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FUNCTIONAL POLYSILOXANES. 3. REACTION OF 1,3-BIS(3-GLYCIDOPROPYL)-1,1,3,3- TETRAMETHYLDISILOXANE WITH AMINO COMPOUNDS

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ABSTRACT

Novel organofunctional disiloxanes were obtained by the reaction between 1,3-bis(3-glycidopropyl)-1,1,3,3-tetramethyldisiloxane and aromatic amino compounds, i.e., aniline and *p*-aminobenzoic acid. The influence of the reaction conditions on the structure of the resulting compounds was followed.

INTRODUCTION

Organofunctional polysiloxanes have received much attention as compatibilizing or modifying agents in polymer blends, surfactants, etc. or as starting materials in the synthesis of block and graft copolymers.

The main synthetic pathways to organofunctional oligosiloxanes are the cationic or anionic equilibration of cyclic siloxanes in the presence of a functional disiloxane acting as an end-blocking agent [1, 2] or the hydrosilation of unsaturated functional compounds with polysiloxanes containing Si—H active groups [1, 3–5].

Previously, the synthesis of carboxyester- or carboxyamido-terminated polydimethylsiloxanes [6] and of chain- or end-chloromethylphenethyl functionalized polydimethylsiloxanes [7] by the transformation of appropriate siloxane prepolymers has been reported.

The present paper deals with the ring opening of glycidoxy groups attached to the siloxane moiety by aniline and *p*-aminobenzoic acid. The aim was the synthesis of oligosiloxanes possessing multiple, different organic functions. 1,1,3,3-Tetramethyldisiloxane was used as the starting model compound.

EXPERIMENTAL

Reagents and Materials

Toluene used for the hydrosilation reaction was purified by the usual procedure and distilled over sodium wire. All other reagents were of commercial grade and used without further purification.

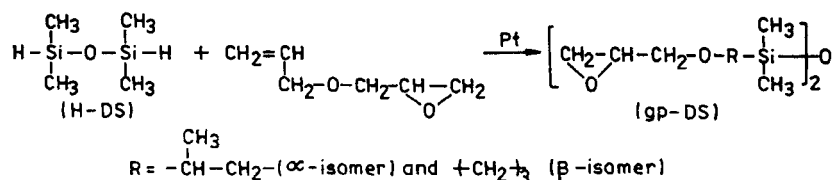
Synthesis of 1,3-bis(3-glycidoxypropyl)-1,1,3,3-tetramethyldisiloxane (gp-DS): The hydrosilation of allyl glycidyl ether (AGE) with 1,1,3,3-tetramethyldisiloxane (H-DS) (AGE/Si-H = 1.2 molar ratio) (Scheme 1) was performed in toluene (total concentration of reagents = 50% by weight) at 100–110°C, in the presence of H₂PtCl₆ (2% by weight in isopropanol) under nitrogen. The reaction was monitored by IR spectroscopy, the disappearance of the 2120–2160 cm⁻¹ band indicating the total consumption of the Si-H group. The hydrosilation was completed after 5 hours. Toluene and any excess AGE were removed by vacuum distillation.

Reaction of gp-DS with aniline was realized by heating the reagents mixture (epoxy/NH₂ = 1/1 or 4/1 molar ratios) in the presence of isopropanol (OH/NH₂ = 1/1 molar ratio) at 80°C, under stirring, over a period of 24 hours. After vacuum evaporation of isopropanol, the products (**1a** and **1b** in Scheme 2) were recovered as yellow-brown liquids in 99% yield.

Reaction of gp-DS with p-aminobenzoic acid was performed by heating the reagents mixture in the presence of isopropanol (OH/NH₂ = 1/1 molar ratio) for 5 hours, at 60°C, under stirring. As the reaction proceeds, the initial heterogeneous mixture becomes homogeneous. Using different epoxy/NH₂ initial ratios (4/1 and 2/1), products **2a** and **2b** (Scheme 3) were obtained as a yellow viscous liquid and a yellow glassy solid, respectively, after vacuum distillation (20 mmHg, 60°C) of isopropanol. The products were purified by dissolving them in methanol, filtering, and evaporating the solvent by vacuum. Yields were higher than 98%.

Analysis

¹H-NMR spectra were registered on a JEOL-C60 HL apparatus. IR absorptions of the synthesized products were obtained on a Specord M 80 spectrometer. Molecular weights were determined on a Knauer Vapour Pressure Osmometer, in



SCHEME 1. Hydrosilation of AGE with H-DS.

