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UV-visible spectroscopic study of the reaction kinetics of methylpiperazine-modified poly(vinyl chloride)s for use as fixed-state proton carrier membranes

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Aminated poly(vinyl chloride)s (AmPVCs) were synthesized for use as fixed-site proton carrier membranes. Reactions between PVC and methylpiperazine (MePIP) in dimethylformamide (DMF) were studied using UV-VIS spectroscopy over time, temperature, and in the presence of the catalyst, potassium fluoride (KF). Based on the spectra of AmPVCs in THF, the peak attributions were assigned and the extinction coefficients were calculated to determine the vinyl MePIP groups and polyenes with different number of conjugated double bonds (n). The rate constants for the accumulation of vinyl MePIP groups (k_N), polyenes with $2 \leq n \leq 7$ (k_n), and total conjugated double bonds (k_D) were calculated at 90°C. The k_N constant was only about one half as much as k_D, and $k_n > k_{n+1}$ (for $2 \leq n \leq 7$). Assuming an Arrhenius relationship, the activation energies (ΔE) were calculated for the formation of the vinyl MePIP groups and polyenes with $2 \leq n \leq 13$ over different temperature ranges and in the presence or absence of KF. The first double bond formation was always favoured over the substitution reaction at any temperature and were independent of the presence of KF. As for the propagation of double bonds, short chains grew easier than long chains; but after a certain n, they grew with the same energy barrier. When the EMF-pH responses of AmPVC membranes were studied, no clear dependence was observed between the Nernstian responses of the membranes and the amount of conjugated double bonds (D) or the D/R_N, where R_N was the amount of vinyl MePIP groups. Nernstian responses were obtained for membranes made from AmPVCs with $0.003 \leq R_N \leq 0.04$ and $0.6 \leq D/R_N \leq 1.7$. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(vinyl chloride); reaction; UV-VIS-spectroscopy)

INTRODUCTION

In recent years many publications have appeared in which modified poly(vinyl chloride) (PVC) were used as fixed-site proton carrier membranes[1–3]. Consequently, PVC has found a new use as a precursor for novel polymeric syntheses. In this work PVC was modified by a heterocyclic saturated amine, 1-methylpiperazine (MePIP), and fixed-site proton carrier membranes were prepared from the modified polymer.

Since the advent of aminated PVCs as ion conductive membranes, investigators have noted their discolouration[4]. The presence of conjugated double bonds in these polymers were presupposed, since substitution of the amine moiety (a SN2-type reaction) and elimination of HC1 (an E2-type reaction) occurred concurrently. Although some authors studied the elimination reaction in PVC in the presence of strong bases[5], the processes of amination and elimination have not been investigated simultaneously. So the direct process (the amination) and a side or parallel process (the elimination) were studied, using UV-VIS spectroscopy. The best conditions of the amination were provided: high nucleophilicity and basicity of the N-containing reagent, MePIP; an excess MePIP over the polymeric halide; a 'good' aprotic solvent, *N*,*N*-dimethylformamide (DMF); and the presence of a catalyst, potassium fluoride (KF). The SN2 and the E2 reactions were compared by their rate constants and activation energies. Two questions were addressed: why did the side reactions occur despite unfavourable conditions? And did double bonds influence the ion conductive properties of these materials? In the present work the reactions between the PVC and MePIP were investigated *versus* time, temperature, and the presence of a catalyst. After membranes were prepared from these formulations, their pH responses were measured in appropriate potentiometric cells. The interaction between N containing groups, conjugated double bonds, and ion conductive properties were discussed.

EXPERIMENTAL

General amination procedure

For each batch, 0.02 mol of PVC beads (MW = 110,000; Polyscience) was reacted with 0.04 mol of 1-methylpiperazine (MePIP; Aldrich) in 50 ml of DMF (HPLC grade; Sigma-Aldrich) under Argon (Ar) flow. In those experiments in which a catalyst was used, 0.002 mol KF (Fluka-Chemika) was added. In some cases, which will be discussed later, 0.0004 and 0.01 mol of KF were also used. Temperatures were maintained from 50 to 110°C. Each reaction time was measured in hours (h). At the end 60 ml methyl alcohol (MeOH) (HPLC grade, Mallinckrodt

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Chrom AR) was added to quench the reaction. The solutions with precipitated polymer were left standing for 24 h. Then the solvent was removed with a Buchner funnel. The polymer was washed by portions of MeOH until the pH of the filtrate became neutral. Finally the aminated PVC product (AmPVCs) was dried in a vacuum overnight.

As distinct from work where authors used piperazine as a reactant[3], this work used MePIP. As a result, crosslinking due to a second tertiary anino group was not found. Therefore, all formulations were soluble in THF.

Membrane preparation

The polymer of AmPVC, the negatively charged sites of potassium tetrakis(*p*-chlorophenyl)borate (KT*p*ClPB; Fluka), and the plasticizer of *o*-nitrophenyloctyl ether (*o*-NPOE; Fluka) were dissolved in tetrahydrofuran (THF), HPLC grade; Fisher Scientific) in the proportions, 100:2:200. For every 300 mg of polymer, its negatively charged sites, and its plasticizer, 4 ml of THF was added. Membrane disks that were about 200 μm in thickness were recovered following solvent evaporation of THF for *ca.* 48 h.

Electromotive force (EMF) measurements

Ion-selective pH electrodes were fabricated from membrane disks that were 0.7 cm in diameter. These were preconditioned for a minimum of 24 h in a pH = 7 TRIS buffer, which contained sodium as an ionic background. Using an Ag/AgCl external reference electrode (Orion Model 90–90), the EMF was measured across the membrane disks at 23°C with a pH/mV-meter (Orion Model 720) from pH = 4 to pH = 12.

The general amination procedure, membrane preparation, and EMF measurements have been detailed in a previous publication[6].

Recording UV-VIS spectra

A UV-VIS spectrophotometer (Model DU–70; Beckman) was used with a wavelength range of 190–900 nm and a scanning speed of 60–2400 nm min^{-1}. The spectra of the polymers were recorded in solutions of THF. Wavelengths (λ) were varied from 200 to 550 nm at a scanning speed of 120 nm min^{-1}.

