

## Guidance of Solution Model Reactions under Nuclear Magnetic Resonance Tracking on Interface Organic Synthesis Reactions

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**Keywords:** Nuclear magnetic resonance; Solution model; Synthetic reaction; Organosilicone

**Abstract:** Silicone materials are a new type of chemical products with a wide variety, excellent performance and wide application. The synthesis of gas-solid fluidized monomer is one of the key technologies in the production of methylchlorosilane, which plays an important role in the industrialization of silicone. Methylchlorosilane is one of the most valuable and used silicone monomers, and it is the foundation and pillar of the whole silicone industry. Studying the bulk polymerization process of amino silicone oil is helpful to confirm the reaction mechanism and determine the structure of the product at each stage, and can also effectively control the reaction and make it proceed in the expected direction. Nuclear magnetic resonance (NMR) spectroscopy is a very powerful analytical technique, which is usually used to analyze the reaction mixture. Using NMR tracking technology to study the reaction process has the advantages of high speed, good repeatability and no termination of the reaction. In this paper, NMR is proposed to track the solution model reaction, and the structures of intermediate products and final products can be determined according to the corresponding NMR spectra, thus guiding the organic synthesis of the interface.

### 1. Introduction

Polyacrylamide is widely used in papermaking, oil displacement, medicine, sewage purification, super absorbent resin, clothing and textile and other fields, especially as an oil field additive, which can be used as oil displacement agent, thickener and so on [1]. Gas-solid fluidized monomer synthesis is one of the key technologies in the production of methylchlorosilane, which plays an important role in the industrialization of silicone [2]. Silicone materials usually refer to polymer compounds with Si-O bond as the main chain and other organic groups attached to the Si atom as side chains [3]. At present, most of the modified polyacrylamide polymers are difficult to dissolve quickly, which limits their industrial application, and the functions of the polymers are relatively simple. The polymers with good emulsification effect have small apparent viscosity and long demulsification time, while the polymers with high apparent viscosity generally have long dissolution time and poor emulsification effect [4]. Studying the bulk polymerization process of amino silicone oil is helpful to confirm the reaction mechanism and determine the structure of the product at each stage, and can also effectively control the reaction and make it proceed in the expected direction [5].

NMR spectroscopy is a very powerful analytical technique, which is usually used to analyze the reaction mixture. NMR analysis can provide abundant information for the determination of molecular structures of intermediate products and target products [6]. With the widespread use of NMR analysis methods, NMR analysis is more and more widely used to track the progress of organic synthesis reactions, which has the characteristics of high sensitivity, integration of tracking monitoring and structural analysis [7]. Interfacial organic synthesis is a hot topic in the research of solid-state organic synthesis and surface functionalization of solid materials. Niu et al. Li Liping made a rough analysis on the emulsifier of amino silicone oil softener [8]. Wang et al. used NMR and chemical degradation methods to analyze the structure of amino silicone oil [9]. Traditional analytical methods often have special requirements for analytical materials, so they cannot be directly used to track surface organic chemical reactions. NMR spectroscopy can not only be used as a method to quantitatively monitor the reaction process, but also provide detailed structural information of the reaction components in

the solution. Other technologies that can identify the functional groups of the analyzed molecules are compared with NMR spectroscopy, but they lack the comprehensive characterization that NMR can provide [10]. These two characteristics make NMR have obvious advantages over other analytical techniques often used for reaction monitoring. In this paper, NMR is proposed to track the solution model reaction, and the structures of intermediate products and final products can be determined according to the corresponding NMR spectra, thus guiding the organic synthesis of the interface.

## 2. Silicone characteristics

Silicone materials usually refer to polymer compounds with Si-O bond as the main chain and other organic groups attached to the Si atom as side chains [11]. In recent years, more and more studies have focused on hydrophobic association of polymers, and hydrophobic polymers can be obtained only by connecting a small number of hydrophobic groups to the hydrophilic main chain of polymers. Methyl chlorosilane is very active in chemical properties and has great potential for comprehensive deep processing. It is the main raw material for preparing silicone oil, silicone rubber, silicone resin and other downstream products in silicone and their silane coupling agents. Silicone can not only resist high temperature, but also low temperature, and can be used in a wide temperature range. Both chemical properties and physical and mechanical properties change little with temperature. Figure 1 shows the main application of silicone.

