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Microwave-Assisted Synthesis of 1,3-*Bis*(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane

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1,3-*Bis*(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane was synthesized under microwave irradiation. The structure of the compound was analyzed by infrared spectroscopy, nuclear magnetic resonance hydrogen spectroscopy and gas chromatography. The optimal reaction condition was obtained by the single factor method. Under the optimal condition, the overall yield could reach 83.9 % and the purity of 1,3-*bis*(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane was 99.1 %. It is found that under microwave radiation the reactions are very rapid with good yield, better quality and less time is required for the completion of the reaction.

Keywords: Microwave synthesis, Hydroxypropyl polysiloxane, Hydrosilylation, Allyloxytrimethylsilane.

INTRODUCTION

Hydroxyalkyl silicone is a carbon-containing functional group polysiloxane. Due to the high reactivity of hydroxyalkyl, it can make polysiloxane link with organic polymers through Si-C bond by react with -OH, -Br, -COOH and -NCO, *etc*. to achieve the purpose of the silicone-modified organic polymer, thereby greatly improving the releasability gloss, lubricity, heat resistance, cold resistance, weather resistance and hydrolysis resistance, *etc*. [1,2]. Therefore, the introduction of the hydroxyalkyl chain polysiloxane segment, is an effective way to make activated carbon having a reactive silicone functional group. The most commonly used is 1,3-*bis*(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane (BHTS).

Because of larger difficulty of BHTS preparation, the preparation method is seldom reported. Predecessors have conducted some research on preparation methods, Knoth used dimethyldichlorosilane, 3-chloropropyl alcohol and sodium to synthesis BHTS [3], for the Si-Cl bond easily hydrolyzed, the total yield was only l3 %. Fang *et al.* [4] increased the total yield to 45.2 % with dimethyl dimethoxy silane instead of dimethyldichlorosilane. Speier prepared BHTS by hydrosilylation of allyl acetate and 1,1,3,3-tetramethyl-disiloxane [5], the yield was just 29 % although the synthetic method was simple. Jiang Hongqin *et al.* used 1,3-*bis*(3-chloropropyl)-1,3-dimethoxy-1,3-dimethyl siloxane as a raw material, after the Grignard, ester substituted and alcoholysis reaction the total yield could reach 75 %, but it was not appropriate for industrial production for using the Grignard reagent which was prepared in harsh conditions [1].

Recently microwave technology is used more widely in various fields of chemistry. Introduce microwave radiation in organic synthesis may accelerate the reaction rate and improve product yield [6-8]. In this paper, BHTS was synthesized under microwave irradiation with temperature-controlled non-pulsed microwave reactor.

EXPERIMENTAL

Allyl alcohol, hexamethyldisilazane (HMDS), 1,1,3,3-tetramethyldisiloxane (HMM), platinum tetrachloride were commercial product. Isopropyl alcohol (A.R.), *p*-toluenesulfonic acid (A.R.), imidazole (A.R.), pyridine (A.R.), sodium hydroxide (A.R.), phenolphthalein (A.R.), *o*-phthalic anhydride (A.R.) were all commercial reagents. Potassium biphthalate was standard reagent.

The reactions were conducted in a MAS-II Microwave Workstation with a maximum power output of 1000 W, equipped with a magnetic stirrer. The product was analyzed by VECTOR-22 infrared spectrometer with resolution of 4.0 cm^{-1} and the average data of ten times test. ^1H NMR spectra were measured on a Varian INOVA-400 NMR spectrometer (^1H, 300 MHz). Content Analysis were performed using a Agilen GC 7890A gas chromatograph, with PH-1 capillary columns (30.0 m × 320 μm, film thickness 0.25 μm), the column temperature were 200 °C, injection port temperature were 270 °C, FID detector temperature were 270 °C, the carrier gas: high purity nitrogen,

the column flow: 1 mL/min, the split ratio: 100:1, sample were injected in split mode, the sample were dissolved in methanol.

Synthesis procedure of BHTS: The general procedure of preparing BHTS is presented in Fig. 1.

