

PRODUCTION OF SILOXANE OILS FROM OCTAMETHYLCYCLO-TETRA SILOXANE USING EQUILIBRIUM RING OPINING REACTION

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الملخص

تم تصنيع زيت السيلوكسان بخمس أوزان جزيئية مختلفة عبر تفاعل فتح المركبات الحلقية التوازن لأوكتاميثيل سيكلوتيتراسيلوكسان (D4). تم تأكيد وجود البنية الكيميائية لمادة زيوت السيلوكسان الخمسة باستخدام كل من مطياف الرنين المغناطيسي النووي (NMR) ومطياف تحويل فورييه الطيفي للأشعة تحت الحمراء (FTIR) وتم تحديد الكتلة الجزيئية باستخدام الرنين المغناطيسي النووي البروتوني $^1\text{H-NMR}$ وكذلك تقنيات التحليل الكروماتوغرافي. أظهرت نتائج الكروماتوغرافي السائلة عالية الأداء (HPLC) التي تم الحصول عليها أيضًا، أنه يمكن إزالة زيوت السيلوكسان الحلقية من زيوت السيلوكسان الخطية باستخدام التقطير تحت الضغط المخلخل، وكانت الكتلة الجزيئية المحددة من $^1\text{H-NMR}$ أصغر من الكتلة الجزيئية المستهدفة.

ABSTRACT

Siloxane oil with five different molar masses was synthesized via equilibrium ring-opening reaction of octamethylcyclotetrasiloxane (D4). The chemical structures of the five siloxane oils material were confirmed using both Nuclear Magnetic Resonance Spectroscopy (NMR) and Fourier-Transform Infrared Spectroscopy (FTIR) techniques and the molecular mass was determined using proton $^1\text{H-NMR}$ as well as chromatographic analysis techniques. The High Performance Liquid Chromatography (HPLC) results obtained also showed that cyclic siloxane oils could be removed from the linear siloxane oils using vacuum distillation, and the molecular mass determined from $^1\text{H-NMR}$ was smaller than the target molecular mass.

KEYWORDS: Siloxane Oil; Ring-Opening; Proton-NMR; Chromatography; Polysiloxane.

INTRODUCTION

Siloxane oils can be regarded as derivative of inorganic silicates by partial substitution with organic groups. These materials are considered to be the most widely studied inorganic polymers. Historically, the first time these types of materials were produced in 1872; however, they did not gain commercial importance until decades later. They were introduced to the market in 1940s [1]. Siloxane oils offer a wide spectrum of properties that cannot be offered by common organic polymers. This is a result of the polar Si-O backbone, combined with the contribution from the organic substituents. The length of the Si-O bond is longer than that for carbon C-O bond by about $0.11 \text{ \AA}$, which provide bend-ability and flexibility to the polysiloxanes chains [2]. The major differences among siloxane oils depend on the molecular weight (MW), on the length of the linear chain, and on the chemical structure of radical side groups, radical end termination of the polymer chains, and the size distribution of the chain. Thus, each type of silicone oil has specific chemical and physical characteristics [3].

Some of the outstanding properties of siloxane oil include an extremely low glass transition temperature (-123°C), high thermal and oxidative stability, high UV resistance, low surface energy and hydrophobicity, low toxicity, good electrical properties, high permeability to many gases and relatively low flammability [4]. Due to the low glass transition temperature and in order to take the advantage of the unique properties of such materials a very high molecular mass is required to achieve good mechanical properties which can be established by physical modification by filler additives, chemical modifications by crosslinking or copolymerizations of the siloxanes with other polymers [5]. Amino silicone oil is applied in textile finishing. Series of amino silicone oil can be obtained satisfactory from wool cotton and chemical fiber. In emulsion form, it provides strong adsorption for the polyester blended yarn, nylon and can tightly combine with active group of fibers. This type of oil plays key role in hair-care cosmetics and shampoos. However, it should be kept away from fire [6].

