

## **Reactions**

### **Selective Elimination Reaction on PVC with Potassium Tert-Butylate**

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#### SUMMARY

Three samples of PVC, having different tacticities, were treated with potassium tert-butylate under mild conditions. By means of  $^{13}\text{C}$ -NMR measurements, the elimination reaction was demonstrated to occur selectively by a small fraction of isotactic and heterotactic triads. On the other hand, the elimination was shown to give rise to a definite type of polyenes which absorb at 240 nm in the UV-Visible spectrum. The intensity of this band was proved to be higher as the overall isotactic content of the polymer increases.

#### INTRODUCTION

Nucleophilic elimination reaction on PVC appears to be an excellent tool to create double bonds without long polyenes being formed provided that mild experimental conditions are used.

The importance of such reaction lies, on the one hand, in that it leads to the formation of allylic chlorines which have been claimed to be very labile structures, and, on the other, in that it might be thought to occur differently depending on the possible conformations in PVC. Actually, it is well known that strong bases like potassium tert-butylate and the presence of good leaving atoms, favour the occurrence of  $\text{E}_{1\text{cB}}$  syn-eliminations (1), which, in the case of some gauche conformations in PVC might involve the formation of cis double-bonds. Now, as these specific double bonds, have been recently proposed to be related to the presence of thermally labile structures in PVC (2), the study of the elimination reaction proves to be very enlightening in the field of PVC degradation and stabilization mechanisms, besides in that of the influence of tacticity on reactivity in analogous reactions of PVC.

The purpose of this work is to demonstrate that the elimination reaction on PVC with potassium tert-butylate occurs selectively with respect to some definite gauche conformations in isotactic and heterotactic triads, as well as to state the relationship between such conformations and the nature of the formed double bonds.

## EXPERIMENTAL

### Preparation of Polymers

Sample A was prepared by bulk polymerization at 90°C using 2-2'azodiisobutyronitrile as initiator, Sample B is the insoluble fraction in acetone of a polymer prepared as Sample A but at 60°C. The acetone soluble fraction was withdrawn because it is similar in both tacticity and molecular weight to Sample A. Sample C was prepared by the same method but using UV irradiation to initiate polymerization at 0°C. The full details have already been published (3).

### Characterization of Polymers

The osmometric measurements were carried out at 34°C with solutions in cyclohexanone using a Knauer membrane osmometer. Data are shown in Table I.

The tacticities were measured by means of the  $^{13}\text{C}$ -NMR spectra obtained at 20.1 Mhz and 100°C using a WP-80 Bruker spectrometer. The polymers were examined as a 10% solution in a 1/4 mixture of deuterated dimethylsulfoxide and o-dichlorobenzene; 10 mm sample tubes were used. The calculations were carried out by measuring the areas with a compensating polar planimeter. The obtained values are given in Table I, where P(SS), P(SI&IS) and P(II) refer to syndio, hetero and isotactic triads respectively.

### Elimination Reaction

The potassium tert-butyrate was readily dissolved in cyclohexanone (0.03 mole/l). Owing to the initially observed thermal effect the solution was left stirring at room temperature for 24 hours, then, the turbidity formed was eliminated by centrifugation. 30 ml aliquots of the so obtained solution were mixed with 20 ml of 0.2 mole/l solutions for each PVC sample in a jacketted reactor thermostated at 60°C. After 5 hours of reaction the polymer was precipitated with methanol, filtrated and vacuum dried at 40°C.

### Ultraviolet-Visible Spectra

The spectra of the eliminated polymers were recorded with 4 g/l solutions in 80:20 (in volume) of tetrahydrofuran-hexamethylenphosphortriamide mixtures, using a Perkin Elmer 554 spectrophotometer, at 40°C in an inert atmosphere. The corresponding unmodified polymers were used as reference.