For the first spectrum of any formulation 0.05 mol l^{-1} solutions of AmPVC (assuming 1 mol of AmPVC $\approx$ 1 mol of PVC = 62.5 g) were dissolved in THF. Wavelengths of the absorbance maxima and values of the absorbance were determined. Only those maxima were used for the concentration calculations that satisfied the Lambert–Beer's law, $A = \epsilon{\cdot}c{\cdot}l$; where A was the absorbance in relative units, ϵ was the extinction coefficient (l mol^{-1} cm), c was a concentration (mol l^{-1}), and l was a light path (cm). Using corresponding dilutions of solutions by THF, working spectra were obtained within these specifications for all wavelengths. All solutions were kept under Ar to prevent water sorption and/or to reduce oxidation.

Attributions and calculations

All formulations had a spectral peak at 211 ± 3 nm, which was attributed to the vibration of electrons in the MePIP ring. This attribution was made on the basis of MePIP and 1,4-Dimethylpiperazine (DMePIP; Aldrich Chem. Co) spectra, which have only one peak with the same λ. To calculate the extinction coefficient of amine-containing groups in AmPVCs, the tertiary amine DMePIP, was used. By preparing known concentrations of DMePIP in THF (*Table 1*), the extinction coefficient of the DMePIP (ϵ_N = 11500 ± 500 l mol^{-1} cm) was determined at 0.05 (mol l^{-1}) PVC. Using this value of ϵ_N, concentrations of vinyl MePIP groups (c_N) were determined in solutions of the AmPVCs, assuming that this unit has the same ϵ_N in AmPVC that the low molecular weight DMePIP has in the presence of PVC. The relative amounts of vinyl MePIP groups in AmPVCs were calculated as the ratio, $R_N = c_N/c_o$, where c_o was the initial concentration of AmPVC in solution.

Table 1 Determination of the extinction coefficients (ϵ_N) for DMePIP in the presence of 0.05 mol l^{-1} PVC

c (mol l^{-1})	λ (nm)	Absorbance	ϵ_N (l mol^{-1} cm)
0.0000918	209.4	0.9261	10088
0.0000918	209.2	0.9167	9986
0.0000673	208.8	0.7695	11464
0.0000673	208.9	0.7352	11434
0.0000459	208.9	0.6762	14732
0.0000459	208.9	0.5971	13009

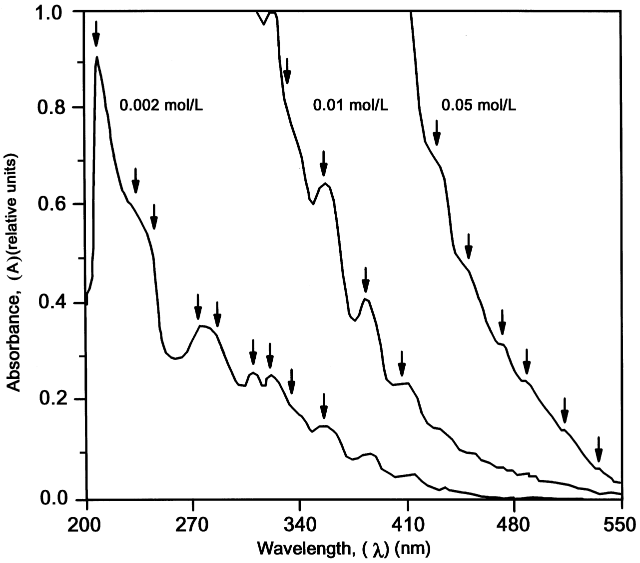

Figure 1 Spectrum of AmPVC that was synthesized at 90°C for 6 h, a portion of which was then dissolved in THF. The arrows indicate the special points at three different concentrations

Although PVC-reaction products can include a small amount of carbonyl and allylic chloride groups, UV-VIS spectra do not show their presence[7,8]. All other spectral peaks of the AmPVCs were attributed to an availability of sequences of conjugated double bonds (polyenes), where n was the number of conjugated double bonds in a certain polyene. After the extinction coefficients were determined for each polyene (ϵ_n), concentrations of each polyene in solution (c_n) were obtained. The relative concentrations of polyenes containing n double bonds (R_n) were expressed as the ratio of their absolute concentrations (c_n) to initial concentrations of AmPVCs in solution (c_o), or $R_n = c_n/c_o$. The total amount of conjugated double bonds (D) was calculated as, equation (1)

$$D = \sum_{n=1}^{n=m} nR_n \qquad (1)$$

where m was the number of double bonds that were found in the longest polyene of a given AmPVC.

