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NMR Spectroscopic Study of Phosphorus-Containing Polymer Sorbent

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Abstract—The nature and distribution of functional groups in the polymer matrix, as well as the nature of the spatial network in the phosphorus-containing polymeric sorbent was studied by the method of NMR spectroscopy.

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The phosphorus-containing polymer sorbents are widely used for extraction, concentration, and separation of heavy and radioactive metals. Their main sorption properties, that is, capacity and selectivity, are defined by such characteristics as the nature of functional groups, their distribution and state of the phosphorus in the matrix, which depend on the selection of initial components, their ratio, the method and conditions of their synthesis [1–3].

The aim of this work was to study the structure of the phosphorus-containing polymer adsorbent based on the polybutadiene. As a research method we selected the NMR spectroscopy, as the most informative in solving the problem [4].

Figure 1 shows ^{1}H, ^{13}C, and ^{31}P NMR spectra of the phosphorus-containig polymer.

As seen, the proton spectrum (Fig. 1a) is composed of three parts: a strong signal at 5.5 ppm of the protons at the double bonds, the signal of lesser intensity at approximately 3.7 ppm, which can be attributed to groups >CHOH and/or >CHCl, and overlapped broad signals in the aliphatic region. The nature of the spectrum confirms that in the region of the double bonds the structure of compound is much more mobile and uniform than aliphatic, which may suggest that the cross-linking is present in the aliphatic part of the compound at the points of binding with the double bonds. The presence of a relatively pronounced signal at 3.7 ppm indicates that there are also oxidized and/or chlorinated groups more mobile than the other aliphatic groups [7–9].

The ^{13}C NMR experiment was carried out using the technique of rotation at the magic angle with strong suppression of the dipole-dipole interactions on the frequency of the proton resonance and with the transfer of polarization from protons to the carbon nuclei, because without this technology the accumulation is ineffective. It is obvious that the resulting spectrum has four broad signals: one belongs to the carbon in the double bond (~130 ppm) and the other, to the saturated aliphatic carbon atoms. From the overall spectrum pattern we can conclude that the compound under study is disordered by the composition and structure (amorphous), with low mobility of all its components. Apparently, at room temperature the compound is in the state below its glass transition temperature, or has a large number of cross-linking, or more likely, both reasons are valid [7–9].

Analysis of the chemical shift and shape of the signals suggests that the compound composition includes, along with the components of butadiene –CH =CH– (~120 ppm) and $–CH_2–CH_2–$ (28–33 ppm), also the carbon atoms connected with oxygen, chlorine and phosphorus. It may be the groups $>CH–O–PO_3H_2$, >CHOH, and >CHO–, whose chemical shifts are in the region of 76–84 ppm; >CHCl with chemical shift ~64 ppm, and the group $>CHPO_3H_2$, which is likely to be characterized by the shoulder in the range of 40–45 ppm of the main aliphatic signal (28.5 ppm) [9, 10].

At the quantitative interpretation of the results it should be borne in mind that the quantitative measurement of the signals obtained using the technique of

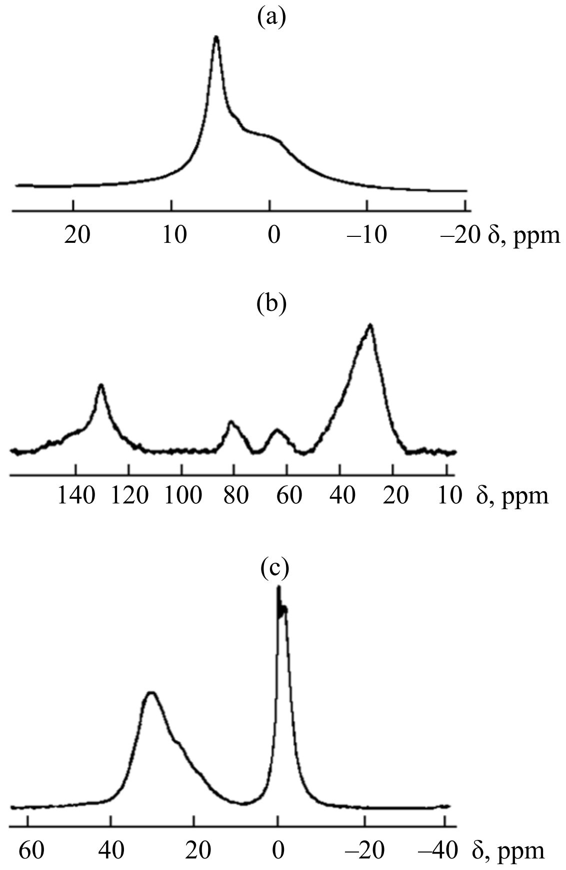

Fig. 1. NMR spectra of the phosphorus-containig polymer: (a) ^{1}H, (b) ^{13}C, and (c) ^{31}P.

