Highly efficient method for synthesis of epoxy functional (poly)siloxanes

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ABSTRACT

Epoxy functional siloxanes have many applications which makes the development of a highly efficient method for their synthesis very desirable. Herein, we report syntheses of these compounds based on the hydrosilylation process, in a biphasic reaction setup without the use of solvents that allows separation of the product, recovery and reuse of the catalyst, which is fundamental from the point of view of "green chemistry". Such a biphasic system was obtained by applying phosphonium ionic liquids which immobilised rhodium complex very well while maintaining its high catalytic activity even after multiple use of the catalyst. The above highly effective and universal method of synthesis enabled to obtain epoxy functional di-, tri-, and polysiloxanes of different content of functional groups with a high selectivity at stoichiometric ratio of reactants. A full characterisation of all products by FT-IR and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic analyses as well as by GPC and refractometric analyses was provided.

KEYWORDS: epoxy functional siloxane, modified silicone, hydrosilylation, ionic liquid, epoxy siloxane characterisation

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INTRODUCTION

One of the most popular classes of modified silicones is that of epoxy functional siloxanes [1-4]. They have been well-known and used for many years in a lot of various applications [5-12]. The high reactivity of the oxirane ring of epoxides makes it possible to obtain a wide range of compounds, e.g. ionic silicone surfactants [10, 11, 13]. Moreover, epoxy functional siloxanes are characterised by a good reactivity in cationic polymerisation and are easily polymerised both in the case of thermally [14] and photoinduced [9, 15-17] polymerisation.

A number of epoxy functional (poly)siloxanes have been synthesised via hydrosilylation of allyl glycidyl ether or 1,2-epoxy-4-vinyl-cyclohexane by oligo- or polysiloxanes. The addition proceeds efficiently in the presence of a whole range of catalysts, mainly platinum [7, 8, 10, 18, 20-27] or rhodium [12, 14-16, 19, 20] complexes which operate in homogeneous systems. As heterogeneous catalysts only polymer-bound Wilkinson catalyst [9] and Pt-nanocluster catalyst [28] were used. All the above reactions were carried out in the presence of solvents such as toluene, n-hexane or 1,4-dioxane, and with 10-20% excess of olefin. The presence of metals in the reaction products, even in trace quantities, is unacceptable, but the separation of the catalyst from the reaction mixture, particularly in the case of polymer systems of high viscosity, is a difficult problem. Therefore efforts are made to apply heterogeneous catalysts or immobilised metal complexes in order to obtain high catalytic activity in many subsequent

reaction runs and easy product isolation at the same time, which is fundamental from the point of view of "green chemistry". Our contribution to this area was the development of effective catalytic systems for hydrosilylation processes, based mainly on transition metal complexes immobilised in ionic liquids [29-32].

Ionic liquids (IL) have been recognised as potential media for the immobilisation of catalysts and have been used with a considerable success in a wide range of laboratory scale reactions [33, 34]. Among all publications on this subject, only papers by Weyershausen *et al.* concern functionalisation of poly(dimethyl, hydromethyl) siloxanes catalysed by platinum complexes in ionic liquid media, mainly imidazolium derivatives [35, 36].

Epoxy functional (poly)siloxanes have a great potential for many applications, therefore the development of a highly efficient method for synthesis of this group of compounds is of significant importance. The present study concerns synthesis of different epoxy functional siloxanes and polysiloxanes by using hydrosilylation processes in the presence of a catalytic system consisting of rhodium siloxide complex immobilised in phosphonium ionic liquid. Moreover, because the most of epoxy functional polysiloxanes obtained so far were not fully characterised, we have performed full spectroscopic characterisation of all derivatives prepared.

EXPERIMENTAL

Materials

All reagents were dried and purified before use by usual procedures. Rhodium complex, [{Rh(μ-OSiMe$_3$)(cod)}$_2$], was prepared as described in Ref. [37] Ionic liquid, propoxymethyltrihexyl phosphonium saccharinate, [TriHexProxMP][sac], was prepared as described in Ref. [38] The IL was dried prior to use under vacuum at 60°C for 8h. Heptamethyltrisiloxane, tetramethyldisiloxane and poly(dimethyl-co-hydromethyl)siloxane were purchased from Gelest, olefins and other reagents from Aldrich. Three polysiloxanes of general formula Me$_3$Si(OSiMe$_2$)$_m$(OSiMeH)$_n$SiMe$_3$ with different chain length and different Si-H content were employed in the study. For m=50 and n=25,

polydispersity index M_w/M_n = 5973/3534; for m=70 and n=30, M_w/M_n = 8520/6386; and for m=82 and n=18, M_w/M_n = 7840/5905.

Analytical equipment

NMR spectra (^{1}H, ^{13}C and ^{29}Si) were recorded on Varian Gemini 300 VT and Varian Mercury 300 VT spectrometers. C$_6$D$_6$ or CDCl$_3$ were used as solvents.

