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PREPARATION AND CHARACTERIZATION OF TERMINAL HYDROGEN SILICONE OIL

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ABSTRACT

The terminal hydrogen silicone oils are often used as raw material for the synthesis of amino, epoxy and polyether terminated silicone oil that is used widely to formulate oil agents for carbon fiber precursor. The terminal Hydrogen silicone oil can be synthesized by using octamethylcyclotetrasiloxane (D4) and hydrogen dual head (dihydro-tetramethyl disiloxane) (HMM) as raw materials and 98% sulfuric acid as catalyst in this article. Our group reported two synthetic scheme of terminal hydrogen silicone oil and studied effect of reaction activity of D4 and HMM on its molecular weight. The first synthetic scheme is to put all starting raw materials into the reactor together and to trigger the reaction by catalyst. The second synthetic scheme is to let HMM of low reaction activity to start reaction and then to initiate the ring opening polymerization of D4.

KEYWORDS

Oil agent, terminal hydrogen silicone oil, ring-opening polymerization.

1. INTRODUCTION

In recent years, the modified silicone oil has been used more and more widely, and terminal hydrogen silicone oil is an important raw material for preparing the modified silicone oil. The terminal hydrogen silicone oil has good flexibility, heat resistance and friction resistance because main chain of the terminal hydrogen silicone oil is the Si-O-Si bond, the longer Si-O bond length, the larger bond angle and the smaller bond energy, no double bond and no substituent group on oxygen atom. In addition, the terminal hydrogen silicone oil contains a large amount of methyl, which can form film at low temperature and give good waterproof property. At the same time, the two ends of the terminal hydrogen silicone oil contain Si-H bonds with strong activity, which can be used to prepare modified silicone oil with different structures. Such as amino modified silicone oil, epoxy modified silicone oil, polyether modified silicone oil, and ternary copolymer block silicone oil (containing siloxane chain, polyether chain and polyether amine chain) [1-3].

At present, the main preparation methods of the terminal hydrogen silicone oil in China include co-hydrolysis, alcoholysis followed by hydrolysis and ring-opening copolymerization. Among them, co-hydrolysis condensation polymerization method has been used in practical industrial production, and most domestic manufacturers also use this method. However, it is necessary to add solvent dilution to reduce the reaction rate when organochlorosilane is hydrolyzed. However, the smell of solvent is difficult to remove, and the gel is easy to be produced when hydrolyzed, and the properties of the product are also unstable, the quality of the product is poor; alcoholys is followed by hydrolysis method can reduce the solvent, but the production cost is high, and the reaction steps are complicated, not suitable for mass production in the factory [4-7]. Ring-opening copolymerization method is an ideal synthetic method with mild reaction conditions, simple technological process and good product quality [8]. Because of the difference in the activity of D4 and HMM, the effect of the feeding sequence of D4 and HMM was investigated to make sure the accurate molecular weight prepared, and the effect of catalyst dosage and temperature on the molecular weight distribution was also investigated.

2. EXPERIMENTAL PART

2.1 Experimental materials and equipment

Octamethyl cyclotetrasiloxane (D4, industrial grade, Xinan Chemical Group Co., Ltd.), hydrogen dual head (dihydro-tetramethyl disiloxane) (HMM , ARL, Guangdong Wengjiang Chemical Reagent Co., Ltd.), concentrated Sulfate (GRL, Xilong Chemical Co., Ltd.), Sodium bicarbonate, (Tianjin Ruijin Chemical Co., Ltd.) Fourier transform infrared spectrometer (Shimadzu, Japan), Advance AV400 MHz digital Fourier transform NMR spectrometer, NDJ-5S rotary viscometer, collector type constant temperature heating magnetic agitator, DF-101S, Gongyi Yuhua instrument Co., Ltd.

2.2 Synthesis of terminal hydrogen silicone oil

Terminal hydrogen silicone oil was prepared by cationic ring-opening copolymerization with octa-methyl cyclotetrasiloxane and dihydro-tetramethyl disiloxane as raw materials, 98% sulfuric acid as catalyst, under the protection of nitrogen, the steps are as follows:

Scheme I: feed 27g D4 and 10g HMM into reactor equipped with magnetic stirrer, the reaction starts after addition of a certain amount of concentrated sulfuric acid and continues for 5 hours at suitable temperature, 5g HMM is then added into reactor again and reaction is kept going for 2 hours. An excess amounts of sodium bicarbonate is added to neutralize concentrated sulfuric acid, and then the filtration is carried out for removing sodium sulfate. Finally, the synthetic products were put into a four-neck flask and heated to 130°C to remove the unreacted small molecules under reduced pressure.