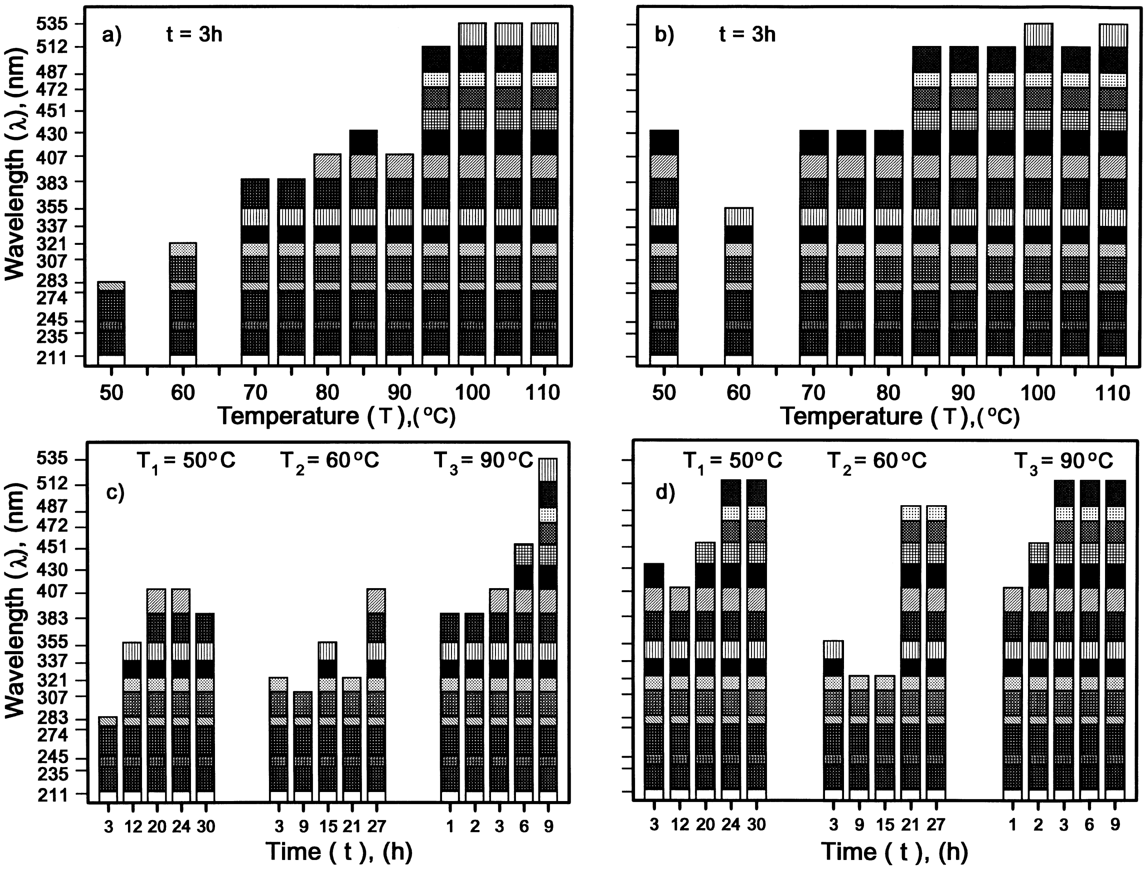

Figure 2 The availability of peaks and other special points in the spectra of the AmPVCs: (a) and (b) for 3 h syntheses at different temperatures; (c) and (d) for different times at 50, 60, and 90°C, (a) and (c) without the KF catalyst; (b) and (d) in the presence of the KF catalyst

RESULTS

In total the spectra of about fifty batches of powders were tested, of which a typical spectrum is given in *Figure 1*. From all spectra about fifteen special points were identified by arrowheads within the region from $\lambda = 200$ to $\lambda = 550$ nm. Each point existed in a narrow interval 6–10 nm, depending on the polymer concentrations. Not only points of the maxima were implied as special points, but all points, were the first derivative of absorbance ($dA/d\lambda$) abruptly changes its value. On the *y*-axis of *Figure 2* the λ's of all special points were denoted, as well as the time, temperature, and in (b) and (d) the presence of catalyst (KF). More special points were observed with longer reaction times or higher temperatures. When the catalyst was present, its influence was observed at low and intermediate temperatures for all time periods.

DISCUSSION

Attribution of peaks and calculation of extinction coefficients for polyenes

All special points, except the first peak at 211 ± 3 nm, were attributed to the availability of conjugated double bonds in AmPVC. Some theoretical and experimental background was used to identify the peak that represented the electron vibration of a certain polyene with *n* conjugated double bonds and its extinction coefficient.

In 1939 Lewis and Calvin formalized the theory that changes in the colour of organic compounds contained *n* conjugated double bonds[9]. Assuming a quasi-classical model, they considered that the molecules represented vibrating electronic systems, which were subject to the same rules of quantitization as an harmonic oscillator. Accordingly, two deductions were made,

$$\lambda_n^2 \propto n \tag{2}$$

and

$$\epsilon_n \propto n \tag{3}$$

where λ_n was a wavelength of the greatest absorption maximum of the polyene sequence containing *n* conjugated double bonds and ϵ_n was its corresponding extinction coefficient. In the mid 50's and early 60's this theory was verified on several homologous series of organic substances[10–12]. Those authors found that spectra of polyenes containing *n* conjugated double bonds consisted of four maxima in order of increasing wavelengths—A, B, C, and D. The spectra of the substances with $n < 6$ had very small A maxima, which completely disappeared at $n \leq 3$. Maxima C and D were the most prominent, although they were not equal in value. In fact for $n \leq 7$, peak D was greater than C; whereas for $n \geq 8$, peak C was greater than D. The linear dependencies were observed between λ_n^2 and *n* for all four maxima of polyenes, when *n* ranged from 2 to 12, and mostly for ϵ_n and *n*, when *n* ranged from 2 to 7. The data for ϵ_n were less reliable, however, because the separation and purification of polyenes with high *n* were difficult.

Unlike organic compounds the polymer chain can include polyenes of different *n* simultaneously. Equations (2) and (3) can be applicable for analyzing polyenes found in polymers, if the following assumptions are made:

