonds the extent of reaction was determined as the percentage of double bonds remaining. In this way a semiquantitative determination of the kinetics of the reaction was possible.

In Figure 1 (a) the UV spectra are shown of samples withdrawn after 48 hr in experiments with varying maleic anhydride concentrations but the same original concentration of polyene PVC. In Figure 1(b) the corresponding curves after

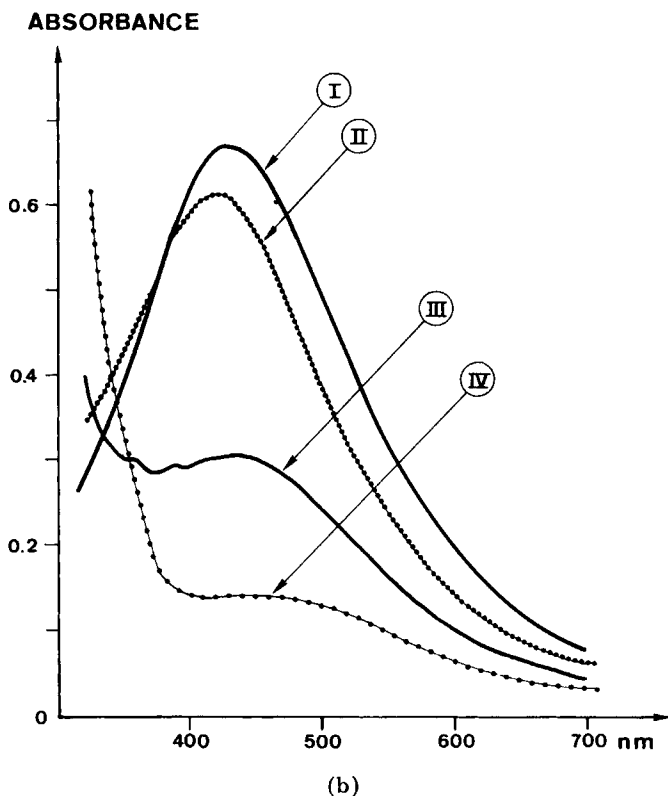


Fig. 1. Continued from previous page.

41 hr reaction for polyene PVC made by thermal dehydrochlorination in DMF are shown. In this case the D_{tot} values could not be determined due to the absence of discreet absorption peaks, and the reaction rates were estimated by comparison of absorbance maxima at 425–440 nm in Figure 1(b).

The rates of the reaction with polyene PVC with short sequences are shown in Figure 2 (a) for varying concentrations of maleic anhydride. Rates for some other dienophiles under comparable conditions are given in Figure 2 (c). The reactions were slow at room temperature and only for dimethyl maleate did the investigated range of polyene sequences react quantitatively. Loan⁴ reported similar results from visual observation of the color. The relative rates of the other dienophiles were of the same order as reported in the literature for their Diels–Alder reactions with low molecular-weight dienes.¹⁰ It was attempted to raise the rate of the reactions by using catalysts and higher temperatures. Already a moderately higher temperature of 40°C caused side reactions, such as cross-linking and further dehydrochlorination.

In the literature catalysts for Diels–Alder reactions have been described.¹⁰ We tried aluminum chloride and ferric chloride. Both catalyzed only further dehydrochlorination, however. Better results were obtained with cobalt naphthenate which approximately doubled the rate of reaction between maleic anhydride and polyene PVC.

While an increase of the maleic anhydride concentration had the expected effect of increasing the reaction rate, an increase in the concentration of polyene