Today, siloxanes are used as rubbers, resins, dielectric multimedia, hydraulic or heat transfer fluids, lubricants, medical materials and as surfactants. They are synthesized commercially by the hydrolysis and subsequent condensation of organohalosilanes or by the acid- or base- catalyzed ring opening reaction of cyclic siloxane monomers particularly octamethylcyclotrisiloxane D_4 and the polymer molecular weight is controlled by introducing a chain transfer agent [1]. Another method of synthesizing polysiloxanes with controlled molecular mass is the living anionic reaction of hexamethylcyclotrisiloxane (D_3) employing an alkyl lithium as the initiator. The ring opening reaction process allows great control over molecular mass by adjusting the stoichiometry of cyclics to the end group reactants or the monofunctional agent. An example of these end group agents is bis (3-aminopropyl) tetramethyldisiloxane, which will be used in this work under anionic conditions, on the other hand protic acids are the most common initiating species used in cationic ring opening reactions. The ring opening reaction reactions can be carried out under anionic or cationic conditions and they are usually classified as either a kinetically or thermodynamically controlled process. In the thermodynamically controlled route D_4 is the appropriate monomer used, whereas the kinetically controlled route D_3 is used [4]. Thermodynamically controlled reactions occur when the system is allowed to reach equilibrium conditions, which results in a redistribution of both linear and cyclic chains for polysiloxanes. The most popular synthetic method of polysiloxanes preparation is ring opening equilibration reaction of D_4 under anionic conditions [7].

The process includes three general steps: firstly initiation step where the base catalyst attacks the silicon to produce the silanolate end-group, secondly propagation-depropagation steps in which the linear and cyclic oligomers molecular mass increases, and finally chain equilibration step where the oligomers molecular mass start to be constant and the cyclic will represent between 10-15 wt% of the produced oligomers [8]. Then the remaining cyclics can be easily distilled under vacuum. During ring opening reaction the growing polymer chain can perform a “backbiting” reaction where it can break the partially ionic Si-O bond present along the linear backbone resulting in the production of cyclics. Studies on this phenomenon have revealed that the equilibrium between the linear chains and cyclics determines the polymer yield, molecular mass and molecular mass distribution [9]. The concentration of the equilibrium cyclics and the linear polymer is independent of the initial monomer concentration. As a consequence dilution of the system with a solvent results in a decrease in the linear chain yield so that the cyclic concentration remains the same,

therefore, the equilibration reaction can only be preformed effectively in bulk [10] as it is carried out in this work. The obtained siloxane oil will have amino end group which provide the ability for the polymer to be further modified to produce amino-modified siloxane oil by bulk polymerization and using potassium hydroxide as a catalyst and 1,3-Diethenyl- 1,1,3,3 tetramethyl disiloxane as a cured agent [11].

EXPERIMENTAL Work

Materials

Octamethylcyclotetrasiloxane (D₄, + 99% purity) was purchased from Fluka Company (Sigma-Aldrich). It was dried by stirring over calcium hydride overnight under nitrogen. A vacuum distillation of the D₄ was carried out at 60–70°C, using a short path distillation apparatus. The dried D₄ was stored under a nitrogen atmosphere in a round bottom flask sealed with a rubber septum and adhesive tape.

Bis(3-aminopropyl) tetramethyldisiloxane (+97% purity) was purchased from Industrial Analytical Company. It was used as received and stored in desiccators over calcium hydride.

Tetramethylammonium hydroxide pentahydrate (+97% purity) was purchased from Sigma-Aldrich. It was used as a catalyst for equilibrium ring-opening reaction.

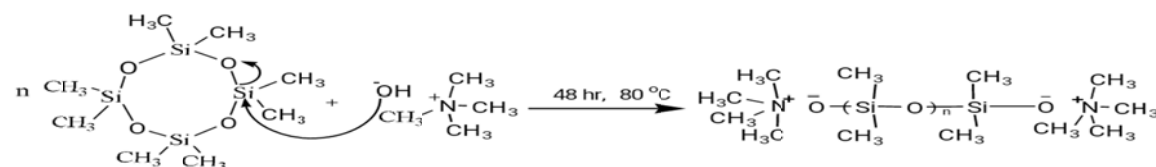
Benzophenone (99% purity,) was purchased from Sigma-Aldrich; and used as received. It was used to deactivate the amine end group of the siloxane oils. Chloroform, tetrahydrofuran (THF), and d-chloroform solvents were purchased from Sigma-Aldrich. These solvents were used as received in the characterization.

