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Size exclusion chromatography with evaporative light scattering detection: Method for the determination of polydimethylsiloxanes II. Application of TSK-GEL $H_{HR}GMH_{HR}$-M column to determine and separate molecular weight of linear polydimethylsiloxanes

Krystyna Mojsiewicz-Pieńkowska *

Medical University of Gdańsk, Faculty of Pharmacy, Department of Physical Chemistry, 80-416 Gdańsk, Al. Gen. Hallera 107, Poland

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Abstract

Issues concerned with molecular weight distribution analysis of linear polydimethylsiloxanes have not been extensively investigated and mastered, yet. Current publications do not provide detailed research data on the evaluation of the polymerization degree of polydimethylsiloxanes (PDMS) present in variable matrices: e.g. pharmaceuticals, cosmetics, foodstuffs nor indicate molecular weights of the polymer used. However, the information on molecular weight, i.e. viscosity, is of primary importance as it directly affects PDMS toxicity, absorption and migration in the living organism. The vast majority of currently applied methods prove to be insufficiently specific for PDMS of a particular molecular weight and therefore alternative analytical methods have to be further researched. In this paper the results of determination of molecular weights in linear polydimethylsiloxanes, using size exclusion chromatography with the evaporative light scattering detector are described. The column calibration curve obtained from low-dispersion standard polystyrene of molecular weights ranging 376–2,570,000 Da was used to determine PDMS molecular weights. Precision and accuracy of determination was obtained. For the mobile phase flow-rate of 0.3 ml/min relative standard deviation RSD ranged to 0.45% and the accuracy of measurement amounted to −0.42%, whereas for flow-rate of 1.0 ml/min RSD ranged to 0.38% and accuracy to +2.15%.

Keywords: Polydimethylsiloxanes; Size exclusion chromatography; Gel permeation chromatography; Evaporative light scattering detection

1. Introduction

The review of literature indicates that the problems of molecular weight distribution analysis of linear polydimethylsiloxanes (PDMSs) have not been well researched to date. There are few publications illustrating detailed investigations related to the polymerization degree of PDMS, which are present in various matrices such as pharmaceuticals or foodstuffs. However, data referring to molecular weight, and at the same time viscosity, are vital, as viscosity directly influences PDMS toxicity, absorption and migration in the living organism [1–14]. The majority of the methods applied to date absorption atomic spectrometry (AAS), emission atomic spectrometry (EAS), infrared spectroscopy (IR), Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance spectroscopy (^{1}H NMR), gas chromatography (GC), reversed-phase high-performance liquid chromatography (RP-HPLC) are not adequately molecular weight distribution analytical to determine PDMS with a given molecular weight [15]. Lack of speciation methods, suitable for the analysis of PDMS, calls for searching alternative analytical methods. Bearing in mind the superior aim of investigations, owing to which the speciation analysis of PDMS in variable matrices (e.g. pharmaceuticals, foodstuffs or biological samples) will be possible the advantages of size exclusion chromatography are just conspicuous. The literature contains very few examples that describe exclusion chromatography for the purposes of the analysis of PDMS, refer to environmental investigations. The problem tackled by several

* Tel.: +48 58 349 31 52; fax: +48 58 349 31 52.
E-mail address: kpienk@amg.gda.pl.

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authors was related to the assessment of pollution of the environment by the silicaorganic compounds that differ in molecular weights. Molecular weights affect the solubility of these polymers in the ecosystem, as well as their volatility [16–21].

Fendinger et al. [16] using exclusion chromatography with inductively charged plasma (GPC-ICP) and high-performance liquid chromatography, also with inductively charged plasma (HPLC-ICP) carried out tests for the:

(a) determination of PDMS as a wastewater pollutant,
(b) observation of PDMS "behavior" in the water environment, and
(c) evaluation of PDMS influence on the environment.

Soil samples were extracted with tetrahydrofuran, which also fulfilled the role of the mobile phase. The purpose of exclusion chromatography was only to separate PDMS from the soil matrix, and the expected products of PDMS hydrolysis (low-molecular fractions which were generated as a result of polymer decomposition) were separated using HPLC-ICP with reverse-phase C_{18}. PDMS were extracted from sediment, amended soil, sludge and influent and their retention times were compared with the retention time of standard PDMS of viscosity 350 cSt.