polarization transfer from protons to carbon nuclei provides a large error since the contribution of each carbon signal is determined, firstly, by the number of protons directly bound to the carbon (but the dependence is not strictly proportional), as well as by the degree of dipole-dipole interactions of each carbon with its proton environment, which, in turn, is determined by the degree of mobility of a certain part of the molecule. In this case, the number of carbon atoms belonging to one or another group, we can determine only with the accuracy of 30–40%.

^{31}P NMR spectrum confirms that the com-pound includes both >$CHPO_3H_2$ group that is characterized by a broad signal at ~30 ppm, and >$CH–O–PO_3H_2$, to which corresponds a signal at ~0 to 1.5 ppm [10]. Since the mobility of the phosphate groups >$CH–O–PO_3H_2$ associated with the polymer via oxygen bridges is much higher than of the >$CHPO_3H_2$ group, this signal is much narrower. However, in this case there are two types of signals differing by width, and consequently, corresponding to the groups of different mobility. Apparently, this testifies to the fact that the phosphate groups may be connected with the atoms adjacent to the point of cross-linking (the signal at –1.5 ppm), and with the more mobile parts of the molecule (the signal at –0.1 ppm). Similarly, the groups >$CHPO_3H_2$ give rise to the main signal at ~30 ppm that apparently characterizes the relatively more mobile groups, and the signals in the area of ~25 ppm manifested as a shoulder on the main signal, characterizing much less mobile groups, lying in the vicinity of cross-linking. Thus the conclusion about formation of cross-links involving carbon atoms directly adjacent to both types of groups obtained at the analysis of the ^{13}C NMR spectra is confirmed by the data of ^{31}P NMR spectroscopy. The overall ratio of groups >$CHPO_3H_2$ to >$CH–O–PO_3H_2$ is approximately 5:3.

Taking into account all the above observations, the structure of the adsorbent can be interpreted as follows: (1) Phosphate and phosphonate groups are attached to the polymer mainly at the double bond. (2) In 1–2 events per 40 carbon atoms the addition is effected as follows: $–CH(O–PO_3H_2)–CHCl–$ and/or $–CH(PO_3H_2)–CHCl–$. (3) Apart from the mode 2, 2–3 additions per 40 carbon atoms are accompanied by the oxidation to form $–CH(PO_3H_2)–CH(OH)–$ and $–CH(O–PO_3H_2–CH(OH)–$ fragments. (4) In addition to the mode 2 and in combination with, or instead, the mode 3, the spatialy close groups can be bound through the oxygen atoms to form the fragments $–CH(O–PO_3H_2)–CH–(O)–CH–CH(PO_3H_2)–$. One such cross-linking per 40 carbon atoms is assumed. If such cross-linking occurs, it is likely that one link per 40 carbon atoms is formed, instead of linking by mode 3.

Thus, on the basis of NMR spectra we revealed the nature and distribution of functional groups in the polymer matrix, as well as the nature of the spatial network of the phosphorus-containing polymer adsorbent.

EXPERIMENTAL

Synthesis of the studied adsorbent was carried out as follows: 5% solution of polybutadiene in CCl_4 was subjected to oxidative chlorophosphorylation by PCl_3 under the action of oxygen [5]. The rate of oxygen supply was 7 l per hour, and the reaction duration, 10 h. This resulted in the formation of a modified substance of three-dimensional structure containing functional groups with P–Cl bonds, which were further processed with water for hydrolysis. The resulting adsorbent was purified along the known procedure [6] and dried at 50°C in a vacuum cabinet.

NMR spectral measurements were carried out on a solid-state Varian Unity Inova 500 WB spectrometer with the following operating frequencies: ^{1}H, 499.82 MHz; ^{13}C, 125.68 MHz; and ^{31}P, 202.32 MHz. For the measurements was used a standard rotor for solid-state 3.2 mm NMR experiments. Rotation at the magic angle was 15 kHz in all measurements. The accumula-tion duration was 1 h for hydrogen and phosphorus, and 4 h for carbon. The time delay between pulses was as follows: hydrogen and phosphorus 3 s, carbon 10 s. Number of scans: hydrogen and phosphorus 1200, carbon 1440.

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