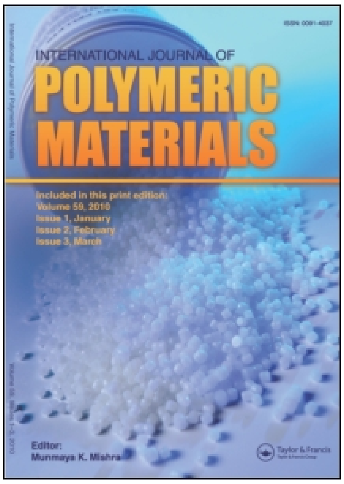

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Microwave-Irradiated Ring-Opening Polymerization of Octamethylcyclotetrasiloxane in the Presence of Water

Bo Yang[a]; Hui He[a]; Riping Chen[a]; Li Ma[a]; Demin Jia[a]
[a] Department of Polymer Materials and Engineering, South China University of Technology, Guangzhou, China

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Bo Yang
Hui He
Riping Chen
Li Ma
Demin Jia
Department of Polymer Materials and Engineering,
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α, ω-dihydroxyl polydimethylsiloxane (DHPDMS) was prepared via anionic ring-opening polymerization of octamethyl cyclotetrasiloxane (D_4) under microwave irradiation (MI) in the presence of water. The conversion and polymerization rate were calculated by the gravimetric method. The effect of microwave power on the polymerization was investigated. FTIR was used to verify the DHPDMS prepared at different irradiation times. The results show that the conversion is the highest when the initial microwave power is preset at 700 W. Compared with conventional heating (CH), the polymerization rate and equilibrium conversion are both enhanced by the introduction of microwave irradiation. The species and concentration of the cyclosiloxane mixture caused by backbiting reaction were determined by gas chromatography/mass spectrometry (GC/MS). The lower concentration of cyclosiloxane in the polymer prepared under MI indicates that side reactions have been reduced and a pure polymer obtained. The molecular weight and polydispersity index (PDI) measured by GPC show that under MI, the molecular weight of DHPDMS is lower and PDI is narrower than those under CH.

Keywords: microwave irradiation, octamethylcyclotetrasiloxane, polydimethylsiloxane, ring-opening polymerization

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Address correspondence to Hui He, Department of Polymer Materials and Engineering, South China University of Technology, 510640 Guangzhou, China. E-mail: pshuihe@scut.edu.cn

INTRODUCTION

The microwave radiation region is located between infrared radiation and radio waves with wavelengths of 1 mm–1 m, corresponding to frequencies between 0.3 and 300 GHz [1,2]. Since Gedye and Giguere published the first papers on the influence of microwaves on chemical synthesis undertaken in a household oven, there has been a steadily growing interest in this research field [3–7]. With the advantages of fast and homogeneous heating, the application of microwaves has opened up many opportunities to improve polymer preparation in recent years [8–10]. The ring-opening polymerization [11–13], step-growth polymerization [14,15] and free radical polymerization [16] have been conducted under MI. Many studies on the microwave-assisted ring-opening polymerizations have been focused on oxazoline [17–19], caprolactone [20–22], and trimethylene carbonate [23]. The study of the anionic ring-opening polymerization of D_4 under MI, however, is still lacking.

Polysiloxane has many attractive properties, such as nontoxicity, low surface tension, excellent weather resistance, high flexibility and good thermal stability. It has become one of the most widely used industrial and commercial polymeric materials [24]. For example, HDPDMS is widely used as room temperature vulcanizable (RTV) adhesive, textile finishing agents, antifoam agents and medical additives. Generally, there are some drawbacks for the HDPDMS prepared by traditional methods in terms of lengthy procedures, insufficient monomer conversion and relatively higher PDI of polymer. In the present study, we attempt to enhance the polymerization rate, increase the equilibrium conversion of D_4 and lower the PDI of the HDPDMS by the introduction of microwaves during polymerization.

EXPERIMENTAL

Materials and Apparatus

D_4 (industrial grade), supplied by Jiangxi Xinghuo Plant, was purified by CaH_2 and distilled prior to use. KOH (AR grade) and acetic acid (AR grade), from Guangzhou Southern Chemical Co. and Tianjin Chemical Reagent Factory, respectively, were used as received. Deionized water was obtained from Guangzhou Qianhui Co., Ltd.