GC analyses were carried out on a Varian 3800 chromatograph equipped with a 30 m capillary column DB-1 and a TCD detector using the following temperature program: 60°C (3 min)-10°C/min-300°C (10 min).

FT-IR spectra were recorded on a Bruker Tensor 27 Fourier transform spectrometer equipped with a SPECAC Golden Gate diamond ATR unit. In all cases 16 scans at a resolution of 2 cm^{-1} were carried out to record the spectra.

GPC chromatograms were performed using a Waters Alliance 2695 GPC system equipped with a Waters 2414 RI detector and a set of three serially connected 7.8 × 300 mm columns (Waters Styragel HR1, HR2 and HR4). Molecular weights and polydispersity indices were calculated on the basis of point to point calibration curve of polystyrene Shodex standards in the range from 1.31×10^3 to 3.64×10^6 Da. THF was used as an eluent in a 0.6 mL/min isocratic flow.

All refractive index measurements were performed on a tabletop ATAGO RX 7000α refractometer.

Analysis of the post-reaction mixture for a possible presence of rhodium was carried out on a Varian Vista-MPX inductively coupled plasma - optical emission spectrometer (ICP-OES).

Preparation of epoxy functional siloxanes and polysiloxanes - a general procedure

The appropriate amount of catalyst (in the ratio of 10^{-5} mole per mole of Si-H) and the ionic liquid (1% based on the total weight of combined substrates) were placed into the reaction vessel and heated to 120°C for 0.5 h in order to dissolve the catalyst in ionic liquid. Then the reaction system was cooled down and the mixture of Si-H functionalised siloxane (or polysiloxane) and olefin was added, followed by heating the reaction

vessel to 60-90°C. After 2 h, the reaction vessel was cooled to room temperature and then the post-reaction mixture was separated from the catalytic system by decantation. The recovered catalytic system (catalyst in ionic liquid) was reused in the next reaction cycle. The mixture was analysed by GC technique (di- and trisiloxanes) or by FT-IR spectroscopy (polysiloxanes) and formation of desired products was verified by NMR analysis. Moreover, refractive indices were measured for all products and, in the case of polymeric products, molecular weights and polydispersity indices were determined using the GPC technique.

Characterisation of epoxy functional (poly) siloxanes

3-(glycidoxypropyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane **(1)**

B.p.= 110°C/4 mm Hg, n^{20}_D = 1.42216.

^{1}H NMR: (C_6D_6, 298K, 300MHz) δ (ppm): 0.07 (s, 3H, -OSi(CH_3)O); 0.11 (m 18H, (CH_3)$_3$SiO); 0.57 (t, 2H, SiCH_2-); 1.69 (m, 2H, SiCH$_2$CH_2-); 2.17 and 2.29 (t, 2H, CH_2-CHO); 3.12 (m, 1H, CH$_2$-CHO); 3.30 and 3.38 (m, 4H, CH_2OCH_2).

^{13}C NMR: (C_6D_6, 298K, 79MHz) δ (ppm): -0.17 (SiCH$_3$); 1.9 (Si(CH$_3$)$_3$); 14.0 (SiCH$_2$-); 23.9 (-CH$_2$-); 43.5 (CH$_2$-CHO); 50.7 (CH$_2$-CHO); 71.9 (OCH$_2$CH$_2$); 74.0 (CHCH$_2$O).

^{29}Si NMR: (C_6D_6, 298K, 59.61MHz) δ (ppm): 7.1 (OSiCH$_2$); -21.3 (Si(CH$_3$)$_3$.

3-(2{3,4-epoxycyclohexyl}ethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane **(2)**

B.p.= 140°C/5-6 mmHg, n^{20}_D = 1.43632.

^{1}H NMR: (C_6D_6, 298K, 300MHz) δ (ppm): 0.10 (3H, SiCH_3); 0.16 (18H, Si(CH_3)$_3$); 0.46 (2H, SiCH_2-); 1.20 (2H, SiCH$_2$CH_2-); 1.30-2.10 (m, 7H CH_2-cyclo); 2.84 (2H, -CH-CHO).

^{13}C NMR: (C_6D_6, 298K, 79MHz) δ (ppm): -0.18 (SiCH$_3$); 1.9 (Si(CH$_3$)$_3$); 14.8 (SiCH$_2$-); 23.9-31.2 (CH$_2$-cyclo); 35.6 (CH-cyclo); 51.9, 52.5 (-CH-CHO).

^{29}Si NMR: (C_6D_6, 298K, 59.61MHz) δ (ppm): 6.9 (SiCH$_2$-); -21.1 (OSi(CH$_3$)$_3$).

1,3-bis(glycidoxypropyl)-1,1,3,3-tetramethyldisiloxane **(3)**

B.p.= 184°C/2 mm Hg, n^{20}_D = 1.45135.