Synthesis of Siloxane Oils

Five siloxane oils with amino functional groups, and different molar masses of (1000, 2000, 4000, 7000, 10000 g/mol), were synthesized, using equilibrium ring-opening reaction based on the method reported in literature using D₄ [7]. The first step in siloxane synthesis is preparing the siloxanolate catalyst, which is used in the second step to prepare the siloxane oils.

Preparation of tetramethylammonium hydroxide siloxanolate catalyst

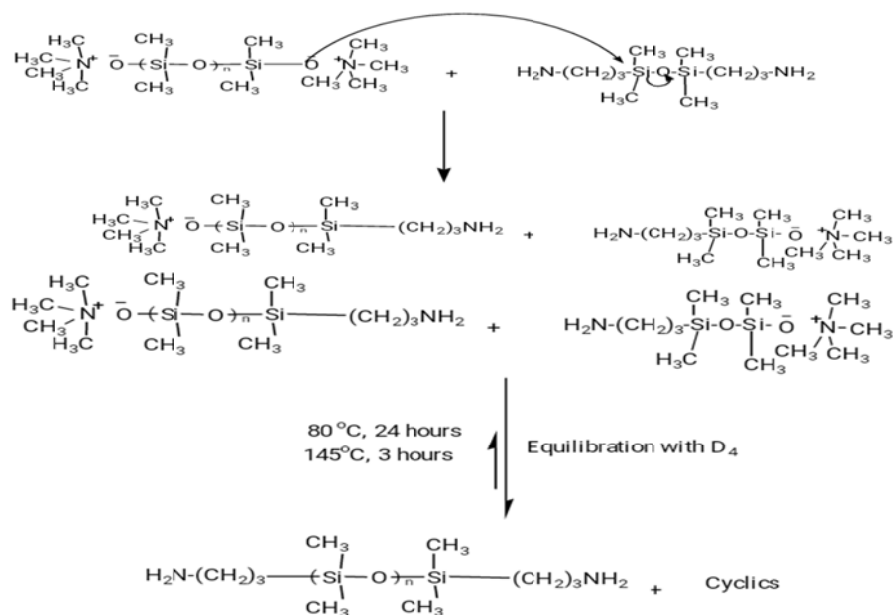
The tetramethylammonium hydroxide siloxanolate catalyst synthesis was carried out by reacting tetramethylammonium hydroxide pentahydrate with D₄, as is illustrated in Scheme (a). Tetramethylammonium hydroxide pentahydrate (0.25 g) was added to the reaction vessel, followed by the addition of D₄ (5 mL), via syringe. The reaction mixture was stirred with nitrogen bubbling through it for 40 h at 80 °C. The nitrogen flow was high enough to aid in the removal of water. Following the reaction, the mixture was cooled to room temperature and diluted with D₄ (5 mL) to reduce the viscosity of the mixture. The catalyst was added almost immediately, to avoid moisture absorption of atmospheric water.



Scheme a: Tetramethylammonium siloxanolate catalyst preparations from D₄.

Synthesis of siloxane oils terminated with an aminopropyl group

The synthetic route that was used in the study for the synthesis of the siloxane oils is an equilibration of the cyclic tetramer D₄ and a difunctional siloxane end-blocking reagent, i.e. bis (3-aminopropyl) tetramethyldisiloxane (Scheme b).



Scheme b: Synthesis of siloxane oils via equilibrium ring-opening reaction.

The synthetic procedure used was as follows:

1. Bis(3-aminopropyl) tetramethyldisiloxane was added to a flame dried 25 mL two-neck round bottomed flask equipped with a magnetic stir bar and rubber septum. The D₄ was added to the flask.
2. The reaction mixture was heated to 80°C and 0.04 mole % (based on the number of moles of D₄) of the siloxanolate catalyst solution was added. The reaction temperature was maintained for 24 h to allow the mixture to equilibrate.
3. The reaction mixture was subsequently heated at 140 °C for 4 h while bubbling nitrogen through it to decompose the catalyst and remove the trimethylamine by-product.
4. The reaction mixture was heated at 125 °C under vacuum for 3–5 h to remove the cyclic compounds (D₃, D₄, D₅ ...) from the equilibrium mixture. The polymer was stored for characterization under nitrogen in a dried round bottom flask sealed with a rubber septum and adhesive tape.