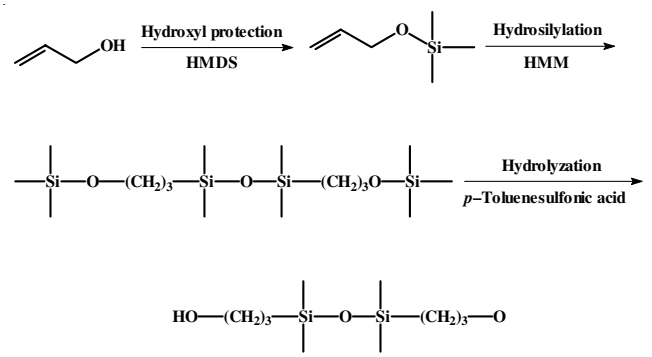

Fig. 1. Synthesis route of 1,3-*bis*(3-hydroxypropyl)-1,1,3,3-tetramethyl-disiloxane

Preparation of allyloxytrimethylsilane (ATMS): In the presence of platinum tetrachloride, allyl alcohol can react with 1,1,3,3-tetramethyldisiloxane reacted to get Si-O-CH_2, which lead to the yield of the main product reduced greatly. So the alcoholic hydroxyl groups need to be protected to avoid the side effects. Trimethylchlorosilane was often used as hydroxyl protection reagent in literature [9], but this method can produce HCl, which may corrode the equipment and that the reaction condition was strict. In this paper the synthetic process was studied using hexamethyldisilazane as hydroxyl protection reagent.

Hexamethyldisilazane was added into four-neck round-bottom flask, which was equipped with thermometer, stirrer and constant pressure funnel and condenser pipe, then setting the microwave reaction parameters, when thermometer reached 75 °C. After that cautiously added dropwise allyl alcohol in 1 h, after that, set reaction temperature to start reaction, then distilled the mixture at atmospheric to collect 100-102 °C fraction, which was ATMS.

Preparation of 1,3-*bis*(3-trimethylsiloxypropyl)-tetramethyl disiloxane (TPMS): Hydrosilylation is occurred between compound with silicon hydrogen bond and olefin/alkyne, which can form corresponding silicon-carbon compounds. By this means, many organic silicon-carbon compounds can be synthesized. It often use hyperoxide, platinum compound, *etc*., one of the most commonly used is platinum compounds/complexes, such as Speier platinum catalyst.

Most of the hydrosilylation use chloroplatinic acid as catalyst, the common dosage was 60-100 mg/kg in platinum (hereinafter the same) [5,10]. For the expensive price of chloroplatinic acid compare to platinum tetrachloride, the platinum tetrachloride was chosen as catalyst under microwave radiation. It was expected to reduce the amount of catalyst to improving the relationship of performance to cost.

A given mass of ATMS and four platinum chloride/isopropyl alcohol catalysts was added into four-neck round-bottom flask, which was equipped with thermometer, stirrer and nitrogen catheter and condenser pipe with calcium chloride anhydrous dry pipe. Bubbling nitrogen to expel oxygen for 20 min, then stirred high speed for 10 min. After that open microwave reactor, set the reaction temperature, when the temperature reached, cautiously added, dropwise, 1,1,3,3-tetramethyl-disiloxane in 1h, holding the temperature for a certain time. Then distilled the mixture to collect 129-131 °C fraction by vacuum distillation (pressure: 0.0998 MPa), which was TPMS, a colourless transparent liquid.

Preparation of BHTS: This kind of reaction often use acetic acid as catalysis, siloxane containing substitution get reaction with excess of methanol, the alcoholysis reaction usually need more than 8 h. In this paper, self-made TPMS was used as raw materiel, double hydroxypropyl polysiloxane were get under microwave irradiation condition. It was more efficient and higher function-price ratio.

0.1 mol TPMS, a given mass of water and *p*-methyl-benzene sulfonic acid catalyst were added into four-neck round-bottom flask which was equipped with thermometer, stirrer and condenser pipe, set up the microwave irritation time, temperature, started stir and heat to certain temperature, holding the temperature for a certain time. After the reaction, the 66-68 °C fraction of the mixture was collected by vacuum distillation (pressure: 0.0984 MPa) to collect BHTS.

RESULTS AND DISCUSSION

Optimization of process of ATMS: Allyloxytrimethyl-silane was synthesized with microwave irradiation. The effect of feed ratios (HMDS/allyl alcohol), reaction temperature and reaction time were investigated and the results are shown in Fig. 2.

Fig. 2a showed that the dosage of hydroxyl protection reagent HMDS greatly affected the yield of ATMS. The allyl alcohol reaction incompletely when the dosage of hydroxyl protection reagent HMDS is small. The more HMDS added the higher yield of ATMS is. Whereas more HMDS not only waste raw material but also cause the difficulty of after treatment. The experiment shows that the advisable weight ratio of HMDS:allyl alcohol is 0.7 :1.