(i) The apparent of polyene sequences with *n* double

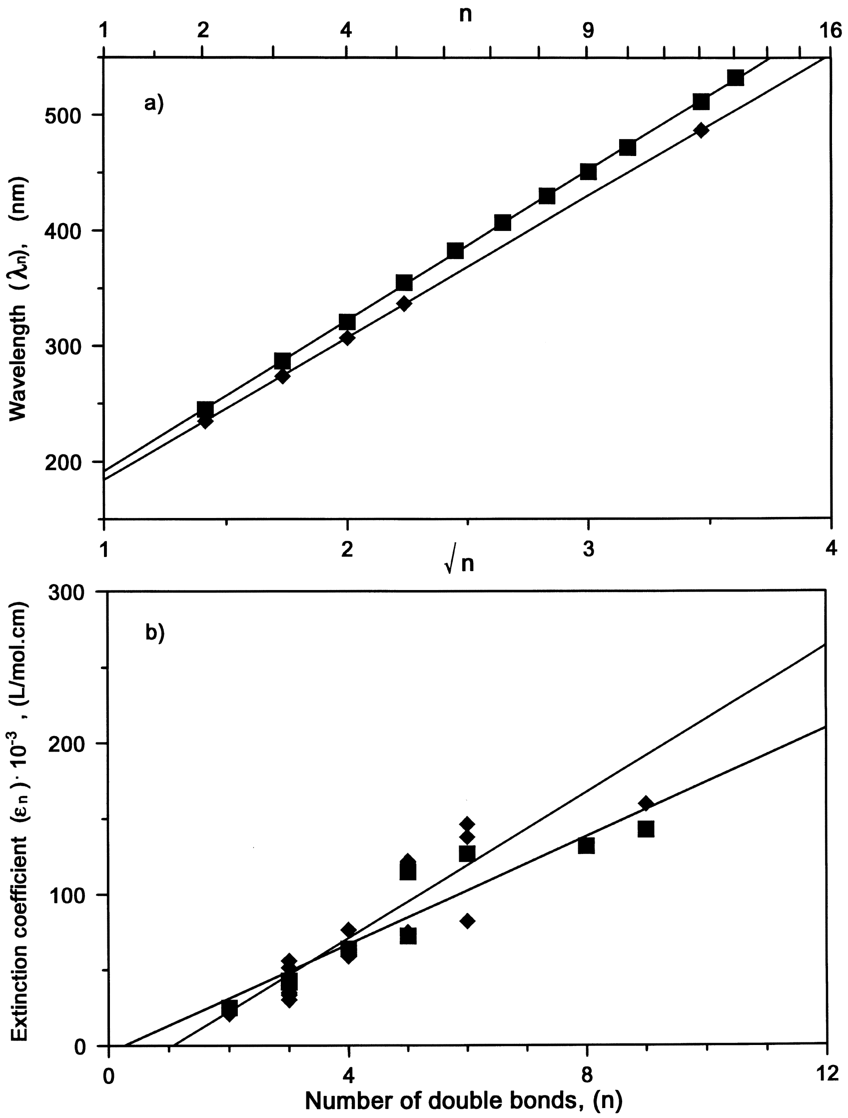

Figure 3 Confirmation of n to two assumptions: (a) the distribution of special points wavelengths between two lines according to the law, $\lambda_n \propto \sqrt{n}$; (b) the dependence $\epsilon_n \propto n$ for experimental data of different low molecular weight polyenes, as found in the literature. In both plots (■) represents peak D and (◆) represents peak C

bonds in a polymer chain can be equated to the availability of independent oscillators, whose properties equal those of low molecular weight substances with the same n. Some authors[7,8,13,14], who studied the thermal degradation of the PVC and poly(vinyl alcohol), successfully used that assumption. This approach was incorporated in this work to determine the amount and distribution of conjugated double bonds in AmPVCs.

(ii) We also assumed that the spectra of AmPVCs exhibited only the most intensive maxima of the related low molecular weight compound spectra (C and D), although they are the sums of the spectra of relative compounds. Exactly as in low molecular weight compounds case, equations (2) and (3) are fulfilled for each type of peak.

(iii) And a third assumption was made: that each maximum reflects the vibration of the only one type of polyene for a given n. That is, the interaction between polyenes in a polymer chain is ignored. As a consequence, the spectral inputs of all other polyenes within the spectrum of a given polyene are ignored.

Returning to the experimental data of this work and according to the first two assumptions, a distribution of special point λs was made between two lines obeying the law, $\lambda_n \propto \sqrt{n}$ (*Figure 3a*). By linear regression analysis straight lines were obtained that were significant having the probability, $p < 0.001$. For $2 \leq n \leq 5$ and $n = 12$, special points belonged to lines C and D. At least one of them was the maximum point for each n. For $6 \leq n \leq 10$ and $n = 13$, points belonged only to the line D. Inexplicably the point $n = 11$ does not exist for either C or D.

Figure 3b shows a linear plot of all extinction coefficients that were found in the literature for maxima C and D at different n for low molecular weight substances[10–12,15,16], for which the regression lines were

$$\epsilon_{n,\mathrm{C}} = 24188n - 25797$$

and

$$\epsilon_{n,\mathrm{D}} = 17886n - 4654$$

The values of $\epsilon_{n,\mathrm{C}}$ and $\epsilon_{n,\mathrm{D}}$ were calculated for all n from 2 to 14. The calculated ϵs together with corresponding λs are given in *Table 2*, which were used for the concentration determination via Lambert-Beer's law. If two special points referred to the same n, the maxima points were

Table 2 Wavelengths (λ) and corresponding extinction coefficients (ϵ) for the quantitative determination of polyene sequences in PVC

n	λ (nm)	ϵ_C (l mol^{-1} cm)	ϵ_D(l mol^{-1} cm)
2	235 ± 4	22600	
3	274 ± 3	46800	
4	307 ± 3	71000	
4	321 ± 3		66900
5	355 ± 2		84800
6	383 ± 3		102700
7	407 ± 3		120600
8	430 ± 3		138400
9	451 ± 2		156300
10	472 ± 3		174200
12	487 ± 2	264500	
12	493 ± 2		210000
13	512 ± 3		227900
14	535 ± 3		245800

ϵ_N = 11 500 (l mol^{-1} cm) at 211 ± 3 nm for vinyl MePIP groups determination

preferred for concentration calculations. Average values were taken for c_4 determined at $\lambda = 307$ and $\lambda = 321$ nm and c_{12} at $\lambda = 487$ and $\lambda = 493$ nm, because no preference was found.

Study of the substitution and elimination reactions

Figure 4 shows the time dependence of accumulations of vinyl MePIP groups (R_N) (*Figure 4a*), total conjugated double bonds (D) (*Figure 4b*), and separate polyenes (R_n) with $n = 2$, and $n = 7$ (*Figure 4c* and *d*) for formulations that were made in the presence and absence of catalyst (KF) at 50, 60 and 90°C. (Although only R_2 and R_7 were shown, other polyenes have the same trends and only differ in their specific values.) All dependencies were linear. In every case more vinyl MePIP groups, conjugated double bonds, and certain polyenes were observed in those formulations that were synthesized in the presence of KF than without it, but these differences diminished as the temperature decreased.

Table 3 Reaction rate constants of the vinyl MePIP group (k_N), total conjugated double bonds (k_D), polyenes with certain n (k_n), and specific ratios at 90°C

N, D, n	k_N, k_D, k_n (h^{-1})		k_N/k_D; k_n/k_{n+1}	
	KF present	KF absent	KF present	KF absent
N	0.00529	0.00522	0.46	0.53
D	0.01150	0.00993	-	-
2	0.00223	0.00234	2.9	3.7
3	0.00077	0.00064	1.9	1.9
4	0.00041	0.00034	2.0	1.9
5	0.00021	0.00018	1.8	2.0
6	0.00012	0.0009	2.0	-
7	0.00006	-	-	-

Based upon the linear regression lines of AmPVC data, the reaction rate constants k (h^{-1}) were calculated from the slope of these lines for the accumulation of vinyl MePIP groups (k_N), and the polyenes with certain n (k_n) ($2 \leq n \leq 7$). In *Table 3* these data are presented for reactions carried out at 90°C along with ratios k_N/k_D and k_N/k_{n+1}. Note that k_N was only about one half as much as k_D but two times more than k_2; so, despite the favourable