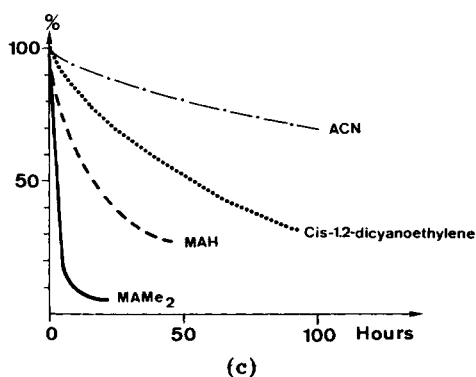
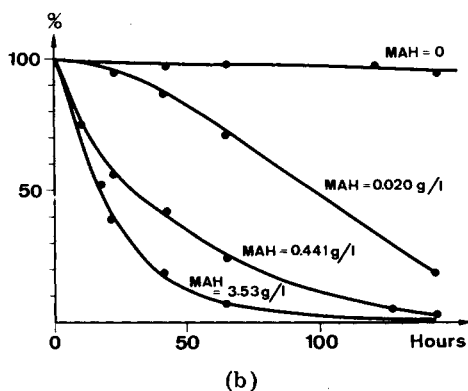
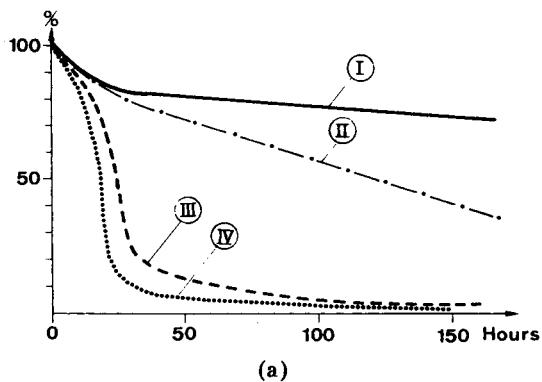


Fig. 2. Rates of disappearance expressed as the percentage of double bonds ($n = 6-10$) remaining (see text) after reaction of polyene PVC. (a) Calculated from spectra in Figure 1 (a). (b) Calculated from spectra in Figure 1 (b) (see text). (c) 0.351 g/l of polyene PVC ($D_{\text{tot}} 4.1$ mole %), made by reaction with alcoholic KOH in THF, with different dienophiles; acrylonitrile, *cis*-1,2-dicyanoethylene, maleic anhydride, and dimethyl maleate. The concentration of dienophile was 2.0 mmole/l in each case.

PVC gave lower reaction rates. Attempts to perform the reaction in solvent-swollen beads failed due to too low rates. A probable explanation is that steric hinders from association of polyene segments made the conditions unfavorable for reaction.

Some of the derivatives obtained by the reaction of polyene PVC with dienophiles were isolated and purified by repeated precipitation from THF solution. Films were cast and subjected to infrared analysis. Those from maleic anhydride gave a carbonyl absorption at 1780 cm^{-1} , where untreated polyene PVC had little absorption. Hydrolysis of the maleic anhydride derivative yielded a polymer containing carboxyl groups. By potentiometric titration in THF by aqueous NaOH the quantity of them was shown to be of the same order of magnitude as