^{1}H NMR: (C_6D_6, 298K, 300MHz) δ (ppm): 0.05 (12H, SiCH_3); 0.53 (4H, SiCH_2-); 1.60 (4H, SiCH$_2$CH_2-); 2.20, 2.21 (t, 2H, CH_2-CHO); 3.12 (m, 1H, CH$_2$-CHO); 3.26 (m, 2H, OCH_2CH$_2$); 3.38 (m, 2H, CHCH_2O).

^{13}C NMR: (C_6D_6, 298K, 79MHz) δ (ppm): 0.02 (SiCH$_3$); 14.6 (SiCH$_2$-); 24.0 (-CH$_2$-); 43.6 (CH$_2$-CHO); 50.7 (CH$_2$-CHO); 71.8 (OCH$_2$CH$_2$); 74.3 (CHCH$_2$O).

^{29}Si NMR: (C_6D_6, 298K, 59.61MHz) δ (ppm): 7.8 (OSi(CH$_3$)$_2$).

1,3-bis(2{3,4-epoxycyclohexyl}ethyl)-1,1,3,3-tetramethyldisiloxane **(4)**

B.p.= 223°C/2-3mm Hg, n^{20}_D = 1.47740

^{1}H NMR: (C_6D_6, 298K, 300MHz) δ (ppm): 0.08 (12H, SiCH_3); 0.43 (4H, SiCH_2CH$_2$-); 1.10 (4H, SiCH$_2$CH_2-); 1.30-2.03 (m, 7H, CH_2-cyclo); 2.86 (2H, -CH-CHO).

^{13}C NMR: (C_6D_6, 298K, 79MHz) δ (ppm): 1.9 (SiCH$_3$); 15.1 (SiCH$_2$-); 25.7 (SiCH$_2$$CH_2$); 27.1, 30.0 32.5 ($CH_2$-cyclo); 35.7 ($C$H-cyclo); 51.2, 52.5 (-$C$H-$C$HO).

^{29}Si NMR: (C_6D_6, 298K, 59.61MHz) δ (ppm): 7.7 (OSi(CH$_3$)$_3$).

poly({glycidoxypropyl}methyl-co-dimethyl)siloxane, m=50, n=25 **(5a)**

Polydispersity index determined by GPC: M_w/M_n = 8021/4746, n^{20}_D = 1.43551.

^{1}H NMR: (C_6D_6, 298K, 300MHz) δ (ppm): 0.20 (75H, SiCH_3); 0.29 (300H, Si(CH_3)$_3$); 0.85 (50H, SiCH_2CH$_2$-); 1.92 (50H, SiCH$_2$CH_2-); 2.32, 2.44 (50H, CH_2-CHO) 3.00 (25H, CH$_2$-CHO); 3.28 (50H, CH$_2$CH_2O); 3.54 (50H, OCH_2CH).

^{13}C NMR: (C_6D_6, 298K, 79MHz) δ (ppm): -0.23 (Si(CH$_3$)$_3$); 1.39 (Si(CH$_3$)$_2$); 1.94 (SiCH$_3$); 13.98 (SiCH$_2$); 23.86 (SiCH$_2$$CH_2$); 43.53 ($CH_2$-CHO); 50.25 (CH$_2$-$C$HO); 71.96 (O$CH_2CH_2$); 74.09 (CH$CH_2$O).

^{29}Si NMR: (C_6D_6, 298K, 59.61MHz) δ (ppm): 7.34 (SiCH$_2$) 21.4 (SiCH$_3$) and 21.9 (Si(CH$_3$)$_3$).

poly({glycidoxypropyl}methyl-co-dimethyl)siloxane, m=70, n=30 **(5b)**

Polydispersity index determined by GPC: M_w/M_n = 9972/5772, n^{20}_D = 1.43452.

^{1}H NMR: (C_6D_6, 298K, 300MHz) δ (ppm): 0.16 (90H, SiCH_3); 0.24 (420H, Si($CH_3)_2$); 0.73 (60H, SiCH_2CH$_2$-); 1.80 (60H, SiCH$_2$CH_2-); 2.21, 2.32 (60H, CH_2-CHO) 2.88 (30H, CH$_2$-CHO); 3.18 (60H, CH$_2$CH_2O); 3.42 (60H, OCH_2CH).

^{13}C NMR: (C_6D_6, 298K, 79MHz) δ (ppm): -0.21 (Si($CH_3)_3$); 1.61 (Si($CH_3)_2$); 1.92 (SiCH_3); 13.98 (SiCH_2); 23.85 (SiCH$_2$$CH_2$); 43.67 ($CH_2$-CHO); 50.29 (CH$_2$-$C$HO); 72.14 (O$CH_2CH_2$); 74.06 (CH$CHCH_2$O).