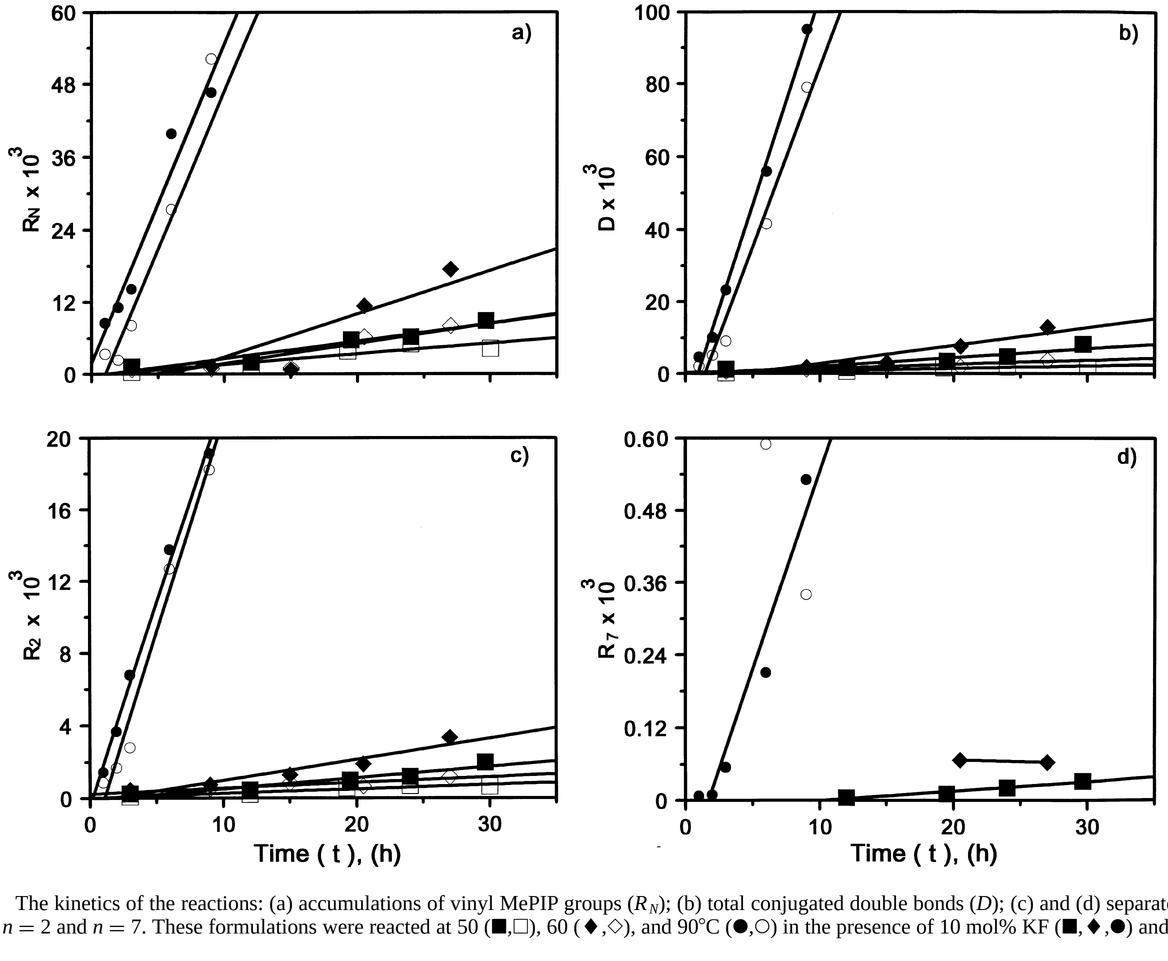

Figure 4 The kinetics of the reactions: (a) accumulations of vinyl MePIP groups (R_N); (b) total conjugated double bonds (D); (c) and (d) separate polyenes (R_n) with $n = 2$ and $n = 7$. These formulations were reacted at 50 (■,□), 60 (◆,◇), and 90°C (●,○) in the presence of 10 mol% KF (■,◆,●) and without it (□,◇,○)