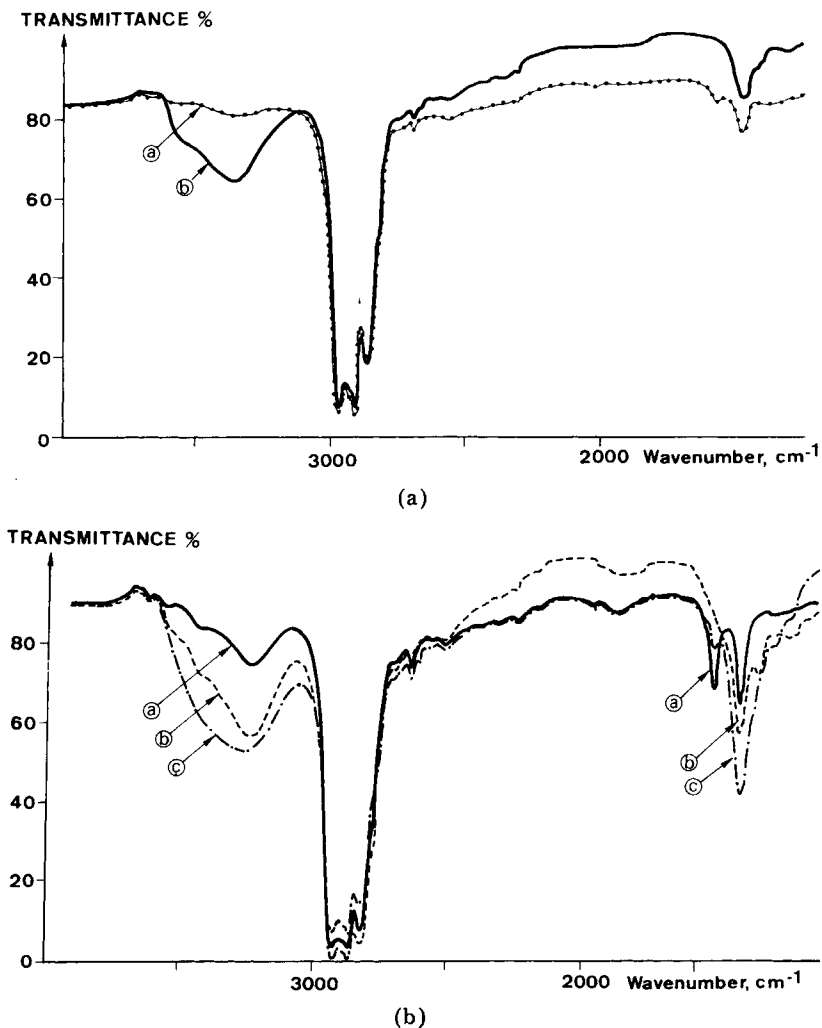


Fig. 3. Infrared spectra of: (a) Polyene PVC (D_{tot} 3 mole %) (a) before and (b) after hydroxylation with OsO_4 . The reaction was carried out in THF at room temperature. Time of reaction 15 hr. Concentrations: polyene PVC 8.989 g/l, OsO_4 1.214 g/l. (b) Polyene PVC [D_{tot} 0.3 (a), 3 (b), and 8 (c) mole %] after hydroxylation with performic acid (see Table I). The polyene PVC was made by reaction with alcoholic KOH on a PVC solution in THF (Experiment 10, ref. 2).

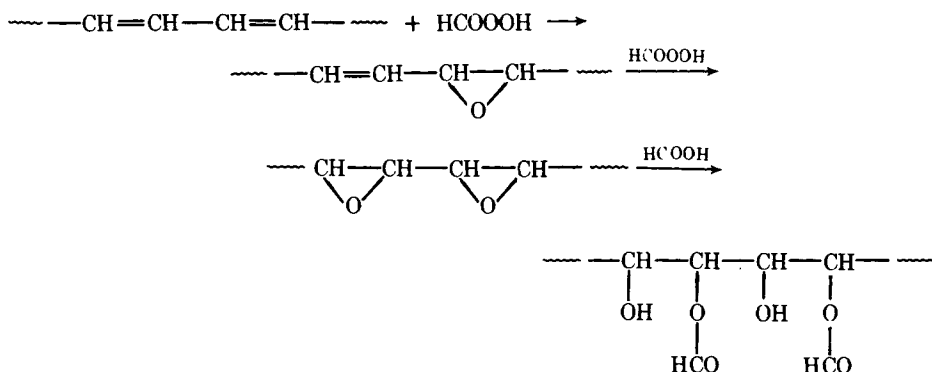
could be expected from a Diels–Alder reaction of the accessible polyene segments. The titration curves showed two equivalence points as expected for a dibasic acid.

HYDROXYLATION

Three different hydroxylation methods were tried on polyene PVC. With potassium permanganate chain scissions were frequent as evidenced by the rapid decrease in viscosity. It was to be expected since PVC itself has been shown to be rapidly degraded by potassium permanganate.¹⁷ The action of osmium tetroxide proved to be more selective. After hydrolysis of the osmate ester a cast film of the product gave the infrared absorption spectrum shown in Figure 3 (a). When compared with the original PVC an absorption peak at 3360 cm^{-1} had formed.

The third method tried was hydroxylation by performic acid. Polyene PVC samples made by all three dehydrochlorination methods (see Experimental) were studied. The hydroxylations were performed in solution in THF or with particles of polyene PVC swollen and suspended in chloroform or benzene. The experimental conditions are given in Tables I–III.

