Chemical dehydrochlorination of poly(vinyl chloride) by LiCl in dimethylformamide

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(Received 30 November 1990; revised 7 February 1991; accepted 14 February 1991)

The dehydrochlorination of poly(vinyl chloride) (PVC) with LiCl in dimethylformamide (DMF) is distinguished by the formation of polyenic products exhibiting an optical absorption peak at a wavelength greater than 500 nm. PVC dehydrochlorinated by other means usually absorbs below 450 nm. Since optical absorption characterizes the polyene sequence length distribution, we can assume that more polyenes with a large number of conjugated double bonds are formed. Investigating the influence of reaction conditions on the formation of long conjugated polyenes, a strong influence of reaction temperature and polymer concentration in the reaction system was found. Polyenes with an absorption peak at 630 nm could be prepared by adding an inert matrix polymer and hydrogen chloride. The mechanism of the formation of long polyene sequences is discussed by means of an ineffective Cl–Cl substitution, which changes the substituent configuration on the PVC backbone and thus creates steric opportunities for dehydrochlorination.

(Keywords: poly(vinyl chloride); chemical dehydrochlorination; polyvinylbutyral; polyene; lithium chloride; dimethyl formamide)

INTRODUCTION

The chemical dehydrochlorination of poly(vinyl chloride) (PVC) is known as an efficient route to prepare conjugated polymers[1–3]. However, it is also known that the physical properties of these products differ from those of the, in principle chemically identical, synthesized polyacetylene (PA). The d.c. conductivity of dehydrochlorinated PVC (dPVC) doped with iodine is several orders of magnitude lower than that of PA. Besides the low crystallinity of the polymer, the short conjugation length of the double-bond sequences is discussed as the main reason for these differences.

The conjugation length and its distribution can be characterized qualitatively by optical spectroscopy (*Figure 1*). PA exhibits an absorption peak around 690 nm. Compared to PA, dPVC absorbs light of higher energy. Different methods of PVC dehydrochlorination in the absence of oxygen using thermal, radiolytic, or chemical initiation produce products with very similar optical absorption characterized by a broad absorption peak located between 350 and 450 nm (corresponding to six and nine conjugated double bonds, respectively). However, the conditions of dehydrochlorination can be changed in order to produce polyenes with a larger conjugation length.

Roth[4] reported PVC dehydrochlorination with lithium chloride and other halides of IA and IIA metals in dimethylformamide (DMF) or mixtures with DMF. They observed that the dehydrochlorination rate as well as the optical absorption of the products can be influenced by the composition of the reaction system. Violet products were formed with an absorption peak at 540 nm using LiCl in pure DMF. Other salts (e.g. LiBr) cause the formation of the 'usual' purple products with an absorption peak at 450 nm. Therefore, via the LiCl–DMF system, polyenes are obtained with larger conjugated sequences than in other dehydrochlorination systems.

However, detailed investigations on the influence of reaction conditions on the polyene sequence length and its distribution are not yet known from other authors, and will be reported in this paper.

EXPERIMENTAL

The dimethylformamide used was dried over molecular sieves and distilled in vacuum.

For the spectroscopic investigations, PVC (BUNA, Scovinyl S6329; M_n (g.p.c.) = 72 900, M_n/M_w = 1.96) and lithium chloride (Lachema n.p., Czechoslovakia) were dissolved in DMF (0.016–0.64 mol l^{-1} and 0.64 mol l^{-1}, respectively). Then the reaction system was kept at constant temperature (295–353 K) and samples were drawn off after predetermined intervals of reaction time. In one series of experiments, polyvinylbutyral (PVB; 40 g l^{-1}) was added to the reaction system.

To carry out the dehydrochlorination at higher temperature (393–417 K), 2 ml of the reaction system was heated in a small, thin-walled vessel for a fixed period of several minutes. The reaction was stopped by rapid cooling with ice–water and the optical absorption spectrum was immediately recorded. To investigate the

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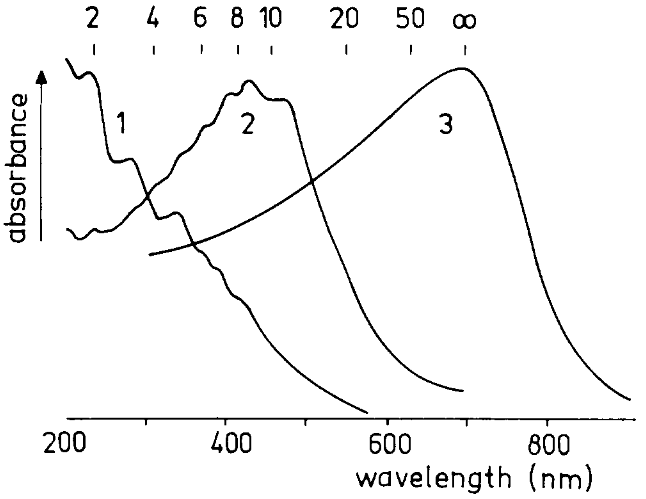