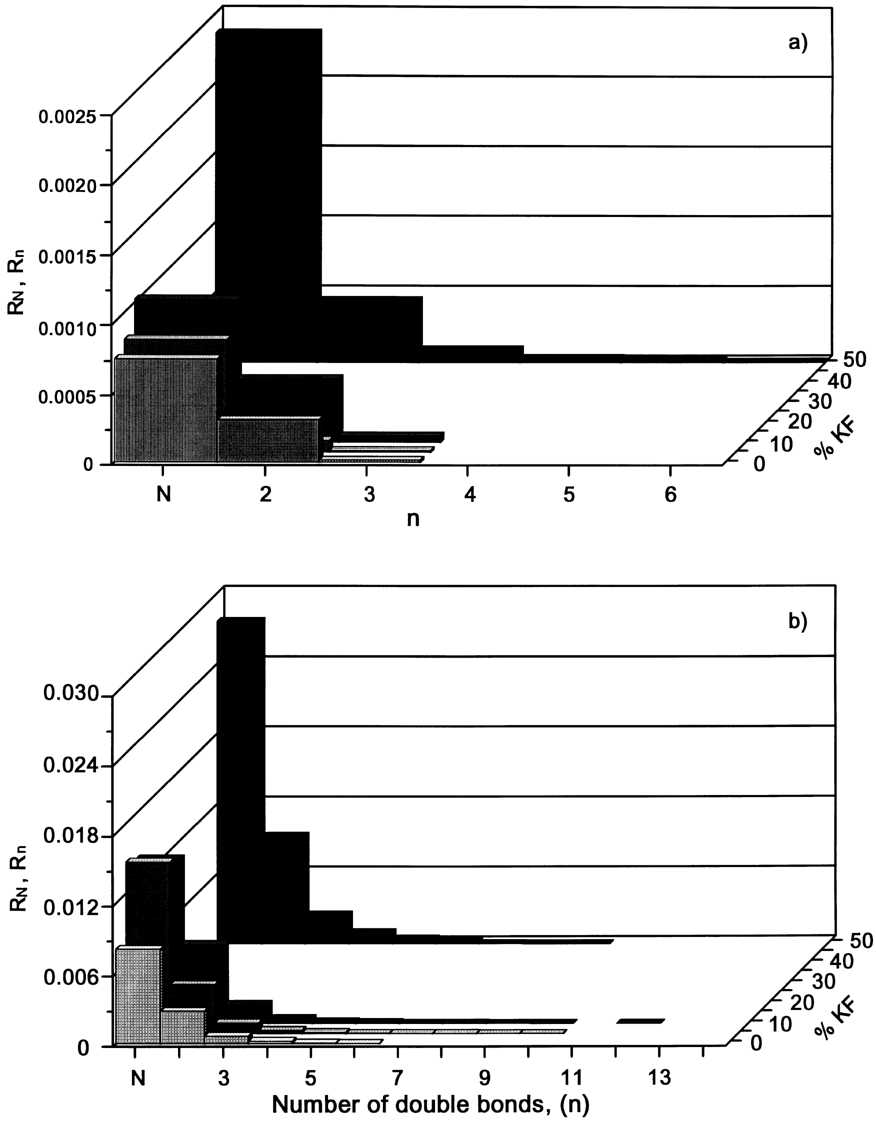

Figure 5 The accumulation and distribution of vinyl MePIP groups (R_N) and polyenes (R_n) with $n = 2,3,\ldots,13$ in formulations made with different amounts of KF: (a) at 60°C; and (b) at 90°C

conditions for substitution, the elimination reaction propagated faster. Also, although the catalyst accelerated both reactions, the KF apparently accelerated the elimination reaction more. Constants of the polyene formation with $n = 2$ were higher than with $n = 3$ by factors of 2.9 and 3.7 times, when reacted in the presence and absence of KF, respectively. When $n \geq 3$, each successive polyene formed, having a rate constant that was about two times less than the previous one. Thus the propagation of the polyene chain decelerated by an inverse relationship ($1/2^{n-1}$) for $n \geq 3$ and showed no indication of autocatalytic process.

Figure 5a and *b* show the influence of the catalyst at 60 and 90°C, respectively, on the amount of vinyl MePIP groups and conjugated double bonds and their distribution. The more catalyst that was used the more vinyl MePIP groups and polyenes that appeared at each *n* and in total. The dependence was not linear, if the amount of the catalyst was more than 10 mol%.

Figure 6 represents the amounts of vinyl MePIP groups (R_N) (*Figure 6a*), total conjugated double bonds (D) (*Figure 6b*), and separate for polyenes (R_n) with $n = 2$, and $n = 13$ (*Figure 6c* and *d*) *versus* temperature for formulations that were reacted for 3 h in the presence and absence of KF. Once again the dependencies of R_n are given only at the end points, R_2 and R_{13}, all others have the same trends and only differ in their specific values. At least three different parts are apparent on these curves. The first part corresponds to temperatures below 70°C. Here the amounts of vinyl MePIP groups, conjugated double bonds, and certain polyene sequences are low and independent of temperature, but depend on the presence or absence of the catalyst. The second part occurs between 70 and 100°C for the substitution reaction and 70 and 90°C for the elimination reaction, where the reactions go faster as temperature increases. Here the influence of the catalyst was substantial. In the third part above 100°C and 90°C, respectively, the yields from amination and elimination were very high and appear independent of KF.

Assuming an Arrhenius relationship, the activation energies (ΔE) (kcal mol^{-1}) were estimated for amination and elimination; and for the latter, for total conjugated double bond formation and for each polyene with certain *n*. If plotted, the curvature of some lines would require two linear regression analyses at the border of the second and third parts of the temperature regions: at 100°C for substitution and 90°C for elimination. Then these lines

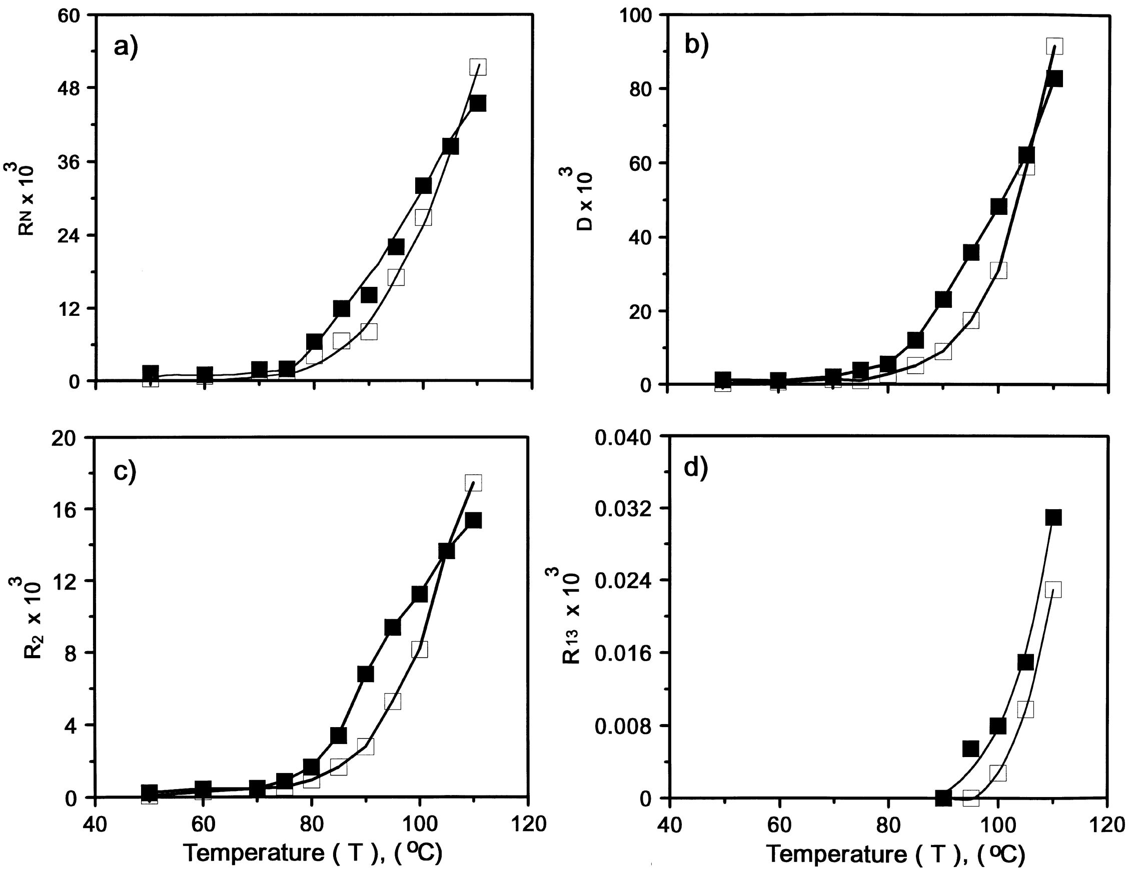

Figure 6 Influence of temperature on the yields of the reactions: (a) accumulations of vinyl MePIP groups (R_N); b) total conjugated double bonds (D); (c) and (d) separate polyenes (R_n) with $n = 2$ and $n = 13$. These formulations were reacted for 3 h in the presence of 10 mol% KF(■) and without it (☐)