As shown in Fig. 2b, at low temperature the reaction speed is slow, so the yield is low. With the increase of temperature, the reaction speed rise, the yield of ATMS correspondingly increased. At 120 °C, the reaction is basically finished. At high temperature unsaturated group self-condensed seriously, which made the yield reduced. In conclusion, the optimal reaction temperature is 120 °C

As show in Fig. 2c, other reaction condition is fixed, the longer reaction time is the higher yield of ATMS. But after 4 h, the yield decreased a little, then it maintained, so the optimal reaction time was 4 h.

Through the above experiment, the optimal reaction condition is as follows: in microwave irradiation, the weight ratio of HMDS:allyl alcohol equal to 0.7:1, reaction temperature is 120 °C, reaction time is 4 h. The yield of ATMS is 95.5 %. The product is clear and purity.

Optimization process of TPMS: 1,3-*Bis*(3-trimethylsiloxy propyl)tetramethyl disiloxane was synthesized with microwave irradiation. The effect of feed ratios (HMDS/allyl alcohol), reaction time, reaction temperature and catalyst dosage were investigated and the results are shown in Table-1.

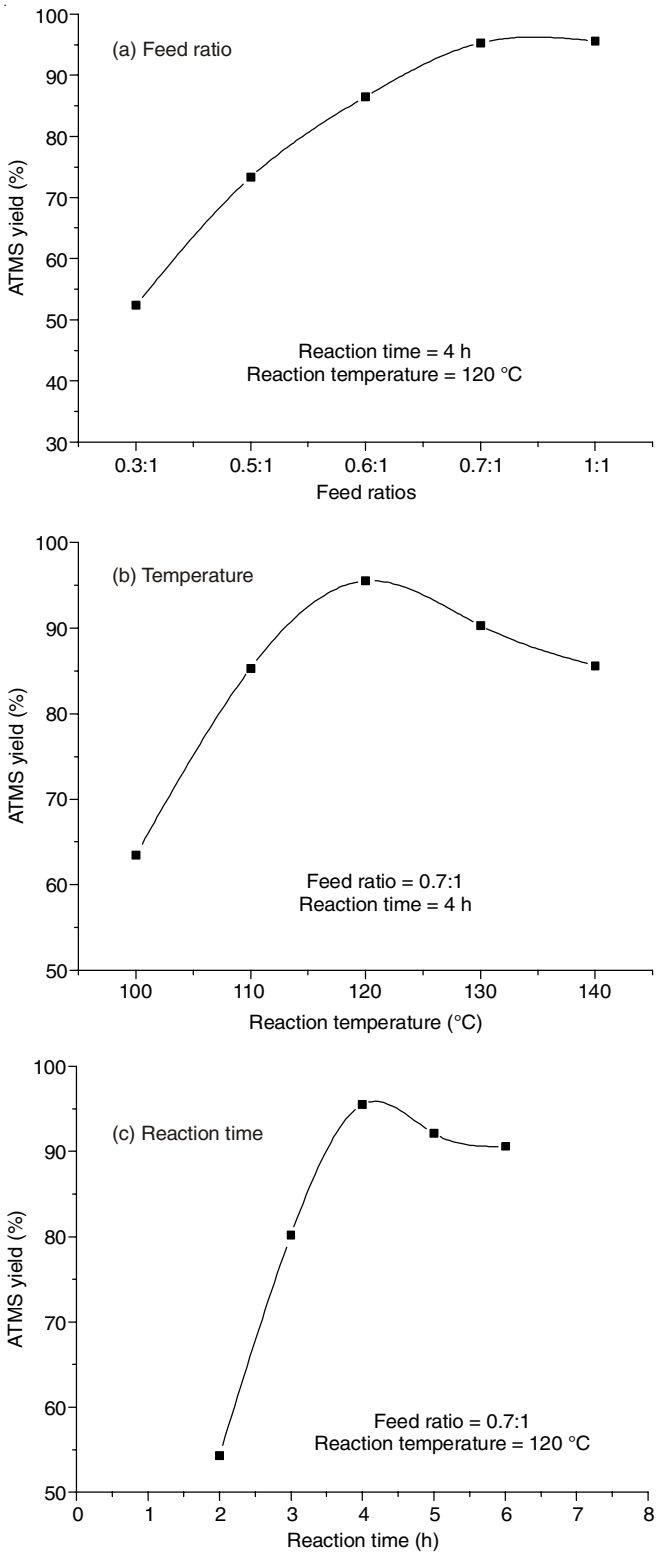

Fig. 2. Effect of process conditions on yield of allyloxytrimethylsilane

The essence of hydrosilylation is that the carbon-carbon double bonds and silicon hydrogen bond take addition reaction by certain molar ratio. But as shown in Table-1, the yield of the product is increased, as the molar ratio of HMM to ATMS from 1.5:1 to 2.4:1. When the molar ratio exceeds 2.4:1, the yield of the product has no remarkable change which indicated that the reaction has been completed. As the HMM increases, the scale of the distillation becomes large, which will cause much energy consumption. The experiment shows that the reaction has been completed, when the molar ratio of HMM to ATMS is 2.4:1 and low-cost.