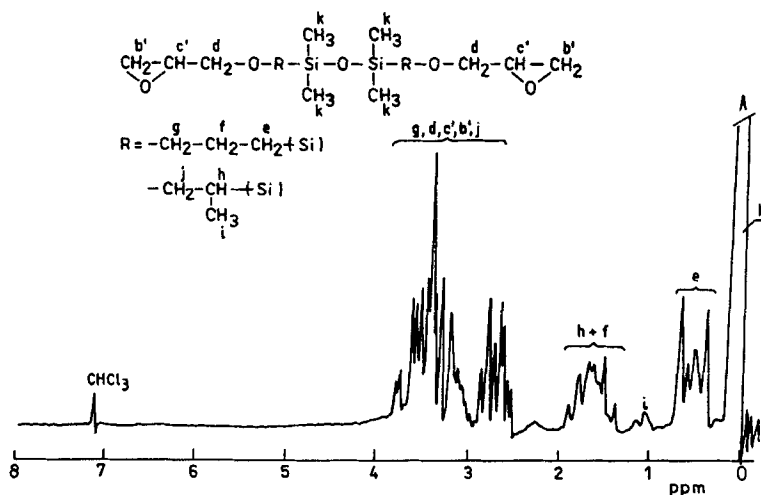
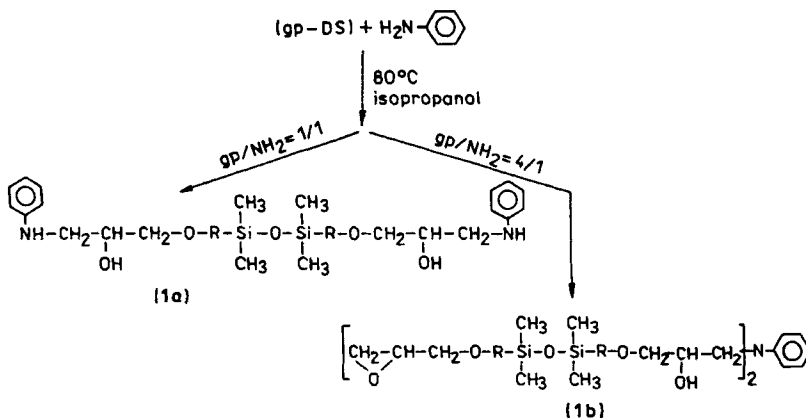


FIG. 1. $^1\text{H-NMR}$ spectrum of the addition product of H-DS to AGE.

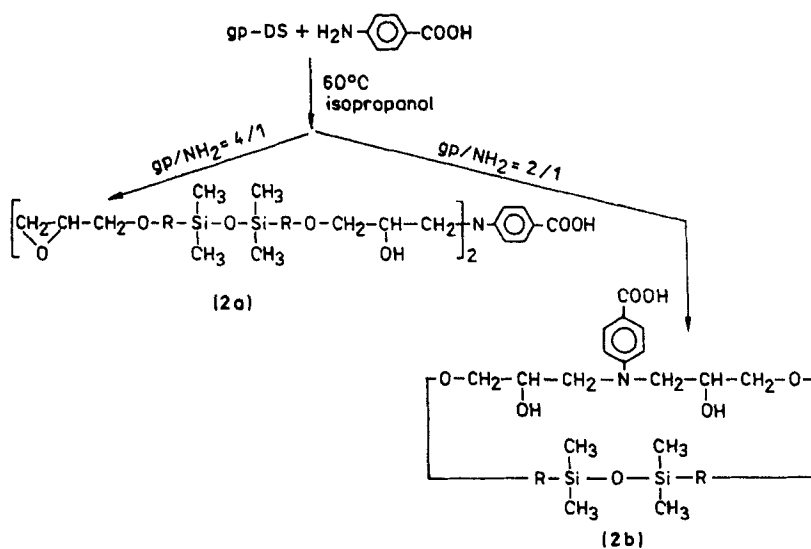
dioxane, at 36°C . Elemental analysis was performed on a Perkin-Elmer 240. The content of carboxylic groups was determined by volumetric analysis (tetramethylammonium alcoholic solution). Epoxy group content was established by reaction with hydrochloric acid and titrating the excess acid with NaOH solution.

RESULTS AND DISCUSSION

The gp-DS was obtained by hydrosilation of AGE with H-DS in the presence of platinum catalyst, at $100\text{--}110^\circ\text{C}$, in toluene (Scheme 1). The reaction product was a mixture of α - and β -addition isomers ($\alpha/\beta \cong 1/6$ molar ratio, as calculated from the $^1\text{H-NMR}$ spectrum). After removing the solvent, the excess AGE, and the



SCHEME 2. Reaction of gp-DS with aniline.



Scheme 3. Reaction of gp-DS with *p*-aminobenzoic acid.