Scheme II: 10 g of HMM and a certain amount of concentrated sulfuric acid were put into reactor equipped with magnetic stirrer, thermometer and bulb type condenser, then heated up to the appropriate temperature. After the reaction occurring for 30min, 27 g of D4 is added and the reaction is kept going for 5 hours. 5 g HMM is added again and the reaction keeps for 2 hour to make the reaction completed totally and the terminal group of silicone oil is hydrogen. An excess amounts of sodium bicarbonate is added

to neutralize concentrated sulfuric acid, and then the filtration is carried out for removing sodium sulfate. Finally, the synthetic products were put into a four-neck flask and heated to 130℃to remove the unreacted small molecules under reduced pressure.

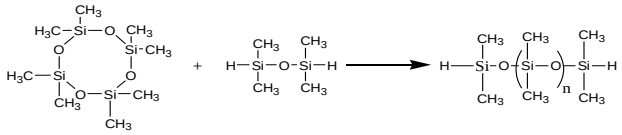

Figure 1: Preparation of hydrogen-terminated silicone oil by cationic ring-opening polymerization

2.3 Determination of viscosity by Brookfield viscometer

At room temperature, the viscosity of the terminal hydrogen silicone oil is measured with a Brookfield rotary viscometer. In industry, measurement of the molecular weight of the product is time-consuming and laborious, but the viscosity is proportional to the molecular weight of polymer, therefore the viscosity can be used to identify molecular weight, which is not only convenient but also low cost.

3. RESULTS AND DISCUSSION

3.1 FT-IR and NMR spectral characterization of terminal hydrogen silicone oil

The chemical structure of the terminal hydrogen silicone oil was characterized by FT-IR and NMR spectrum. Figure 2 shows the infrared spectrum of the product, the strong absorption peak at 2960cm^{-1} is the stretching vibration peak of C-H bond in CH_3; the strong absorption peaks at 2130cm^{-1} and 850cm^{-1} are the stretching and bending vibration peaks of Si-H, respectively; the strong absorption peaks at 1260cm^{-1} and 792cm^{-1} are the stretching and bending vibration peaks of Si-C bond in Si-CH_3, respectively; the stretching vibration peak of Si-O-Si is at 1100cm^{-1}

Fig. 3 shows the NMR spectra of the terminal hydrogen silicone oil . A strong absorption peak at 4.7 is assigned to the Si-H bond of the terminal hydrogen silicone oil and the other absorption peaks are overlapped with the internal standard silicone oil

