Study on Ultrasonic Assisted Mechanism of Ring Opening Polymerization of Octamethylcyclotetrasiloxane (D4)

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Abstract. In this study, the linear high molecular weight polydimethylsiloxanes(PDMS) were synthesized by ultrasonic-assisted bulk ring-opening polymerization method, with D4 as the raw material, hexamethyldisilane(HMDS) as the capping agent and concentrated sulfuric acid as the catalyst. The mechanism of ring-opening polymerization assisted by ultrasound is discussed in detail, through the ultrasonic time, ultrasonic intensity and reaction temperature and other factors. The results showed that D4 ring-opening polymerization and PDMS depolymerization was a pair of reversible equilibrium reaction. Due to the influence of steric hindrance and viscosity, the ultrasonic action appears as the driving effect of D4 ring opening at the initial reaction, and the chain exchange or depolymerization of PDMS at the end of the reaction. Therefore, ultrasonic irradiation is believed to facilitate the rapid synthesis of high molecular weight PDMS at high monomer concentrations.

INTRODUCTION

Ultrasound is a mechanical vibration wave in the frequency range of 20KHz-10MHz. When it propagates in a liquid medium, cavitation can occur, creating a high-energy environment with a very short duration of thousands of K high temperature and hundreds of or thousands of atmospheres in the microdomains, which produce strong shock waves, micro-jet and discharge, causing molecular thermal dissociation, ionization and generate free radicals, resulting in a series of chemical changes [1]. In addition to cavitation, many of the secondary effects of ultrasound, such as mechanical oscillations, emulsification, diffusion, crushing, are also beneficial to the heat and mass transfer processes of the system and promote the reaction [2].

With the application of ultrasound in the field of chemistry, it has been found that the ultrasound has the characteristics of accelerating the chemical reaction, alleviating the reaction conditions, shortening the reaction time and carrying out some chemical reactions which are difficult to be achieved by the traditional methods [3]. Suslick [4] observed with an electron microscope that the ultrasonic wave produced a mechanical effect in the heterogeneous reaction and rapidly crushed the solid, thereby causing the particles to collide at a high speed. Bhanvase [5] studied styrene, methyl methacrylate ultrasonic irradiation micro-emulsion polymerization and found that ultrasonic irradiation micro-emulsion polymerization has the advantages of fast reaction, low dosage of emulsifier, no initiator and narrow particle size distribution. Liu [6] ultrasonic irradiation applied to iniferter polymerization, to achieve the effect of controlled radical polymerization.

Ultrasound-assisted ring-opening polymerization experiments were achieved by Price for D4 monomer, dimethyl ether as a solvent [7]. The reaction rate was found to be significantly increased and a better molecular weight distribution polymer was obtained. However, the mechanism of ultrasound-assisted ring-opening polymerization

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was still not enough. In this paper, the bulk ring-opening polymerization of D4 will be the object of study to discuss the mechanism of action of ultrasound conditions on the polymerization reaction.

EXPERIMENT

The D4 and HMDS were provided by Panshi Datian Chemical Auxiliary Institute; the concentrated sulfuric acid (98%) was provided by the Shanghai Bohe Fine Chemicals Co., Ltd. The experimental ultrasound source was FS-250N ultrasonic wave processor from Shanghai FSH Instrument Co., Ltd. The reaction kettle used a 200 ml large test tube with a magnetic stirrer bath. The polymerization was carried out under the conditions of the ratio D4/ H_2SO_4/ HMDS =1500/8/1 (volume), and the degree of polymerization was judged by measuring the viscosity at different reaction times. The reaction was deemed complete when the viscosity of silicone oil was almost unchanged. Viscosity was measured by NDJ-4 rotational viscometer from Shanghai Precision Instruments Manufacturing Co., Ltd. A series of experiments were carried out by adjusting the ultrasonic intensity and the reaction temperature for ultrasonic assisted mechanism of ring opening polymerization of D4.

RESULTS AND DISCUSSION

The experimental data (65℃) of the change of viscosity with or without ultrasound irradiation were shown in Fig.1. The viscosity of D4 system without ultrasonic irradiation showed no significant change in the first 60 minutes, and the viscosity reached 2.0×10^4 mpa•s at 120 minutes, which indicated that the degree of ring-opening polymerization was lower at 65℃. However, the viscosity of D4 system undergoing ultrasonic irradiation changed obviously. the viscosity of the system reached 2.0×10^4 mpa•s at 60 minutes, which means that the reaction time was doubled. The comparative experiments shown that the role of ultrasound irradiation can indeed accelerate the D4 ring-opening polymerization.