Table (1) shows the quantities of D₄ and bis(3-aminopropyl) tetramethyldisiloxane that were used to synthesize the siloxane oils of desirable molar mass. The quantity of D₄ and bis(3-aminopropyl) tetramethyldisiloxane required to obtain siloxane oils with specific molar masses were determined according to the well-known method in literature [10, 12].

Table 1: Quantities of D₄ and bis(3-aminopropyl) tetramethyldisiloxane required to obtain siloxane (10 g) with various target molar masses

Target M _m (g/mol)	Bis(3-aminopropyl) tetramethyldisiloxane (g)	D ₄ (g)
1000	2.50	8.63
2000	1.24	10.07
4000	0.62	10.78
7000	0.36	11.10
10000	0.25	11.21

5. Chromatography technique was used to verify the removal of cyclic compounds resulting from equilibration, and to measure the molar mass of the siloxane oils. ^1H -NMR was used to verify the molar masses of the siloxane oils.

Characterization Techniques

Nuclear magnetic resonance spectroscopy (NMR)

The chemical composition of the obtained amino and ester terminated siloxane oils were determined using NMR (^1H and ^{13}C -NMR) (a Varian Unity Inova). ^1H -NMR spectra were measured on a Varian 300 MHz instrument using deuterated chloroform as solvent. All the spectra were referenced to the solvent chemical shift at δ 7.26 ppm. The absolute molar mass of the siloxane oils was also calculated using ^1H -NMR spectra (with the absence of the internal standard TMS in d-chloroform solvent). This is necessary to later avoid any confusion with the siloxane peak (chemical shifts) assignments (the signals from the methyl groups of the siloxane oils and copolymers would have overlapped with the TMS reference peak). ^{13}C -NMR spectra were obtained in the same manner as the ^1H -NMR spectra but long runs were used (overnight runs). All the ^{13}C -NMR spectra were referenced to the solvent chemical shift at δ 77.0 ppm. All the chemical shifts in the NMR spectra were assigned to the corresponding chemical structures according to the Cambridge Soft. Chem. Office 2006, using an NMR prediction software program.

Fourier-transform infrared spectroscopy (FTIR)

The chemical composition of the obtained siloxane oils was determined using FTIR. FTIR was used to follow, and characterize, the emergence and disappearance of the amine group (NH_2) as the molar mass of the siloxane oils increased. Siloxane samples were prepared by placing a drop of the material between two sodium chloride discs. The infrared spectra were obtained with a Perkin Elmer 1650 Fourier-transform infrared spectrophotometer, and recorded in the range from 500 to 4000 cm^{-1} , using 32 scans.

High performance liquid chromatography (HPLC)

HPLC was used to verify the removal of cyclic compounds resulting from equilibration reaction during siloxane synthesis. The separation was performed using a dual pump HPLC comprising the following units: a Waters 2690 separations module (Alliance), Agilent 1100 series variable wavelength detector, and PL-ELS 1000 detector, and UV detector was adjusted to 254 nm, which corresponds to the absorption of the aromatic ring [13]. Data were recorded and processed using PSS Win GPC unity (Build 2019) software. A PLgel (Polymer Laboratories) 3 μm mixed-E column was used at 30 $^\circ\text{C}$. THF was used as solvent at a flow rate of 1.0 mL/min. The polymer samples were prepared by dissolving 10 mg of siloxane in 2 mL THF. The samples were filtered through a Gelman Glass Acrodisc or a Gelman GHP Acrodisc prior to introduction to the column [14].

RESULTS AND DISCUSSION

Chemical characterization of siloxane oils

Figure (1) shows typical ^1H -NMR spectrum of a siloxane oils terminated with an amine group. Five different chemical shifts (τ) can be distinguished in the spectrum at τ 0.07, 1.2, 1.5, 2.0 and 2.6 ppm. The chemical shift at τ 0.07 ppm corresponds to the protons in the methyl group bonded to silicon (CH_3), and the chemical shift at τ 2.0 ppm corresponds to the protons in the end group (amine group (NH_2)). The other three

chemical shifts are related to protons in the methene groups positioned between the silicone atom and the amine group.