^{29}Si NMR: (C_6D_6, 298K, 59.61MHz) δ (ppm): 7.31 (SiCH$_2$) 21.4 (SiCH$_3$) and 21.9 (Si($CH_3)_3$).

poly({glycidoxypropyl}methyl-co-dimethyl)siloxane, m=82, n=18 (**5c**)

Polydispersity index determined by GPC: M_w/M_n = 8822/5029, n^{20}_D = 1.42451.

^{1}H NMR: (C_6D_6, 298K, 300MHz) δ (ppm): 0.18 (54H, SiCH_3); 0.25 (492H, Si($CH_3)_3$); 0.70 (36H, SiCH_2CH$_2$-); 1.80 (36H, SiCH$_2$CH_2-); 2.20, 2.32 (36H, CH_2-CHO) 2.87 (18H, CH$_2$-CHO); 3.17 (CH$_2$CH_2O); 3.42 (OCH_2CH).

^{13}C NMR: (C_6D_6, 298K, 79MHz) δ (ppm): -0.25 (Si($CH_3)_3$); 1.29 (Si($CH_3)_2$); 1.89 (SiCH_3); 13.97 (SiCH_2); 23.82 (SiCH$_2$$CH_2$); 43.38 ($CH_2$-CHO); 50.26 (CH$_2$-$C$HO); 71.93 (CH$_2CH_2$O); 74.06 (O$CH_2$CH).

^{29}Si NMR: (C_6D_6, 298K, 59.61 MHz) δ (ppm): 7.34 (SiCH$_2$); 21.4 (Si($CH_3)_2$); 21.9 (Si($CH_3)_3$).

poly({2(3,4-epoxycyclohexyl)ethyl}methyl–co-dimethyl)siloxane, m=50, n=25 (**6a**)

Polydispersity index determined by GPC: M_w/M_n = 7928/4556, n^{20}_D = 1.45304.

^{1}H NMR: (C_6D_6, 298K, 300MHz) δ (ppm): 0.19 (75H, SiCH_3); 0.28 (300H, Si($CH_3)_3$); 0.53 (50H, SiCH_2CH$_2$-); 1.34 (50H, SiCH$_2$CH_2-); 1.35-2.14 (175H, H-cyclo); 2.87-2.93 (50H, -CH-CHO).

^{13}C NMR: (C_6D_6, 298K, 79MHz) δ (ppm): -0.23 (SiCH_3); 1.40 (Si($CH_3)_2$); 14.7 (SiCH_2); 24.2 (SiCH$_2$$CH_2$); 27.3, 30.4 32.5 (CH$_2$-cyclo); 35.8 (CH-cyclo); 51.1, 52.5 (-CH-CHO).

^{29}Si NMR: (C_6D_6, 298K, 59.61MHz) δ (ppm): 6.9 (SiCH$_2$) 21.4 (SiCH$_3$) and 21.9 (Si($CH_3)_3$).

poly({2(3,4-epoxycyclohexyl)ethyl}methyl–co-dimethyl)siloxane, m=70, n=30 (**6b**)

Polydispersity index determined by GPC: M_w/M_n = 9254/5258, n^{20}_D = 1.44789.

^{1}H NMR: (C_6D_6, 298K, 300MHz) δ (ppm): 0.17 (90H, SiCH_3); 0.26 (420H, Si($CH_3)_3$); 0.63 (60H, SiCH_2CH$_2$-); 1.28 (60H, SiCH$_2$CH_2-); 1.31-2.52 (210H, H-cyclo); 2.72-2.88 (60H, -CH-CHO).

^{13}C NMR: (C_6D_6, 298K, 79MHz) δ (ppm): -0.19 (SiCH_3); 1.42 (Si($CH_3)_2$); 14.7 (SiCH_2); 24.6 (SiCH$_2$$CH_2$); 27.3, 30.4, 32.5 (CH$_2$-cyclo); 35.8 (CH-cyclo); 51.1, 52.5 (-CH-CHO).

^{29}Si NMR: (C_6D_6, 298K, 59.61MHz) δ (ppm): 7.0 (SiCH$_2$) 21.4 (SiCH$_3$) and 21.9 (Si($CH_3)_3$).

poly({2(3,4-epoxycyclohexyl)ethyl}methyl–co-dimethyl)siloxane, m=80, n=18 (**6c**)

Polydispersity index determined by GPC: M_w/M_n = 8006/4973, n^{20}_D = 1.43522.

^{1}H NMR: (C_6D_6, 298K, 300MHz) δ (ppm): 0.20 (54H, SiCH_3); 0.27 (492H, Si($CH_3)_3$); 0.64 (36H, SiCH_2CH$_2$-); 1.28 (36H, SiCH$_2$CH_2-); 1.35-2.57 (126H, H-cyclo); 2.80-2.93 (36H, -CH-CHO).

^{13}C NMR: (C_6D_6, 298K, 79MHz) δ (ppm): -0.25 (SiCH_3); 1.30 (Si($CH_3)_2$); 14.75 (SiCH_2); 27.23 (SiCH$_2$$CH_2$); 29.8, 30.6, 32.2 (CH$_2$-cyclo); 35.6 (CH-cyclo); 51.1, 52.4 (-CH-CHO).