The reactions were performed at room temperature and led to discoloration of the polyene PVC in one day. An ultraviolet spectrum of a sample after 25.1 hr is shown in Figure 4. The absorption peaks due to polyene sequences had disappeared completely. Infrared spectra of films made by hydroxylation of polyene PVC samples with degrees of dehydrochlorination (D_{tot}) of 0.3%, 3%, and 8% are shown in Figure 3 (b). The absorption in the hydroxyl region (3360 cm^{-1}) increased with the degree of dehydrochlorination. In contrast to those hydroxylated with osmium tetroxide they also absorbed in the carbonyl region at 1725 cm^{-1} . It is reasonable to assume that the reaction had taken a similar course to that observed in reactions between performic acid and an alkene, i.e., both hydroxyl and formiate ester groups were introduced into the polymer.¹² The following reaction scheme serves to illustrate a probable mechanism.



The molecular-weight distributions were followed by GPC analysis of the polyene PVC samples and the hydroxylated products. In Figure 5 the GPC curves for a polyene PVC (alcoholic KOH in dioxane) with 1.5% dehydrochlorination, its ozonolysis product, and its reaction product with performic acid are

TABLE I
Experimental Conditions in Hydroxylation Reactions of 0.625 g Polyene PVC in 50 ml THF Under Nitrogen Blanket^a

Polyene PVC D_{tot} , mole %	Time, hr	HCOOH moles added	H ₂ O ₂ moles added	$\frac{\text{H}_2\text{O}_2}{\text{C}=\text{C}}$ initially	Remarks
0.3	0	1.13×10^{-2}	0.4×10^{-2}	133	Yellow to red solution
	15	3.4×10^{-2}	0	—	Pale yellow
	22	0	0	—	White
3	0	3.2×10^{-2}	1.2×10^{-2}	40	Dark red
	15	9.6×10^{-2}	0	—	Light red
	22	0	0	—	White
8	0	8×10^{-2}	3.2×10^{-2}	40	Black, reddish
	15	26.0×10^{-2}	3.2×10^{-2}	—	Dark brown
	22	0	0	—	Pale yellow

^a Polyene PVC made by reaction of alcoholic KOH on PVC in THF (experiment 10, ref. 2).

shown. While ozonolysis reduced the molecular weight drastically, hydroxylation only changed it slightly as seen by the broadening of the curve.

In Figure 6 the number average molecular weights and the heterogeneity index (HI) are shown as a function of the degree of dehydrochlorination. In this case the polyene PVC samples were made by treatment of alcoholic KOH in dioxane (experiment 25, ref. 2). The hydroxylations were made by performic acid acting on polyene PVC particles swollen in chloroform (Table II). For comparison the data for the original PVC and the ozonolyzed products of the polyene PVC samples are shown. The number average molecular weights and the heterogeneity indices were essentially unchanged in the hydroxylated samples as the

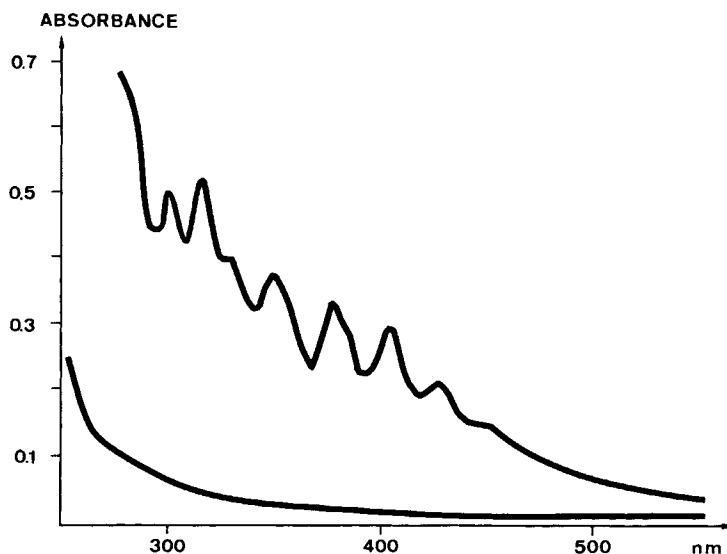


Fig. 4. Ultraviolet spectra for polyene PVC (D_{tot} 1.5 mole %), made by reaction of alcoholic KOH on dioxane swollen PVC (experiment 25, ref. 2). (a) Before hydroxylation. Concentration 0.625 g/l. (b) After hydroxylation for 25.1 hr with performic acid in chloroform. Concentration 0.625 g/l.

