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Preparation and Characterization of Functionzliaed Silicone Oil for High Temperature Mold Release Agent

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Abstract: Silicohydrogen addition method was utilized to prepare long-chain alkyl silicone oils using high hydrogen-containing silicone oil, α-methylstyrene, and 1-tetradecene as raw materials and chloroplatinic acid as catalyst. FTIR and ^{1}H-NMR were used to characterize the structure of the products, and the effects of reaction temperature, reaction time, catalyst dosage, and n(Si-H): n(C=C) on the Si-H conversion were investigated experimentally to determine the optimal reaction process. The experimental results showed that the optimized process conditions were n(Si-H): n(C=C) =1:1.1, reaction time of 6 h, reaction temperature of 150 °C, catalyst dosage of 2 ppm, and the Si-H conversion of the product was 96.3%.

Keywords: Silicone Oil; Long-chain Alkyl Phenyl; Hydrogenation; Preparation; Polymer.

1. Introduction

Methyl silicone oil has excellent electrical insulation, weather resistance, physiological inertness and low surface tension, but also has a low viscosity-temperature coefficient, high compression resistance [1-5]. However, there are certain disadvantages: poor compatibility of methyl silicone oil with organic materials and additives, heat resistance is not prominent enough, limiting its further application, for these defects, for silicone oil modification, alkyl functionalized silicone oil is obtained from methyl silicone oil in part of the methyl by the olefinic double bond and phenyl substitution, and other common silicone oil, compared with the advantages of high and low temperature resistance, and lubrication and irradiation resistance is excellent. The alkyl and phenyl silicone oils have better high temperature resistance, higher refractive index, and better lubricity than the long chain alkyl silicone oils [6-10]. Ningbo Runhe Chemical Industry Co., Ltd [11] openly published a preparation method of long-chain alkylphenyl-modified silicone oil to obtain a new type of advanced mold release agent. Yizheng Xinyuan New Material Technology Co Ltd [12] also reported the preparation of a long-chain alkylphenyl-modified hydrogen-containing silicone oil release agent. The introduction of long-chain alkyl groups endowed silicone products with special properties such as better mold release, lubricity, defoaming, anti-adhesion, and affinity for organic materials, and enhanced the hydrophobicity of silicone oils, as well as improved their surface properties [13-17], and the introduction of phenyl groups could improve their hydrophobicity [18-21].

In this work, modified phenyl hydrogenated silicone oils were prepared from high hydrogenated silicone oils and 1-tetradecene, α-methylstyrene by silica-hydrogen addition reaction. The structure of the modified specimen was characterized by FTIR and 1H NMR techniques, and the process optimization of the synthesis process of the product was carried out in terms of reaction temperature, reaction time, n(Si-H): n(C=C), catalyst incorporation, and dosing method and the best process parameters were obtained.

2. Experimental Section

2.1. Raw Material

1-tetradecene: analytically pure, Aladdin; α-methylstyrene: analytically pure, Aladdin; high-hydrogen silicone oil: industrially pure, Shin-Etsu, Japan, active hydrogen content of 1.6% (w); isopropyl alcohol: analytically pure, Tianjin Fuyu Fine Chemical Co.

2.2. Methods of Analysis

(1) Nuclear magnetic resonance (NMR): the structure was characterized using a nuclear magnetic resonance (NMR) instrument with the solvent $CDCl_3$.

(2) Infrared spectroscopy (FTIR): the use of BRUKERV70 FTIR spectrometer to characterize the structure, wave number 400 cm-1 ~ 4000 cm-1.

(3) Si-H conversion: hydrogen-containing silicone oil reacts with alkali solution to displace hydrogen, the volume of hydrogen is read from a hydrogen cylinder, and the amount of hydrogen is calculated from the gas equation.

Reagent: 20% sodium hydroxide solution: 95% ethanol solution = 1:1 mixed well

Instruments: Long's nitrogen determination, instrument thermostatic water bath Y-shaped reaction flask, precision thermometer (0-50℃) graduation value of 0.1℃, syringe 0.5mL with No. 5 closed needle

Calculation formula:

$$x = \frac{\left(P - \frac{T}{6}\right) \times v \times 273 \times 1.008}{(273 \div t) \times 22400 \times 1013.25 \times m} \times 100$$

Operation steps:

(1) Use a syringe to draw 0.1-0.3 grams of sample, wipe the needle clean, plug it with silica gel, weigh it, accurate to 0.0002 grams, remove the silica gel, insert the needle carefully into the side of the reaction bottle, inject the sample

into the reaction tube, take it out carefully and then plug it with silica gel, weigh it again, and the difference between the two masses will be the weight of the sample.

