



Synthesis of new organoelement copolymers based on polydimethylsiloxanes and aminophosphonates

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ARTICLE INFO

Article history:

Received 2 May 2018

Received in revised form

21 June 2018

Accepted 25 June 2018

Available online 28 June 2018

Keywords:

Polydimethylsiloxane

Aminophosphonates

3-Aminopropyl(diethoxy)methylsilane

Acetic acid

Functionalized siloxanes

ABSTRACT

Based on commercially available 3-Aminopropyl (diethoxy)methylsilane new alkoxy silane with functional aminophosphonate group - diethyl (2-((3-(diethoxy (methyl)silyl)propyl)amino)propan-2-yl)phosphonate were synthesized and characterized. Obtained functional alkoxy silane were transformed to tetrasiloxane in active medium in the presence of acetic acid and then copolymerized with octamethylcyclotetrasiloxane (D4). The chemical structure of the resulting polymer was studied and confirmed by a combination of physical methods, namely, ¹H, ¹³C, ³¹P and ²⁹Si NMR, GPC, and IR spectroscopy. The thermophysical and rheological properties of the polymer were also studied.

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1. Introduction

The interest in the synthesis and study of the properties of compounds based on phosphorus compounds has grown considerably in the past decade [1]. Among these, a particular place belongs to 1-aminophosphonates that found use not only in agriculture but also in medicine [2]. These compounds also became popular owing to the Kabachnik-Fields reaction that occurs without side products and allows one to obtain a required compound in a quantitative yield [3].

Synthesis of polymeric structures is a matter of current interest since it expands our capability to create new materials, devices, formulations, etc. Incorporation of a new element into the structure of a polymer may offer a new set of properties due to the specifics of the respective element. For the moment, siloxanes, specifically polydimethylsiloxane (PDMS), are among the most popular polymers. Items and materials based on PDMS are used by consumers in almost every large industrial sector [4].

However, the literature currently offers only a few publications

on the synthesis of hybrid organic-inorganic materials containing a 1-aminophosphonate moiety within PDMS [5,6]. It has been shown in studies by Jiang S. and Chao P. that incorporation of a 1-aminophosphonate organic substituent into a polymer matrix containing a siloxane moiety favours the emergence of the self-extinguishing properties in the polymer. Thus, incorporation of a functional aminophosphonate moiety into the structure of a pure polydimethylsiloxane frame is an interesting task since it allows one to expect that new materials with practically useful properties would be obtained. Apart from the self-extinguishing effect, one can expect that viscosity would change and hence new elastomeric materials may be obtained.

It should be noted that two synthetic methods were used in the published studies to obtain self-extinguishing materials: the sol-gel method and the hydrosilylation reaction. The co-oligomerization with octamethylcyclotetrasiloxane (D4) is also an important method for incorporation of a functional moiety into PDMS. However, the method for synthesizing polydimethylsiloxanes with an aminophosphonate moiety by polymerization with opening of a siloxane ring was not reported to date.

In this publication we suggest a new synthetic approach for the preparation of a polydimethylsiloxane with statistically distributed 1-aminophosphonate moiety along the polymer chain, using the

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Kabachnik-Fields reaction and ring opening polymerization. The chemical structure of the resulting polymer was studied and confirmed by a combination of physical methods, namely, NMR, GPC, and IR spectroscopy. The thermophysical properties of the polymer were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The rheological properties of the polymer were also studied.

2. Materials and methods

All the starting materials were purchased from Acros and Sigma Aldrich. Solvents were dried and purified according to standard procedures. ^1H , ^{13}C , ^{31}P and ^{29}Si NMR spectra were recorded using a Bruker Avance 300 NMR spectrometer in CDCl_3 , chemical shifts are reported with reference to residual chloroform (7.26 ppm, ^1H).

3. Results and discussion

Previously we have considered a synthetic method for incorporating a 1-aminophosphonate moiety into the structure of (3-aminopropyl)triethoxysilane, however it was accompanied by partial hydrolysis of alkoxy groups at the silicon atom, which prevented the synthesis of an individual functionalized monomer with an alkoxy group in the organic substituent at the silicon atom [7]. In this study, we suggested a modified method for synthesizing diethyl 2-((3-(diethoxy (methyl)silyl)propyl)amino)propan-2-yl)phosphonate **4**. The Kabachnik-Fields reaction (Scheme 1) was performed in the presence of anhydrous magnesium sulfate, with intense stirring in toluene.