^{29}Si NMR: (C_6D_6, 298K, 59.61MHz) δ (ppm): 6.9 (SiCH$_2$) 21.4 (SiCH$_3$) and 21,9 (Si($CH_3)_3$).

RESULTS AND DISCUSSION

Epoxy functional siloxanes and polysiloxanes, making the subject of our study, were prepared by hydrosilylation catalysed with a system consisting of rhodium siloxide complex [{Rh(μ-OSiMe$_3$)(cod)}$_2$] immobilised in propoxymethyltrihexyl phosphonium saccharinate, [TriHePrOP][sac], (see Fig. 1).

Such a system was chosen on the grounds of results obtained in our earlier studies of hydrosilylation processes catalysed by platinum and rhodium complexes immobilised in different ionic liquids.

At the first stage, hydrosilylation of allyl glycidyl ether and 1,2-epoxy-4-vinylcyclohexane with 1,1,1,3,5,5,5-heptamethyltrisiloxane or 1,1,3,3-tetramethyldisiloxane proceeded as shown in Scheme 1.

In all cases biphasic systems were obtained which enabled easy separation of the catalytic system after the reaction was completed, thus making it possible to reuse the catalyst. The catalytic system
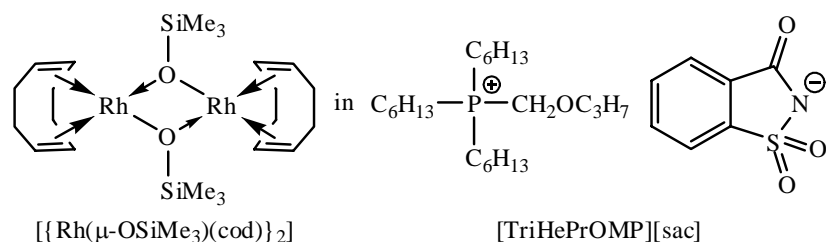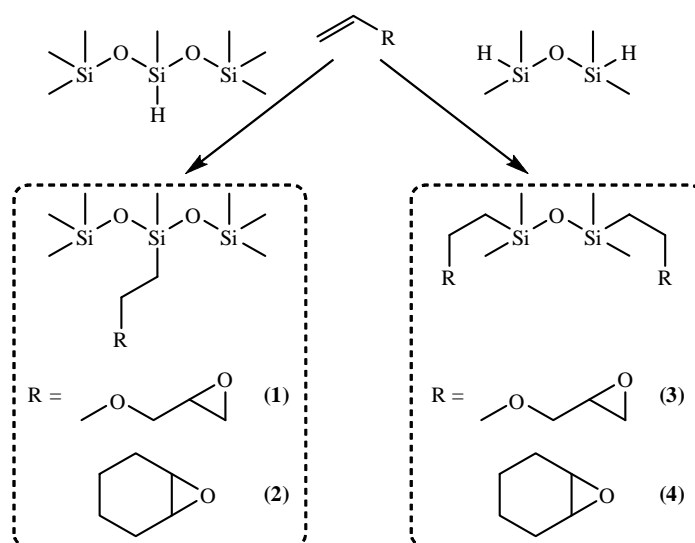
Fig. 1. Catalytic system based on rhodium siloxide complex in phosphonium ionic liquids.

Scheme 1. Syntheses of epoxy functional siloxanes.

based on rhodium siloxide complex [{Rh(μ-OSiMe₃)(cod)}₂] immobilised in ionic liquid [TriHePrOMP][sac] was capable of performing ten runs of the process using the same portion of the catalyst without a noticeable reduction in catalytic activity. Yields of 3-(glycidoxypropyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane **(1)** and 3-(2-{3,4-epoxycyclohexyl}ethyl)-1,1,1,3,5,5,5-hepta-methylotrisiloxane **(2)** were 99-93% in each subsequent run (Fig. 2).

It is worth of mentioning that the yield of disubstituted derivatives is slightly lower than that of the derivatives obtained by hydrosilylation with heptamethyltrisiloxane, although still very high since it is 96-89% (in 10 runs) in the case of 1,3-bis(glycidoxypropyl)-1,1,3,3-tetramethylodisiloxane **(3)** and 95-88% in that of 1,3-bis(2{3,4-epoxy-cyclohexyl}ethyl)-1,1,3,3-tetramethyldisiloxane **(4)** (Fig. 3).

