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Influence of metallic palladium on thermal properties of polysiloxane networks

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ABSTRACT

Polysiloxane networks differing in cross-link densities were prepared by hydrosilylation of linear polysiloxanes containing various amounts of vinyl groups uniformly distributed in their chains. Thus, D_2V polymer with a vinyl group at every third Si atom in the macromolecule and $4D_3V_3$ copolymer with vinyl groups located in a block constituting one fifth of its chain were reacted with hydrogensiloxanes of different molecular structures and functionalities in the presence of Karstedt catalyst. The process was conducted at excessive amounts of Si–H groups with respect to vinyl ones which ensured that unreacted Si–H groups remained in the polysiloxane networks formed. Such systems were treated with palladium(II) acetate solution in THF. As established by X-ray diffraction and FTIR spectroscopic studies, the redox reaction between Pd^{2+} ions from the solution and Si–H groups of the networks occurred which resulted in the appearance of metallic Pd particles in the systems. Systematic investigations conducted using thermogravimetry coupled with mass spectrometry allowed to conclude that the presence of Pd modifies thermal properties of polysiloxane networks, influencing mainly redistribution of Si bonds taking place during thermolysis of the systems. It was found that higher cross-link densities of the D_2V polymer-derived networks than those of the $4D_3V_3$ copolymer-based ones are beneficial for thermal stability of the systems with incorporated Pd. The type of the cross-linking agent, in turn, decides on residual mass remaining after pyrolysis of the Pd-containing samples conducted at 1000 °C in Ar flow.

1. Introduction

Because of their unique properties, polysiloxanes are among the most important synthetic polymers. These inorganic-organic macromolecular compounds have extremely flexible chains resulting from freedom of rotation around Si–O bonds, exhibit high permeability to gases and are chemically stable [1]. They are also nontoxic, physiologically inert materials that find numerous biomedical applications [2]. Furthermore, cross-linked polysiloxanes can be used as precursors for SiCO ceramics [3].

Polysiloxanes are known for their outstanding thermal properties [4]. In particular, they show very good stability at high temperatures. The onset of their degradation is usually close to or above 300 °C; their thermal stability depends on substituents attached to Si atoms, kind of polymer end-groups as well as conditions of heat treatment [5–9]. Composition and atmosphere of heating affect also the type of products formed during thermal degradation of polysiloxanes and, consequently, the char yield obtained after this process. For example, poly(dimethylsiloxane) (PDMS), i.e. the simplest and the most widely applied polymer of this group, in an inert atmosphere gives no residue because its decomposition is accompanied by the evolution of exclusively volatile compounds (cyclic siloxanes) [5,6]. After decomposition under aerobic conditions, ca. 30%–60% of the material remains as a solid residue (SiO_2), whereas CO_2 and H_2O are released as volatile products [5,6]. These differences have been attributed to cross-linking of PDMS occurring in the presence of oxygen at elevated temperatures which prevents polymer chains from scissions necessary for the formation of cyclosiloxanes [5,6].

Thermal properties of polysiloxanes can be modified by incorporation of additives and fillers which also influence flame retardancy of these polymers [10]. Among additives, the use of platinum has been described in several papers. Thus, platinum from platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, i.e. Karstedt catalyst, added to silicone rubber (lightly cross-linked PDMS filled with SiO_2) has been found to improve flame

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retardant properties of the material by facilitating further polymer cross-linking which results in the increased char yield [11]. Similar effect, observed in the case of SiO_2-filled uncross-linked PDMS, has been explained by synergistic role of platinum and silica in the PDMS cross-linking process [12]. Platinum ions originating from H_2PtCl_6 incorporated into the cross-linked poly(methylphenylsiloxane) have been demonstrated, however, to lower thermal stability and char yield of the initial material [13].

Another platinum group metal, palladium, has been introduced into polysiloxanes in order to obtain catalytically active systems [14–20]. In these studies, Pd ions have been incorporated into appropriately functionalized polymers [14–16] and Pd metal particles - into poly(methylhydrosiloxane) [17–20]. Deteriorative influence of Pd ions on thermal stability of the polymer matrix has been reported; the effect, however, has not been studied in detail [14].

The present investigations have been aimed at evaluating the influence of palladium on thermal stability and char yield of regular polysiloxane networks. The networks have been obtained by cross-linking of two linear polysiloxanes containing vinyl groups regularly distributed at Si atoms in their chains: D_2V polymer and $4D_3V_3$ diblock copolymer using the - well-known in organosilicon chemistry [21] - hydrosilylation reaction. Linear ($^{H}MM^{H}$), branched (QM^{H}_4) and cyclic (D^{H}_4) hydrogensiloxanes have been applied as cross-linking agents. In this way, polysiloxane networks of various cross-link densities have been obtained. Metallic Pd has been introduced into these systems from palladium(II) acetate solution in THF employing redox properties of the Si–H groups present in them.

It should be noted that polysiloxane networks-Pd systems prepared and investigated in the work can be potentially applied as heterogeneous catalysts and as flame retarders. In both applications, thermal properties are of crucial importance.

2. Experimental

2.1. Materials

The monomers: hexamethylcyclotrisiloxane (D_3) and 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V_3) were purchased from SIGMA-Aldrich and ABCR, respectively, whereas 1,3,3,5,5-pentamethyl-1-vinylcyclotrisiloxane (D_2V) was synthesized according to the procedure presented in Ref. [22]. They were dried over CaH_2 and vacuum-distilled before use in the polymerizations.