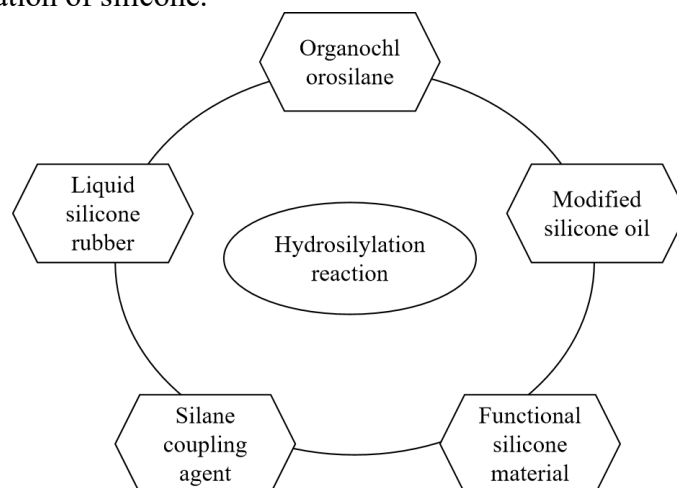


Figure 1 Main applications of silicone

Si is a poor conductor of heat, and the product chlorosilane is easy to decompose at high temperature to generate high-boiling substances, and the reaction temperature is easy to rise because the heat can't be taken away. When the temperature rises to a certain extent, the catalyst will be irreversibly deactivated. Therefore, temperature is a very important technical parameter in the direct synthesis process. The association of hydrophobic groups in water makes the polymer have unique rheological and interfacial properties. Silicone products have good electrical insulation performance, and their dielectric loss, voltage resistance, arc resistance, corona resistance, volume resistance coefficient and surface resistance coefficient are among the best among insulating materials, and their electrical properties are little affected by temperature and frequency.

Silicone not only has excellent heat resistance, but also has excellent water repellency, which guarantees the high reliability of electrical equipment when it is used under wet conditions. Hydrophobic modification of polyacrylamide is the focus of research. According to the different groups added, such as long-chain alkyl, acrylate, anion and cation groups, it can not only enhance its temperature and salt resistance, but also make the polymer have certain emulsifying properties and increase crude oil recovery.

Among the most inactive compounds known, polysiloxane compounds in silicone materials are one of them. They are very resistant to biological aging, have no rejection reaction with animals, and have good anticoagulant properties. Compared with liquid, solid samples have dipole-dipole interaction, chemical shift anisotropy and electric quadrupole moment interaction because molecules

can't move freely or are blocked, which leads to the broadening of spectral lines, covering up many fine structures containing useful information and greatly reducing spectral line resolution. The integration of upstream and downstream industries in silicone is low, and its ability to resist risks is poor. While building individual projects in silicone, enterprises generally don't consider downstream deep processing projects, which aggravates the problem of low integration between upstream and downstream industries in silicone.

### 3. Guidance of NMR tracking on interfacial organic synthesis reaction

The monomer synthesis reactor in silicone has experienced the development process from fixed bed to stirred bed to fluidized bed. At present, the fluidized bed is mostly used for mass production of methylchlorosilane, because the reaction materials in the fluidized bed reactor have good gas-solid contact atmosphere and heat transfer performance, high solid content and low axial backmixing. Generally, it can be divided into intake section, preheating section, reaction section, cooling section, product collection section and tail gas recovery section. Among them, the reaction section usually adopts single-stage heating mode, and the outer wall is covered with copper blocks to ensure that the temperature distribution is relatively uniform in the longitudinal direction during preheating and reaction. The inner tube passes through the lower ceiling and is connected with the upper ceiling, and the hot fluid collects in the space above the upper ceiling and flows out of the reactor from the side wall of the reactor. Two-stage finger tubes can also be connected in series by using the flower plate structure, but three-layer flower plate should be used when the second-stage finger tubes are connected in series. When the flower plate structure is adopted, the gas flow cannot flow through the flower plate, and the gas outlet is arranged on the top side wall of the reactor, and the gas flows out in the radial direction.