Figure 1 Optical absorption spectra of polyenes: (1) thermo-oxidatively dehydrochlorinated PVC; (2) oxygen-free dehydrochlorinated PVC; (3) poly(acetylene)

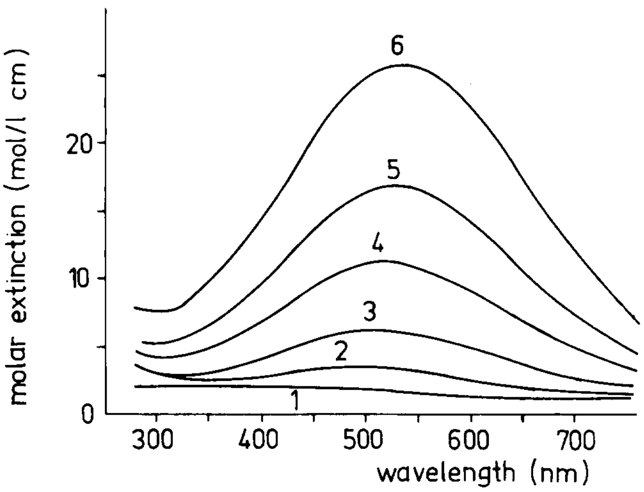


Figure 2 Typical set of optical absorption spectra recorded during the starting stage of PVC dehydrochlorination with LiCl in DMF: [PVC] = 0.16 mol l^{-1}; [LiCl] = 0.64 mol l^{-1}; $T = 353$ K; (1) $t =$ 0.2 h; (2) 0.4 h; (3) 0.5 h; (4) 0.7 h; (5) 0.8 h; (6) 1 h

induced dehydrochlorination, the recording was repeated after a certain period (days), keeping the reaction mixture at 295 K or adding the reaction mixture to another one containing only non-dehydrochlorinated PVC. In another series of experiments PVC, PVB and LiCl were dissolved in DMF. Hydrogen chloride (prepared by the reaction of ammonium chloride with sulphuric acid and dried with sulphuric acid) was bubbled into an equal amount of the solvent, until a concentration of 1 mol l^{-1} was reached. To start the reaction, these two solutions were mixed.

All reactions were carried out in a nitrogen atmosphere.

The degree of dehydrochlorination was determined from the chlorine content of the reaction products or by potentiometric titration of the HCl formed during reaction. The optical absorption spectra were recorded using a Beckmann DB-G spectrophotometer. In order to compare the spectra of different reaction systems, absorption (A) was converted into molar extinction (ε) using the formula:

$$\varepsilon = A/cd \qquad (1)$$

where c is the original PVC concentration and d is the thickness of the absorbing layer.

RESULTS

Development of optical absorption

The start of the formation of conjugated polyenes can be characterized by optical spectroscopy. A typical set of dPVC spectra as a function of the level of dehydrochlorination is shown in *Figures 2* and *3*. In *Table 1* the dehydrochlorination conversion and the peak position are listed.

In the course of the reaction, this development of optical absorption passes through three stages. During the *first stage*, the absorption peak is shifted to longer wavelengths, while the intensity increases. After this, in the *second stage*, the shape of the spectra and the peak position remain constant, and further dehydrochlorination results only in an increase in the absorption. Consequently, at first polyenes with a small conjugation length are formed. In further dehydrochlorination, they increase until a distribution is reached characteristic of the actual set of reaction conditions. The formation of the polyene sequence length distribution (*PSLD*) (first phase) is generally finished at a conversion below 3% (compare *Figure 2* and *Table 1*).