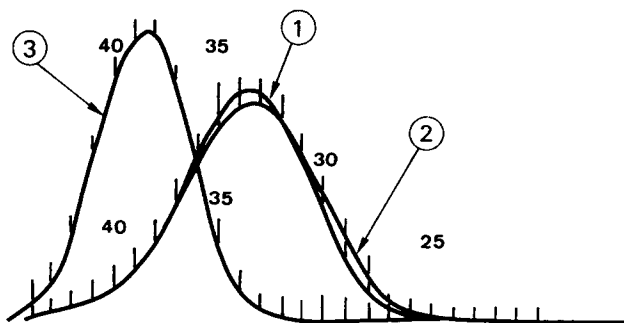


Fig. 5. GPC curves for polyene PVC, D_{tot} 1.5 mole %, made by reaction of alcoholic PVC on dioxane swollen PVC (experiment 25, ref. 2). (1) Polyene PVC, (2) polyene PVC after hydroxylation, (3) polyene PVC after ozonolysis.

degree of dehydrochlorination increased. A slight tendency towards higher values was observed.

When the reactions were made in solution in THF on samples with higher degrees of dehydrochlorination, the changes were more pronounced, i.e., the molecular weight decreased. This was also the case when large molar excesses of performic acid was used. However, the decrease was always moderate and

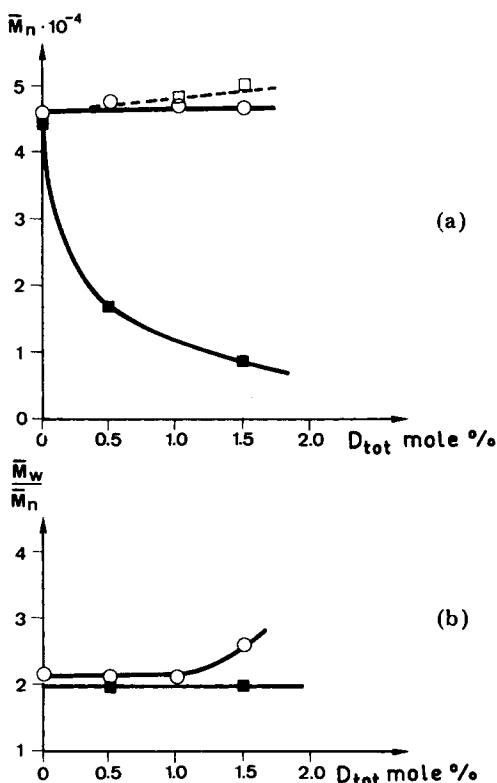


Fig. 6. (a) Number average molecular weights (\bar{M}_n), and (b) heterogeneity indices (\bar{M}_w/\bar{M}_n) for polyene PVC (O) of varying D_{tot} , made by reaction of alcoholic KOH on dioxane swollen PVC (experiment 25, ref. 2); the corresponding hydroxylated products (□) and the corresponding ozonolyzed products (■).

TABLE II
Experimental Conditions in Hydroxylation Reactions of 35 g Polyene PVC Swollen in 200 ml Deaerated Chloroform Under Nitrogen Blanket^a

Polyene PVC D_{tot} , mole %	Time, hr	HCOOH moles added	H ₂ O ₂ moles added	$\frac{H_2O_2}{C=C}$ initially	Remarks
	0	0.67	0.025	8.9	Red
0.5	25.2	0	0.013	—	Yellow
	49	0	0	—	Pale yellow
1.0	0	0.67	0.050	8.9	Red
	17	0	0	—	White
1.5	0	0.67	0.050	6.0	Dark red
	25.2	0	0.013	—	Pale yellow
	45.3	0	—	—	Pale yellow
	48	0	0	—	Pale yellow

^a Polyene PVC made by reaction of alcoholic KOH on PVC in dioxane (experiment 25, ref. 2).

the molecular weights well above those of corresponding ozonolyzed samples. Thus relatively few of the polyene sequences had undergone chain scission reactions.