The microwave reactor, model MAS-I, was manufactured by Shanghai Sineo Microwave Chemistry Technology Co., Ltd. The electromagnetic energy was produced by a magnetron at 2.45 GHz. The reactor was equipped with an online IR temperature sensor and compressed air system for cooling. The microwave power could be preset between 100 and 1000 W and automatically adjusted to control the reaction temperature.

Synthesis of DHPDMS

D_4 (250 g, 0.84 mol), catalytic amounts of KOH (0.89 mmol) and deionized water (5.6 mmol) were charged into a round-bottom flask. The vessel, equipped with a mechanical stirrer, a nitrogen inlet and a condenser, was placed in the cavity of microwave reactor. The parameters (such as reaction time, microwave power) of the microwave reactor were fixed. The mixture was premixed under vigorous stirring for 15 min before polymerization and then irradiated with microwaves at 130°C in conjunction with air-cooling to keep the desired temperature for polymerization. The polymerization was quenched by acetic acid.

In the case of conventional heating, the flask was placed in an oil bath at the same temperature as the microwave reaction for polymerization.

MATERIALS CHARACTERIZATION

Conversion Measurement

The conversion of D_4 monomer was calculated by the gravimetric method. The polymer was the precise weight (1.5–2.0 g) to form a film by using a dry clean culture dish. The culture dishes were then dried under vacuum at 180°C for 6 h to remove the unpolymerized monomer and other volatiles. When the samples cooled down to room temperature, conversion was calculated as follows:

$$Conversion(\%) = \frac{W - W_0}{W^* - W_0} \times 100\%$$

where W^* and W are the gross weights before and after drying, respectively. W_0 is the weight of the culture dish.

Infrared Spectroscopy (FTIR)

FTIR was performed on a Nicolet FTIR 760 spectrometer using a coated KBr disk to verify the DHPDMS prepared at different microwave irradiation time. The unpolymerized monomer and other volatiles were eliminated in a vacuum desiccator before measurement.

FTIR spectra were obtained at room temperature in the transmission mode between 500 cm^{-1} and 4000 cm^{-1} with a resolution of 2 cm^{-1}.

Gas Chromatography/Mass Spectrometry Measurement (GC/MS)

Samples of polymer of known weight (approximately 2 g) were dissolved by using analytical grade toluene. Methanol was then added to the mixture to separate the polymer from impurities. The analysis of solvent extract of impurities was made by using an HP 6890 GC with 5973 mass selective detector (MSD). Chromatographic separation was performed on a HP-5MS fused silica capillary column (5% phenyl methyl siloxane, 30.0 m × 0.25 mm). Chromatographic conditions: initial temperature 50°C, 2 min isothermal, 15°C/min up to 250°C. Carrier gas: He (purity 99.995%), constant flow 1.0 ml/min. Identification of mass spectra and assignation of GC-MS peaks was carried out by a library search (NIST, vers.1.7). The concentration of the cyclosiloxane mixture was calculated from the initial weights of samples and relative abundance of each cyclosiloxane.

Gel Permeation Chromatography Measurement (GPC)

The molecular weight and PDI of DHPDMS were determined, using a Waters 515-2410 gel permeation chromatograph equipped with HT4-HT5 columns, calibrated with polystyrene standard samples. Toluene was used as the eluting solvent and the flow rate was kept at 1.0 ml/min at 30°C.

RESULTS AND DISCUSSION

Effect of Microwave Power on Polymerization

Before polymerization, the reaction temperature (130°C) and irradiation time (90 min) were fixed. The effect of microwave power on the D_4 monomer conversion is demonstrated in Figure 1. At the low microwave powers, 100 W to 400 W, the system takes a long time to reach the desired temperature. Therefore, the conversion is below 50%. The rise of microwave power levels increases the conversion of monomer. When the initial microwave power is set at 700 W, the monomer conversion reaches a maximum value, 91.9%. However, powers higher than 700 W could not elevate the conversion any more. Hence, the power, 700 W, was chosen for the subsequent research.