After further increase in the absorption in the second stage, the transition to the *third stage* follows. This is characterized at first by a relatively slow growth of the low-energy part of the absorption. Because the reaction was carried out in an oxygen-free medium, the shift of

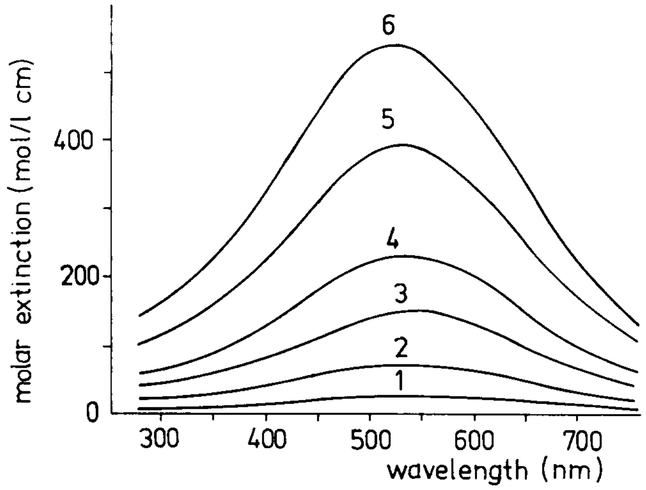


Figure 3 Typical set of optical absorption spectra recorded during PVC dehydrochlorination with LiCl in DMF: [PVC] = 0.16 mol l^{-1}; [LiCl] = 0.64 mol l^{-1}; $T = 353$ K; (1) $t =$ 1.0 h; (2) 1.7 h; (3) 2.5 h; (4) 3.4 h; (5) 4.5 h; (6) 6.0 h

Table 1 Degree of dehydrochlorination (U) and peak position (λ_P) of the optical absorption spectra in *Figures 2* and *3* (t_R is reaction time)

t_R (h)	U (%)	λ_P (nm)
0.2	0.03	(464)
0.4	0.08	(482)
0.5	0.21	500
0.7	0.31	515
0.8	0.39	522
1.0	0.59	529
1.7	1.41	533
2.5	2.68	535
3.4	4.32	530
4.5	6.50	527
6.0	9.27	514

the *PSLD* towards shorter sequences cannot be effected, for example, by oxidation. Chemical crosslinking can be excluded as well. Taking into consideration also the following absorption development, coagulation of the polymer molecules seems to be a more probable explanation of this effect. The strong interaction between long sequences of conjugated polyenes is well known from investigations dealing with polyacetylene[5]. The gelation observed during thermal dehydrochlorination of PVC in DMF[6] can be explained in the same way. The hydrogenation of the gel forms products having a degree of polymerization (g.p.c.) similar to that of the original PVC[6]. Therefore, it can be concluded that the interaction between the polyene sequences is physical rather than chemical.

The tendency towards coagulation continues until the particles have reached an extension of several hundreds of nanometres. At this stage the analysing light is scattered and breakdown of absorption follows due to further particle growth and sedimentation of the reaction product.

The transitions between these stages depend on the reaction conditions. Especially, the PVC concentration and temperature influence the transition to the third stage. In the studied range of reaction conditions, this transition occurs at a conversion of 5–10%.

Obviously, in the third stage the optical spectrum does not characterize the *PSLD* satisfactorily. Moreover, there are further limitations to the interpretation of the optical absorption spectra of these polyene mixtures. Conjugated polyenes with a defined number of double bonds exhibit a relatively broad absorption consisting of several peaks[5,7,8]. In a mixture the absorption of one polyene type overlaps the absorption of the others. While the main absorption peaks of short polyene sequences can be distinguished[9], the spectra of longer polyenes differ only a little from one another and, consequently, discrimination becomes impossible because of the dense overlap.

Temperature dependence

The thermal dehydrochlorination of PVC in DMF was investigated, for example, by Bengough *et al.*[10] and Wirsen *et al.*[6]. They performed the degradation usually at the boiling point of DMF (426 K) or at 403 K.

In these reactions, products were formed with an absorption peak around 475 nm. In contrast, carrying out the dehydrochlorination in solvents such as benzophenone, tritolyl phosphate or ethyl benzoate[10] or in the solid state, the formed polyenes absorb below 450 nm. Moreover, a higher reaction rate is reported for the reaction in DMF, which is explained by the basic character of the solvent as well as by catalysis by the dimethylammonium chloride formed in the reaction of DMF with the hydrogen chloride from the dehydrochlorination[10].

For direct comparison, dehydrochlorination with the LiCl–DMF system was carried out also at 393, 403 and 413 K. The most extensive low-energy shifted peaks were found to be located at 507, 509 and 512 nm (at 413, 403 and 393 K, respectively), compared with 535 nm at 353 K (*Figure 2*), indicating a strong temperature dependence of the *PSLD*. However, even at high temperatures the polyenes formed in the LiCl–DMF system are still longer than those formed by thermal dehydrochlorination in DMF or in a reaction system containing bases for initiation.

