Investigating the oxidative chlorophosphorylation of butadiene rubber by NMR spectroscopy

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Oxidative chlorophosphorylation is one way to synthesise phosphorus-containing organic compounds and polymers [1-11]. In spite of the fact that publications addressing the synthesis of phosphorus-containing compounds have presented extensive information on different low-molecular-weight compounds and have studied the mechanism of the reaction and the chemical structure of the products obtained [1-6], studies of polymers have been limited only to individual polymers of the polyolefin type (polyethylene, polypropylene, polyvinyl acetate, etc.) and contain information relating mainly to the properties of the polymers obtained [7-11].

Investigations by the present authors along these lines have addressed the phosphorylation of synthetic butadiene rubber (SKD) [12, 13]. It was established that, during the oxidative chlorophosphorylation of SKD by the action of PCl₃ in the presence of oxygen, functionally active groups with a P-Cl bond are introduced into the polymer matrix, as in the case of polyolefin polymers, but, in contrast to the latter, the modified rubber has a three-dimensional structure. Here, as a result of chemical transformation by the P-Cl bonds, on the basis of the modified SKD it is possible to produce polymers possessing sorption properties [14, 15].

It is generally accepted that the main sorption properties of phosphorus-containing sorbents - their capacity and selectivity - are determined in many ways by the type of functional groups, the nature of their distribution, and the state of phosphorus in the matrix. Therefore, the study of the general laws governing the oxidative chlorophosphorylation of SKD and the structure of the hydrolysis product of the modified rubber is of interest both from the scientific and from the practical viewpoint.

¹H, ¹³C, and ³¹P NMR spectroscopy were used in the investigation.

To prepare the initial rubber for the experiments, the latter was dissolved in CCl₄ with subsequent precipitation in methyl alcohol in order to remove the different kinds of impurity. CCl₄ and PCl₃ were purified by distillation, and oxygen was dried by passing it through concentrated sulphuric acid. To a 5% (by mass) solution of SKD in CCl₄ was added PCl₃ in a SKD:PCl₃ ratio of 1:5, and oxygen was passed through the reaction mixture at a rate of 7 L/h. Under the selected synthesis conditions, heterogenisation of the reaction mixture occurs ~1 h after the start of the reaction. The total duration of the reaction is of the order of 10 h, as a result of which a modified rubber with a three-dimensional structure is formed.

For the NMR investigations, use was made of specimens both with a low and with a high phosphorus content.

Specimens with a low phosphorus content (FSKD-1, FSKD-2, FSKD-3) were sampled successively from the reaction mixture after certain time intervals at the initial stage of the process, when the initial mixture was homogeneous.

To produce specimens with a high phosphorus content (FSKD-4), the reaction was brought to an end (~10 h), the liquid phase was removed from the reaction mixture, and hydrolysis of the modified rubber was carried out, with its subsequent washing until a neutral reaction and drying in a vacuum oven at 40°C.

For soluble specimens (FSKD-1, FSKD-2, FSKD-3), ¹H, ¹³C, and ³¹P spectra were taken on a Bruker-300 spectrometer operating respectively at frequencies
of 300, 75, and 121.4 MHz. The spectrometer was connected to an HP computer. The 1H NMR spectrum was obtained with pulses of 7.3 µs width (20°C), with a pulse delay of 3 s; 5% (by mass) solutions of the reaction products in CCl₄ were used. The 13C NMR spectrum was taken with 1H [13C] suppression, with a pulse width of 9 µs (20°C), a pulse delay of 1 s, and CCl₄ as the solvent (external reference D₂O). The concentration of the solution amounted to 5% (by mass). The chemical shift was calculated on the basis of the external (CH₃)₄Si DEPT signal obtained using the standard DEPT program (Bruker).

For the crosslinked specimens (FSKD-4), NMR spectral measurements were conducted on a Varian Unity Inova 500 WB solid-state spectrometer with the following working frequencies: 1H NMR - 499.82 MHz, 13C NMR - 125.68 MHz, 31P NMR 202.32 MHz. For the measurements, use was made of a standard rotor for solid-state NMR measurements every 3.2 mm. The magic-angle rotation frequency was 15 kHz for all measurements. The phosphorus build-up was 1 h, and the carbon build-up was 4 h.

1H, 13C, and 31P NMR spectral data of soluble specimens are given in Tables 1 and 2.

As can be seen from Table 1, at the initial stage, the reaction proceeds both with replacement of the hydrogen atoms located at the α-position in relation to the double bond and with direct addition to it. Subsequently, it proceeds only with addition by the double bond. According to data of spectra, in the modified specimen FSKD-3 the following groups are present: >CH-POCl₂, >CHCl, >CH-O-POCl₂, >CHOH, >CHO-.

In accordance with literature sources, oxidative chlorophosphorylation is initiated by attack of the C1 radical [1, 2, 4, 6]. If data of 1H, 13C, and 31P NMR for the reaction products are taken into consideration, under these conditions it is possible for two macroradical intermediates R₁ and R₂ to be formed, each of which is transformed into the corresponding chlorophosphorylation products A, B, C, and D (Scheme a).

As can be seen from the scheme shown, when the macroradical intermediates R₁ and R₂ interact, primarily with PCl₃, this will lead to the formation in the macromolecule of phosphonate groups, and then of phosphate groups on interaction with O₂. On the basis of theories of polarity or "philicity", the more stable radical will primarily be subjected to the action of oxygen [5]. Taking into account that macroradical R₂ is more stable than macroradical R₁, the likelihood of the formation of products A and D from macroradicals R₁ and R₂ is greater than the likelihood of the formation of products C and B from macroradicals R₂ and R₁.

