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Various types of polysiloxanes studied by positron annihilation lifetime spectroscopy ☆

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HIGHLIGHTS

- Free volume sizes in various siloxane compounds were studied by PALS.
- Based on PALS, cross-link densities of polysiloxane networks were evaluated.
- PALS results were compared with those of swelling and IR measurements.
- PALS allows establishing presence of free carbon in polysiloxane-derived ceramics.

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ABSTRACT

In the work, linear poly(vinylsiloxanes) with regular distributions of vinyl groups along chains, the networks obtained by their hydrosilylation with various hydrogensiloxanes, products of pyrolysis of such networks as well as the networks prepared *via* reaction of low-molecular siloxanes have been studied by positron anihilation lifetime spectroscopy (PALS).

Based on free volume sizes determined by this method, relations between cross-link densities in the investigated systems have been established. They have been compared with the results of swelling experiments conducted in the work and to efficiency of cross-linking reaction evaluated in our previous FTIR investigations of the systems. It has been found that PALS and swelling measurements lead to the same conclusions concerning cross-link densities in the networks prepared from low-molecular siloxanes. Discrepancies have been observed in the case of polymer-derived systems. Additionally, it is demonstrated that PALS is capable of revealing the presence of free carbon phase in SiCO materials formed upon pyrolysis of polysiloxane networks.

Introduction

The beginnings of positron annihilation lifetime spectroscopy (PALS) date back to the 1940s when γ-radiation formed upon annihilation of positrons injected into metal samples was studied for the first time [1,2]. Nowadays, PALS is a well-established experimental technique that offers the possibility to examine structure of materials at the atomic or molecular level. It is widely used in the investigations of metals and their alloys [3–5], semiconductors [6], inorganic oxides, glasses and minerals [7–10] as well as polymers and polymer-containing systems [11–14].

The method employs the fact that the positron, i.e., the antiparticle of the electron, emitted by a radioactive source (usually ^{22}Na isotope), upon interaction with the studied material is thermalized (i.e. loses its energy to reach that of atomic or molecular thermal motions) and then, after random walk, annihilates with an electron. Positron lifetime is measured as the time interval between the detection of a 1.275 MeV photon, emitted from ^{22}Na nucleus almost simultaneously with the positron, and one of the annihilation photons of 0.511 MeV. Generally, positrons can annihilate from the free state or a state localized in different crystalline defects. However, in molecular solids, where valence electron density is extremely low, the bound state of the positron and the electron, called Positronium (Ps), can be formed. The self-annihilation of Ps, which occurs in vacuum, depends on the positron and electron spin alignment: the singlet state, called para Positronium (p-Ps), annihilates with the average lifetime of 0.125 ns and the triplet

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state, called orto Positronium (o-Ps) lives much longer, ca. 145 ns. In molecular solids both states can be formed, however, the lifetime of o-Ps state shortens to a few ns, because the positron can annihilate with an electron of the surrounding molecules in the so called *pick-off* process. It is well established that Ps is formed in the free volume in amorphous regions of molecular solids; moreover the lifetime of *o*-Ps depends on the radius of the free volume [15]. Annihilation of free positrons, i.e. those which do not form Ps, usually gives the lifetime shorter than 0.5 ns.

Based on the positron lifetimes resolved from lifetime spectrum it is possible to evaluate directly the dimensions, dimension distributions and concentrations of subnanometer-sized free volumes, i.e. voids, existing in polymers. Owing to this, PALS may be the method of choice when phenomena proceeding with or properties related to changes in free volume sizes in polymeric systems, such as glass transition [16,17], gas permeability [18,19], diffusion of chemicals [20], degradation [21,22], plasticization [23], or mechanical properties [24,25] are investigated.

In the present work, PALS has been applied in the studies of various types of polysiloxanes, i.e. organosilicon compounds containing Si–O bonds in the macromolecules. Two linear poly(methylvinylsiloxanes) – D_2V and V_3 polymers – with regular distributions of vinyl groups along their chains, the networks obtained by cross-linking of these polymers as well as the networks prepared from low-molecular siloxanes were subjected to investigations. The main goal of the studies was to evaluate the cross-linking density in the studied materials based on free volume sizes. This parameter is important since, as was shown in our previous papers [26–28], all the examined systems can be used as precursors to SiCO ceramics. Suitability of polymer networks for such application is closely connected with their cross-linking density.

In the work, PALS investigations have been preceded by swelling experiments, which allow to determine the cross-link densities in the studied material. Cross-link densities derived from both methods as well as from our previous FTIR spectroscopic studies of these polysiloxane networks [26–28] have been compared. Additionally, the effect of heat treatment on the positron lifetime parameters in the materials has been studied. For this reason, PALS spectra of the products obtained from the selected polysiloxane network pyrolyzed at various temperatures have been measured.

It should be noted that even though cross-linked polysiloxanes have been studied by PALS before [29–32], up to our knowledge this is the first report in which the use of this technique in the investigations of preceramic polysiloxane networks of regular compositions is demonstrated.