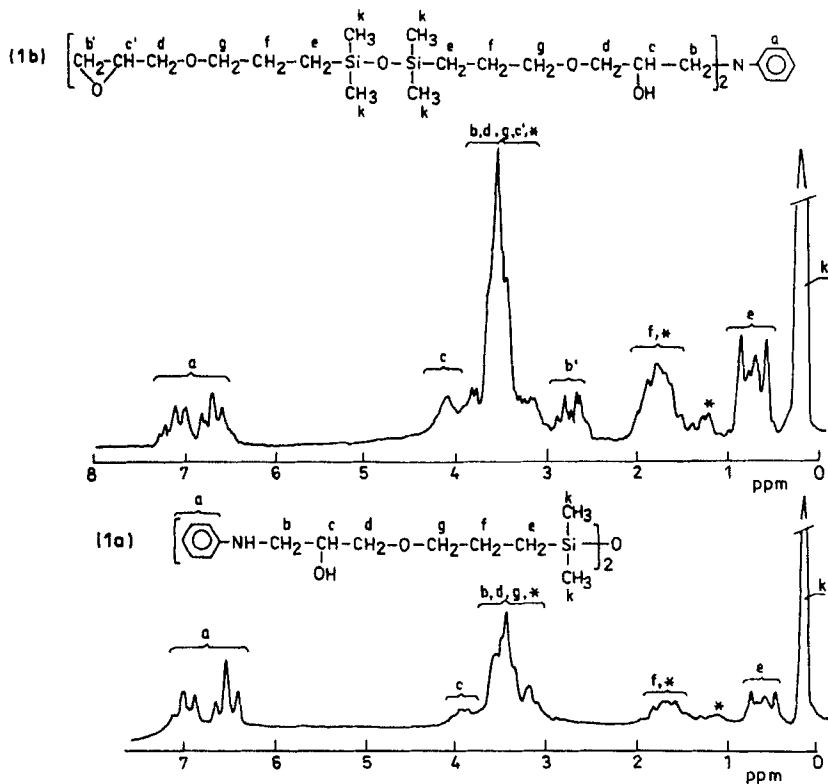


FIG. 2. ¹H-NMR spectra of the reaction products of gp-DS with aniline; (1a) epoxy/NH₂ = 1/1 and (1b) epoxy/NH₂ = 4/1.

solvent of the catalyst, no side products were observed in the $^1\text{H-NMR}$ spectrum (Fig. 1).

Disiloxanes containing two, three, or four different hydroxy, amino, epoxy, or carboxy functional groups were prepared by the reaction between gp-DS and aniline or *p*-aminobenzoic acid, according to Schemes 2 and 3.

The reaction of gp-DS with aniline occurred at 80°C in the presence of isopropanol. Isopropanol acts both as an activating agent and as a blocker of the possible reactions between the preformed OH groups and the epoxy cycle [8]. Depending on the epoxy/ NH_2 initial ratio, disiloxanes containing hydroxy and secondary amino

