The influence of a matrix polymer on the chemical dehydrochlorination of poly(vinyl chloride) in solution

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Poly(vinyl chloride) (PVC) has been dehydrochlorinated by potassium butoxides in the presence of poly(vinyl butyral) as a solved matrix. A stable colloid solution of highly dehydrochlorinated PVC was obtained. U.v.–Vis spectroscopic studies show the formation of continuously growing conjugated polyene sequences up to a high degree of dehydrochlorination in the reaction with potassium tert.-butoxide and an optical absorption peak at 503 nm was observed. The role of alkoxide groups attached to the backbone of the matrix polymer is discussed.

(Keywords: poly(vinyl chloride); chemical dehydrochlorination; poly(vinyl butyral); polyene, colloid solution)

INTRODUCTION

The chemical dehydrochlorination of PVC and other elimination reactions of suitable polymers are well known as routes to preparing conjugated polymers. Several investigations have been made into the dehydrochlorination of PVC, e.g. by potassium hydroxide in THF/ethanol[1], by alkali hydroxide under phase transfer conditions[2], by sodium amide[3] or by alkali alkoxides[4,5]. The dehydrochlorination products formed by such reactions exhibit several properties that differ from those of synthesized poly(acetylene)[6,7], which is in principle chemically identical. These differences are probably due to chemical and physical defect structures in the polymer chains originating from the starting material as well as being induced by the elimination reaction. A similar feature, however, is the intractability of the polyenic products. During the dehydrochlorination of PVC in solution a powdery product deposits which is insoluble in any known solvent.

Several investigations have dealt with the preparation of solubilized poly(acetylene) by graft polymerization[8], block copolymerization[9,10] or by polymerization in the presence of a solved matrix polymer[11,12]. This paper describes the preparation of poly(acetylene)-like structures by dehydrochlorination of poly(vinyl chloride) in solution with potassium butoxides in the presence of a polymer acting as a solved matrix.

EXPERIMENTAL

All the solvents used were distilled and dried rigorously. n-Butanol and tert.-butanol were stored over molecular sieves. Tetrahydrofuran was stored in a nitrogen atmosphere and freshly distilled before use.

Poly(vinyl chloride) (PVC) and poly(vinyl butyral) (PVB) were commercial products (BUNA Scovinyl S6329, Hoechst Mowital B30H containing 19 mol% residual vinyl alcohol units). The alkoxides were prepared immediately before use by dissolving potassium pieces in the corresponding alcohol. All reactions were done in a nitrogen atmosphere at 295 K.

To dehydrochlorinate PVC without a matrix (reaction type 1) a potassium tert.-butoxide or potassium n-butoxide solution (1.31 mmol in 20 ml tert.-butanol or n-butanol, respectively) was added to a PVC solution in THF (1.28 mmol in 200 ml). To dehydrochlorinate PVC in the presence of a matrix 1 g PVB was dissolved in a PVC solution (1.28 mmol in 160 ml THF). The reaction was started by the addition of a potassium n-butoxide solution (5.1 mmol in 80 ml n-butanol, reaction type 2) or a potassium tert.-butoxide solution (5.1 mmol in 80 ml tert.-butanol, reaction type 3).

At specific reaction time intervals 10 ml samples were withdrawn. Then 150 ml water was added to dissolve the potassium chloride formed during dehydrochlorination. The content of this chloride in every sample was determined by argentometric titration. The polyene formation was followed by optical spectroscopy using a Beckman spectrophotometer DB-G.