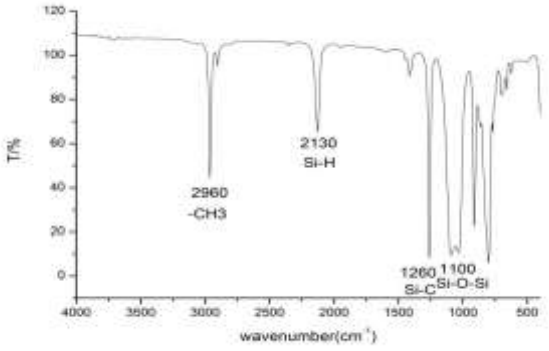

Figure 2: Infrared spectra of hydrogen-containing silicone oil

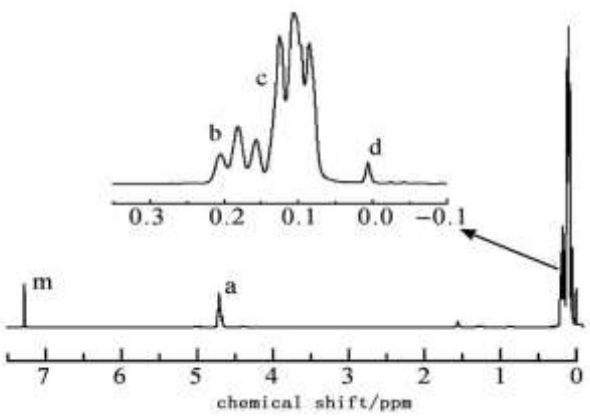

Figure 3: Nuclear magnetic spectrum of hydrogen-containing silicone oil

3.2 Viscosity of terminal hydrogen silicone oil at different temperatures

Concentrated sulfuric acid was used as a catalyst and the amount was 1.5% of the amount of both D4 and HMM. Cationic ring-opening polymerization of D4 was used to prepare terminal hydrogen silicone oil. The effects of different reaction temperatures on the viscosity of the product were investigated in detail. The results are shown in tables 1 (synthetic scheme I) and 2 (synthetic scheme II):

Table 1: Preparation of the terminal hydrogen silicone oil at different reaction temperatures based on synthetic scheme I

number	Reaction temperature / ℃	Viscosity /cp
1	25	11
2	30	16
3	35	15
4	40	15
5	45	15

Table 2: Preparation of hydrogen-containing silicone oil at different reaction temperatures based on synthetic scheme II

number	Reaction temperature / ℃	Viscosity /cp
1	25	17
2	30	16
3	35	15
4	40	15
5	45	14

3.3 Viscosity of terminal hydrogen silicone oil under different catalyst dosage

The effects of amount of catalyst on the viscosity of the product were investigated at 30 ℃. The results are shown in tables 3 (synthetic scheme I) and 4 (synthetic scheme II).

Table 3: Preparation of hydro-terminated silicone oil with different amount of catalyst based on synthetic scheme I

number	Catalyst dosage /%	Viscosity /cp
1	1.2	14
2	1.5	16
3	1.8	17
4	2.0	13
5	2.3	12

Table 4: Preparation of hydro-terminated silicone oil by different amount of catalyst based on synthetic scheme II

number	Catalyst dosage /%	Viscosity /cp
1	1.2	14
2	1.5	16
3	1.8	15
4	2.0	12
5	2.3	11

The experimental results are showed as table 1 to 4, the synthetic scheme, reaction temperature and the amount of catalyst have effect on the viscosity of the terminal hydrogen silicone oil. Based on the design of synthesis of 500 molecular weight of terminal hydrogen silicone oil, the conclusion will be drawn that the synthetic scheme I is chosen and the reaction temperature is from 30℃ to 40℃ and the amount of catalyst is about 1.5% to 1.8%

4. CONCLUSION

Terminal hydrogen silicone oil was prepared by ring-opening polymerization with D 4 as a starting material, HMM as end capping reagent and concentrated sulfuric acid as catalyst. The chemical structure of the terminal hydrogen silicone oil was identified by FT-IR and NMR spectra. The optimum synthetic procedure and conditions were as following: D4 and HMM were added to the reactor at 30 ℃ to 40 ℃, and

the amount of catalyst was 1.5% to 1.8 %, and reaction time was 5 hours.

REFERENCES

[1] Zhitao, L. 2013. Structure and application properties of terpolymer block silicone oil. Printing and dyeing, 39 (5), 39-42.

[2] Jie, Y., Jiangping, H., Huaqian, Y. 2016. Study on the synthetic process of Ternary Block copolymerized Silicon Oil. Silicone material, 30 (5), 393-399.

[3] Xuemin, H., Haiyan, Z., Changfa, X. 2013. Preparation and application of amino polyether silicone oil SEA. Journal of Textile, 10, 107-111.

[4] Haines, G.R., Puckett, D.E., Wood, L.H. 1995. Process for preparing cyclic organohydrogen siloxanes: US, 5395956, 03, 07.

[5] Anderson, P.P., Perry, R.J., Razzano, J.S. 1997. Production of low molecular weight linear hydrogen siloxanes: US, 5670596.09, 23.

[6] Lindner, T., Geisberger, G., Pachaly, B. 2000 Process for preparing methylhydrogenpolysioxanes having trimethylsilyl end groups: US, 6143912. A11, 07.

[7] Guoqiao, L., Songmin, X. 2010. Synthesis process and application of organosilicon. Beijing: chemical Industry Press, 382.

[8] Qi, L., Jinquan, Y., Dengzheng, L. 2010. A method for the production of methyl hydrogen-containing silicone oil:CN, 102408566. 04, 11.

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