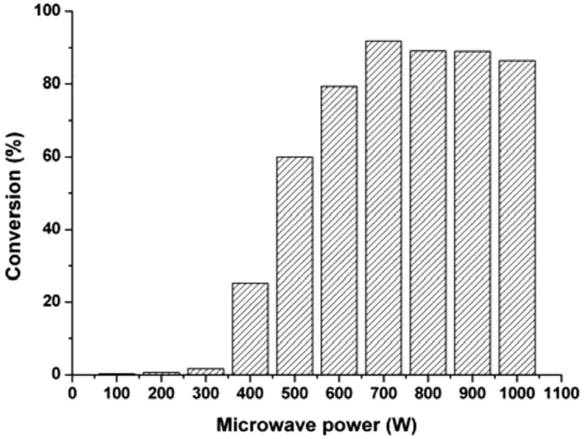

FIGURE 1 Effect of microwave power on conversion of D_4.

FTIR Characterization

FTIR technology was used to characterize the polymers prepared at 700 W for different microwave irradiation times. As shown in Figure 2, the spectra of DHPDMS are different from the D_4 monomer. The characteristic peak at $1076\,cm^{-1}$ for Si−O−Si stretch vibration in

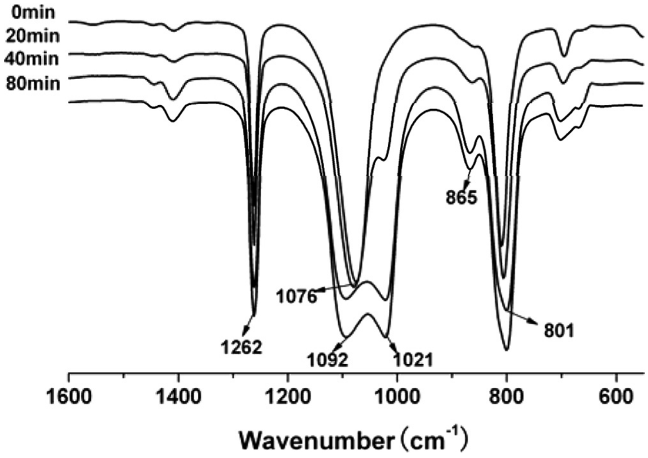

FIGURE 2 FTIR spectra of D_4 and DHPDMS prepared at different irradiation times.

cyclosiloxane divides into two peaks, 1021 cm^{-1} and 1092 cm^{-1}, which represent the linear siloxane formation. The absorption around 865 cm^{-1} is assigned to the Si–O stretching of Si–OH. With increased irradiation time, the amount of Si–OH also increases, as can be seen obviously in the spectra. The 1262 cm^{-1} and 801 cm^{-1} bands are associated with Si–CH_3 symmetric deformation and stretching vibrations. The FTIR spectra indicate that DHPDMS was synthesized successfully in a single step under microwave irradiation.

Conversion of D_4 Monomer in Two Processes

The polymerization of D_4 is known as an anionic ring-opening polymerization [25], which primarily includes three steps: initiation, propagation and termination, as seen in Figure 3.

Figure 4 presents the reaction time dependence of the monomer conversion during polymerization under MI and CH. Based on the characteristics of anionic ring-opening polymerization and the results attained from the experiments, the Boltzmann mode was selected to fit the results [26]. As shown in Figure 4, the curves fit the results well and the shapes are similar. The three stages of polymerization mentioned above under MI and CH also can be distinguished. However, the duration of both initiation and propagation decreases and the ultimate conversion increases by the introduction of microwaves. The polymerization rate curves under two different processes were calculated by the differential of the conversion curve, as seen in Figure 5. The conversion of D_4 monomer under MI is significantly higher than the corresponding results of conventional polymerization. For example, within the first 60 min of polymerization under microwaves,

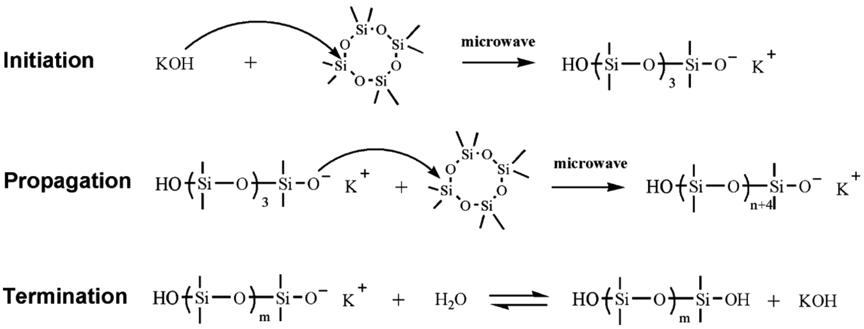

FIGURE 3 Course of anionic ring-opening polymerization of D_4 under microwave irradiation.