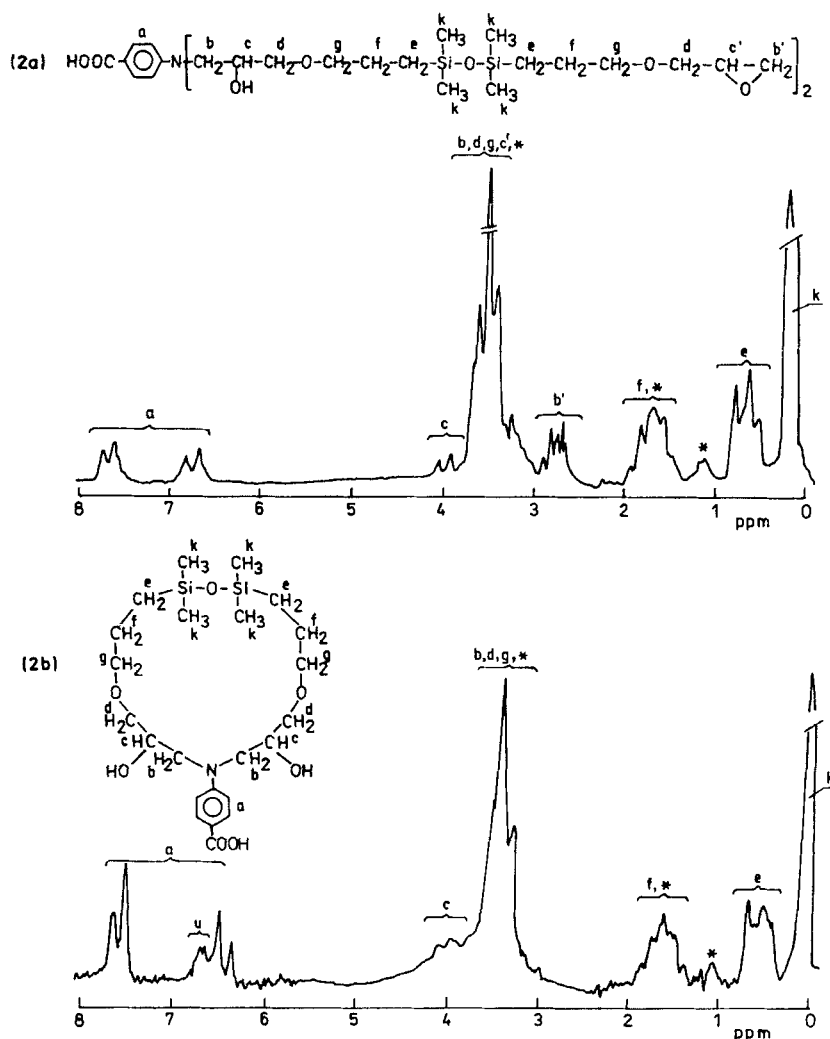


FIG. 3. $^1\text{H-NMR}$ spectra of the reaction products of gp-DS with *p*-aminobenzoic acid; (2a) epoxy/ $\text{NH}_2 = 4/1$, and (2b) epoxy/ $\text{NH}_2 = 2/1$; u = unknown structure (see the text).

TABLE 1. IR, Molecular Weight, and Chemical Analysis Data of the Functional Disiloxanes

Sample code	IR characteristic absorptions, cm^{-1}	Molecular weight, theoretical/found (VPO)	Chemical analysis (theoretical/found)					
			Carbon, %	Hydrogen, %	Silica, %	Nitrogen, %	Epoxy, mol/100 g	Carboxy, mol/100 g
gp-DS	915 (epoxy); 1050–1100 (siloxane); 1120 (ether); 1260 (Si–CH ₃)	362.6/360	—	—	—	—	0.55/0.55	—
1a	—	548.9/531	61.3/61.2	8.8/8.8	10.2/10.1	5.1/5.0	—	—
1b	750, 1515, 1610 (Ph); 915 (epoxy); 1050–1100 (siloxane); 1120 (ether); 1190 (N–CH ₂); 1230 (N–Ph); 1260 (Si–CH ₃); 3300–3500 (OH)	818.4/835	55.8/54.7	9.2/8.9	13.7/13.7	1.7/1.8	0.24/0.24	—
2a	905 (epoxy); 1050–1100 (siloxane); 1185 (N–CH ₂); 1260 (Si–CH ₃); 1530, 1605 (Ph); 1680, 1700 (C=O); 3300–3450 (OH)	862.4/824	54.4/54.3	8.7/8.8	13.0/13.1	1.6/1.5	0.23/0.23	0.12/0.11
2b	—	499.8/482	55.3/55.4	8.2/7.9	11.2/11.0	2.8/2.8	—	0.20/0.20

(**1a**) or hydroxy, tertiary amino, and epoxy functional groups (**1b**) were obtained (Scheme 2).

The *p*-aminobenzoic acid proved to be more reactive than aniline. Its reaction with gp-DS in the presence of isopropanol is completed at 60°C over a period of 5 hours. The structure of the resulting compounds depends on the initial ratio between epoxy and amino groups (Scheme 3). For an epoxy/NH₂ = 4/1 ratio, a linear compound (**2a**) having four different functional groups was formed, while for an epoxy/NH₂ = 2/1 ratio, a cyclic structure (**2b**) appeared. The structures of the synthesized compounds were established by ¹H-NMR spectroscopy (Figs. 2 and 3) and IR spectroscopy, and they were confirmed by molecular weight determinations and chemical analysis (Table 1).

The data in Table 1 show good agreement between the theoretical and determined values (molecular weight and chemical analysis data). The proposed structures are also sustained by the IR characteristic absorptions.

For gp-DS, a $\cong 1/6$ molar ratio between α - and β -isomers was established from the NMR spectrum (Fig. 1). For all other spectra, the contribution of the α -isomer is noted by the symbol *. The ¹H-NMR spectra of compounds **1a**, **1b** (Fig. 2), **2a** and **2b** (Fig. 3) confirm the proposed structures. However, in the case of compound **2b**, in the aromatic region the spectrum shows a mixture of products with the *p*-aminobenzoic group linked in different ways. No epoxy rings are evidenced by the spectrum, so a possible structure should consider a linear product having one epoxy cycle from gp-DS opened by the *p*-aminobenzoic acid and one opened by water traces existing in the reaction mixture.

CONCLUSIONS

Ring-opening reactions of epoxy groups linked to disiloxane moiety were performed with aniline and *p*-aminobenzoic acid. The chemical transformations were proved to be almost quantitative and yielded highly functionalized disiloxanes, able to be used in subsequent reactions. Data on the transformation of higher molecular weight polysiloxanes will be published soon.

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