Influence of PVC concentration

The development of the *PSLD* also depends on the polymer concentration in the reaction system. Not only the reaction rate is influenced, but the maximum peak position as well. At a low PVC concentration (16 mmol l^{-1}) the peak is located at relatively short wavelength (508 nm). During the reaction it shifts towards longer wavelength after a period of hours. Increasing the PVC concentration, the up-shift is finished earlier and the preferred formation of shorter polyene sequences follows. But in the early stage of the reaction an absorption peak can be observed at a wavelength up to 550 nm (640 mmol l^{-1} PVC).

All these facts indicate the presence of two different effects. One of them results in an increase of the conjugation length. The other process, acting against this, consists of interaction between the polyene sequences, including the formation of coagulates and ultimately the precipitation of the reaction product. While the processes limiting polyene sequence growth are known, the nature of the other processes is not obvious and will be discussed in detail below.

At first we take into consideration only one part of this process. In the experiments, a wide concentration range is included (1:40). This means that the viscosity of the reaction system is remarkably higher at higher PVC concentration. For this reason the mobility of the polymer molecules and segments of molecules becomes more and more restricted, inhibiting the polyene sequence interaction if their concentration is low due to low conversion.

Adding an inert polymer in order to increase the viscosity of the reaction system, the maximum wavelength peak is developed at all PVC concentrations at an early stage of the reaction. The trends observed (the higher the polymer concentration, the more up-shifted the peak position) are more distinct. At a higher PVC concentration (640 mmol l^{-1}), an absorption peak was found at 567 nm. A long-wavelength absorption like this did not arise in a reaction without additional polymer. Consequently, the formation of long polyene sequences cannot be explained by a viscosity effect alone.

For further elucidation of the conditions favouring long polyene formation, reactions were carried out with an 'induced' dehydrochlorination.

Induced dehydrochlorination

It has been shown that a low reaction temperature favours the formation of longer polyenes. Carrying out a dehydrochlorination in the LiCl–DMF system at room temperature, or even below, it should be possible to prepare still longer polyenes exhibiting a conjugation length greater than that described above. However, dehydrochlorination in this reaction system is very slow at room temperature. A PVC solution in DMF (1%) containing 0.16 mol l^{-1} LiCl does not change its optical absorption for at least 150 days. Considering the activation energy of this reaction[11], the ratio of the rate constants at 353 and 295 K can be estimated to be 5000, i.e. an absorption spectrum as established after 1 h in a reaction like that represented in *Figure 2* would be measured after more than 200 days!

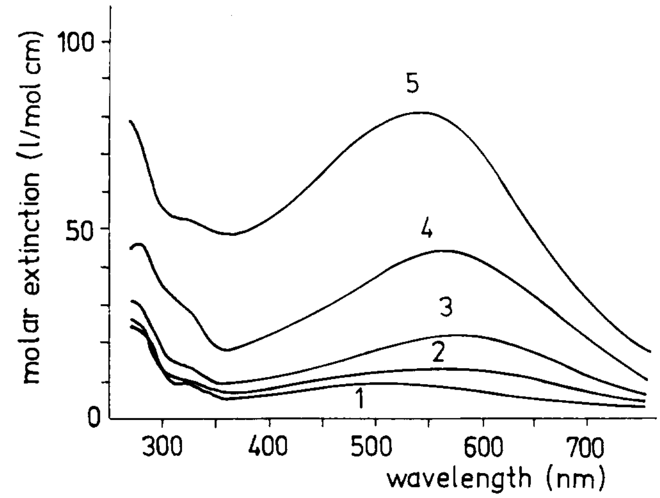


Figure 4 Development of the optical absorption after a short period of heating at 413 K: [PVC] = 0.16 mol l^{-1}; [LiCl] = 0.64 mol l^{-1}; [PVB] = 40 g l^{-1}; T = 295 K; (1) t = 1.5 min; (2) 18 h; (3) 96 h; (4) 242 h; (5) 1930 h