In all cases experiments were discontinued after 10 catalytic cycles carried out in the presence of the same portion of catalyst, in spite of the fact that it still maintained its high catalytic activity. The reactions proceeded with a high selectivity (β-adduct was the only product) and isolation of the reaction product was easy due to formation of biphasic system. High catalytic activity of the system, even at room temperature, made it possible to perform the reaction at a relatively low temperature (from 25 to 60°C), due to which undesired side reaction of olefin isomerisation was not observed. It is worth to add that at elevated temperatures, hydrosilylation is often accompanied by olefin isomerisation and this fact results in a higher consumption of expensive olefin. One of the most important differences between hydrosilylation processes described in the present paper and those reported earlier is the
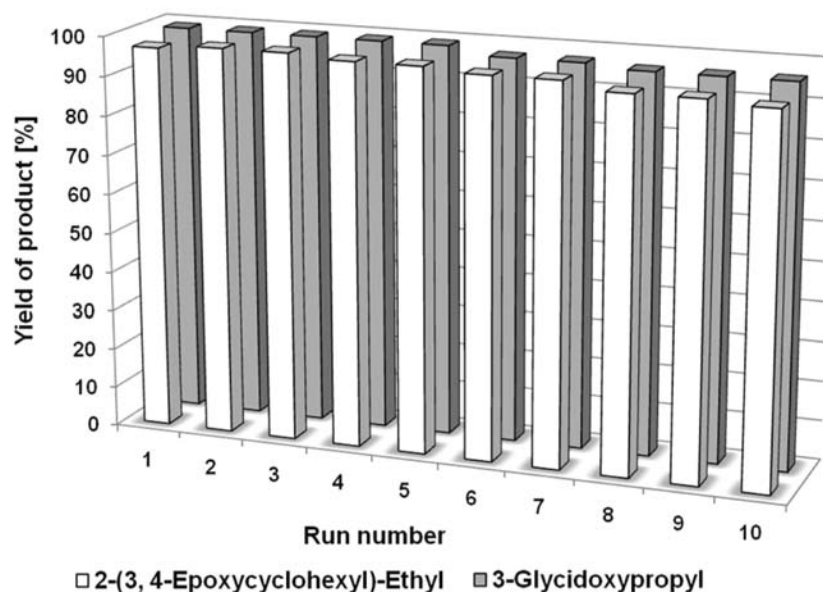
Fig. 2. Yields of products of hydrosilylation of allyl glycidyl ether and 1,2-epoxy-4-vinylcyclohexane with 1,1,1,3,5,5,5-heptamethyltrisiloxane during 10 subsequent reaction runs carried out in the presence of the same portion of catalyst.
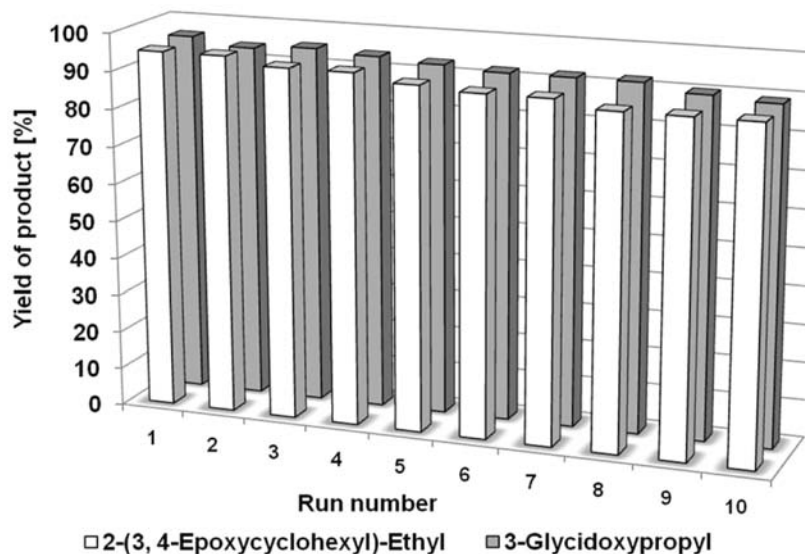

Fig. 3. Yields of products of hydrosilylation of allyl glycidyl ether and 1,2-epoxy-4-vinylcyclohexane with 1,1,3,3-tetramethyldisiloxane during 10 subsequent reaction runs carried out in the presence of the same portion of catalyst.

absence of a solvent, due to which, after the reaction completion and product decantation, practically pure compound is obtained with no need of distilling off the solvent. However, to perform spectroscopic characterisation, the products were isolated by distillation under reduced pressure, which enabled to determine their boiling points, too.

Most of epoxy functional polysiloxanes, obtained by hydrosilylation processes, are low molecular weight compounds which usually have epoxy groups in terminal positions. In the case of

synthesis of high molecular weight polysiloxanes with epoxy groups in side chains, processes of hydrosilylation were applied relatively rarely [15]. Moreover, kinetic studies reported in the literature [39] have pointed to a very interesting fact that the presence of a vicinal hydrogenmethylsiloxane unit in polyhydromethylsiloxanes results in a higher reactivity compared to those containing isolated groups. This is why in order to verify the effectiveness of our catalytic system we have applied poly(hydrogenmethyl-*co*-dimethyl)siloxane of various length of siloxane chain and different content of Si-H groups, according to the Scheme 2.