Experimental

Materials

D_2V and V_3 polymers and their networks constituted the first group of materials studied in the work. Because of the appropriate choice of the monomers applied for their synthesis, both polymers had regular chain compositions. In D_2V polymer a vinyl group was attached to every third Si atom, whereas in V_3 polymer – to each Si atom.

D_2V and V_3 polymers were prepared by kinetically-controlled anionic ring-opening polymerization of the corresponding cyclotrisiloxanes: 1,3,3,5,5-pentamethyl-1-vinylcyclotrisiloxane (D_2V) and 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (V_3). The number–average molecular weight of the polymers (M_n) determined by gel permeation chromatography (GPC) in toluene using polystyrene standards was equal to 21 600 g/mol (D_2V polymer) and 24 600 g/mol (V_3 polymer).

Polysiloxane networks from D_2V and V_3 polymers were obtained by hydrosililative cross-linking of the macromolecules conducted in toluene at 60 °C under Ar atmosphere in the presence of Karstedt's catalyst. Three hydrogensiloxanes: 1,1,3,3-tetramethyldisiloxane (${}^{H}MM^{H}$), 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) and octa(hydridodimethylsiloxy)silsesquioxane ($Q_8(M^H)_8$) served as cross-linking agents. In all reactions, molar ratio of Si–H groups to Si-vinyl groups was equal to 1.

Other polysiloxane networks investigated in the work were prepared by hydrosilylation of low molecular siloxanes: 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D_4^{Vi}) with ${}^{H}MM^{H}$ and D_4^{Vi} with D_4^H. The reactions were carried out without solvent, under Ar atmosphere in the presence of Karstedt's catalyst using the following temperature regime: 25 °C for 48 h and 70 °C for additional 3 h. The following ratios of Si–H to Si-vinyl groups were applied in the cross-linking processes: 1.5 ($D_4^{Vi}/{}^{H}MM^{H}$ system) and 2 (D_4^{Vi}/D_4^H system).

V_3 polymer cross-liked with ${}^{H}MM^{H}$ was pyrolyzed in the quartz furnace under flowing Ar atmosphere at the following temperatures: 240 °C, 570 °C, 623 °C, 670 °C, 1000 °C. The heating rate to the selected temperature was equal to 5 °/min and the holding time at this temperature was equal to 15 min. Then, still in the furnace, the samples were slowly cooled down to the room temperature.

The detailed synthetic procedures as well as reagents used in the experiments can be found in our previous papers [26–28,33].

It should be noted that at room temperature D_2V and V_3 polymers were liquid, whereas all other investigated materials were solid materials.

$D_2V/{}^{H}MM^{H}$, D_2V/D_4^H, $D_2V/Q_8(M^H)_8$, $V_3/{}^{H}MM^{H}$, V_3/D_4^H, $V_3/Q_8(M^H)_8$ symbols, whenever used in the following text, denote D_2V or V_3 polymer cross-linked with the appropriate hydrogensiloxane. Symbols $D_4^{Vi}/{}^{H}MM^{H}$, D_4^{Vi}/D_4^H refer to the networks obtained by hydrosilylation of D_4^{Vi} with ${}^{H}MM^{H}$ and D_4^H, respectively.

Methods

Swelling experiments

Swelling of the polysiloxane networks obtained was tested at room temperature in toluene. In the experiments, into the known volume of the powdered sample placed in a calibrated, stoppered vial, solvent was added in the excessive amount to ensure complete swelling of the network. Equilibrium swelling was considered to be attained when no further change in the volume of the analyzed sample was observed (24 h). Swelling degree was expressed as the ratio: $(v - v_0/v_0) \times 100\%$; where v_0,v_0 – volumes of the swollen and the initial sample, respectively. Cross-linking densities (n^{FR}) of the polysiloxane networks studied were calculated according to the Flory–Rehner equation:

$$n^{FR} = \frac{-[v_2 + v_2^2\chi_1 + ln(1 - v_2)]}{V_1(v_2^{1/3} - 0.5v_2)} \quad (1)$$

where $v_2 = v_0/v$ is the polymer volume fraction in the swollen sample, χ_1 is the Flory–Huggins polymer–solvent interaction parameter. Due to the lack of the appropriate data for the networks studied, χ_1 was assumed to be equal to 0.48, which is its value for poly(dimethylsiloxane)–toluene system [34,35] and V_1 is the molar volume of toluene.

Molecular weight of the chains between cross-links, defined as $M_c = \varrho/n^{FR}$, where ϱ is the polymer network density, was calculated with the assumption that $\varrho = 1\ g/cm^3$ since the values close to 1 have been established for various polysiloxane networks [34,35].

PALS measurements

Positron lifetime spectra were measured using a conventional *fast–fast* spectrometer with BaF_2 scintillators. The time resolution of the system was 280 ps (FWHM). The 30-Ci activity positron