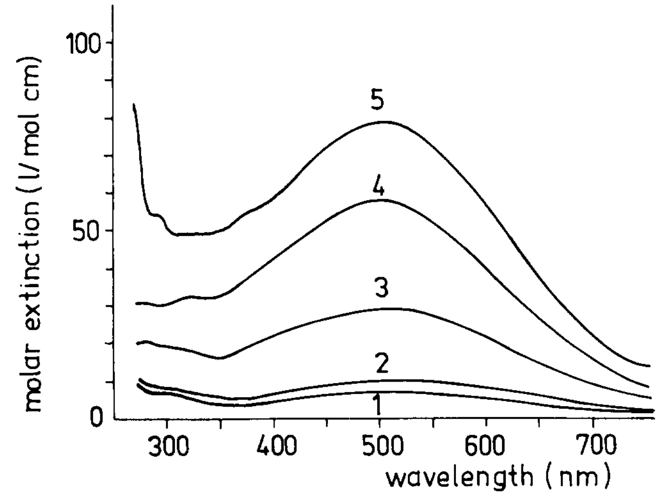


Figure 5 Development of the optical absorption after a short period of heating at 413 K without PVB: [PVC] = 0.16 mol l^{-1}; [LiCl] = 0.64 mol l^{-1}; T = 295 K; (1) t = 1.5 min; (2) 18 h; (3) 242 h; (4) 1320 h; (5) 1930 h

A quite different situation was found if initiation sites are present in the PVC chain. In this case the dehydrochlorination proceeds at low temperature at a considerable reaction rate. In order to initiate the dehydrochlorination, the reaction system was heated for a short period and then rapidly cooled to room temperature. *Figure 4* shows typical optical absorption spectra after conducting such a procedure. The first spectrum was recorded immediately after a 1.5 min heating at 403 K and cooling.

The very low absorption increase in the high-energy region during the first 24 h reveals that no trienes and tetraenes and only small amounts of polyenes consisting of less than eight double bonds are formed. The maximum increase takes place in the region around 630 nm. These facts suggest that in this stage long conjugated polyenes are formed preferentially from shorter ones introduced into the reaction system by heating. In the further course of the dehydrochlorination, it is impossible to distinguish whether the polyenes are formed by the growth of shorter ones or due to new initiation.

After 50 days the reaction system gelled, excluding a further recording of the optical absorption. At this time 2% of the PVC was already dehydrochlorinated.

However, the described effects can be observed only in the presence of PVB as matrix polymer. In the absence of PVB, the dehydrochlorination proceeds more slowly and a shift of the absorption peak towards greater wavelength does not occur (*Figure 5*).

Another way to initiate the dehydrochlorination at room temperature was found by addition of a solution containing already dehydrochlorinated PVC to the original reaction system. Small amounts (<2%) suffice to induce a dehydrochlorination with a rate comparable with that in a reaction conducted using the above-described procedure (*Figure 6*). Compared to *Figure 4* a greater absorption is observed, especially in the low-wavelength region, suggesting a dehydrochlorination from intact PVC chains. Considerations on the absorption and concentration of the active components in the reaction system support this suggestion. The dehydrochlorination in *Figure 6* was initiated by the addition of 2 vol% of the reaction system represented by spectrum 1 in *Figure 4*. The yield of dehydrochlorination can be estimated to be less than 0.1% (compare *Figure 2* and *Table 1*). Consequently, at the beginning, the molar extinction of the reaction system in *Figure 6* was about 0.2 l mol^{-1} cm^{-1} at 500 nm. During dehydrochlorination the absorption increases at least 500-fold. Therefore, dehydrochlorination seems to occur not only at the end of a polyene sequence but also on a perfect PVC segment, i.e. the reaction does not proceed only at activated sites.

Since, under similar conditions, PVC is dehydrochlorinated much more slowly without the addition of substances inducing the reaction and dehydrochlorination is not just the growth of polyene sequences in an E1 reaction, the hydrogen chloride split off from the PVC seems to take part in the reaction. Replacing LiCl in the reaction system by hydrogen chloride, dehydrochlorination of PVC cannot be observed under the same conditions as applied in the presence of LiCl. This fact is in agreement with results reported by Roth[4]. However, adding hydrogen chloride to the LiCl–DMF system, the dehydrochlorination is distinctly accelerated (*Figure 7*). Moreover, an absorption peak is formed at 630 nm.