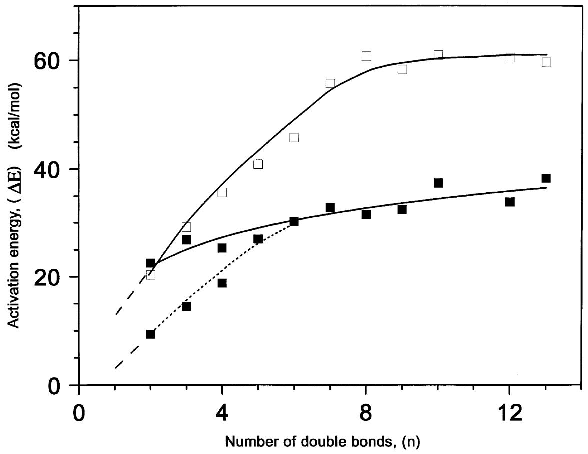

Figure 7 The activation energies (ΔE) for polyene sequence formation at $1 \leq n \leq 13$ in the presence (■) and absence (☐) of KF. The solid lines represent $T = 70$–90°C for $n = 2,3,\ldots,13$, the dotted line represents $T >$ 90°C for $n = 2$, 3, and 4, and the dashed lines represent the extrapolated data to $n = 1$.

would be bent for the substitution reaction in the presence and absence of the catalyst, but for the elimination reaction these lines would be bent only in the presence of KF for lnD, lnR_3 and lnR_4. Values for both temperature regions could be used for the ΔE calculations, where the bends of the experimental points existed.

Figure 7 shows the variation in ΔE for different polyenes synthesized in the presence and absence of KF. The data for polyenes, which were synthesized without KF, had the only values over the entire temperature interval 70–110°C for each n. The corresponding data for polyenes synthesized in the presence of KF were plotted for the temperature interval 70–90°C (solid lines) and above 90°C (dotted line) for $n =$ 2, 3, and 4. These ΔE data were extrapolated by necessity to $n = 1$ (dashed lines). (This extrapolation was possible because the formation of the first double bond was governed by the same process as the formation of any other double bond, although this process was not measured under the chosen experimental conditions by UV-VIS spectroscopy.) As expected, the ΔEs of the conjugated double bond formation were less in the presence of catalyst than without it. The ΔEs increased when n increased. Consequently the small polyenes initiated and propagated more readily than the large polyenes, the most favourable reactions being the polyene reactions having $n = 1$ or 2, especially at temperatures above 90°C in the presence of KF. But if $n \geq 8$, the formation of the next double bond was independent of n for formulations synthesized without KF. The ΔEs of the substitution reaction within the temperature region of 70 and 100°C were 17.3 and 23.5 kcal mol^{-1} in the presence and absence of KF, respectively, which changed to 9.9 and 18.3 kcal mol^{-1} above 100°C. Thus ΔEs of the substitution reaction were comparable to those of the elimination reaction (*Figure 7*) for low n (i.e., $n = 1$, 2 and 3) at both temperature regions and yet were higher than the first double bond formation (*Figure 7*). Therefore, the formation of the first double bond was more favourable than adding MePIP rings.

The AmPVCs were synthesized for use as fixed-site proton carrier membranes. *Figure 8a* illustrates that a Nernstian response can be attained by these membranes at a rather low level of vinyl MePIP groups ($R_N = 0.003$–0.004),