(2) On the other side of the Y-type reaction bottle, use a pipette to suck up 4-5 ml of mixed reagent, and plug the mouth of the bottle with a rubber stopper to prevent leakage. Place the reaction bottle in a water bath at a constant temperature for about 1 minute. The water bath temperature should be the same as the cannula temperature room temperature.

(3) Adjust the zero point, check the leakage situation open the upper part of the gas measuring tube to make it connected with the atmosphere, to the zero point, do not move the level bottle, rotate the three-way valve to make the reaction tube and gas measuring tube connected, and then to the zero point, if not in the zero point, then repeat the above operation until it is exactly in the zero point.

(4) Take out the reaction bottle from the thermostatic water bath, press the stopper tightly, tilt it left and right to make the specimen and the mixed reagent react fully until the liquid level of the gas measuring tube is no longer under, put the reaction bottle back into the thermostatic water bath, and then put it back into the thermostatic water bath, and then keep it at a constant temperature for 5-10 minutes, then lift up the calibrated bottle so that the liquid level is put at the same level with the liquid level of the gas measuring tube, and then take a reading, and at the same time, record the temperatures of the gas measuring tube and the water bath, the atmospheric pressure, and the room temperature.

2.3. The Principle of Synthesis

At a certain temperature, a certain amount of high hydrogen-containing silicone oil and α-methylstyrene were added to the flask with stirring and preheating, and then the catalyst was added, and the remaining α-methylstyrene was added at a temperature of 100°C~130°C, and then the temperature was raised to 150°C, and the holding time was 0.5~2 hour; after the end of the holding time, some of the 1 -tetradecene was added and then the remaining catalyst was added, and the remaining 1 -tetradecene was added a small amount of times to complete the process, and then held for 1 hours. At the end of the heat preservation, the unreacted low molecules were removed by decompression at a certain temperature and negative pressure for a period of time, and the colorless and transparent long-chain alkyl silicone oil was obtained by cooling, and the structural formula of the reaction is shown in Fig. 1 as follows.