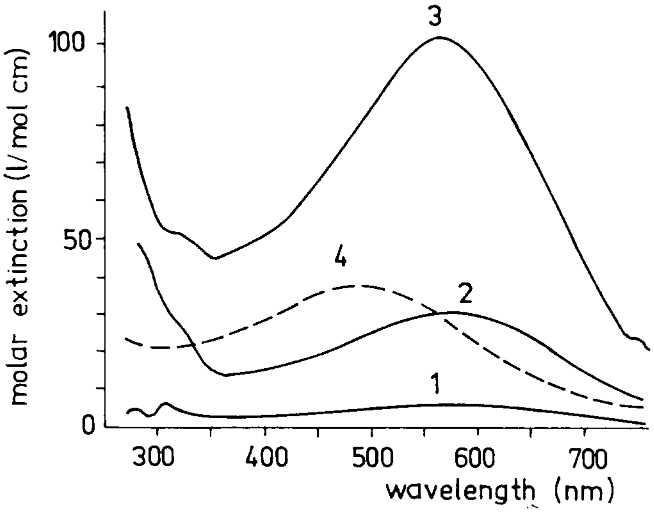


Figure 6 Development of the optical absorption after addition of reaction solution containing slightly dehydrochlorinated PVC: [PVC] = 0.16 mol l^{-1}; [LiCl] = 0.64 mol l^{-1}; [PVB] = 40 g l^{-1}; T = 295 K; (1) t = 242 h; (2) 815 h; (3) 1930 h; (4) 1930 h without PVB

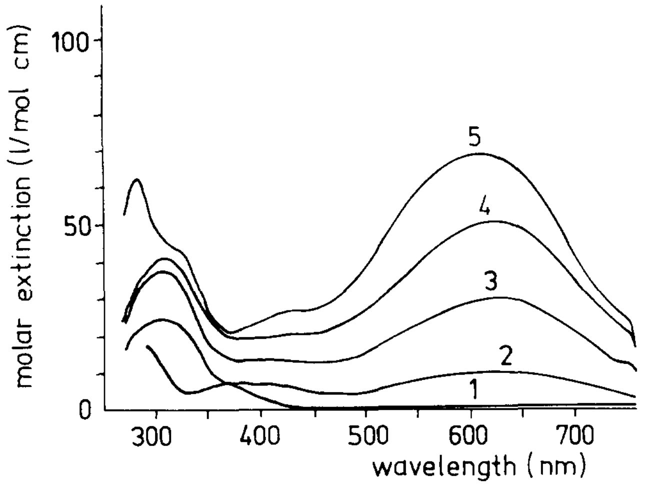
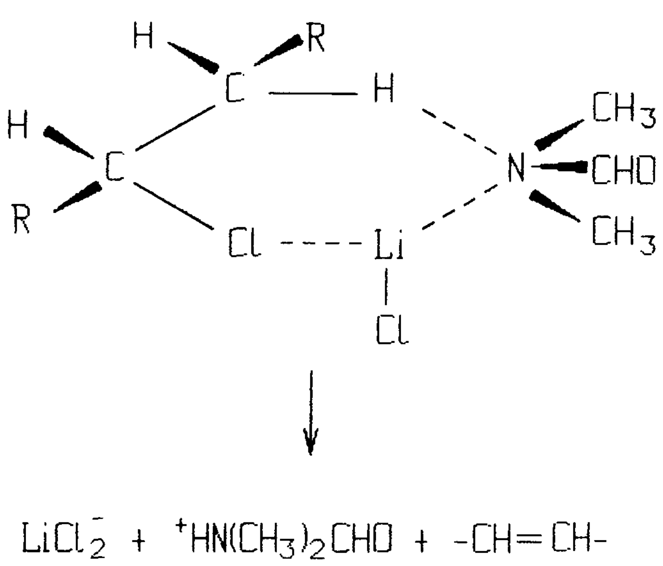


Figure 7 Development of the optical absorption after addition of hydrogen chloride: [PVC] = 0.16 mol l^{-1}; [LiCl] = 0.64 mol l^{-1}; [PVB] = 40 g l^{-1}; $T = 295$ K; (1) $t = 142$ h; (2) 336 h; (3) 672 h; (4) 984 h; (5) 1620 h



Scheme 1

The concentration of HCl in the range investigated does not affect the peak position, though the absorption in the region below 400 nm becomes higher with increasing HCl concentration.

DISCUSSION

Detailed investigations on the mechanism of dehydrochlorination in the LiCl–DMF system are not known. But a scheme (*Scheme 1*) suggested by Holysz[12] is obvious and well accepted.

The dehydrochlorination of PVC discussed in this paper represents a complex reaction not permitting precise information to be obtained about the attack of the reagent molecules on the polymer chain. On the other hand, only a better understanding of the mechanism permits elucidation of the features in this reaction system. Therefore, we first display the facts from our investigations and those reported by Roth, which reflect the conditions needed for the occurrence of the unusual *PSLD*.