TABLE-1
OPTIMIZATION PROCESS OF 1,3-*BIS*(3-TRIMETHYLSILOXY PROPYL)TETRAMETHYL DISILOXANE

Parameter		Yield (%)
Molar ratio HMM:ATMS [Catalyst: 60 mg/kg, temp.: 70 °C, time: 2 h]	1.5:1	46.2
	1.8:1	65.3
	2.1:1	79.7
	2.4:1	83.6
	2.8:1	83.2
	3.2:1	83.4
Reaction time (min) [Molar ratio: 2.4:1, catalyst: 60 mg/kg, temp.: 70 °C]	30	35.3
	50	52.4
	70	64.3
	90	83.8
	110	83.4
	120	83.5
Reaction temperature (°C) [Molar ratio: 2.4:1, catalyst: 60 mg/kg, time: 2 h]	50	36.4
	60	75.6
	70	83.5
	80	85.4
	90	88.1
	100	87.7
	110	83.8
Catalyst dosage (mg/kg) [Molar ratio: 2.4:1, temp.: 90 °C, time: 2 h]	5	38.1
	10	70.8
	20	91.7
	30	91.5
	40	89.3
	50	85.1

As shown in Table-1, the yield of the product were increased rapidly as the microwave radiation time went on. But when the time reach 90 min, the yield of the product tends to be constant value, so the optimum reaction time is 90 min.

Table-1 revealed that the reaction were finished at 90 °C. With rising temperature, the energy of the system increased and it accelerate the reaction. At high temperature unsaturated group self-condensed seriously, the catalyst chloroplatinic acid separated out from isopropanol at high temperature. All these made the yield of ATMS reduce. In conclusion, the optimal reaction temperature is 90 °C.

Thus, the conversion rate increased rapidly with the increase of catalyst dosage. After the dosage of catalyst surpassed 20 mg/kg, instead of increase, the yield of product decreased. With more platinum, the unsaturated double bonds of ATSM self-condensed or isomerized easily, it lower the yield of the product. And platinum is precious metals, the dosage impact on the cost of production greatly, therefore, the appropriate dosage of catalyst is 20 mg/kg.

Optimization of process of BHTS: 1,3-*Bis*(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane was synthesized with microwave irradiation. The effect of the amount of water, hydrolysis temperature, hydrolysis time and catalyst dosage were investigated and the results are shown in Fig. 3.

It can be seen from Fig. 3a, the conversation rate increase rapidly with the increase of water dosage. After the dosage of water surpassed 4.68 g, the conversion rate of product began to decrease. At beginning, the water is not enough to react with TMPS by theory, so the conversation rate increases with