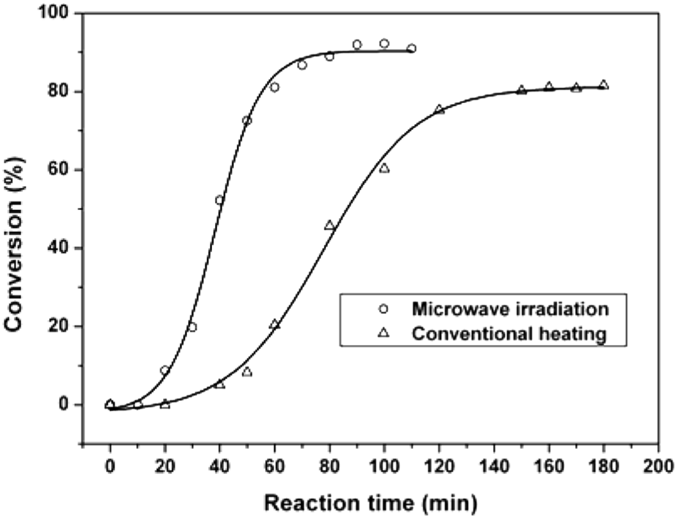

FIGURE 4 Kinetics curves of D_4 polymerization under MI (700 W) and CH.

the conversion is higher than 80%, but only about 20% under CH. The time when polymerization rate reaches its highest point is about 40 min, compared to 80 min in oil bath.

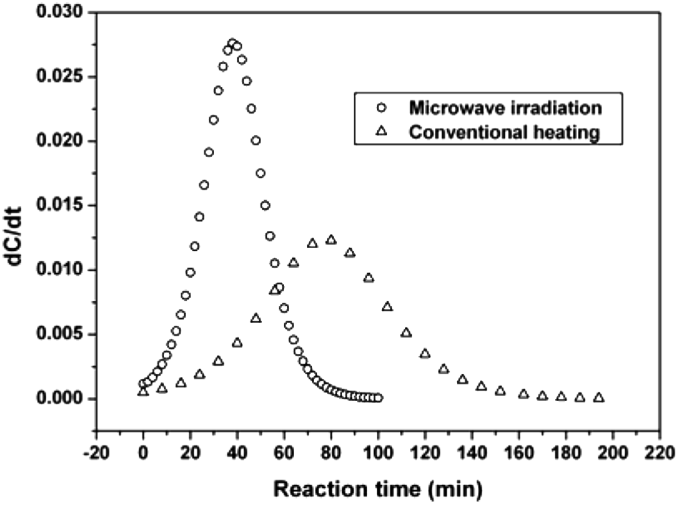

FIGURE 5 Polymerization rate curves under MI (700 W) and CH.

The cause of higher conversion and faster polymerization rate may be attributed to the effect of microwaves. The effect of microwave irradiation is based on two major mechanisms, namely dipolar polarization mechanism and conduction mechanism [1]. Although D_4 has weak dipole characteristics necessary for absorbing microwave due to its structure [27], a solution containing ions is formed when the KOH dissolves in water. In the microwave field and at a certain temperature, the anionic active centers are formed following the OH^- initiation. The anionic active centers, which possess both the characteristic of dipole moments and ions in their ends, are sensitive to the electric fields. They attempt to align themselves and the molecules rotate in phase with the oscillating electric field. Therefore, the active centers become more ready to approach other D_4 monomers to propagate. In the CH process, the active centers formed have less energy than that under microwave radiation, i.e., they align and attack the D_4 monomer inefficiently. On the other hand, the active centers are easy to embed in the polymer under mechanical mixing, and side reactions called backbiting reactions [25] take place. The details will be discussed later. That is why the ultimate conversion of D_4 is enhanced under MI.

GC-MS of Solvent Extracts

The purified D_4 monomer was investigated by GC-MS, the total ion chromatogram is given in Figure 6. After purification, there is not any other cyclosiloxane monomer except D_4. The toluene extracts of DHPDMS prepared by MI and CH in their ultimate conversion were

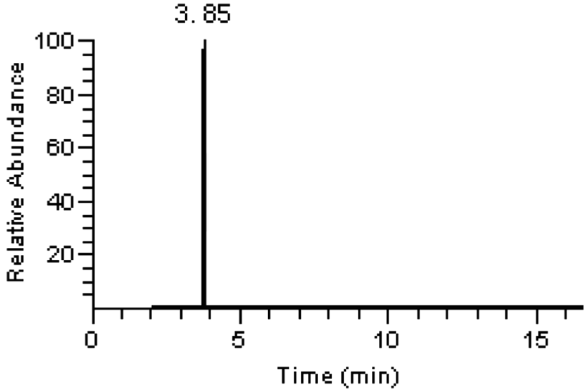

FIGURE 6 Gas chromatography of purified D_4 monomer.

