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High-performance liquid chromatography with nuclear magnetic resonance detection applied to organosilicon polymers

Part 2: Comparison with other methods[☆]

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Abstract

LC–NMR utilizing ^{1}H and ^{29}Si NMR spectroscopy is ideally suited for the analysis of silicones. It is shown that reversed phase gradient LC–NMR surpasses standard gel permeation chromatography (GPC) and diffusion ordered spectroscopy (DOSY) in the analysis of model hydride terminated polydimethylsiloxane. ^{1}H and ^{29}Si NMR in the stopped-flow arrangement leads to full identification of the components. Concentration gradient introduces a dependence of the ^{29}Si shifts on solvent composition, this dependence can be substantially reduced by a proposed method of referencing. It is shown that the ADEQUATE version of powerful but insensitive 2D INADEQUATE experiment can be used for complete line assignment.

Keywords: LC–NMR; NMR; ^{1}H NMR; ^{29}Si NMR; DOSY; ADEQUATE; Silicones; Polysiloxanes; Chemical shift; Solvent effect; Referencing

1. Introduction

Polysiloxanes, often called silicones, are industrially the most important class of organosilicon compounds with their global annual production in 2002 estimated at 850 thousand metric tons [3]. Various methods are used for analysis and characterization of the starting monomers, oligomers and final polymers or copolymers [4]. Among them, high-performance liquid chromatography (in the GPC or SEC form) is the accepted method for the determination of molecular weight distribution in polymers and ^{29}Si NMR is recognized as the most powerful method for structure determination of isolated components [5,6]. In some cases analysis of mixtures of oligosiloxanes by ^{29}Si NMR spectroscopy was carried out using model compounds and statistical considerations for assigning the lines in the spectra of the mixture [7–9]. Mixtures with a small number of components can be analyzed without physical separation by combining ^{29}Si NMR with diffusion ordering (DOSY) [10,11]. More complicated mixtures or mixtures containing components which do not differ in their diffusion rates must be separated into individual components before their identification by ^{29}Si NMR can be ever attempted. Convenient procedure is offered by LC–NMR—which combines high-performance liquid chromatography (HPLC) with NMR detection. Conventional ^{1}H NMR is used in this combination as exemplified in the study of polydimethylsiloxane synthesis by radical polymerization [13]. We have recently demonstrated [1] that it is feasible to combine HPLC separation with indirect detection of ^{29}Si NMR signals (^{1}H{^{29}Si} NMR) through which a full component identification can be achieved.

In this paper we would like to present further development of the LC–^{1}H{^{29}Si} NMR method and compare it with the other two approaches and, at the same time, report the first results of double quantum correlation experiment performed on an oligosiloxane in the LC–NMR flow probe. As the model polysiloxane we have chosen a commercial product—hydride terminated polydimethylsiloxane, HSiMe$_2$–OSiMe$_2$–(OSiMe$_2$)$_{n-2}$–OSiMe$_2$–O–SiMe$_2$H denoted shortly as M$^{\mathrm{H}}$–D$_n$–M$^{\mathrm{H}}$. We shall use notation of Harris and Robins [7] for numbering the D units in accordance with their position from the nearest end-group, M$^{\mathrm{H}}$D(1)D(2)D(3)...

[☆] For Part 1 see ref. [1]. Presented in part at EUROMAR Conference 2006 [2].

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2. Experimental

2.1. Materials

Acetonitrile (AcN) (LC–NMR grade), chloroform-*d* ($CDCl_3$) (99.5% D, water content <0.01%), hexamethyldisilane (HMDSS), octamethyltrisiloxane (OMTSO, $(Me_3SiO)_2$–$SiMe_2$ or M–D–M), dodecamethylpentasiloxane (DoMPS, Me_3Si–$(OSiMe_2)_3$–O–$SiMe_3$) as well as the model polymer hydride terminated polydimethylsiloxane, $HSiMe_2$–$OSiMe_2$–$(OSiMe_2)_{n-2}$–$OSiMe_2$–O–$SiMe_2H$ or M^H–D_n–M^H, $M_n = 580$, were purchased from Sigma–Aldrich. All the reagents were used as received.

2.2. HPLC apparatus and method

The reversed-phase HPLC experiments were conducted on a Varian LC Star chromatograph (consisting of ProStar 230 solvent delivery module, ProStar 330 photodiode array detector and LC–NMR analyte collector) controlled by Star Chromatography Workstation 2 with Star Chromatography software and LC–NMR system software (vnmr 6.1C).

A Bondesil C18 column (Varian, USA; 150 mm × 4.6 (i.d.) mm, particle size 5 μm) and acetonitrile–chloroform solvent mixture were found to yield satisfactory results with the flow rate of 0.5 ml/min held constant through the whole separation; the (volume) ratio of acetonitrile: chloroform linearly increased from initial 9:1 to 1:9 in 40 min. A NMR reference compound was added in 0.01% (v/v) concentration into both solvents.