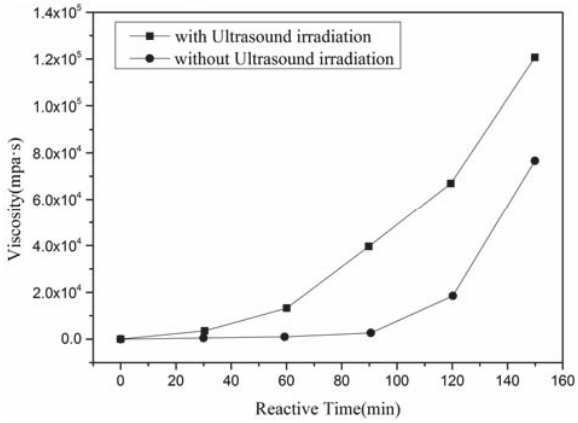

FIGURE 1 The comparative experiments with or without ultrasound irradiation at 65℃

If the force acting on the monomer completely, in which the role of ultrasound intensity and product viscosity changes related to the accelerated performance, the definition of the role of ultrasound on the reaction R, which was calculated as follows:

$$R = \frac{d^2\left(V - V_0\right)}{dt^2} \tag{1}$$

The "V" is the product viscosity under different ultrasonic conditions, "V0" is the product viscosity without ultrasonic, and "t" is the reaction time. The viscosity difference on the second derivative of the time can be obtained with the role of ultrasound trends over time. Under the reaction temperature of 65 ℃ and 85 ℃, the effects of different ultrasonic intensities were shown in Fig. 2 and Fig. 3, respectively. The second-order differential curve

without ultrasonic effect is a horizontal line with ordinate of 0. Values above the horizontal indicate a promotion of ring-opening polymerization, and values below the horizontal indicate inhibition of ring-opening polymerization. This shown that the ultrasonic effect was very conducive to increase the degree of polymerization, the molecular weight rapidly increased the viscosity of the system rapidly increased in the early ring-opening polymerization, and then reached the maximum value at 30 minutes. In the middle of the ring-opening polymerization, ultrasound also shown an inhibitory effect, a decrease in the rate of molecular weight increased, or the polymer chains depolymerized under ultrasound and then reached the minimum value at 120 minutes. At the end of the ring-opening polymerization, chain growth and depolymerization were balanced and the viscosity of the polymer no longer changes significantly. In the early stages of reaction, high levels of D4 monomer tended to form polymeric chains due to steric hindrance and concentration. With the decrease of D4 content, the tendency of depolymerization to ring reaction and chain exchange reaction increased, which was not conducive to the high degree of polymerization of PDMS. Through the above analysis shows that the ring-opening polymerization of D4 and PDMS depolymerization reaction was a pair of competing equilibrium reaction under the action of ultrasound, which is no essential difference with the thermal efficiency. Comparing Fig. 2 and Fig. 3, the area of the area above the horizontal line "0" of the reaction at 65℃ was much larger than that at 85 ℃. This also shows that the effect of ultrasound at low temperature is more obvious.