Table I  
Characterization of Polymers

Sample	$\bar{M}_n \cdot 10^{-3}$	P(SS)	P(SI&IS)	P(II)
A	21.5	0.295	0.487	0.218
A-E	-	0.318	0.479	0.203
B	50.7	0.319	0.494	0.187
C	85.0	0.378	0.468	0.154

## RESULTS AND DISCUSSION

The  $^{13}\text{C}$ -NMR measurements for Sample A and for this sample after elimination (Sample A-E, Table I) clearly demonstrate that elimination selectively involves the isotactic triads and, to a lesser extent, the heterotactic. It is worthy of note that the reaction time was long enough for the reaction to be considered completed at the used temperature (4).

Taking into account that Samples B and C are less abundant in these triads, they are expected to undergo a lower elimination than Sample A under similar experimental conditions. In fact, the elimination extents obtained for Samples B and C were not great enough for being reliably determined by  $^{13}\text{C}$ -NMR analysis.

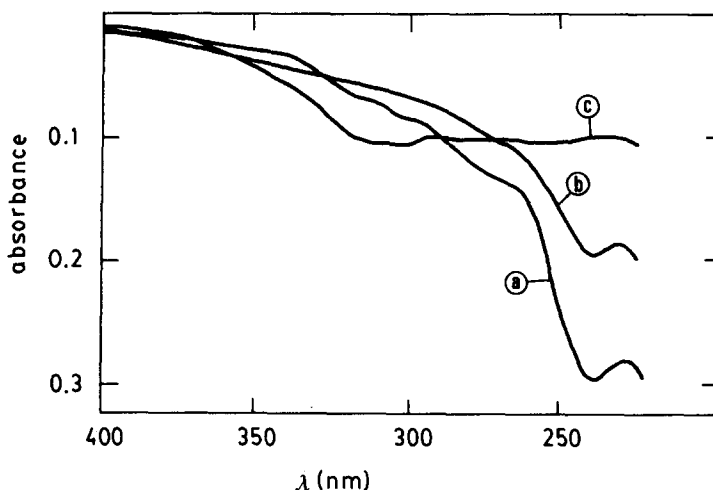


Figure 1. UV-Visible Absorption Spectra of Polymers after Elimination. (a) Sample A ; (b) Sample B ; (c) Sample C .

On the contrary, UV-Visible spectroscopy reveal that the three samples, after elimination under the same conditions, are very different in polyene content, that is, in elimination extent. Actually, as shown by Figure 1, the elimination gives rise to short polyenes which absorb at about 240 nm and their content appears to be higher as the isotactic content of the polymer increases. Although Sample C exhibits some absorption at 306 and 321 nm, the content of the corresponding polyenes is assumed to be very low because of the high molar coefficient of absorption at this region relative to the 240 nm band (5).

With reference to the band at 240 nm in the UV-Visible spectrum of degraded PVC, there hardly exists reliable information in the literature, which makes its attribution rather difficult. Nevertheless, it has been found that model

compounds with three conjugated double bonds, show absorptions at 240, 248, 257 and 268 nm and the intensity of the former bands relative to the two latter, was suggested to be dependent on the content of some cis-isomers (6). Conversely, absorptions at 306 and 321 nm, like that observed for Sample C (Figure 1) are characteristic for polyenes of 4 and 5 trans double bonds in degraded PVC (5).

The above considerations make it very reasonable to relate the band at 240 nm, observed for Samples A and B, to polyenes containing at least one cis double bond. Furthermore, this attribution is strongly supported by the above described results that elimination occurs selectively by isotactic and heterotactic conformations (Table I) and that the intensity of the band at 240 nm increases with increasing isotactic content (Figure 1). As a matter of fact, gauche conformations in GTTG<sup>+</sup> isotactic triad and the heterotactic TTTG (7) are very likely to eliminate through a syn-elimination mechanism and, consequently, to give rise to cis-double bonds.

In connection with the above results, it is worthy of note that the GTTG<sup>+</sup> conformations exhibit alike behaviour in thermal degradation, on condition that very low degradation extents are considered (2). This correlation makes the results in the present work very enlightening on PVC degradation mechanisms.

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