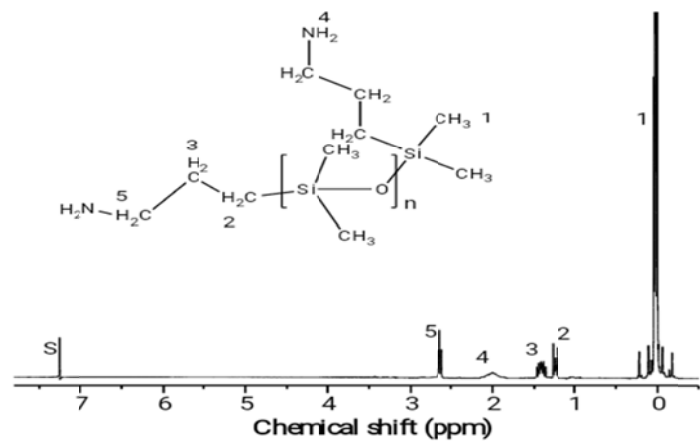


Figure 1: Typical ¹H-NMR spectrum of a siloxane oils terminated with an amine group (-NH₂).

Figure (2) shows a ¹³C-NMR spectrum of the siloxane oils terminated with an amine group. There are four well defined chemical shifts, at TM0, 12, 26 and 45 ppm. The chemical shift at TM 0 ppm corresponds to the carbon atom in the methyl group bonded to silicon (CH₃), the chemical shift at TM12 ppm corresponds to the carbon atom attached to the silicon atom, and the last chemical shift at TM45 ppm corresponds to the carbon atom attached to the amine group (NH₂) at the chain end. The chemical shift at TM26 ppm corresponds to the carbon atom in the methene group placed between the methene attached to the silicone atom and the methene attached to the amine group.

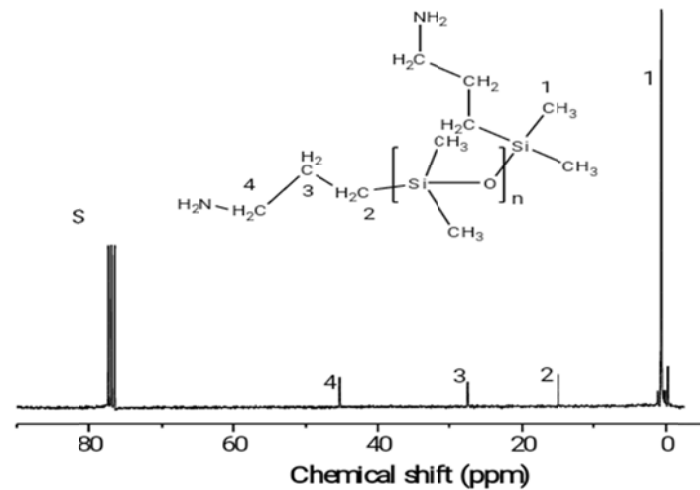


Figure 2: Typical ¹³C-NMR spectrum of a siloxane oils terminated with an amine group (-NH₂).

Figure (3) shows the FTIR spectra of the siloxane oils of two different molar masses (1000 and 7000 g/mol) bands, before the esterification process. The assignments are indicated in the figure. In the case of the low molar mass siloxane oils the amine absorption appears more clearly than in the case of the high molar mass siloxane oils (dotted curve in the figure). The FTIR result confirms results that have been reported by Jeffrey [15], for siloxane terminated with amine groups.

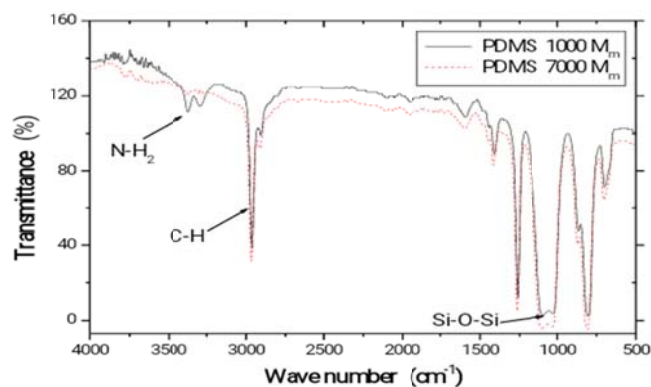


Figure 3: FTIR spectra of siloxane oils terminated with amine end groups of two different M_n (1000 and 7000 g/mol).