Three polysiloxanes, in which m=50 and n=25, m=82 and n=18 as well as m=70 and n=30, were employed in the study. In all cases studied, high activity of the catalytic system used was observed, however, it should be added that the higher Si-H content the higher conversion of raw materials (i.e. higher reactivity) as presented in Fig. 4.

High activity of the catalytic system enabled to perform the process at 90°C, while maintaining the mole ratio of Si-H: olefin = 1:1. The advantage of reactions carried out with polysiloxanes was a considerably better separation of the post-reaction mixture from the catalytic system due to increased hydrophobicity of long polysiloxane chain compared

to di- and trisiloxanes. Moreover, the rhodium complex immobilised in ionic liquid was insensitive to traces of water present in raw materials, contrary to the situation observed when homogeneous systems were applied. The process was monitored by means of FT-IR spectroscopy on the grounds of a gradual disappearance of the band at about 2100 cm^{-1} that is characteristic of Si-H group. FT-IR spectra of starting and post-reaction mixtures are shown in Fig. 5 by way of illustration.

The obtained results permit to state explicitly that the complete conversion of Si-H in individual catalytic runs occurred within 2-4 hours. The obtained products, i.e. poly({glycidoxypropyl}methyl-*co*-dimethyl)siloxane (**5**) and poly({2-(3,4-epoxycyclohexyl)ethyl}methyl-*co*-dimethyl)siloxane (**6**) were isolated and fully characterised spectroscopically and by GPC analysis, which confirmed the assumed structures. Analysis of post-reaction mixtures by ICP-OES technique, carried out in order to check for a possible presence of rhodium, proved no rhodium in them. The above results show that the ionic liquid employed in the experiments immobilizes the rhodium complex very well and protects it from leaching as well as it does not decrease its high catalytic activity.
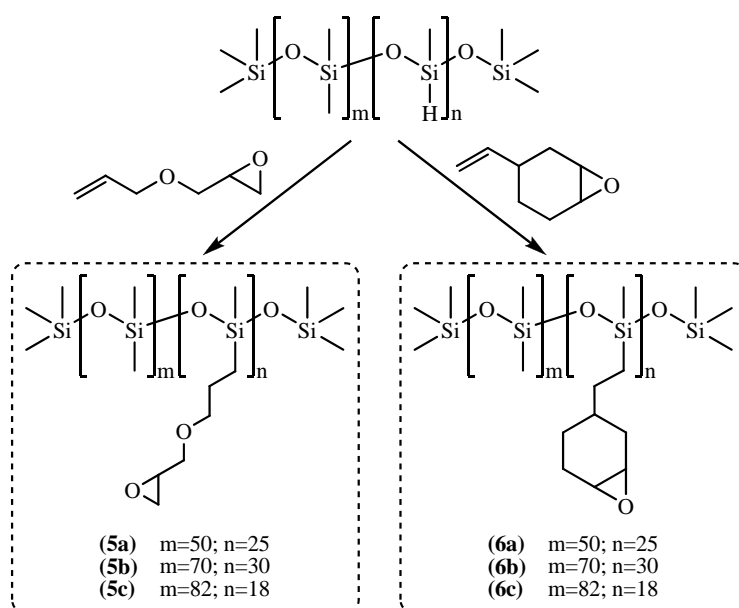
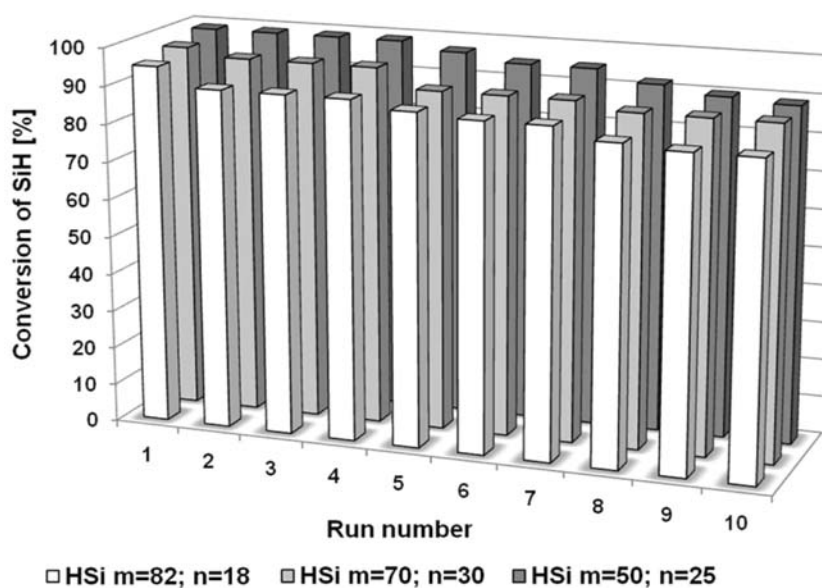**Scheme 2.** The syntheses of epoxy functional polysiloxanes.