The chromatographic peaks were detected with a high sensitivity by on-flow ^1H NMR. (Photodiode detector cannot be used, as methylsilicones exhibit no UV/vis absorption.) NMR detection employed a modified commercial flow probe. The outer coil circuitry of the standard Varian $^1H\{^{13}C,^{31}P\}$ 60 μl PFG IFT Indirect Triple Resonance NMR flow probe was double tuned to ^{13}C and ^{29}Si frequencies by a redesigned BB-channel leaving the outer r.f.-coil and variable capacitors unchanged. No other modification of standard Varian LC–NMR equipment was necessary to perform the described experiments. The selected chromatographic peaks were subjected to three stop-flow $^1H\{^{29}Si\}$ NMR experiments conducted in this probe similarly as was ADEQUATE experiment. Details of all NMR experiments are described in Section 2.3. All the separations and NMR detections were carried out at ambient temperature (22 °C).

GPC (or SEC) measurements were performed using Pump Deltachrom (Watrex Comp.), autosampler Midas and two 300 mm columns in series (PL gel MIXED-B LS, particle size10 μm, separating in the range of molecular weights approximately 400–10,000,000 g/mol). Evaporative light scattering PL-ELS-1000 (Polymer Laboratories) was used as a detector. The injection-loop volume was 0.1 ml. Tetrahydrofuran was the mobile phase. The data were accumulated and processed using the TriSEC 3.0 Software (Viscotek Co.). The calibration dependence for polybutadiene samples in the range cca $600 < M$ (g/mol) < 1700 was fitted by $\log(M) = 11.69–0.506\,V$, where M is molecular weight and V is elution volume in ml.

2.3. NMR spectrometer and details of NMR measurements

The NMR spectra were acquired on a Varian INOVA 500 spectrometer running under vnmr 6.1C software including the flow package for control of LC–NMR experiments. The spectrometer was equipped with a X,Y,Z-Performa gradient module, had four r.f. channels, two of them fitted with waveform generators. The operating frequencies were 499.9, 125.7, and 99.3 MHz for ^1H, ^{13}C, and ^{29}Si NMR, respectively. In all cases the standard software was used. The spectra of the mixture before component separation and their dependence on solvent composition were measured in a 5 mm switchable broad-band probe using the same methods of referencing as used in the flow probe. The ^{29}Si NMR spectra were measured by INEPT [13] with the routine parameters for trimethylsilyl derivatives [14]. Under these conditions the signal of M^H unit is inverted. Possible losses in sensitivity due to non-optimum parameters for other methylsilyl groups are negligible [15].

The on-flow ^1H measurements used spectral width of 10 kHz covering the full ^1H NMR spectrum, relaxation delay 0–1.0 s, acquisition time 1.0–2.0 s, one scout scan preceded 1–4 scans accumulated for each spectrum, and WET [16] was used for solvent signal suppression. Data were zero-filled to 32 K and the initial three data points were obtained by backward projection (32 LP coefficients). Mild Gaussian broadening together with elimination of the residual signal of AcN by digital solvent subtraction were applied before Fourier transform; spline baseline correction was applied to the spectra. No other data processing was employed.

The stop-flow ^1H NMR spectra were measured similarly except that spectral width of 8000 Hz, acquisition time 4 s, and FID zero filling to 128 K were used.

The three gHMQC experiments used a slightly modified phase sensitive gHMQC pulse sequence [17] with ^{29}Si broadband decoupling (GARP [18] using decoupling field of 800 Hz) during 1.5 s acquisition time. In all three experiments only methyl protons were excited by a weak rectangular proton pulses (γB1 approximately 360 Hz) to eliminate effects of homonuclear coupling of SiH protons to methyl protons in the end polymer units. The spectral width in F2 (^1H) dimension was only 1000 Hz, which left the solvent signal outside and showed only correlations to the excited methyl protons. Polarization and refocusing delays were both 71.4 ms long as corresponds to optimal setting for $^2J(^1H,^{29}Si) = 7$ Hz. Gaussian broadening with the constant 1.6 was applied along F2 axis. The first of the three experiments was an “overview” experiment with spectral width 2500 Hz in F1 dimension scanning all ^{29}Si signals in the spectrum with usually 2 × 64 t1 increments and consequently with a poor resolution along the F1 axis. Then two detailed experiments with higher resolution in the F1 dimension were performed. In these experiments the spectral width in F1 dimension was reduced to 300 Hz and in processing 2 × 128 t1 increments the Gaussian broadening constant of about 0.3 was used. The first detailed experiment had silicon (decoupler) transmitter frequency carefully adjusted in the region of D units to cover all D unit signals present and to include the reference ($\delta = -18.4$ to -21.4). The second had decoupler frequency set