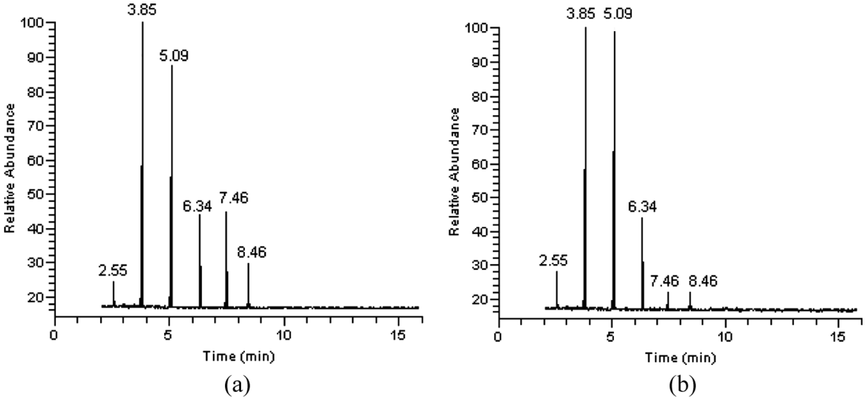

FIGURE 7 Gas chromatography of extracts of DHPDMS prepared by (a) MI and (b) CH.

also measured by GC-MS, as shown in Figure 7. With the aid of library matching, Figure 7 gives evidence for the presence of cyclic siloxane species with a distribution of D_n. D_n refers to the cyclic siloxane species with the subscript representing the number of Si–O bonds within the repeat unit and D refers to the dimethylsiloxane unit.

The mass spectra representative of D_n are shown in Figure 8. The results indicate that the anionic active centers backbite the chains and produce kinds of cycles both under MI and CH, as illustrated in Figure 9. The peak areas of cyclic siloxane at different retention times were integrated and the concentrations of D_n calculated. The results are given in Table 1. Compared with the CH, the concentration of D_3, D_4, D_5, D_6 and the total concentration of D_n in polymers prepared by microwaves are lower. The results prove that under the electric field of microwave, the active centers tend to attack other monomers to propagate rather than backbite the chain to form cyclic siloxanes. That is, the microwave in the system effectively reduces the side reactions.

Molecular Weight and PDI of DHPDMS in Two Processes

The conversions, M_n, M_w and PDI values at different reaction times under the two processes are summarized in Table 2. The PDIs of HDPDMS prepared under MI are narrower than those under CH, which is attributed to uniform temperature throughout the reaction mixture and the effect of the microwave electric field. Generally, the reactions under CH have a temperature gradient. In contrast, the