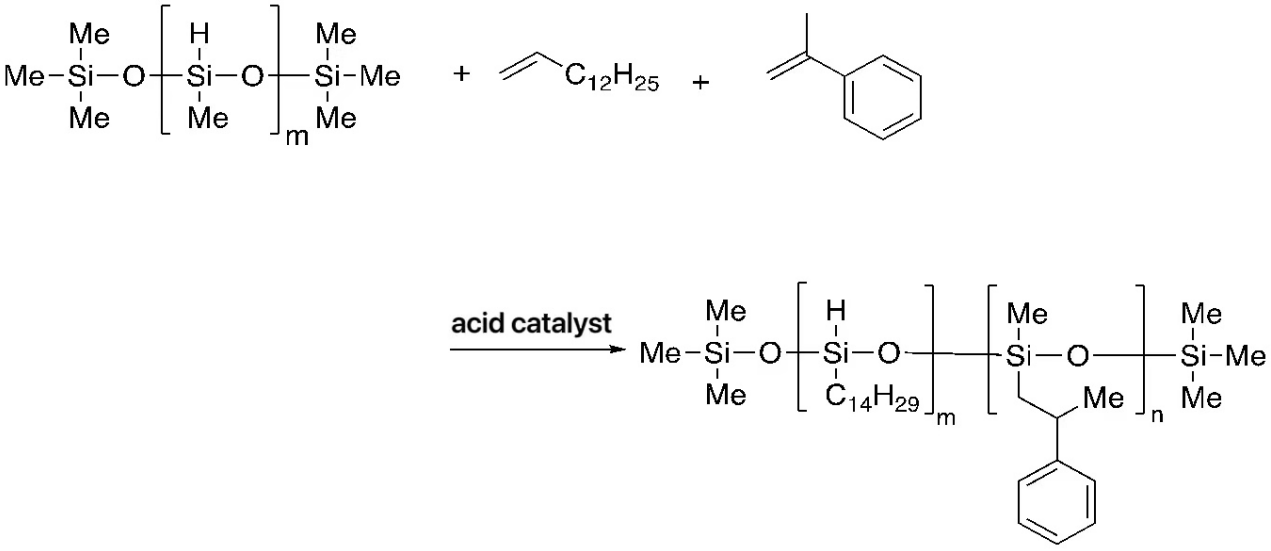


Fig 1. Equation for the preparation of long-chain alkyl silicone oils

3. Results and Discussion

3.1. Structural Characterization

3.1.1. Nuclear Magnetic Resonance (NMR) Characterization

The long-chain alkyl silicone oils were analyzed by hydrogen spectroscopy using NMR, and the results are shown in Fig. 2. The NMR spectrum of the product long-chain alkyl-modified silicone oil is shown in Fig. The ^{1}H-NMR spectrum was well attributed, from which it can be seen that: the characteristic absorption peaks near δ=0 in the NMR hydrogen spectrum of the product were from Si-CH_3; the absorption peaks near δ=0.50 were from Si-$CH_2(CH_2)_{12}CH_3$; the absorption peaks near δ=0.80 were from Si-$CH_2(CH_2)_{12}CH_3$; δ=1.27 from Si-$CH_2(CH)CH_3$; δ=3 from Si-$CH_2(CH)CH_3$; δ=7.26 from the solvent deuterated chloroform; δ=4.7 is the position of the characteristic Si-H peak, which does not appear in the hydrogen spectrum, indicating the success of the silica-hydrogen addition reaction. This indicates that the long-chain alkyl-modified silicone oil was successfully prepared by the silica-hydrogen addition reaction.

Table 1. ^{1}H-NMR chemical shifts of groups in long chain alkyl silicone oils

Chemical shift	Hattribution
0.0-0.1	Si-CH_3
0.5	Si-CH_2
0.8-1.0	Si-$CH_2(CH_2)_5CH_3$
1.1-1.4	Si-CH_2CCH_3
3.0	Si-$CH_2C(CH_3)$ H

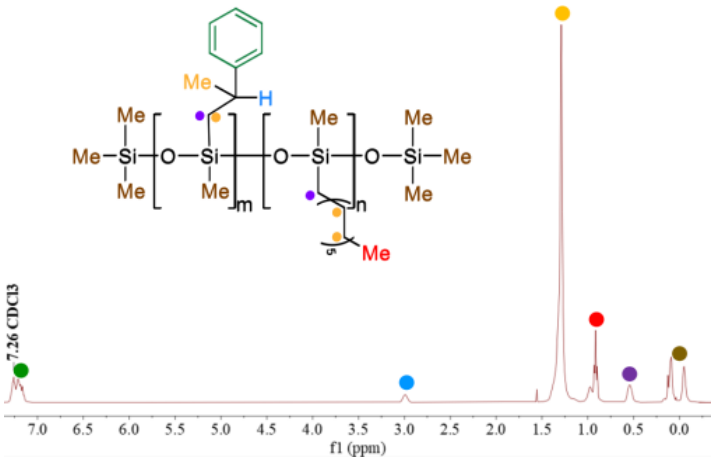


Fig 2. ^{1}H-NMR spectrum of long-chain alkyl silicone oils

3.1.2. Infrared Spectral Characterization

The long-chain alkyl silicone oils were analyzed using infrared spectroscopy, and the results are shown in Figure 3. The infrared spectrum of the product long-chain alkylphenyl silicone oil is shown in Fig. From the figure, it can be seen that there is no obvious Si-H absorption peak appearing near the location of Si-H characteristic absorption peak at 2157 cm-1, which indicates that Si-H is almost completely reacted, and the symmetric telescopic vibration peak of -CH2 near 2855 cm-1, the anti-symmetric telescopic vibration peak of -CH2 near 2920 cm-1 and the characteristic peak of phenyl at about 870 cm-1, which proves that tetradecene and α-methyl styrene were successfully grafted to the side-chain of silicone oil, and the product is a long-chain alkylphenyl-modified silicone oil.