The course of the reaction was monitored by ^{31}P NMR, based on the disappearance of diethyl phosphite signals and appearance of 1-aminophosphonate signals. The chemical structure of compound **4** was confirmed by ^1H , ^{13}C , ^{31}P , ^{29}Si NMR, IR, and elementary analyses. The presence of one signal at δ_{P} 31.02 in the ^{31}P NMR spectrum and one signal at δ_{Si} -20.22 in the ^{29}Si NMR spectrum indicated that **4** was an individual compound. No formation of hydrolysis products or high-molecular compounds was observed.

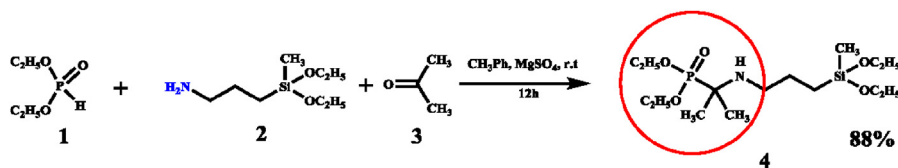
The polycondensation of dimethyldiethoxysilane with a

dialkoxysilyl derivative of aminophosphonate results in a mixture of low-molecular products with cyclic and linear structures. To solve this problem, we decided to use the siloxane ring opening reaction that allows a more uniform product to be obtained. In order to implement the polymerization approach, we obtained, isolated and identified a cyclotetrasiloxane with methyl and (3-((2-(diethoxyphosphoryl)propan-2-yl)amino)propyl) substituents at silicon atoms. It has been shown previously that the condensation of alkoxy silanes in acetic acid, which is also called “active medium” [8–10], is a unique synthetic approach for synthesizing oligoorganosiloxanes, since it allows the course of the reaction to be controlled due to the process homogeneity that results from the specifics of the kinetics of particular cascade process phases. By performing the reaction in acetic acid environment we performed the condensation of compound **4** until the full conversion of alkoxy groups to give compound **5** (Scheme 2).

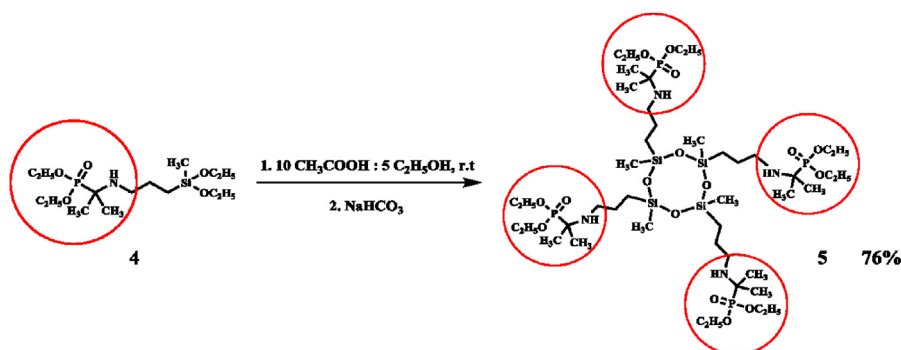
The chemical structure of compound **5** was confirmed by ^1H , ^{13}C , ^{31}P , ^{29}Si NMR, IR spectroscopy, and elementary analyses. According to the ^1H NMR spectrum (Fig. 1), one can see that the reaction carried out in the “active medium” did not give a mixture of isomers. Furthermore, the multiplet signal of SiCH_2 methylene group protons at δ 0.52 (Fig. 1) indicates that an ordered siloxane structure is formed.

The signals of peaks in the ^{29}Si NMR spectra are important parameters for the characterization of organosilicon compounds. Fig. 2 presents the spectrum of compound **5**. The chemical shift matches the D^{P}_4 structure. The presence of one signal at δ -20.18 in the ^{29}Si NMR spectrum and one signal at δ 0.52 in the ^1H NMR spectrum of product **5**, as well as comparison of the chemical shifts with published data [11–13], allowed us to conclude that *cis*-cyclotetrasiloxane was formed.

Copolymerization of cyclic organosilicon compounds containing functional groups in the organic substituents at silicon atoms, with D_4 is a process that occurs in the presence of ionic (anionic and cationic) catalysts. Cationic catalysts with an electrophilic center (Purolite CT-175 sulfocationite resin, sulfuric and trifluoromethanesulfonic acids, etc.) are widely used in reactions with non-functional siloxanes (alkyl, acyl) or siloxanes with a carbonyl group [14]. Anionic catalysts (tetramethylammonium



Scheme 1. Synthesis of (2-((3-(diethoxy(methyl)silyl)propyl)amino)propan-2-yl)phosphonate **4**.



Scheme 2. Condensation of (2-((3-(diethoxy(methyl)silyl)propyl)amino)propan-2-yl)phosphonate **4**.

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