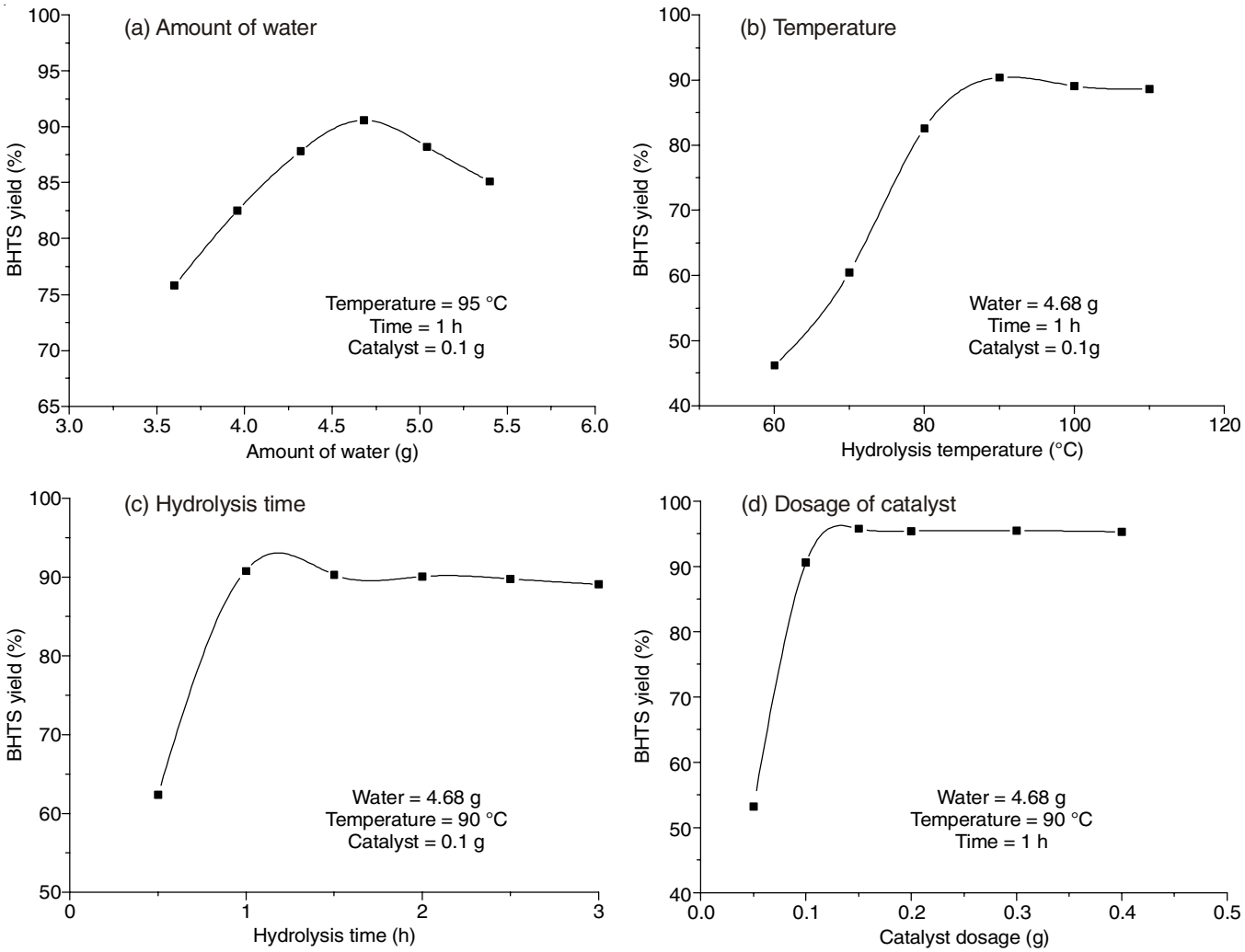

Fig. 3. Effect of process conditions on yield of 1,3-*bis*(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane

waters added. When the amount of water surpasses 4.68 g, the extra water may react with the product by the acid catalyst, so the conversion rate decreases. Therefore, the appropriate dosage of water is 4.68 g.

It can be see from Fig. 3b, the reaction temperature influences the yield of product remarkably. Under 90 °C, the yield of product increases rapidly as temperature go on. When the temperature surpass 90 °C, the yield of product decreases as temperature increases. At higher temperature, some side effects of the hydroxide radical may occur. Meanwhile the water volatilization lost greatly at higher temperature, would effect the yield of product oppositely. So the optimal temperature is 90 °C.

It can be seen from Fig. 3c, at the beginning of the reaction, the yield of the product increases rapidly as the hydrolysis time increase. But after 1 h, the yield of the product changes very small. Some side effects of the hydroxide radical may occur at high temperature within long time. So the optimal reaction time is 1 h.

Fig. 3d shows the yield of the product rise rapidly as the dosage of *p*-methylbenzene sulfonic acid increase. As the catalyst dosage surpass 0.15 g, the yield of the product changes small. So the optimal dosage is 0.15 g.

The optimization of process of BHTS are as follows: 39.4 g (0.1 mol) TMPS, 4.68 g water and 0.15 g *p*-toluenesulfonic acid are added in three-flask with stir, thermometer, reflux condensing tube, set the microwave reaction temperature 90 °C, with stirring, keep the temperature for 1 h. The BHTS yield can reach 95.8 %.

The infrared spectra (Fig. 4) shows an absorption peak at 3328 cm^{-1} which is attributed to the stretching vibration absorption of OH, absorption peak in 1178 cm^{-1} which is attributed to the bending vibration absorption of Si-$(CH_2)_3$- and absorption peak in 1051 cm^{-1} which is caused by the stretching vibration absorption of Si-O-Si in BHTS.