In order to exclude the possibility that the observed optical absorption is due to polyene complexes as discussed for the thermal dehydrochlorination of PVC[13,14], we performed two types of experiments. Both militate against coloured polyene complexes: LiCl added to a solution of PVC dehydrochlorinated with potassium t-butoxide to a low conversion, as well as LiCl added to a reaction system for the PVC dehydrochlorination with potassium t-butoxide, do not effect the formation of violet-coloured products. Moreover, the precipitation of PVC slightly dehydrochlorinated in the LiCl–DMF system with water or aqueous ammonia and subsequent solvation in tetrahydrofuran (THF) do not change the optical absorption.

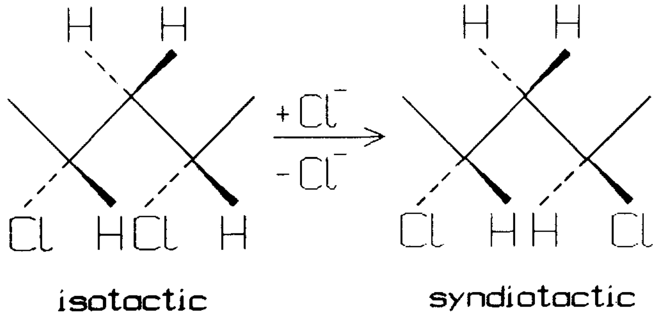
Consequently, the observed optical absorption is very probably due to the absorption of polyenes with a large conjugation length.

Roth[4] reported that the addition of solvents such as THF, dioxane, or methyl ethyl ketone to the DMF resulted in the formation of violet products too, but the reaction rate is decreased. We pointed out that such products are also formed in the reaction system of LiCl in dimethylsulphoxide. On the other hand, in the presence of small amounts of water or ethanol, the PVC is dehydrochlorinated to the 'usual' purple products.

Exchanging LiCl by non-aqueous magnesium chloride, violet polyenes are formed, while other salts (e.g. LiBr) depress long polyene formation[4]. Lithium hydroxide does as well, but in the latter case the formation of water by neutralization of the hydrogen chloride seems to be responsible.

Summarizing these facts, we can conclude that the formation of long conjugated polyenes requires an aprotic solvent and a chloride with a small cation. The reaction rate depends on the polarity of the reaction medium. Because the chloride ion is a strong base in a polar, aprotic medium, it seems to play an important role in the formation of long conjugated polyenes in this reaction system. But what are the special features of chloride as a base?

As is known, elimination competing with substitutions is favoured in the case of a strong basic, voluminous agent. In the reaction system discussed here, the basicity of the agent equals that of the leaving group. They are identical. Consequently, substitutions become very probable under these conditions. The most important difference to other bases lies in the fact that, in the investigated reaction system, substitution are ineffective reactions, i.e. they do not change the chemical composition of the substrate. While the chemical composition of the PVC remains constant after such an ineffective substitution, the steric conditions in the molecule are changed (*Scheme 2*).



Scheme 2

On the supposition that the substitution takes place via an S_N2 mechanism, this reaction results in inversion of the substituent arrangement at this carbon atom, i.e. the tacticity of the polymer segment is changed. Comparing the steric conditions for an S_N2 reaction in an isotactic and a syndiotactic PVC sequence, it becomes obvious that the α-carbon atom is more accessible in an isotactic sequence. Investigations by Millan *et al.*[15,16] confirm this. Consequently, substitutions take place preferentially on isotactic sequences, enriching syndiotactic ones. According to Millan *et al.*[17] and Behnisch *et al.*[18], syndiotactic sequences are easily dehydrochlorinated to long conjugated polyenes because the steric demands of the transition to *trans*-polyenes are markedly low especially in the case of an all-*trans* conformation of the PVC sequence. Therefore, ineffective chloride–chloride substitutions change the steric conditions on the PVC chain in a way supporting the formation of long conjugated polyenes.

The effects observed in the thermal dehydrochlorination of PVC in DMF can be explained as well. In that case the chloride formed during the reaction possibly effects the changes in secondary structure. Indeed, the chloride concentration is low compared with that in the LiCl–DMF system and the reaction is carried out at a higher temperature. Therefore, substitution takes place on a smaller scale compared with elimination.

At lower temperature substitution is favoured compared with elimination, and elimination proceeds at a low rate, leaving time for large-scale configuration changes. These changes are also promoted by a high chloride concentration. Consequently, the longest polyenes are formed in a reaction with a high chloride concentration at low temperature and—this seems to be an essential condition—if the interaction between the polyene sequences resulting in coagulation and precipitation is prevented by a matrix.

