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Study of the structure of polyphenylsiloxanes containing the metal-ions by physical–chemical methods

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ABSTRACT

The study of the structure of polylphenylsiloxanes containing magnesium, cobalt, nickel, and zinc has been performed by the methods of PAS, XRD, and XPS. Using the XRD data, the areas of cross-section of polymer molecules (according to the Miller–Boyer method) and coherent scattering (CS) volumes have been calculated. The data of positron annihilation spectroscopy (PAS) allowed calculation of the specific volumes of positron (V_{e^+}) and positronium (V_{ps}) “traps”. A direct proportional dependence of the volume of the “trap”, in which single positron annihilation takes place, on the positron lifetime and an inverse dependence on the density of metal-siloxanes have was demonstrated. The number of positron annihilations per elementary unit volume has been calculated. Here, for polycobaltphenyl-siloxane and polyphenyl-siloxane the number of oxane fragments, in which annihilation takes place, is equal to 3, whereas for polynickel- and polyzincphenyl-siloxane it is equal to 4. The number of elementary units (e.u.) in the CS volume for magnesium, cobalt, and polyphenyl-siloxane is equal to 10, while for nickel and zinc – to 12, which must be related to higher density in case of nickel-siloxane and to larger CS volume for zinc-siloxane.

The T_3 and T_2 values in the ^{29}Si NMR spectrum for polyphenyl-siloxane coincide with the respective data for polynickel- and polycobaltphenyl-siloxanes and differ significantly from those for polyzincphenyl-siloxane. The increase of the number of T_1-and T_2-fragments for zinc is related to the increase of the percentage of octahedral polyhedra of these ions, while for nickel and cobalt – to a greater degree, to the tetrahedral structure of these ions.

The study of polyzincphenyl-siloxane by the method of X-ray photoelectron spectroscopy has been performed, and the presence of two types of zinc atoms has been demonstrated: the content of zinc atoms with $2p^3/_2$ was 64.3%; the content of those with $2p^1/_2$ was 35.7%. The latter corresponds to the content of the tetrahedral surrounding of T_1 and T_2 silicon atoms in the ^{29}Si NMR spectrum.

1. Introduction

Stair-shaped polyorganyl-siloxanes (POS) and polymetalorganyl-siloxanes (PMOS) comprise a rather comprehensively studied class of organosilicon compounds [1–5]. Despite this, the structures of polymer compounds synthesized in the dimethyl sulfoxide (DMSO) and under conditions of mechanical activation in a solid phase have been studied insufficiently [6,7].

At present, to study the structure of POS, the methods of ^{29}Si NMR and PAS are used [8]. Such a probe-type method as PAS allows determination of ordered and disordered specific volumes in polymers [9–12].

Complexes of transition metals are immobilized on the surface of silicon oxide in the processes of heterogeneous catalysis [13,14], which requires the study of formation of the M-O–Si bond in the solid phase. Earlier, different POS and PMOS with different substituents by the silicon atom were investigated by the ^{29}Si NMR method [15]. To investigate the structures of polymetalorganyl-siloxanes, the methods of diffractometry and positron annihilation spectroscopy were used [16].

At the present stage, the demand to study the structure and morphology of POS and PMOS is determined by the tasks related to

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creating novel materials, since these classes of compounds are known to have some unusual technological parameters [17,18] and serve as objects of industrial-scale manufacture [19]. That is why the present work was devoted to application of spectral methods in study of polymetalphenyl-siloxanes containing nickel, cobalt, and zinc.

2. Experimental

Polyphenyl-siloxane (PPS) was synthesized by the method of [19]. Polynickel-, polycobalt-, and polyzincphenyl-siloxanes were synthesized by the method of [6] at the silicon:metal ratio of 2:1. The results of the element analysis of the obtained polymers are shown in Table 1.

The IR spectra of sorbent samples were recorded using a Spectrum-1000 device (Perkin Elmer) with KBr pellets.

Diffractograms were registered using an Advance D8 device (Bruker) with CuKα-radiation in the angle range $2^\circ < 2\theta^\circ < 90^\circ$ in the point-scanning mode. The maximal deviation of the reflection positions determined using NIST SRM 1976 was less than 0.01° 2θ.

The density was determined by the pycnometry method in hexane.

Measurements of the lifetime and intensity of annihilation of positrons were carried out using a fast delayed coincidence spectrometer with plastic scintillation detectors of a size of 25 × 15 mm and FEU 87 photoelectron multiplier based on a NOKIA-LP-4840 analyzer. The spectrometer time resolution ($2\tau_0$) is 270 ps for the ^{60}Co source at 30% width of the energy “window”.