The shape of a peak coming from sludge and influent testified to the fact that the sample contained a wider range of molecular weights, nonetheless a suitable distribution could not be obtained. Therefore in addition, chromatography in the reverse phases was used. From the determination tests using two chromatographic methods it could be stated that PDMS present in the environment disintegrated into low-molecular compounds. Unfortunately, with chromatography in the reverse phases only polar low-molecular silanols could be identified [17], but not PDMS of a high-molecular weight occurring as an active substance in drugs or as a functional additive E-900 in food.

Many works of Lehmann and co-workers [18–21] also confirmed the ability of PDMS found in soil to degrade. Low-molecular PDMS, which originate as a result, are water-soluble and subsequently freely penetrate the environment in water. The authors used exclusion chromatography to isolate from the matrix a fraction including PDMS, and next PDMS could be separated with HPLC. It was found out that Si–CH_3 bonds are not degraded, whereas Si–O–Si are. Results showed that PDMS is unstable in the soil. This knowledge confirms the fact that PDMS is prone to transform, although it was believed to be a very stable, non-reactive, non-degradable or non-biodegradable polymer.

Dorn and Skelly Frame [17], similarly like in the test described above, joined size exclusion chromatography with the inductively charged plasma to separate and determine polydimethylsiloxanes. Samples from variable environmental matrices do not contain PDMS in high concentrations and therefore, a suitable type of detection which could allow to detect even the slightest amounts of silicaorganic compounds in water and organic solutions was searched. Chromatographic distribution of polymers of a great degree of polymerization and large molecular weights was carried out using a set of two columns: TSK-GEL GMH_{XL} with styrene–divinylbenzene packing, at the mobile phase low speed 0.7 ml/min. The mobile phases in this test were non-polar solvents: xylene and tetrahydrofuran. These solvents were suitable for the extraction of PDMS which differ in molecular weights and they did not disturb the determination using ICP detector. PDMS polymers of molecular weights 1500, 18,000 and 40,000 Da were dissolved in xylene and created a mixture of three solutions.

Andersson et al. used size exclusion chromatography with a refractometric detector [22] for the quantitative determination of polydimethylsiloxanes in pharmaceuticals. The aim of their research was to separate PDMS from smaller molecules, like carboxypolymethylene, which was the element of the pharmaceutical preparation matrix. The authors obtained one chromatogram including one peak, but they did not identify which molecular weight it responds to. It can be presumed that the extract from the pharmaceutical preparation responds quantitatively to a standard formula, known as Antifoam M manufactured by Dow Corning.

Size exclusion chromatography is also applied to the analysis of the ophthalmologic samples. The aim of tests carried out by Lakits et al. was to determine whether PDMS of viscosity 5000 cSt, used as a substitute of a vitreous body in patients, is chemically stable [23]. Earlier findings about detected presence of low-molecular products from PDMS degradation in silicone oils, and some disturbing signals of presumed toxicity of these compounds leading to chronic diseases of the eye, forced the researchers to assess the stability of the methylsilicone oil (PDMS). The material for tests was samples of the methylsilicone oil obtained from the vitreous bodies of 25 patients, in whom this material was used for ca. 9.2 months (maximum to 26 months). From the tests carried out on several columns the authors stated that using silicone materials in ophthalmology is safe, due to the fact that no peaks were observed with retention time longer than it was established for the PDMS standard of viscosity of 5000 cSt. Such a conclusion seems to be too hasty, because the authors in their paper did not include validation of the analytical method specifying, firstly and foremostly, the detection limit. It cannot be ruled out that PDMS degrades into lower PDMS molecular weights and that very small concentration may be below the method detection limit.

Exclusion chromatography was also used for the tests of implants. Liu et al. [24] tested PDMS of a linear structure which were used as implants. They were fully characterized using two methods, exclusion chromatography with refractometric detector and mass spectrometry. Tests were aimed not only to establish molecular weights of the polymers and their decomposition but also to confirm the size of polymers, and end function groups. Size exclusion chromatography was used to collect the eluate fraction including PDMS of variable molecular weights, and PDMS identification was carried out by means of mass spectrometry.

This paper describes test results which testify to the possibility of using size exclusion chromatography with the evaporative light scattering detector to separate and determine molecular weights of polydimethylsiloxanes of linear structure.