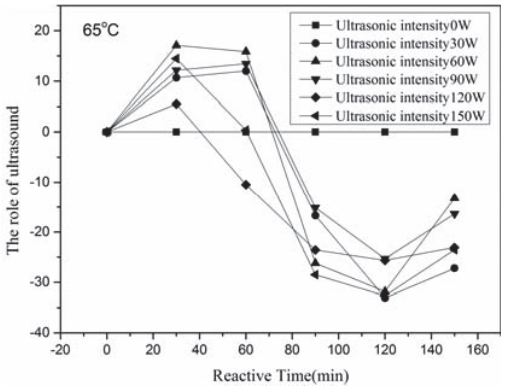

FIGURE 2 The change the role of ultrasound at 65℃

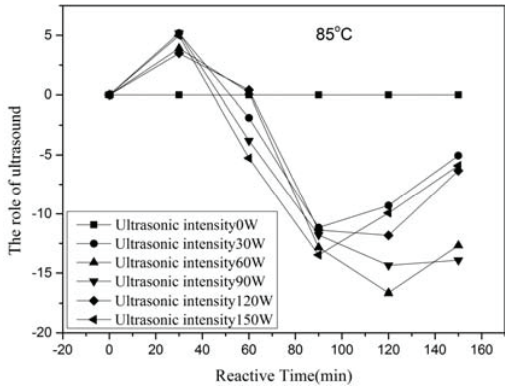

FIGURE 3 The change the role of ultrasound at 85℃

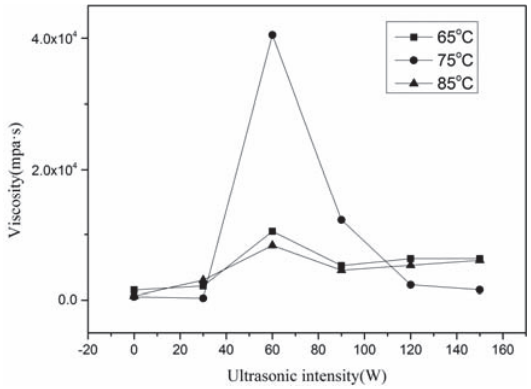

FIGURE 4 The Product viscosity at 30 minutes

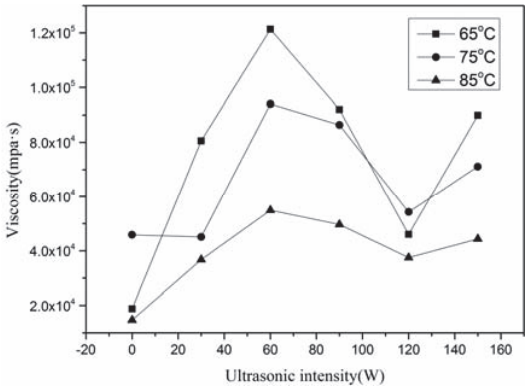

FIGURE 5 The Product viscosity at 120 minutes

In order to study the effect of different ultrasonic intensities on the polymerization reaction, the viscosity of the product at each polymerization temperature was compared to 30 min (max) and 120 min (min), as shown in Fig. 4, Fig. 5 respectively. In D4 ring-opening polymerization, the viscosity of the system did not appear to increase with increasing ultrasonic intensity, but the maximum appeared at 60W. It was shown that the optimum conditions for the ultrasonic intensity was 60W in this reaction. If the ultrasonic intensity was lower than 60W for reaction, the

ultrasonic force was insufficient, and the growth ability of the molecular chain was weaker. If the ultrasonic intensity was higher than 60W and the ultrasonic force was too high, the main chain of the polymer tended to break, which tended to depolymerization reaction. In the early polymerization (Fig. 4), this performance was more obvious, especially at 70 ℃ system viscosity quickly rose to 4.0 mpa•s at 30 minutes.

The reaction temperature is an important condition for the ring opening polymerization of D4. When the ultrasonic intensity of 60W, the product viscosity curve shown in Figure 6.

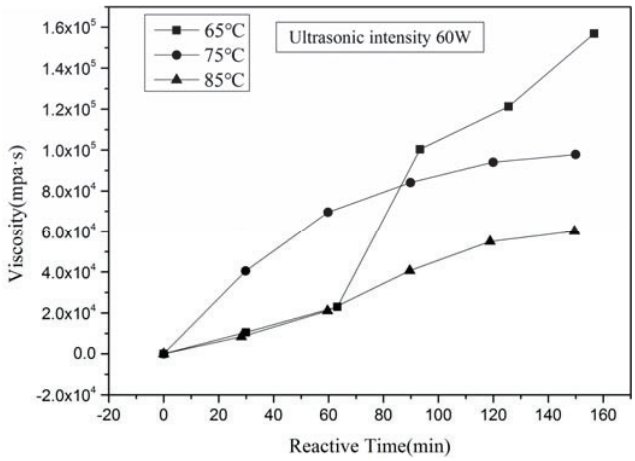

FIGURE 6 The change of viscosity at 60W

It can be seen from the Fig. 6 that when the ultrasonic intensity 60W and the polymerization temperature 65°C, the reaction rate was the fastest and the viscosity of the product was the highest. it was indicated that the optimum reaction temperature for the ultrasonic assisted effect.

CONCLUSION

A series of PDMS experiments with D4 ring-opening polymerization under different ultrasonic intensities and temperature conditions were successfully carried out. It was found that the effect of ultrasound was consistent with the effect of heat, the promoting effect was in the early stage of polymerization and the inhibition was in the late stage of polymerization. For the bulk polymerization system, the best ultrasound-assisted conditions are temperature 65 ℃, ultrasonic intensity 60W.

ACKNOWLEDGMENTS

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