Nuclear magnetic resonance hydrogen spectroscopy: It can be seen from Fig. 5 that there are 5 proton peaks. The no. 1 proton's chemical shift is in high field because it belongs to the methyl which is connected with the silicon proton. The methylene which the no. 2 proton belongs to is connected with another methylene except for silicon proton, so its chemical shift is to the lower field. The carbon which the no. 4 proton belongs to is connected with hydroxyl, therefore its chemical shift is to the lowest field, in 3.469 ppm. The methylene which the no. 3 proton belongs to is connected with alkyl and its chemical shift is in 1.531 ppm. The chemical shift which is in 3.728 ppm belongs to hydroxyl hydrogen. From the data all above, it can be seen that the synthesized product has the desired structure.

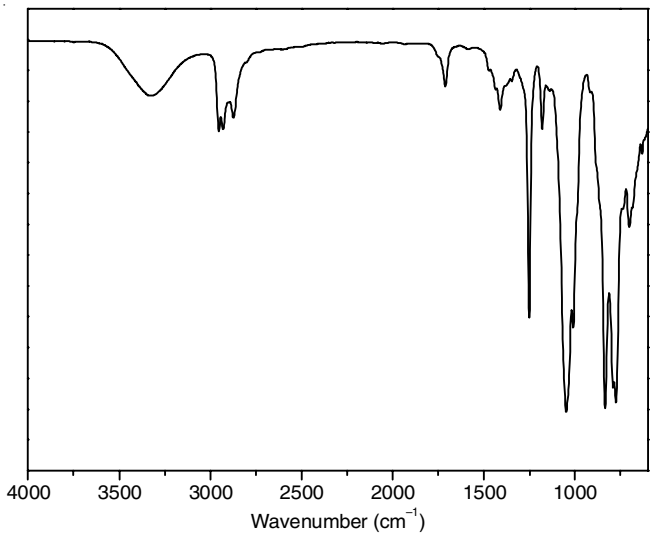

Fig. 4. FT-IR of 1,3-*bis*(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane

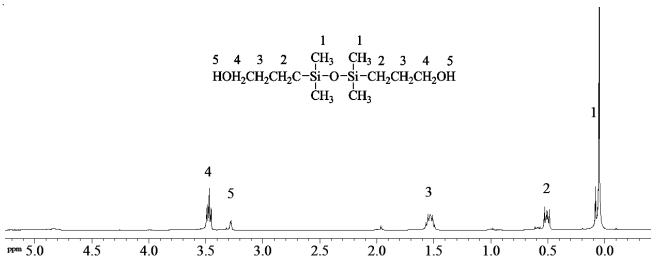

Fig. 5. ^{1}H NMR of 1,3-*bis*(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane

Gas chromatography: The content of BHTS is 99.1 % calculated by the area normalization method (Fig. 6).

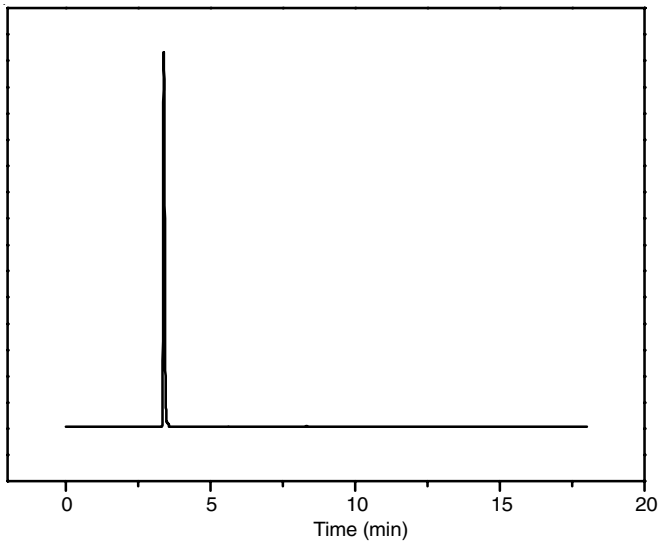

Fig. 6. Gas chromatography of 1,3-*bis*(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane

Conclusion

Microwave radiation is applied to synthesize BHTS from allyl alcohol and HMM. Product structure is analyzed and identified by IR, ^{1}H NMR and GC spectrometry. It is found that under microwave radiation the reaction is rapid with good yield, better quality and less time is required for the completion of the reaction [3-5,10].

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