Determination of siloxane molar mass and the removal of cyclic components

HPLC with an ELSD detector was used to ensure that distillation under vacuum can successfully separate the cyclic products (cyclic compounds of siloxane) from the linear products (siloxane oils) after the ring opening equilibrium reaction. Before HPLC analysis the siloxane oils end group was deactivated.

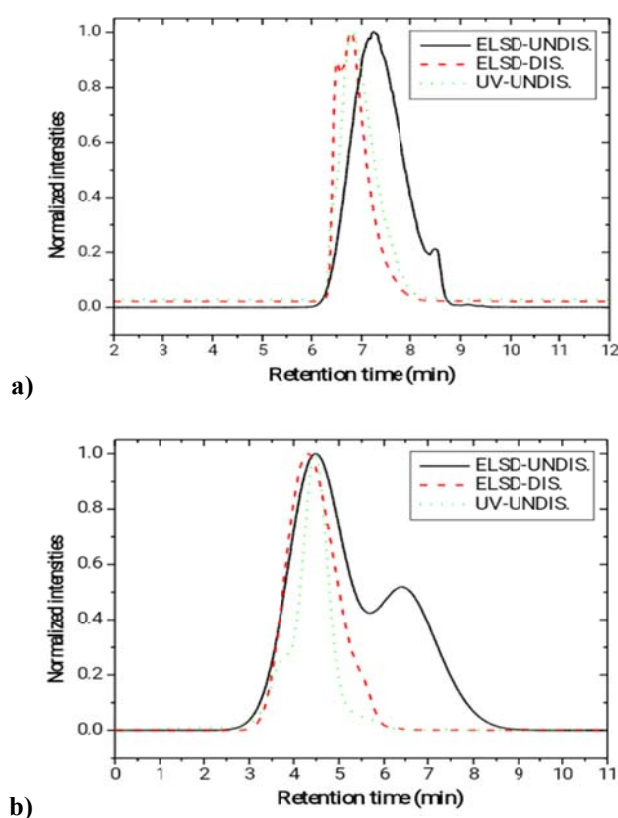


Figure 4: HPLC results of the undistilled and distilled siloxane oils of (a) 1000 g/mol target molar mass and (b) 7000 g/mol target molar mass.

Figure (4) shows a typical example of the HPLC results obtained for undistilled and distilled siloxane oils. It is clear that cyclic siloxane oils can be removed using vacuum distillation. A UV detector was also used to monitor the linear siloxane oils, which are terminated with benzene rings. The benzene ring has UV absorption at approximately 254 nm [13]. However, no complete overlapping was obtained for any of

the siloxane oils; thus, even though cyclic compounds of siloxane can be removed there is no way to be completely sure that all cyclic compounds have been removed from the reaction mixture. The obtained results are identical to those obtained in a previous work by Ressia et al, in 2001 [16], when linear siloxanes polymer was synthesised.

From HPLC the average molar masses and polydispersity of the siloxane oils were also determined. The obtained results are summarized in Table (2). The obtained molar mass values (M_n) here are clearly greater than the values of the target molar masses, and also larger than the estimated molar mass values (M_n) by $^1\text{H-NMR}$ technique. This is due to the fact that HPLC results are relative to the linear polystyrene standards and are not absolute molar masses values.

Molar masses for the amine-terminated siloxane oils were determined by $^1\text{H-NMR}$ after thermal decomposition of the siloxanolate catalyst and removal of the cyclic components by distillation. Results were confirmed by chromatographic analysis as is discussed later in this section. From the integration of the chemical shifts in the $^1\text{H-NMR}$ spectra the molar mass can be calculated. Five $^1\text{H-NMR}$ spectra of siloxane with five different molar masses are shown in Figure (5).