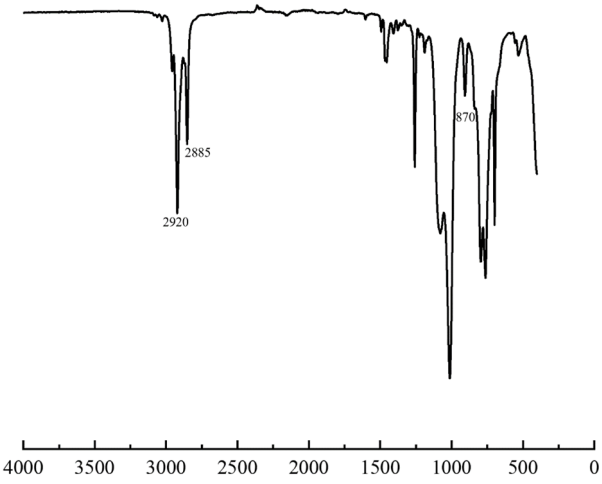


Fig 3. FTIR spectrum of the product

3.2. Impact of Factors

3.2.1. Effect of Catalyst Dosage on the Preparation of Long-chain Alkyl Silicone Oils

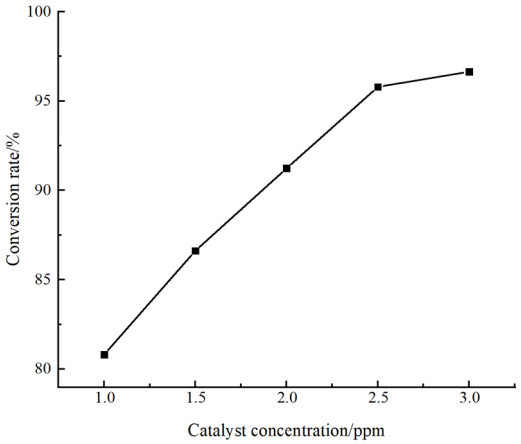


Fig 4. Effect of catalyst dosage on the conversion rate

Tetradecene, α-methylstyrene, and hydrogen-containing silicone oil were used as raw materials for the silica-hydrogen addition reaction, and other reaction conditions were fixed to study the effect of different catalyst dosages on the conversion rate of the prepared long-chain alkylbenzene-based silicone oils, and the results are shown in Fig. 4.

Examining the effect of catalyst dosage on the reaction, it can be seen from the figure, with the increase of catalyst dosage, the conversion rate also shows an increasing trend, but gradually also tends to be stable, less catalyst is not conducive to the silica-hydrogen addition, but too much catalyst dosage, although the conversion rate is helpful, but it will lead to the product color yellow, affecting the appearance of the product, so the comprehensive consideration of the experiments to choose the catalyst dosage for the 2ppm.

3.2.2. Effect of n(Si-H): n(C=C) on the Preparation of Long-chain Alkyl Silicone Oils

Tetradecene, hydrogen-containing silicone oil was used as the raw material for the silicohydrogen addition reaction, and other reaction conditions were fixed to investigate the effect on n(Si-H): n(C=C) on the Si-H conversion, and the results are shown in Fig. 5:

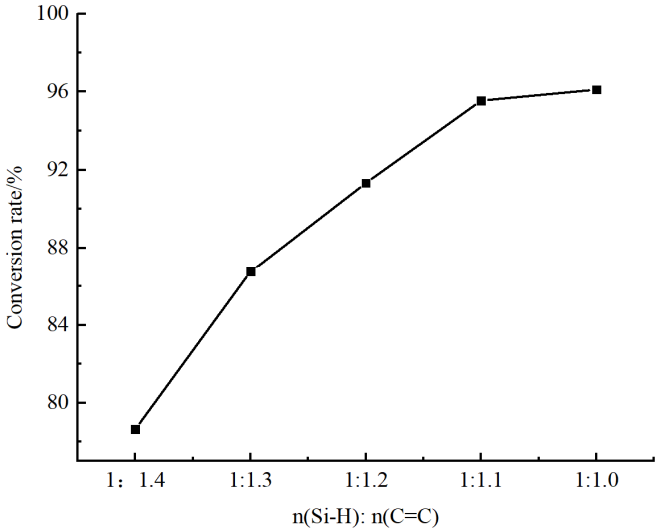


Fig 5. Effect of n(Si-H): n(C=C) on the conversion ratio

With the increase of olefin input, the Si-H conversion rate showed a tendency to increase and then decrease, and the conversion rate reached the highest when n(Si-H): n(C=C) = 1:1.1, but with the further increase of the input amount, the conversion rate decreased significantly, due to a variety of other factors, too much α-methylstyrene will occur in the phenomenon of self-polymerization, the amount of olefin involved in the reaction is reduced, and also lead to the turbidity of the system, so the integrated n(Si-H): n(C=C)=1:1.1 was chosen.

3.2.3. Effect of Reaction Time on the Preparation of Long-chain Alkyl Silicone Oils

Tetradecene, hydrogen-containing silicone oil was used as the raw material for the si-hydrogen addition reaction, and other reaction conditions were fixed to investigate the effect of reaction time on the Si-H conversion rate, and the results are shown in Fig. 6. From the results of the figure, it can be seen that with the prolongation of the reaction time, the Si-H conversion rate shows a tendency of increasing first and then stabilizing. When the reaction time is 6h, the reaction has completed the vast majority of the conversion rate is as high as 96.3%, with the extension of the reaction time, the conversion rate continues to rise, but too long a reaction time is almost no gain. Reaction time is too short, is not conducive to the reaction is fully carried out, but the reaction time is too long is easy to cause the raw material self-polymerization and other side reactions, comprehensive consideration, the appropriate reaction time is 6h.