As mentioned in a previous paper, the polyene PVC became insoluble at degrees of dehydrochlorination above about 1% when the reaction was made thermally in DMF.² We carried it well beyond the gel point, disintegrated the gels, and performed the subsequent reactions on suspensions of particles swollen by solvents. Hydroxylations were made with benzene and ozonolysis with chloroform as swelling agent. The products of both reactions were soluble in THF and could be analyzed by GPC. The results are shown in Figure 7 where also the molecular weights and heterogeneity indices of the soluble polyene PVC samples are given. For the soluble PVC samples D_{tot} was determined according to Vaiman.¹⁸

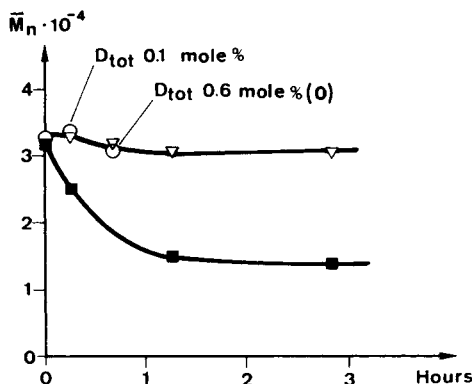
The hydroxylated samples had nearly the same molecular weights as the

TABLE III
Experimental Conditions in Hydroxylation Reactions of 10 g Swollen in 150 ml Deaerated Benzene Under Nitrogen Blanket^a

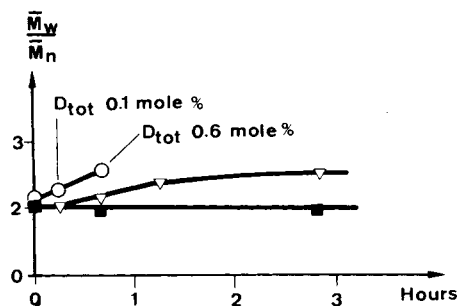
Polyene PVC made by heating at 130°C in DMF, min	Hydroxylation time, hr	HCHOOH moles added	H ₂ O ₂ moles added	Remarks
15	0	0.54	0.019	Pink solution
	18	0	0	White
40	0	0.54	0.037	Dark brown solution
	18	0	0	White
75	0	1.08	0.19	Black gel
	21.5	0	0	Pale yellow solution
170 ^b	0	1.33	0.20	Black gel
	18	0	0	White

^a PVC dehydrochlorinated at 130°C in DMF (experiments 26 and 27, ref. 2).

^b 25-g black gel swollen in 250 ml benzene.



(a)



(b)

Fig. 7. (a) Number average molecular weights (\bar{M}_n), and (b) heterogeneity indices (\bar{M}_w/\bar{M}_n) for polyene PVC (O) made by heating to 130°C in DMF for different times (experiments 26 and 27, ref. 2) the corresponding hydroxylated products (∇), and the corresponding ozonolyzed products (\blacksquare). At low conversions the DMF degraded products were soluble and D_{tot} was determined.

original PVC. It was remarkable since the intermediate polyene PVC samples had gelled and were insoluble in the solvents tried. The obvious explanation is that the cross links responsible for gelation were of a physical nature and due to crystallization of the polyene segments. Further evidence was provided by the ozonolysis experiments which yielded soluble products. This could be expected if the crystallizing segments were destroyed by ozonolysis. Hydroxylation prevented crystallization since side groups (formate and hydroxyl groups) were introduced which hindered aggregation. Furthermore, since gelation occurred the functionality of the polymer chains must be above two; there were more than two polyene segments in the gel-forming molecules, supposing that each segment only participated in one crystallite formation. Another possibility is that some of the longer polyene segments participated in more than one physical cross-link.

In order to find out if a completely dehydrochlorinated PVC could be made soluble by hydroxylation, a PVC solution in THF was treated with sodium amide in liquid ammonia as described by Tsuchida *et al.*¹⁴ The black intermediary product was swelled in benzene and reacted with performic acid. It was decolorized to a yellowish white mass which was insoluble but swelled considerably in both THF and water. Apparently covalent bonds had been formed during the reactions.