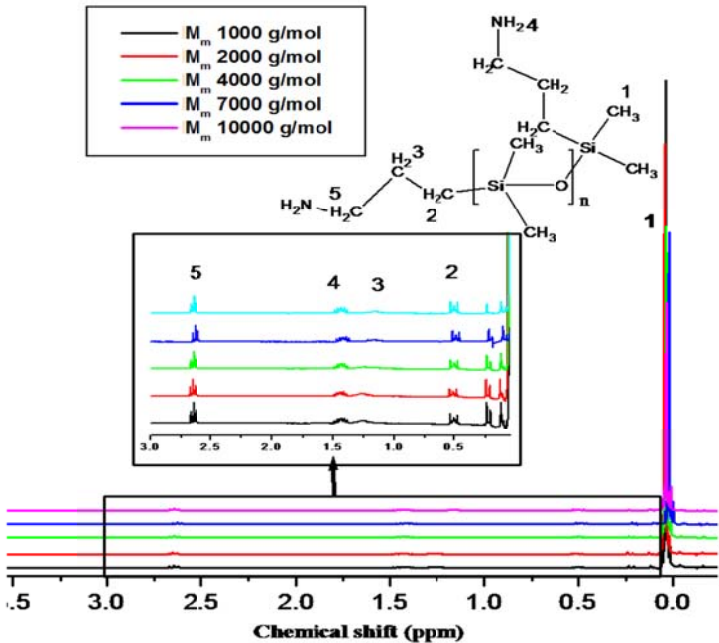


Figure 5: $^1\text{H-NMR}$ spectra of siloxane oils of various molar masses.

The molar masses of the resultant amine-terminated siloxane oils were determined for $^1\text{H-NMR}$ data after thermal decomposition of the siloxanolate catalyst and removal of the cyclics by distillation according to the method introduced by David in 2001 [17]. The molar mass values were calculated using $^1\text{H-NMR}$ spectral data as follows:

1. Let the sum of the integration of the chemical shifts due to the four – CH_2 protons (m 2.6 ppm) attached to the chain end = V. Thus integration of the chemical shift for one proton in the chain end $X = V / 4$,
2. The molar mass of the end group is $M_m(\text{EG}) = 116 \text{ g/mol}$,
3. Let the integration of the chemical shifts due to the six – CH_3 protons (m 0.07 ppm) attached to the backbone = W. Thus the area for one proton in each single repeating unit in the backbone is $Y = W / 6$,
4. The molar mass of the repeat unit $\text{SiO}(\text{CH}_3)_2$ is $M_m(\text{RU}) = 74.16 \text{ g/mol}$,

- Immediately at the chain end group one atom of oxygen is missing, as is shown in the left side of the oil chain in the Figure (5). Therefore the molar mass of one oxygen (O) atom must be subtract from the total molar mass $M_m(O) = 16 \text{ g/mol}$,
- The M_m was determined by substituting the above values in the following equation:

$$M_m = [(Y/ X) M_m (RU)] + M_m (EG) - M_m (O)$$

A summary of the obtained results is tabulated below.

Table 2: Comparison of the target and the determined molar masses of siloxane oils

Target M_m (g/mol)	M_m^a (g/mol)	M_w^b (g/mol)	M_n^b (g/mol)	M_w^b/M_n^b
1000	940	1554	1213	1.28
2000	1950	2846	2194	1.30
4000	3400	5270	4250	1.24
7000	6050	9980	7120	1.41
10000	9100	12640	10195	1.24

^a Measured by ¹H-NMR, ^b Measured by HPLC

Table (2) shows that the M_m determined from ¹H-NMR is lower than the target M_m for all of the siloxane oils and as the molar mass increases this difference between the target and the determined molar mass becomes larger. This may indicate that less cyclic molecules were formed during the synthesis of low molar mass siloxane than in the higher molar mass siloxane oils. This could be because in the case of siloxane synthesis with high molar mass the quantity of D₄ that is used in the reaction feed is greater than in the case of siloxane with low molar mass. This can contribute to an increase in the concentration (by weight) of cyclic molecules when the reaction reaches the equilibrium stage. This is because fewer siloxane molecules were formed in the case of the higher siloxane molar mass chains than were formed in the case of the lower siloxane molar masses chains from the same weight of D₄.

CONCLUSIONS

In this work five different molar masses of siloxane oils were successfully synthesized via equilibrium ring-opening polymerizations. The chemical structures of the five siloxane oils material were confirmed using both NMR and FTIR techniques and the molecular mass was determined using proton ¹H-NMR as well as chromatographic analysis techniques. The Chromatography results showed that cyclic siloxane can be removed using vacuum distillation. The molecular mass determined from ¹H-NMR was smaller than the target molecular mass with percentage of error less than 10%, which is considered as acceptable value in engineering area.

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