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SYNTHESIS OF POLY(DIMETHYLVINYLSILOXY)VINYLSILOXANE

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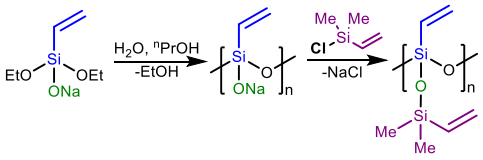
Abstract

A three-stage synthesis of a highly functional polymer matrix, namely, poly(dimethylvinylsiloxy)vinylsiloxane is presented. At the first stage, monosodiumoxy(diethoxy)(vinyl)silane was obtained. The second stage involved the hydrolytic polycondensation (HPC) of monosodiumoxy(diethoxy)(vinyl)silane to obtain poly(sodiumoxy)vinylsiloxane. At the final stage, poly(sodiumoxy)vinylsiloxane was treated with chloro(dimethyl)vinylsilane (CDMVS). All the compounds obtained were characterized by gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy.



Key words: highly functional matrix, hydrolytic polycondensation, monosodiumoxy(dialkoxy)(organo)silanes.

Introduction

Monosodiumoxy(alkoxy)(organo)silanes are organosilicon monomers containing various functional groups at the silicon atom, differing in their chemical nature: the ionic group -ONa and the covalent group -OR, which allows for using them sequentially at different stages during the synthesis of new compounds [1]. It was shown [2] that the successful chemical transformations of monosodiumoxy(dialkoxy)(organo)silanes, which synthetic potential is quite broad [3], with the participation of only alkoxy groups can lead to the formation of a highly functional polymer matrix containing sodiumoxy groups at each silicon atom. Earlier the HPC method was used to obtain a poly(sodiumoxy)methylsiloxane matrix with a regular distribution of sodiumoxy groups along the chain [1].

This work is devoted to the synthesis of a poly(sodiumoxy)vinylsiloxane matrix and its subsequent transformation into poly(dimethylvinylsiloxy)vinylsiloxane, the presence of two types of vinyl groups in which opens up great opportunities for the production of new polymer systems with complex architectures.

Results and discussion

As a monomer for the synthesis of a highly functional polymer matrix, monosodiumoxy(diethoxy)(vinyl)silane was obtained by reacting a triple excess of triethoxyvinylsilane with sodium hydroxide according to the published procedure [4]. To produce a highly functional polymer matrix, the hydrolytic polycondensation of monosodiumoxy(diethoxy)(vinyl)silane was accomplished. During the reaction, a stoichiometric amount of water in dry propan-2-ol was slowly added to a solution of monosodiumoxy(diethoxy)(vinyl)silane in the same solvent.

The reaction of poly(sodiumoxy)vinylsiloxane with CDMVS afforded poly(dimethylvinylsiloxy)vinylsiloxane bearing functional vinyl groups on both sides of the chain, which exhibit different reactivity in the presence of platinum complexes due to the presence of methyl groups at the silicon atom in the side substituent [5].

According to the results of ^{1}H NMR spectroscopic analysis (Fig. 1a), the ratio of the integral intensities of the vinyl and dimethylsilyl group resonances in the resulting polymer was 6:6, which corresponds to the calculated value. The ^{29}Si NMR spectra (Fig. 1b) revealed the signals in the range from –2 to –5 ppm and from –80 to –85 ppm, which are characteristic of O<u>Si</u>Me$_2$CH=CH$_2$ and <u>Si</u>(CH=CH$_2$)O$_{1.5}$ groups, respectively. The following molecular weight characteristics (MWC) of the resulting polymer were determined by GPC: M_n = 2300, M_w = 3100, M_w/M_n = 1.38.