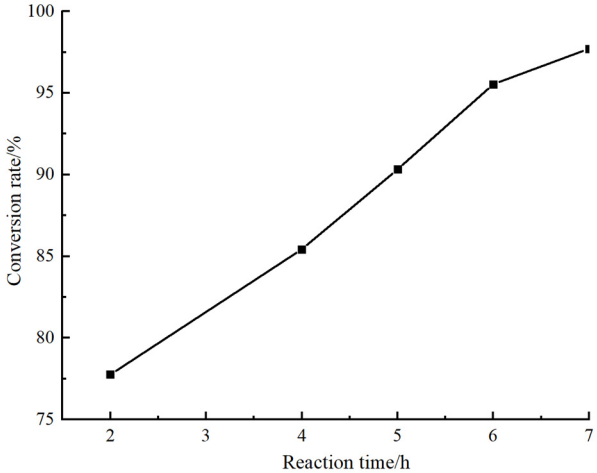


Fig 6. Effect of reaction time on conversion

3.2.4. Effect of Reaction Time on the Preparation of Long-chain Alkyl Silicone Oils

Tetradecene, hydrogen-containing silicone oil was used as the raw material for the si-hydrogen addition reaction, and other reaction conditions were fixed to investigate the effect of different reaction temperatures on the Si-H conversion rate, and the results are shown in Fig. 7. From the results of the figure, it can be seen that with the increase of reaction temperature, the Si-H conversion rate shows a tendency of increasing and then decreasing. When the reaction temperature is maintained at 150 ℃, the conversion rate is close to 95.3%, a high level; with the reaction temperature continues to rise, the conversion rate shows a clear downward trend, this is due to the high temperature in the raw material of hydrogen-containing silicone oil in the active group Si-H under the action of the catalyst is very easy to dehydrogenation cross-linking, the formation of gel, resulting in the system viscosity increases, is not conducive to reaction, and the raw material of the olefin at high temperatures will also occur in the self-polymerization, resulting in insufficient reaction. The raw olefin will also self-polymerize at high temperature, resulting in insufficient reaction. Selecting too low a reaction temperature is not conducive to give full play to the catalytic effect of the catalyst, resulting in a lower conversion of Si-H. For comprehensive consideration, the optimum reaction temperature is 150 ℃.

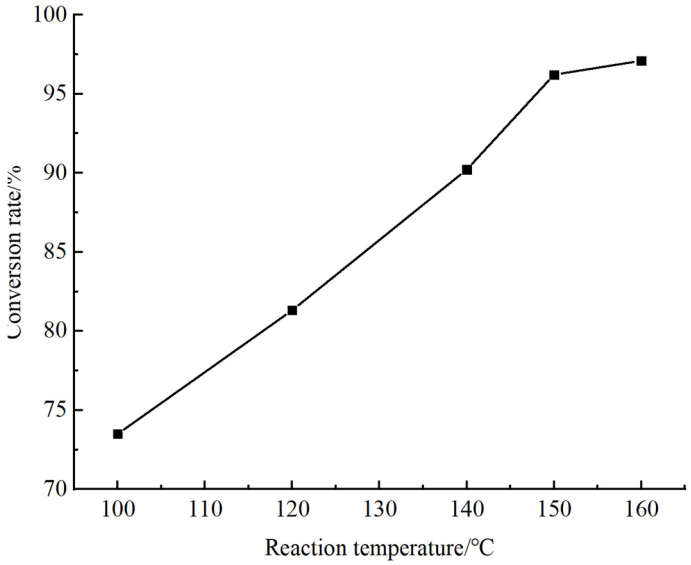


Fig 7. Effect of reaction temperature on conversion

4. Summary

(1) Long-chain alkyl phenyl silicone oils were successfully synthesized using 1-tetradecene, α-methylstyrene, and high hydrogen-containing silicone oil as raw materials and chloroplatinic acid as catalyst. FTIR and ^{1}H-NMR characterization results showed that α-methylstyrene and 1-tetradecene were successfully grafted onto polysiloxane chains.