Below, we will consider the spectrum of specimen FSKD-4. Figure 1 presents 1H, 13C, and 31P NMR spectra of crosslinked specimen FSKD-4. In the proton spectrum of FSKD-4 (Figure 1a) there is an intense signal from diene groups at 5.5 ppm, a signal of lower intensity at roughly 3.7 ppm, which can be assigned to >CHOH and/or >CHCl groups, and a mixture of broad signals in the aliphatic region. The nature of the spectrum confirms that, in the region of double bonds, the compound is much more mobile and homogeneous in structure than in the aliphatic region, which may lend support to the assumption that crosslinks are present in the aliphatic part.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Ratio of area of resonance field of aliphatic protons to area corresponding to resonance field of olefinic protons</th>
<th>Chemical shifts of new signals by comparison with initial rubber (ppm)</th>
<th>Groups corresponding to chemical shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>SKD</td>
<td>2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>FSKD-1</td>
<td>2</td>
<td>~2.3</td>
<td>&gt;CH⁺</td>
</tr>
<tr>
<td>FSKD-2</td>
<td>2.8</td>
<td>~2.3</td>
<td>&gt;CH⁺</td>
</tr>
<tr>
<td>FSKD-3</td>
<td>3.4</td>
<td>~2.3</td>
<td>&gt;CH⁺</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>~2.8</td>
<td>&gt;CH⁺P</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>~4.1 and 4.5</td>
<td>&gt;CHOCl</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>~4.8</td>
<td>&gt;CHO</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters of spectra</th>
<th>Chemical shifts of new signals by comparison with initial polymer, ppm</th>
<th>Groups corresponding to chemical shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>13C NMR</td>
<td>~43</td>
<td>&gt;CH-POCl₂</td>
</tr>
<tr>
<td></td>
<td>~57-63</td>
<td>&gt;CHCl</td>
</tr>
<tr>
<td></td>
<td>~78-87</td>
<td>&gt;CH-O-POCl₂, &gt;CHOH, &gt;CHO⁻</td>
</tr>
<tr>
<td>31P NMR</td>
<td>~49.5-51.5</td>
<td>&gt;CH-POCl₂</td>
</tr>
<tr>
<td></td>
<td>~7.5-8.0</td>
<td>&gt;CH-O-POCl₂</td>
</tr>
</tbody>
</table>
of the compound - at points of addition by the double bond. The presence of a comparatively pronounced signal at 3.7 ppm indicates that there are also oxidised and/or chlorinated groups possessing higher mobility than the remaining aliphatic groups.

From Figure 1b it can be seen that the obtained spectrum of specimen FSKD-4 has four broad signals: one in the region of the double bonds (~130 ppm) and the remainder in the aliphatic region. According to the general form of the spectrum, it can be said that the compound is disordered in composition and structure (amorphous), and also that all its components have extremely low mobility. The polymer probably has a high number of crosslinks and at room temperature is in the glassy state.

Analysis of the chemical shifts and their shapes makes it possible to assume that in the composition of the compound, along with butadiene fragments -CH=CH- (~120 ppm) and -CH2-CH2- (28-33 ppm), there are carbon atoms bound with oxygen, chlorine, and phosphorus. These may be >CH-O-PO3H2, >CHOH, and >CHO- groups, the chemical shifts of which lie in the region 76-84 ppm, a >CHCl group with a chemical shift of ~64 ppm, and also a >CHPO3H2 group which most likely characterises the shoulder from the main aliphatic signal (at 28.5 ppm), the chemical shift of which lies in the region ~40-45 ppm.

In quantitative interpretation of the results it must be borne in mind that quantitative measurements of spectra obtained with the use of the technique of polarisation transfer from protons to carbon nuclei have a high percentage error, as the contribution of each carbon signal is determined primarily by the amount of directly bound protons with the given carbon (but the dependence is not strictly proportional), and also by the degree of dipole-dipole interactions of each carbon with its proton surroundings, which in turn is determined by the degree of mobility of the specific part of the molecule. In the present case, the number of carbon atoms belonging to a particular group can be indicated with an accuracy of up to 30-40%.

The solid-state 31P NMR spectrum for specimen FSKD-4 (Figure 1c) confirms that in the compound there are both >CHPO3H2 groups characterised by a broad signal at ~30 ppm and >CHO-PO3H2 groups, to which signals in the region from ~0 to ~1.5 ppm correspond. This appears to indicate that the phosphate groups may lie both in regions directly adjacent to crosslinks (the signal at ~1.5 ppm) and in more mobile parts of the molecule (the signal at ~0.1 ppm). Similarly, for the >CHPO3H2 group, the main signal at ~30 ppm seems to characterise the comparatively more mobile of these groups, while the signal in the region of ~25 ppm in the spectrum, appearing in the form of a shoulder to the main signal, characterises even less mobile groups.

Figure 1. NMR spectra of the crosslinked specimen FSKD-4: (a) 1H; (b) 13C; (c) 31P
lying in direct proximity to crosslinks. Consequently, the assumption, based on analysis of $^{13}$C NMR spectra, that the carbon atoms directly adjacent to both types of group are active in crosslink formation is confirmed. Here, the total ratio of $>\text{CHPO}_3\text{H}_2$ to $>\text{CH-O-PO}_3\text{H}_2$ groups amounts roughly to 5:3.

Thus, the conducted investigations make it possible to interpret the mechanism of the reaction and the structure of the polymer obtained.

REFERENCES


Received 2.12.2011