(Obviously the chloride concentration is limited by the low dissociation level of the LiCl if only the salt is present in the reaction system whereas the HCl dissociation is more extensive.)

Autocatalysis in thermal dehydrochlorination of PVC in DMF reported by Bengough can be explained by means of the ineffective substitution model better than including the influence of dimethylammonium chloride[10].

Therefore, many details of the investigated reaction can be explained using this model. However, there are more mechanisms influencing the *PSLD*, e.g. the temperature dependence of the conformation sequence distribution[19] and the dependence on the nature of the reaction medium, not yet investigated in detail. But these effects are not strong enough to explain such a drastic change in the *PSLD* compared with other reaction systems.

Wirsen *et al.*[6] suggested another explanation. They attributed the formation of long conjugated polyene sequences in DMF to the existence of favourable initiation sites formed during synthesis of the polymer and differing in nature. According to the ozonolysis–g.p.c. data[6] these initiation sites should have reacted below an overall dehydrochlorination of 1%. Further polyene sequence growth is realized by dehydrochlorination in the neighbourhood of the double bonds (possibly via an E1 mechanism). Growth is supposed to be limited by 'crashes' between growing polyene sequences. In DMF only one-third of all initiation sites are converted into double bonds, resulting in an increase of polyene sequence lengths due to the lower probability for termination by a 'crash' between two growing sequences. However, taking into consideration that a typical PVC chain consists of several hundreds of monomeric units, such a termination reaction should gain importance at a higher degree of dehydrochlorination. Indeed, the limitation of polyene sequence growth begins far below 1% conversion, as can be seen in the optical absorption spectra. Furthermore, from the kinetic point of view, this supposition implies an activated step after the formation of an isolated double bond, but there is no evidence for this assumption.

Also an ionic interaction of the chloride ions or LiCl with the polyenes should be able to influence the *PSLD* by a mechanism similar to that discussed for HCl catalysis during thermal dehydrochlorination of PVC[20,21]. The effects observed in the thermal dehydrochlorination and in the reaction discussed in this paper differ distinctly. On the other hand, HCl catalysis in thermal PVC dehydrochlorination can be discussed by means of the ineffective substitution model.

All in all, the model assumed in this paper allows one to explain all the effects observed in the LiCl–DMF dehydrochlorination of PVC satisfactorily and more comprehensively than other attempts in the literature.

REFERENCES

1 Soga, K. *Synth. Met.* 1983, **6**, 275
2 Preichaud, A., Dhainout, S., Bernier, P. and Lefrant, S. *Synth. Met.* 1988, **24**, 7
3 Kise, H. *J. Polym. Sci., Polym. Chem. Edn.* 1982, **20**, 3189
4 Roth, J. P. *J. Polym. Sci. (C)* 1963, **4**, 1347
5 Knoll, K. and Schrock, R. R. *J. Am. Chem. Soc.* 1989, **111**, 7989
6 Wirsen, A. and Flodin, P. *J. Appl. Polym. Sci.* 1978, **22**, 3039
7 Sandheimer, F., Ben-Efraim, D. A. and Wolovsky, R. *J. Am. Chem. Soc.* 1961, **83**, 1675
8 Knous, S. A. and Schrock, R. R. *Macromolecules* 1988, **21**, 1885
9 Daniels, V. D. and Rees, N. H. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 2115
10 Bengough, W. I. and Grant, G. F. *Eur. Polym. J.* 1968, **4**, 521
11 Holländer, A., Thesis, Institute of Polymer Chemistry 'Erich Correns', 1990
12 Holysz, R. R. *J. Am. Chem. Soc.* 1953, **75**, 4432
13 Schlimper, H. *Plaste Kaut.* 1966, **13**, 196
14 Schlimper, H. *Plaste Kaut.* 1967, **14**, 657
15 Millan, J., Martinez, G. and Mijagos, C. *J. Polym. Sci., Polym. Chem. Edn.* 1985, **23**, 1077
16 Martinez, G., Mijangos, C., Terroba, P. and Millan, J. *J. Polym. Sci., Polym. Chem. Edn.* 1988, **26**, 1629
17 Millan, J., Martinez, G. and Mijangos, C. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 305
18 Behnisch, J. and Zimmermann, H. *Makromol. Chem.* 1989, **190**, 2347
19 Koenig, J. L. and Antoon, M. K. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 1379
20 Martinsson, E., Hjertberg, T. and Soervik, E. *Macromolecules* 1988, **21**, 136
21 Starnes, W. H. and Edelson, D. *Macromolecules* 1979, **12**, 797