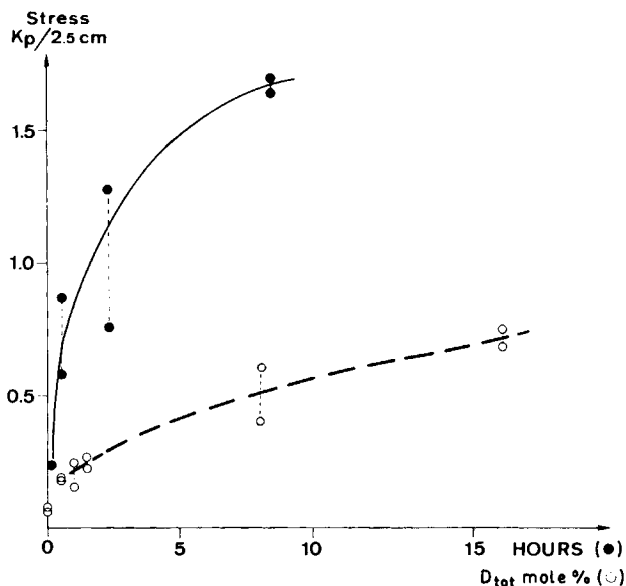


Fig. 8. The adhesion of hydroxylated polyene PVC samples which before hydroxylation had the D_{tot} given. Open circles (O) are for polyene PVC made by reaction of alcoholic KOH in THF or dioxane. Full circles (●) represent hydroxylated samples of polyene PVC made by thermal dehydrochlorination in DMF.

Poly(vinylene glycol) is insoluble in most solvents due to crystallization.¹⁸ Since segments of poly(vinylene glycol) should be present in hydroxylated polyene PVC insolubilization would be likely to occur when the segments are long enough. We hydrolyzed performic acid treated polyene PVC with long segments (from thermal dehydrochlorination in DMF) to remove the formiate ester groups by hydrolysis with HClO_4 . Insolubilization occurred since clear solutions in THF could not be obtained from samples with long hydroxylated segments.

ADHESION

The introduction of polar groups into PVC can be expected to increase its adhesion to polar substrates. We tested the adhesion of our carboxylated (Diels-Alder reaction with maleic anhydride followed by hydrolysis) and hydroxylated (with performic acid) PVC derivatives to glass and stainless (18/8) steel surfaces. The results of tests with hydroxylated derivatives are shown in Figure 8. As mentioned previously we found D_{tot} difficult to determine for the DMF samples owing to gelation at an early stage of the reaction. However, after hydroxylation the hydroxyl group concentration could be estimated by IR analysis in relation to hydroxylated PVC made from polyene PVC of known D_{tot} (dehydrochlorinated by alcoholic KOH in THF). The curves based on relative hydroxyl content are in good agreement with those obtained by calculating D_{tot} with the formula given by Fikhman.¹⁹ The force required to separate the film from the steel surface increased with the degree of substitution (given as degree, or for DMF time, of dehydrochlorination in the figure). The samples obtained by thermal dehydrochlorination had much higher adhesion than the ones ob-

tained by alkaline dehydrochlorination. The differences were considerable indicating fundamental structural differences between the two types of derivatives. This is in accordance with the observation of differences in average segment lengths after thermal degradation in DMF and alkaline degradation, respectively.

The carboxylated derivatives had higher adhesion than the hydroxylated ones. For them also the adhesion increased with the degree of substitution and the derivatives from thermal dehydrochlorination had considerably higher values than those from alkaline dehydrochlorination.

For both types of derivatives the ones obtained by thermal dehydrochlorination in DMF had the highest adhesion. A reasonable explanation seems to be that the length of the segments containing the polar groups plays an important role for adhesion. It can be deduced from our results that a few long segments are more efficient for promotion of adhesion than a greater number of short segments. It is highly probable that similar effects will be seen for other physical properties. Since it is possible to vary the length of the segments without changing their number, this type of derivatives open up interesting possibilities to study microphase separation and its influence on the physical properties.

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