RESULTS AND DISCUSSION

Figure 1 shows the progress of polyene optical absorption during the dehydrochlorination of PVC with potassium tert.-butoxide in THF (type 1 reaction). Under these conditions no sedimentation of the reaction product causing a breakdown of the optical absorption was observed for several hours. While a coagulation effect probably stops the shift of the absorption peak toward longer wavelengths at an early stage of dehydrochlori-

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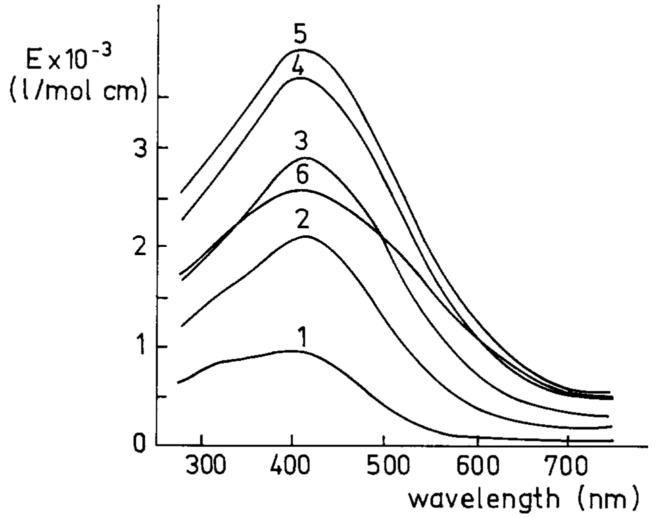

Figure 1 Optical spectra of poly(vinyl chloride) dehydrochlorinated with potassium tert.-butoxide (reaction type 1) for: 1, 0.25 h; 2, 0.75 h; 3, 1.5 h; 4, 3.0 h; 5, 4.0 h; 6, 6.0 h

Table 1 Characteristic parameters of the dehydrochlorination products of a type 1 reaction with potassium tert.-butoxide (see *Figure 1*) and potassium n-butoxide

Reaction time (h)	Conversion (%)	Peak position (nm)
0.25	29.3	394
0.75	58.6	408
1.5	73.7	408
3.0	87.8	408
4.0	90.0	408
6.0	92.9	408
120.0	54.3[a]	387[a]

[a] Potassium n-butoxide

nation (*Table 1*), sedimentation starts only at a fairly high conversion. Nevertheless, at this late stage sedimentation takes place. If potassium n-butoxide is used as the dehydrochlorination agent, sedimentation begins after 120 h at a conversion of 54%. The absorption peaks are located at 405 and 387 nm for the tert.-butoxide and the n-butoxide, respectively.

To prevent sedimentation of the reaction product several polymers were tested as a matrix for poly(vinyl chloride) dehydrochlorination by potassium butoxides. In most cases (e.g. polystyrene and poly(ethylene oxide)) the product deposits as in a reaction without a matrix.

Suitable reaction conditions were found using PVB as a matrix polymer. The set of optical spectra in *Figure 2* was recorded during PVC dehydrochlorination by potassium-n-butoxide in the presence of a PVB matrix (type 2 reaction). The shape of the spectra is similar to that of a type 1 reaction (*Table 2*). A breakdown of optical absorption in the type 2 reaction does not occur for at least 330 h, during which time 83% of the vinyl chloride units are transformed into C=C double bonds.

The use of potassium tert.-butoxide as a dehydrochlorination agent in the presence of PVB results in significant changes in the development of optical absorption (*Figure 3*). We observed an absorption peak at a wavelength >500 nm depending strongly on the reaction conditions. For a type 3 reaction at a higher temperature (e.g. at 305 K), with a higher concentration of PVC or base, the absorption peak does not rise to 500 nm.

While in the reactions of types 1 and 2 the shape of the spectra is established at a low stage of conversion, i.e. further reaction does not significantly change the distribution of polyene sequence length, the type 3 reaction exhibits a simultaneous growth of double bond concentration and conjugation length. In *Figure 4* difference spectra of the type 3 reaction are plotted, indicating the increase of absorption in a defined interval of reaction time. This plot shows clearly the growth of conjugation length during dehydrochlorination up to a conversion of at least 67% (*Table 3*).