Fig. 4. The yield of product of hydrosilylation of allyl glycidyl ether by poly(hydrogenmethyl-*co*-dimethyl)siloxane of various length of siloxane chain and different content of Si-H groups during 10 subsequent reaction runs carried out in the presence of the same portion of catalyst.
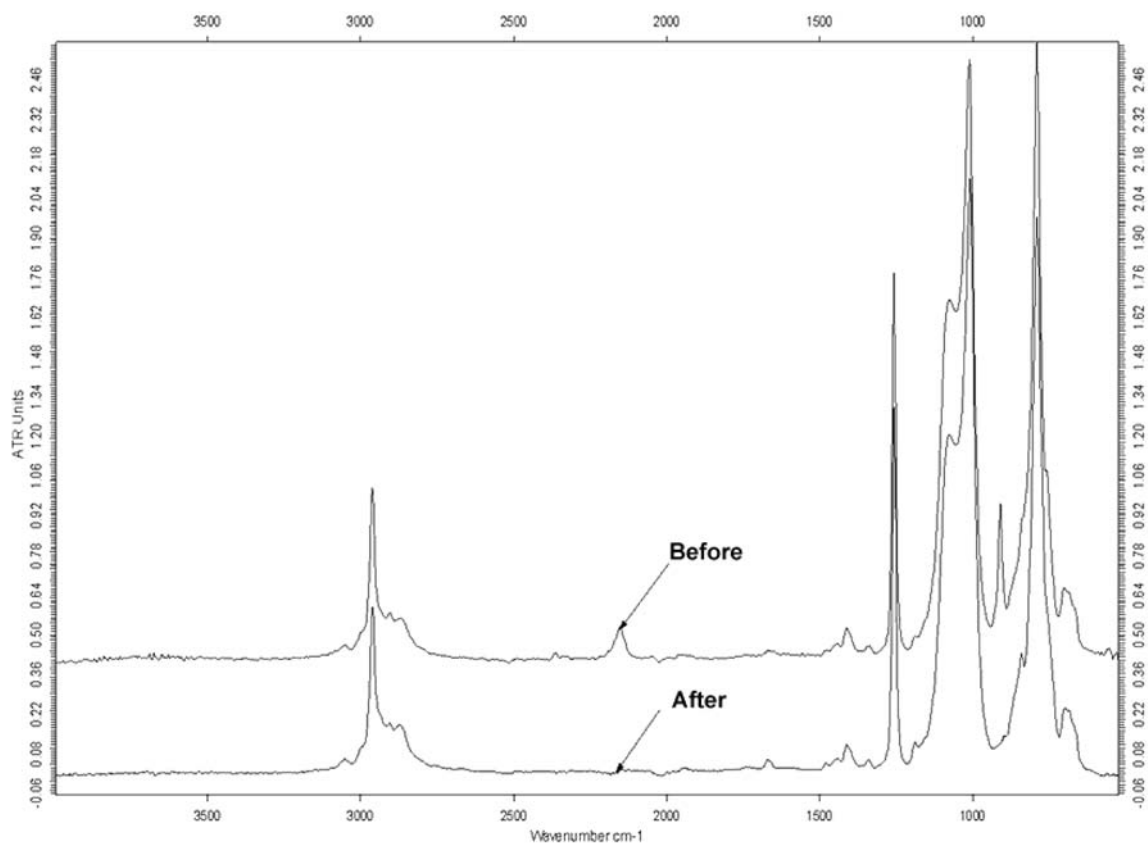

Fig. 5. FT-IR spectra of starting and post-reaction mixtures used in hydrosilylation of allyl glycidyl ether with poly(dimethyl-*co*-hydromethyl)siloxane (m=70, n=30).

CONCLUSIONS

The developed method is one of the simplest and the most effective methods for the preparation of various epoxy functional polysiloxanes which are classified among the most important functionalised and reactive silicones. A very effective catalytic system for the above processes appeared to be rhodium siloxide complex [{Rh(μ-OSiMe$_3$)(cod)}$_2$] immobilised in ionic liquid (propoxymethyltri-hexylphosphonium saccharinate) which enabled to perform 10 reaction runs in the presence of the same portion of the catalyst without a noticeable reduction in its activity. The above catalytic system forms a biphasic system with reactants which enables easy isolation of products by decantation. The important advantage of the process is the fact that it proceeds without using any solvents at stoichiometric ratio of reactants, and this is why the process is considerably more environment friendly than all methods of synthesis of this class of compounds known to date. Good points are also high yields of products and already mentioned easy isolation from the catalytic system which makes the products ready to direct use for most applications.

All products were isolated and fully characterized by FT-IR, ^{1}H, ^{13}C and ^{29}Si NMR spectroscopic analyses as well as by refractometric analysis. Such a full characterization of most of derivatives obtained was performed for the first time.

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