(2) Orthogonal experiments were used to determine the optimal process conditions for the synthesis of long-chain alkyl-modified phenyl hydrogen-containing silicone oils. Under the process conditions of reaction time of 6.0 h, reaction temperature of 150 °C, catalyst addition of 2 ppm, and n(Si-H): n(C=C) =1:1.1, the conversion of Si-H bonds was as high as 96.32%.

Acknowledgments

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References

[1] Deng S S. Application of dimethyl silicone oil in improving the anti-foaming property of electric pump lubricant [J]. Hunan Electric Power 2006, 26(3): 16 -18.

[2] Yan Hui, Diao Yong. Application of dimethicone and its derivatives in antifoam agents[J]. Fine and Specialty Chemicals, 2010, 18(1): 19-23.

[3] Lv W B, Mou Q H, Liu X L et al. Status and application of domestic phenyl silicone oil products[J]. Organosilicon Materials,2009, 23(6): 402-405.

[4] Yang Liu, Zhang D Q, Hong Hong. Synthesis and properties of dodecyl/phenyl silicone oil[J]. Fine Chemical Industry, 2015, 32 (10):1081-1085.

[5] Zhu G J, Wang Fan, Zhang X J et al. Effect of sulfur-containing extreme pressure antiwear agents on tribological properties of phenyl silicone oil[J]. Organosilicon Materials, 2014, 28(5): 367-369.

[6] Du J H, Song R J, Li Bin. Synthesis of methylphenyl hydrogen-containing silicone oils and their thermal stability[J]. Synthetic Chemistry,2013, 21(5): 615-618.

[7] Xing SM, Wang YL. Organosilicon synthesis process and product application[M]. Beijing: Chemical Industry Press 2000, 456.

[8] Lin Yin, Yan B Z. Preparation of long-chain alkyl silicone oils[J]. Journal of Beijing University of Chemical Technology: 2004, 31(2): 82-86.

[9] Browing G V. Grease preparation[P]. US: 2616850, 1949.

[10] Huang W R. Silicone oils and secondary processed products [P]. Silicone oils and secondary processed products [M]. Beijing: Chemical Industry Press: 2004, 99.

[11] Ningbo Runhe Chemical Industry Co. Preparation method of long chain alkylphenyl modified silicone oil: 200810181325.9 [P]. 2009-04-08.

[12] Yizheng Xinyuan New Material Technology Co. Preparation method of a long-chain alkylphenyl-modified hydrogen-containing silicone oil release agent: 104497312 A [P]. 2015-04-08.

[13] Maciejewski H, Wawrzynczak A, Dutkiewicz M, et al. Silicone waxes-synthesis via hydrosilylation in homo- and heterogeneoussystems [J]. J Mol Catal A: Chem, 2006, 257 (1/2): 141 - 148.

[14] Perrin F X, Nguyen T B V, Margaillan A. Linear andbranched alkyl substituted octakis (dimethylsiloxy) octasilsesquioxanes: WAXS and thermal properties[J]. Eur Polym J, 2011, 47(7): 1370 - 1382.

[15] Louis E, Jussofi e I, Kuhn F E, et al. Karstedt catalyst-catalyzedstep growth c o-polyaddition of 1, 9-decadiene and 1.1.3.3-tetramethyldisiloxane [J]. J Org Chem, 2006, 691(9): 2031-2036.

[16] Mei H, Chen G, Zhu Q, Dong P, et al Improving properties of silicone rubber composites using macromolecular silane coupling agent[J]. Journal of applied polymer science, 2016, 133(19): 43415-43425.

[17] Yang Xu. Preparation and application of long-chain alkyl and polyether co-modified silicone oil [D]. Xi'an: Shaanxi University of Science and Technology, 2013.

[18] Guo Rui, Zhang Fei, Wang E M, et al. Synthesis of binary copolymer thick oil emulsion breaker[J]. Fine Petrochemicals, 2015, 32(1): 26 - 29.

[19] Ren Z H, Luo Yue, Chen D J. Emulsion breaking effect of non-polyether-based emulsion breakers[J]. Fine Petrochemicals, 2011, 28(2): 52-55.

[20] Wang E M, Guo Rui, Xie C M, et al. Synthesis and characterization of polysiloxane thick oil emulsion breakers[J]. Fine Chemical Industry, 2014, 31(7): 894-897.

[21] Yin D N, Zheng Cheng, Zhang LP, et al. Synthesis and characterization of polyether-modified trisiloxane surfactants [J]. Journal of Chemical Engineering, 2010, 61(7): 1565 -1570.