Table 2 Characteristic parameters of the dehydrochlorination products of a type 2 reaction represented by the optical spectra in *Figure 2*

Reaction time (h)	Conversion (%)	Peak position (nm)
24	11.5	(365)
67	38.1	387
165	56.4	387
213	70.8	387
331	83.7	387

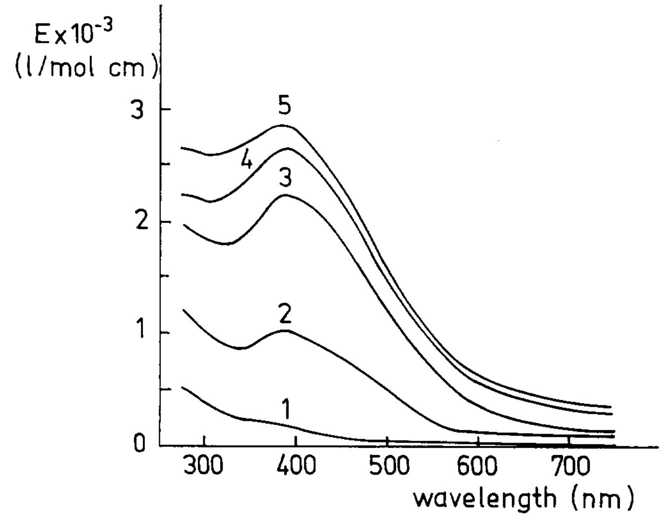

Figure 2 Optical spectra of poly(vinyl chloride) dehydrochlorinated with potassium n-butoxide in the presence of poly(vinyl butyral) (reaction type 2) for: 1, 24 h; 2, 67 h; 3, 165 h; 4, 213 h; 5, 331 h

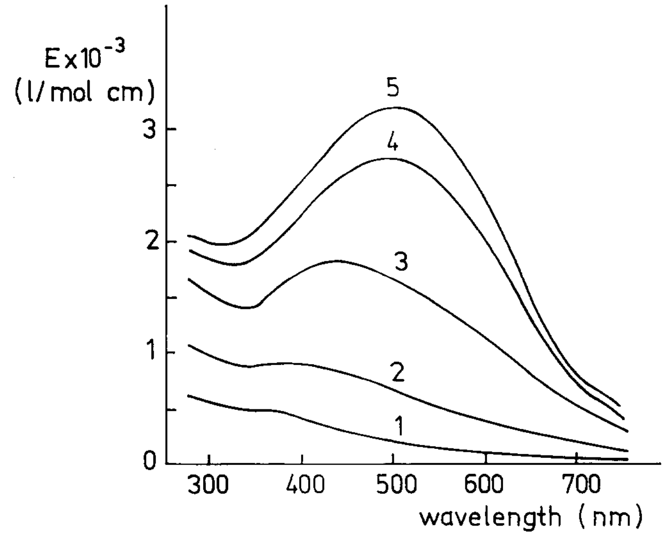

Figure 3 Optical spectra of poly(vinyl chloride) dehydrochlorinated with potassium tert.-butoxide in the presence of poly(vinyl butyral) (reaction type 3) for: 1, 10 h; 2, 15 h; 3, 23 h; 4, 60 h, 5, 177 h

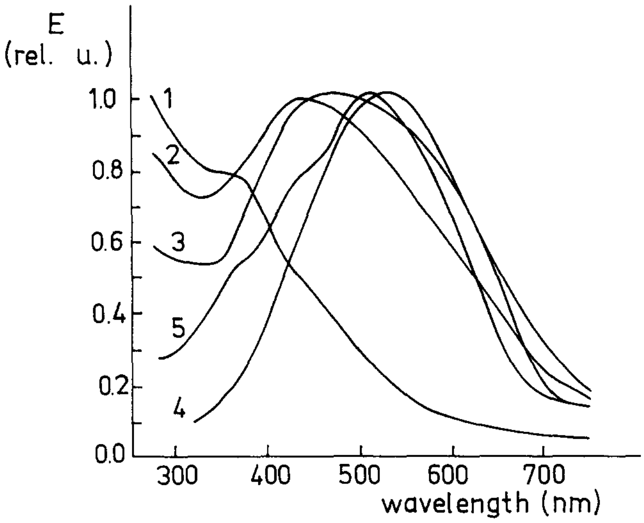

Figure 4 Difference spectra of the spectra in *Figure 3* related to the corresponding maxima. 1, 10–0 h; 2, 15–10 h; 3, 23–15 h; 4, 60–23 h; 5, 177-60 h