The initiator, *n*-buthyllithium (*n*-BuLi) and the chain terminating agent, chlorotrimethylsilane (CTMS) were supplied by SIGMA-ALDRICH and ABCR, respectively and applied in the syntheses without further purification.

Triethylamine (Et_3N) was purchased from SIGMA-ALDRICH, dried over P_2O_5 and distilled under atmospheric pressure before use.

Cross-linking agents: 1,1,3,3-tetramethyldisiloxane ($^{H}MM^{H}$), 2,4,6,8-tetramethylcyclotetrasiloxane (D^{H}_4), tetrakis(dimethylsiloxy)silane ($Q(M^{H})_4$) were provided by ABCR and applied as received.

Karstedt catalyst, i.e. platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, applied in the cross-linking processes, was supplied by Aldrich (Poland) as the solution in xylene (2% of Pt) and used in the experiments as received.

Palladium(II) acetate was purchased from ACROS. It was applied in the experiments without any preliminary purification procedure.

Solvents: tetrahydrofurane (THF) and toluene were bought from POCh (Poland). Before use, THF was dried using benzophenone and sodium, and then distilled under Ar, whereas toluene, after preliminary drying over $CaCl_2$, was distilled from the suspension with P_2O_5.

2.2. Synthetic methods

The polymers, further on in this work referred to as D_2V polymer and $4D_3V_3$ copolymer, were obtained by kinetically-controlled anionic ring-opening polymerization of D_2V and sequential, kinetically-controlled anionic ring-opening copolymerization of D_3 and V_3 at their molar ratio equal to 4:1, respectively. The reactions were carried out under inert atmosphere (Ar).

In the polymerization of D_2V, 0.186 mol of D_2V, $1.57\cdot10^{-3}$ mol of *n*-BuLi, $7.89\cdot10^{-3}$ mol of CTMS and $7.17\cdot10^{-3}$ mol of Et_3N were used. The process was carried out at −16 °C. Details of the procedure can be found in Ref. [23].

In the D_3 and V_3 copolymerization, 0.091 mol of D_3, $9.42\cdot10^{-4}$ mol of *n*-BuLi, 0.02 mol of V_3, $3.94\cdot10^{-3}$ mol of CTMS and $3.58\cdot10^{-3}$ mol of Et_3N were applied. The procedure was as follows: D_3 and THF were first vacuum-distilled into a Schlenk reactor, then - under flowing Ar – *n*-BuLi was added into the obtained solution. The polymerization was carried out at room temperature until 80% conversion degree of the monomer was reached (controlled by gas chromatography). After that, freshly vacuum-distilled V_3 was added to the reactor, which was placed in a cryostat at 0 °C. The polymerization was continued to 80% conversion degree of V_3. Then the reaction was stopped by addition of CTMS and Et_3N. The synthesized $4D_3V_3$ copolymer was purified by dissolution in methylene chloride and precipitation in methanol. Finally, all the volatile compounds were removed from it during heating at 60 °C on a vacuum line.

Average molecular weight of D_2V polymer was equal to 13 000 g/mol, whereas that of $4D_3V_3$ copolymer - 19 800 g/mol, (determined by GPC, polystyrene standards, eluent: methylene chloride). Both polymers had similar molecular weight distribution, $M_w/M_n = 1.2$.

^{29}Si NMR spectra of the polymers (not shown) contained the signals at −21 and −35 ppm assigned to Si atoms in $Si(CH_3)_2$ and $Si(CH_3)(CH{=}CH_2)$ units [24], respectively. D_2V polymer regularity calculated based on its spectrum according to the method proposed in Ref. [22] was equal to 84.1%. This means that the composition of this polymer was highly regular, with a vinyl group attached to every third Si atom in most units of the macromolecule. The ratio of the units originating from D_3 to those of V_3 in $4D_3V_3$ copolymer was equal to 1: 0.25, i.e. precisely as expected.

The polymers were cross-linked by hydrosilylation, in which various hydrogensiloxanes: $^{H}MM^{H}$, D^{H}_4, $Q(M^{H})_4$ and Karstedt catalyst were used. Molar ratio of Si–H groups from the cross-linker to $-CH{=}CH_2$ groups from the polymer amounted to 1.5:1. Cross-linking processes were carried out without any solvent (D_2V polymer) or in toluene ($4D_3V_3$ copolymer, 1 ml of toluene per 0.5 g of the copolymer), under inert atmosphere (Ar), at the temperature of 60 °C for 48 h. The reactions were catalyzed by $0.2\cdot10^{-6}$ mol of Pt introduced into the system from Karstedt catalyst per 0.5 g of the polymer subjected to cross-linking.

Palladium was introduced into the prepared cross-linked polymers from the solution of palladium(II) acetate in THF ($4.7\cdot10^{-3}$ mol dm^{-3}). In the experiments, the cross-linked polymers were treated with such amounts of palladium(II) acetate solution to get 1 wt% of Pd in the system. The reactions were carried out at room temperature for 48 h. After the reaction, the Pd-containing material was separated from the solution, washed with THF and dried on a vacuum line. It should be mentioned at this point that - out of two possible ways of Pd incorporation into the polysiloxane networks studied, i.e. during or after cross-linking of the polymers - the method adopted in the present work which used previously cross-linked polymers seems to be more advantageous. This is because the reaction between Pd^{2+} ions from palladium(II) acetate solution and the cross-linked polymer is the only chemical process that can take place in the system. Moreover, the previously obtained polymer