To measure the positron lifetime in objects under study, a ^{44}Ti cyclotron source with the activity of 10–15 μCi was used. The time spectra processing was carried out using a PALEIT program.

^{29}Si NMR spectra of polymers in the solid phase were recorded using a Bruker Advance AV-300 device with the proton resonance frequency of 300 MHz. At spectra recording, the sample magic angle spinning (MAS) technique was used.

Diamagnetic samples were recorded using the technique of cross-polarization with suppression of dipole-dipole interactions, while for samples containing metals with unpaired electrons the Hahn echo technique was used.

Tetramethyl silane was used as a reference system for silicon and carbon nuclei; the chemical shift (CS) zero point was defined in a separate experiment. The CS determination error did not exceed 1–2 ppm depending on the peak resolution. Spectra were recorded at 300 K.

X-ray photoelectron spectra of polymetalphenyl-siloxanes were recorded using a superhigh-vacuum photoelectron spectrometer (Omicron) with a hemispheric analyzer of a curvature radius of 125 mm. An X-ray tube with a magnesium anode served as a radiation source (MgKα – 1253.6 eV). The pressure in the chamber during the experiment did not exceed 9×10^{-9} mbar. The energy scale calibration was performed on the carbon level Cls. The spectra processing was carried out using the CASA XPS program [20].

3. Results and discussion

3.1. Diffractometry of PPS and PMPS

The samples of polyphenyl-siloxane and polymetalphenyl-siloxanes were investigated by the diffractometry method (Fig. 1).

Based on the XRD data, the cross-section areas of polymers and coherent scattering areas (CSA) were calculated. The calculation data are shown in Table 2.

Ordered areas, within which macromolecular chains are packed in a band-like fashion, are known to exist in the polymers supramolecular structure [23,24]. These are the so-called coherent scattering areas (CSA), whose determination enables one to conclude on ordering in the polymer supramolecular structure.

The CSA size was calculated using the Selyakov–Shearer formula:

$$D = \frac{0.89 \cdot \lambda}{\cos(\theta) \cdot FWHM}, \tag{1}$$

where: D – the CSA size;

λ – the X-ray radiation wavelength;
θ – the scattering angle;
FWHM – the full width at half maximum.

In calculation of the cross-section area, the Miller–Boyer equation was used [21]:

$$\lg(d) = 0.61 \cdot \lg(s) + 0.06, \tag{2}$$

where: $d = d_{001}$; s – the cross-section area of the polymer chain.

According to [22], the first reflection corresponds to the interchain distance, while the second one – to the intrachain distance. As seen from the data of Table 2, interchain distances for polymetalphenyl-siloxane samples increase in comparison with that of polyphenyl-siloxane due to the increase of the coordination polyhedron of the metal ion, whereas intrachain distances undergo virtually no changes. The latter indicates to the fact that the metal ion is located between layers. A direct proportional dependence of lg(d) on lg(s) corroborates the effect of the metal ion coordination polyhedron (see Fig. 2).

Coherent scattering volumes (CSV) were found from the equation:

$$V_{CSV} = S_{cross\text{-}sec} \cdot L_{CSV}, \tag{3}$$

where: S – the polymer chain cross-section area;

L – the CSA size.

The obtained data are shown in Table 3.

Table 1
Data of element analysis of polyphenyl-siloxane and polynickel-, polycobalt-, and polzincphenyl-siloxanes.

Polymer	Element content, %								Si/M	Unit formula
	Found				Calculated					
	Si	C	–OH	M	Si	C	–OH	M		
PPS	22.9	48.6	6.7	–	21.7	49.0	7.5	–	0	$[(PhSiO_{1.5})_{0.7}][PhSi(OH)O]_{0.3}$
PNiPS	16.9	42.1	–	17.5	16.1	43.6	3.0	17.7	2.06	$[(PhSiO_{1.5})_2NiO]_n \cdot 0.6\ H_2O$
PCoPS	15.9	42.5	–	17.9	16.8	43.4	3.6	17.7	1.96	$[(PhSiO_{1.5})_2CoO]_n \cdot 0.65\ H_2O$
PZnPS	16.1	43.7	–	19.0	16.0	42.6	2.4	18.8	1.92	$[(PhSiO_{1.5})_2ZnO]_n \cdot 0.5\ H_2O$