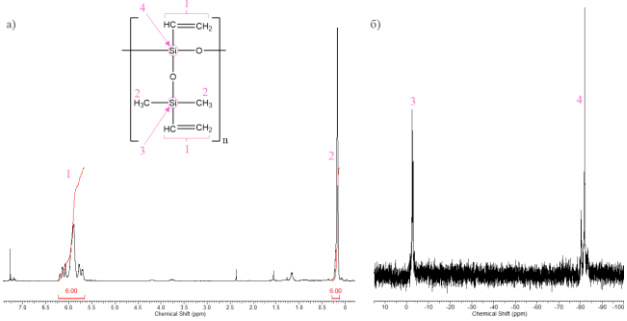


Figure 1. ^{1}H NMR (***a***) and ^{29}Si (***b***) NMR spectra of poly(dimethylvinylsiloxy)vinylsiloxane.

Experimental section

General remarks

Sodium hydroxide (97%, Acros Organics) and CDMVS (97%, Acros Organics) were purchased from commercial sources and used without further purification. Toluene, propan-2-ol, and triethoxyvinylsilane were purified prior to use according to the standard methods [6].

The GPC analysis was performed on a chromatographic system consisting of a high-pressure pump, STAYER series 2 (Aquilon, Russia), a SmartlineRI 2300 refractive index detector (KNAUER, Germany), and a JETSTREAM 2 PLUS column thermostat (KNAUER, Germany). The thermostat temperature was 40 °C ± 0.1 °C. The eluent in use was toluene + 2% THF, and the flow rate was 1.0 mL/min. The columns (300 × 7.8 mm) were filled with Phenogel sorbent (Phenomenex, USA), the particle size was 5 μm, the pore size ranged from 10^3 to 10^5 Å. The results obtained were processed using the MultiKhrom 1.6 GPC program (Ampersend, Russia).

The ^{1}H NMR spectra were recorded on a Bruker WP 250 SY spectrometer (Germany). The ^{29}Si NMR spectra were recorded on a Bruker AVANCE II 300 spectrometer (Germany). The solvent was $CDCl_3$. The spectra were processed using the ACD LABS software.

Syntheses

Monosodiumoxy(diethoxy)(vinyl)silane was synthesized according to the published procedure [4].

Poly(sodiumoxy)vinylsiloxane. Monosodiumoxy-(diethoxy)(vinyl)silane (20 g, 0.1087 mol) and dry propan-2-ol (50 mL) were placed in a flask equipped with a magnetic stirrer and a dropping funnel under an argon atmosphere. Upon vigorous stirring, a stoichiometric amount of water (1.96 mL, 0.1087 mol) in dry propan-2-ol (9 mL) was slowly added. The reaction time was 5 h.

Poly(dimethylvinylsiloxy)vinylsiloxane. A solution of poly(sodiumoxy)vinylsiloxane (9.92 g, 0.0901 mol) in dry toluene (30 mL) was added to a solution of CDMVS (11.4 g, 0.0946 mol) in dry toluene (5 mL) at –50 °C under an argon atmosphere. After the reaction completion, the resulting mixture was filtered. The solvent was removed on a membrane pump, the residual amount of solvent was removed on an oil pump. The product obtained was a transparent viscous liquid. ^{1}H NMR ($CDCl_3$): δ 5.63–6.22 (m, 6H, $SiCH=CH_2$), 0–0.25 (m, 6H, SiMe) ppm. ^{29}Si NMR ($CDCl_3$): δ –2–(–5) ($-OSiMe_2CH=CH_2$), –80–(–85) ($Si(CH=CH_2)O_{1.5}$) ppm. GPC: M_n = 2300, M_w = 3100, M_w/M_n = 1.38.

Conclusions

Hence, poly(sodiumoxy)vinylsiloxane, obtained by the hydrolytic polycondensation, was treated with CDMVS to furnish poly(dimethylvinylsiloxy)vinylsiloxane—a highly functional polymer matrix bearing different types of vinyl groups in its composition. The selective use of the vinyl groups offers great opportunities for the synthesis of new polymers for various purposes.

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