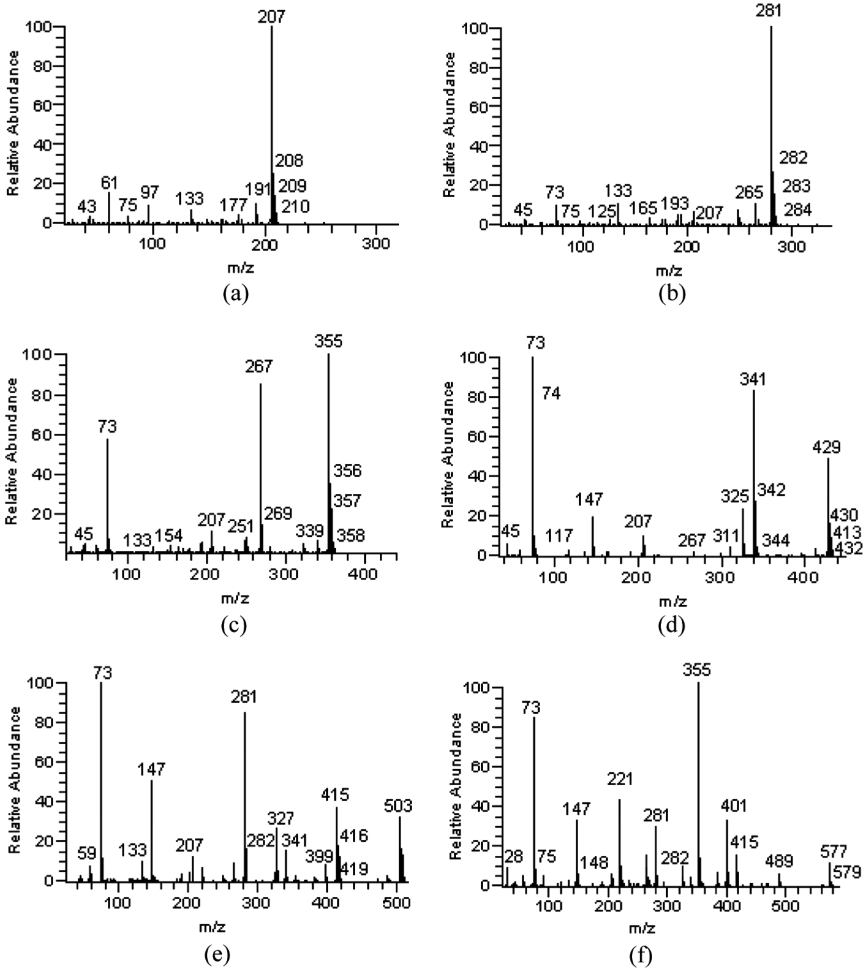

FIGURE 8 Mass spectrum showing peaks indicative of D_n in the polymer: (a) D_3, (b) D_4, (c) D_5, (d) D_6, (e) D_7, (f) D_8.

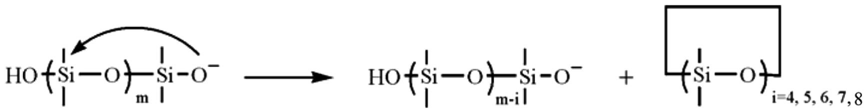

FIGURE 9 Formation of D_n through backbiting reaction of active center.

TABLE 1 Concentration of D_n in Polymer Obtained by MI and CH

D_n	D_3, mol/L	D_4, mol/L	D_5, mol/L	D_6, mol/L	D_7, mol/L	D_8, mol/L	Total, mol/L
RT/min	2.55	3.85	5.09	6.34	7.46	8.46	—
MI	0.004	0.142	0.105	0.029	0.027	0.015	0.329
CH	0.038	0.242	0.188	0.052	0.011	0.007	0.538

TABLE 2 M_n, M_w and PDI of DHPDMS Prepared by MI and CH

Process	Reaction time (min)	Conversion (%)	M_n ($\times 10^4$)	M_w ($\times 10^4$)	PDI
MI	40	52.2	7.7	10.9	1.41
	60	81.1	12.4	18.3	1.47
	80	88.9	14.1	20.5	1.45
CH	100	60.3	10.9	22.6	2.08
	120	75.3	12.5	24.5	1.96
	160	81.0	13.5	26.8	1.98

inner heating of the system under MI leads to very fast and homogenous heating, resulting in less side reactions and uniform products.

The obtained polymers in two processes with close conversion have distinct molecular weights. For example, when the conversion reaches 81%, the M_w of polymer prepared under MI is about 18.3×10^4, lower than 26.8×10^4 attained under CH. The differences in molecular weight could be explained by the destruction of complexes containing silanolate active centers. Complexes are formed in terms of a donor-acceptor type interaction between active centers [28]. The formation of complexes leads to the inertness of active centers. However, under the electric field in microwave, the active centers attempt to align themselves and move in phase quickly with the oscillating electric field. The complexes are hard to form, which results in a greater amount of active centers than under the condition of CH. Hence, the molecular weights of the polymer prepared under MI are lower.

CONCLUSIONS

DHPDMS was successfully and rapidly synthesized by the microwave-irradiated ring-opening polymerization of D_4 using KOH as a catalyst and in the presence of water. Compared with conventional heating, the polymerization rate and ultimate conversion of the monomer were all enhanced by the introduction of microwave irradiation. Due to the electric field and homogenous heating, the active centers got more energy to propagate, the side reactions were reduced and the polymers attained under MI were purer than those prepared under CH. The process will make a promising path to prepare DHPDMS in both laboratory research and industry.

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