The relationship between fluid pressure drop and flow rate is approximately linear:

$$\frac{\Delta p}{H} = 150 \frac{(1-\varepsilon)^2}{\varepsilon^2} \frac{\mu \cdot u}{d_v^2} + 1.75 \frac{(1-\varepsilon)}{\varepsilon^3} \frac{\rho_f \cdot u^2}{d_v} \quad (1)$$

When the fluid velocity  $u$  reaches a certain critical value, the pressure drop  $\Delta p$  and the flow velocity  $u$  no longer follow the Ergun formula, but slightly decrease after reaching the maximum pressure drop  $\Delta p_{\max}$ , and then tend to a certain value, which is the bed static pressure:

$$\Delta p = \frac{W_b}{A_c} \quad (2)$$

At this time, the bed is in a critical state of transition from fixed bed to fluidized bed, and the corresponding fluidization velocity is critical fluidization velocity  $u_{mf}$ . After that, the bed pressure drop remained almost unchanged and did not change significantly with the further increase of fluid velocity.

A filter screen should be installed at the lower part of the reaction device, and Shi Ying cotton and quartz sand should also be installed when filling the reaction tube to prevent the reaction contact from being blown out by the feed gas, thus ensuring the overall stability of the bed. During the reaction, the dried and preheated MECL will flow into the reactor after the flow rate is controlled by the gas mass flowmeter above, and directly contact with the Si powder and the catalyst sample to start the reaction. In the preheating section, the serpentine coil is needed to ensure the uniform temperature distribution. In this paper, long-chain alkyl triphenylsilane with terminal reactive groups was assembled at the interface of semiconductor SiO<sub>2</sub>/Si to form a self-assembled film, and then the organic functional groups were transformed on the surface of the self-assembled film. The best experimental conditions for the conversion of organic functional groups at the interface were obtained by solution model reaction and its NMR analysis data. Ultra-fast multi-dimensional spectrum technology based on spatial coding meets the requirements of collecting multi-dimensional NMR

spectrum data in the environment of non-uniform magnetic field, and at the same time greatly improves the shape, sensitivity and adaptability of spectrum peak to non-uniform magnetic field, which is helpful to analyze non-uniform biological or chemical systems, which also makes ultra-fast two-dimensional sampling technology more universal.

The advantages of the reactor with flower-plate-distributed finger tubes are: quasi-single-tube heat transfer can be realized, so that the heat transfer between the surface of each finger tube and the reaction fluid is relatively uniform, the radial and axial temperature gradients are small and the heat transfer rate is relatively constant. If the catalyst can not be returned to the fluidized bed reactor in time, it will have adverse effects on the quality control and yield of products. The products after the reaction are all in the form of gas at the reaction temperature, and will be further condensed into liquid through a condenser tube, and then flow out and collected by a toluene collecting bottle, so that the crude monomer formed so far is separated in the liquid phase. After that, the product was qualitatively and quantitatively detected by Agilent 7890A chromatography. For the single-phase model, only one set of conservation equations of momentum and continuity needs to be solved. In order to realize the change from single-phase model to multi-phase model, additional conservation equations must be introduced and some modifications must be made to the original settings. These modifications include the introduction of multiphase volume fraction and the mechanism of momentum exchange between phases.

#### 4. Conclusions

With the widespread use of NMR analysis methods, NMR analysis is more and more widely used to track the progress of organic synthesis reactions, which has the characteristics of high sensitivity, integration of tracking monitoring and structural analysis. The monitoring of chemical reaction process is particularly important in the study of reaction mechanism. The combination of NMR spectroscopy and electrochemistry can be applied to the study of chemical reaction process, and the in-situ experiment can realize the real-time detection of chemical reaction products, and then study the reaction mechanism. In this paper, the application of NMR hydrogen spectrum to determine the optimal reaction conditions of solution model reaction is proposed to guide the organic functional group transformation at the solid interface. Ultra-fast multi-dimensional spectrum technology based on spatial coding meets the requirements of collecting multi-dimensional NMR spectrum data in the environment of non-uniform magnetic field, and at the same time greatly improves the shape, sensitivity and adaptability of spectrum peak to non-uniform magnetic field, which is helpful to analyze non-uniform biological or chemical systems, which also makes ultra-fast two-dimensional sampling technology more universal. With the development of ultra-fast technology in the future, the ultra-fast combined liquid flow device will further detect the rapid reaction, which will not only lower the spectral width limit of the sample to be detected, but also refresh the time limit of the observed reaction.

#### Acknowledgements

The key research project of Anhui Natural Science in 2021(KJ2021A1299)

The key research project of Anhui Natural Science in 2022(2022AH053017)

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