Table 3 Characteristic parameters of the dehydrochlorination products of a type 3 reaction represented by the optical spectra in *Figure 3*

Reaction time (h)	Conversion (%)	Peak position (nm)
10	12.1	350
15	23.7	390
23	40.1	435
60	67.4	503
177	80.3	498

Usually the limitation of the growth of double bond conjugation length in dehydrochlorination of poly(vinyl chloride) is discussed in terms of defects in chemical structure as well as of influences of conformation[13]. Defects in chemical structure, such as branches or head to head connections of monomer units, are present in such a small concentration[13] that they cannot be the only reason for the limitation of conjugation length. Since the mobility of the backbone segments is less restricted in solution than in solid state, the importance of conformational hindrance should be lower, keeping the product dissolved. Therefore, the conjugation length can be expected to become longer in a reaction like that described. But the function of the PVB seems to be different in a type 2 and a type 3 reaction, as seen in the optical spectra. The rates of the reactions using potassium n-butoxide with or without a PVB matrix are very similar. In contrast, the reaction rate in dehydrochlorination with potassium tert.-butoxide in the presence of the PVB matrix is about two orders of magnitude lower than in the reaction without a matrix.

It is worth remembering that PVB actually consists of vinyl butyral units, vinyl alcohol units and vinyl acetate units. While the butyral and the acetate groups can be expected to be inert in the reaction system, the hydroxyl groups of the vinyl alcohol should undergo the following reaction:

$$\text{P–OH} + \text{Bu–OK} \rightleftharpoons \text{P–OK} + \text{Bu–OH} \tag{1}$$

Because most of the PVB hydroxyl groups are secondary groups, the equilibrium is shifted to the left for n-butoxide (type 2) and to the right in the presence of tert.-butoxide (type 3). If PVB is dissolved in THF the addition of potassium tert.-butoxide results in the precipitation of a viscous product soluble in alcohols. The addition of the n-butoxide does not affect any visible changes. Therefore, no change in the reaction route seems to take place in the type 2 reaction. In contrast, due to the molar excess of the vinyl alcohol units, the alkali exchange can be expected to proceed to a large extent in a type 3 reaction, resulting in a strong decrease of the potassium tert.-butoxide concentration in the reaction system. The lower reaction rate can be explained either simply by the decrease of the potassium tert.-butoxide concentration or by the action of the polymeric potassium alkoxide as the actual dehydrochlorination species, i.e. in this case the dehydrochlorination of poly(vinyl chloride) is a reaction between two polymers and for that reason is slower than the reaction with the low molecular weight tert.-butoxide itself.

In hydrogen chloride autocatalysed thermal PVC dehydrochlorination the formation of long polyenes is discussed in terms of the chloride stabilization of the growing polyenyl cation[14,15]. In a type 3 reaction discussed in this paper the polymeric alkoxide groups may have a similar function in the formation of longer polyenes. Furthermore, this interaction or possibly a covalent ether bridge between PVB and the polyene formed from such a complex could be the reason for the resistance of these products to sedimentation.

Nevertheless, in this case also, coagulation occurs. A typical electron micrograph of a film cast from the solution of the type 3 reaction is shown in *Figure 5*. The particles are polydisperse, with sizes ranging from 50 to

Figure 5 Transmission electron micrograph of an ultra-thin layer of the composite formed in a type 3 reaction

200 nm. During the reaction there is obviously a transition from dissolved PVC to colloid particles of poly(acetylene-co-vinyl chloride). Therefore, it is possible that one of the functions of the PVB is based on the stabilization of the colloid particles as described for a poly(acetylene) latex synthesized by polymerization of acetylene[12]. The particle size in this latex is reported to be in a similar range to that in our case.

Moreover, the PVB matrix exhibits an additional effect. In the solid state, e.g. in a film cast from the reaction solution, the PVB retards the oxidation of the polyenes. The optical properties of such a composite film are stable in air for at least several weeks. On re-dissolving the film in ethanol or tetrahydrofuran after such a storage time, no differences between the optical spectrum of this solution and that of the primary solution can be observed.

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