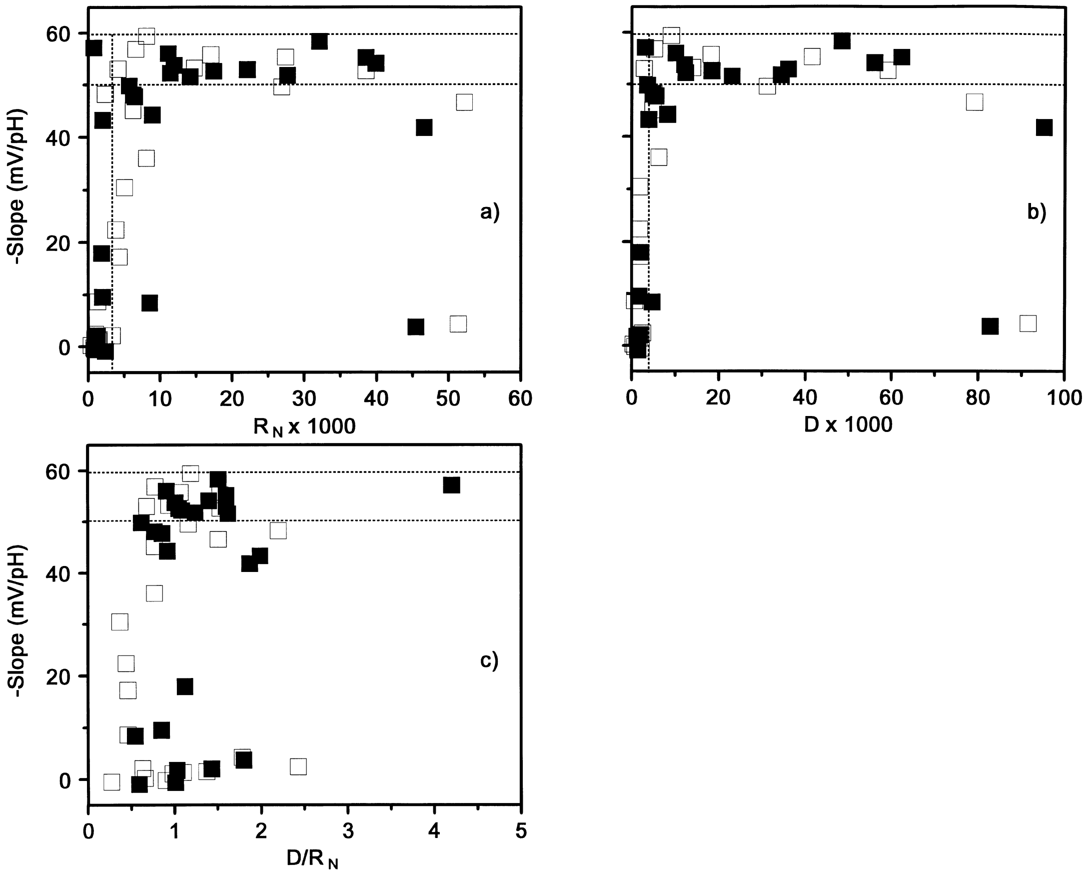

Figure 8 Slopes of the potentiometric-pH responses in the presence (■) and absence (□) of KF *versus*: (a) the vinyl MePIP group content (R_N); (b) the total conjugated double bond content (D) for all formulations; (c) the ratio D/R_N. The two horizontal dotted lines encompass the region of acceptable Nernstian behaviour; whereas the vertical dotted lines repreesnt the minimum value of R_N or D at which the Nernstian response is possible, i.e., at 0.003–0.004

independent of the presence of catalyst. Further increases in R_N, from about 0.003 to 0.04, do not change the pH responses. As R_N increases further, the pH response decreases once again as a result of the poor structural quality of low molecular weight AmPVCs, as was shown previously[6]. The influence of double bonds on ion conductive properties of AmPVC still is not very clear (*Figure 8b*), since the amination and elimination happen simultaneously. *Figure 8a* and *b* appear to be the same, but no dependence is noted between the double bond contents and ion conductive properties in the absence of the fixed-site proton carriers—that is, the vinyl MePIP groups. The influence of the D/R_N ratios on the EMF-pH responses (*Figure 8c*) showed that either good (Nernstian) or bad responses could be obtained for the same D/R_N ratios. However almost all Nernstian responses were observed for membranes having $0.6 \leq D/R_N \leq 1.7$.

CONCLUSIONS

(1) Using UV-VIS spectroscopy, the vinyl MePIP groups and polyenes with different *n* (number of conjugated double bonds) could be detected in the AmPVCs from extinction coefficients that corresponded to low molecular weight substances.

(2) The vinyl MePIP group, double bond content, and their distribution were studied in the AmPVCs *versus* time, temperature, and presence of KF. All three factors increased the number of vinyl MePIP groups, increased the conjugated double bond contents, and extended the distribution.

(3) The rate constants of the accumulation for vinyl MePIP groups (k_N), polyenes with $2 \leq n \leq 7$ (k_n), and total conjugated double bonds (k_D) were found at 90°C along with the ratios k_N/k_D and k_n/k_{n+1}. Here k_N was only about one half as much as k_D and $k_n > k_{n+1}$ for $2 \leq n \leq 7$. Therefore, the elimination reaction was more favoured over substitution, although the autocatalytic mechanism of elimination was not found.

(4) Three temperature regions were detected wherein the temperature and presence of the catalyst influenced differently the substitution (below 70°C, 70–100°C, and above 100°C) and elimination (below 70°C, 70–90°C, and above 90°C) reactions.

(5) Activation energies (ΔE) for the formation of vinyl MePIP groups and polyenes with $2 \leq n \leq 13$ were found. They were 17.3 and 23.5 kcal mol^{-1} in the presence and absence of KF, respectively, within the temperature region of 70–100°C for the substitution reaction; and 9.9 and 18.3 kcal mol^{-1} above 100°C. For different polyenes they ranged from 9 to 62 kcal mol^{-1}, depending on the values of *n*, the temperature region, and the presence of the catalyst. All ΔEs are lower in presence of the catalyst than in its absence. A deduction was made that the formation of the first double bond was favoured over a substitution reaction. As for propagation of the sequence of the double bonds, short chains grew easier than long up to a certain *n*, at which point they grew with the same energy barrier.

(6) Nernstian responses were obtained for membranes made from AmPVCs with $0.003 \leq R_N \leq 0.04$ and $0.6 \leq D/R_N \leq 1.7$.

REFERENCES

1. Lindner, E., Cosofret, V. V., Kusy, R. P., Buck, R. P., Rosatzin, T., Schaller, U., Simon, W., Jeney, J., Toth, K. and Pungor, E., *Talanta*, 1993, **40**, 957.
2. Kusy, R. P., Whitley, J. Q., Buck, R. P., Cosofret, V. V., and Lindner, E., US Patent No. 5 403 895, April, 1995.
3. Kusy, R. P., Whitley, J. Q., Buck, R. P., Cosofret, V. V. and Lindner, E., *Polymer*, 1994, **35**, 2141.
4. Kusy, R. P., Whitley, J. Q. and Lee, S., *J. Vinyl & Additive Technology*, 1995, **1**, 223.
5. Bergbreiter, D. E. and Xu, G.-F., *Polymer*, 1996, **37**, 2345.
6. Roudman, A. R., and Kusy, R. P., Influence of potassium fluoride on the syntheses of methylpiperazine-modified poly(vinyl chloride)s for use as fixed-site proton carrier membranes, *J. Biomed. Mater. Res.*, in press.
7. Mukherjee, A. K. and Gupta, A., *J. Macromol. Sci.-Chem.*, 1981, **A16**, 1162.
8. Abbas, K. B. and Sorvik, E. M., *J. Appl. Polym. Sci.*, 1975, **19**, 2991.
9. Lewis, G. N. and Calvin, M., *Chem. Revs.*, 1939, **25**, 273.
10. Bohlmann, F., *Chem. Ber.*, 1954, **86**, 63.
11. Nayler, P., and Whiting, M. C., *J. Chem. Sos.*, 1955, 3037.
12. Sondheimer, F., Ben-Efraim, D. A. and Wolovsky, R., *J. Amer. Chem. Soc.*, 1961, **83**, 1975.
13. Daniels, V. D. and Rees, N. H., *J. Polym. Sci. (Pol. Chem. Ed.)*, 1974, **12**, 2115.
14. Smirnov, L. V. and Popov, K. R., *Vysokomol Soed.*, 1971, **A13**, 1204.
15. Cais, M., in *The Chemistry of Alkenes*, ed. S. Patai. John Wiley & Sons, London, New York, Sydney, 1964, p. 981.
16. Bohlmann, F., *Chem. Ber.*, 1951, **84**, 545.