

EFFECT OF POLYMERIZATION CONDITIONS ON THE MOLECULAR WEIGHT OF POLYPHENYLSILSISQUIOXANE*

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ABSTRACT

Samples of polyphenylsilsisquioxane (PPSQ) using CaF_2 or MgF_2 as the main catalysts had been prepared under different polymerization conditions. The results were treated on an orthogonal design $L_9 (3^4)$. All weight-average molecular weights ($\bar{M}_w$) of PPSQ had been measured by gel permeation chromatography (GPC). Effects of polymerization conditions including reaction temperature, composition of the dual catalysts (CaF_2 or MgF_2 and DCC), mixture of solvents and reaction time on $\bar{M}_w$ of PPSQ have been discussed. The quantity of the catalysts is the most important factor that affects $\bar{M}_w$ of PPSQ. Reaction temperature is the second important factor. Appropriate polymerization condition has been established to get PPSQ with high $\bar{M}_w$.

INTRODUCTION

Polyphenylsilsisquioxane (PPSQ), one kind of these ladder polymers with flexible skeleton chain structure, has many outstanding properties, i.e. thermal and oxidative stability, electrical insulating property, selective permeability to gases as well as easiness to be soluble in most mild organic solvents. These good comprehensive properties entitle PPSQ and its copolymers to have specific applications in coating, membrane and semiconductor industries.

While much effort has been expended in developing applications of PPSQ, only a few studies on the effect of polymerization conditions on molecular weight of PPSQ have been reported in recent years. Since the synthesis of PPSQ using KOH as the catalyst by Brown^[1,2], Hata obtained this ladder polymer using alkaline - earth metals and their fluorides as

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catalysts^[3]. But Hata did not study the effect of polymerization conditions on $\bar{M}_w$ of PPSQ. However, $\bar{M}_w$ of PPSQ determined by GPC in most papers are apparent devoid of the universal calibration treatment. Shi and his coworkers had studied the synthesis, solution property, characterization of structures, thermal stability and decomposition of PPSQ^[4-9]. In this paper, PPSQ using two alkaline-earth metal fluorides (CaF_2 and MgF_2) and dicyclohexyl carbodiimide (DCC) as catalysts under different polymerization conditions were prepared and their molecular weight were measured by gel permeation chromatography (GPC). The choice and variation of polymerization conditions were determined by an orthogonal design $L_9(3^4)$ with four factors and three levels for each factor. The effect of polymerization conditions on the molecular weight of PPSQ has been analyzed on the basis of the experimental results.

EXPERIMENTAL

1. Materials

Monomer phenyl trichlorosilane purchased from Japan Tokyo Kasei Kogyo Co. was purified by distillation (150—152°C/200mmHg). Other reagents and solvents are commercially available. Their purity is of analytical grade.

2. Synthesis of PPSQ and its prepolymer

Prepolymer of PPSQ was prepared by means of hydrolysis similar to the procedure of Brown et al.^[1,2]. A mixture of some solvents (Table 1) was dropped into a flask containing 10g prepolymer of PPSQ and a small amount of catalysts. While being stirred, the solution was heated to 100°C and continued from 100°C to 130°C for half an hour. Then the reaction temperature was increased to the designed one (Table 1). After standing for a given time, the reaction solution was cooled to room temperature. 20ml toluene was added to it. After the reaction solution was filtered, the final products were precipitated by methanol. The samples were then dried in a vacuum oven at 50°C till its weight unchanged.

3. Measurement

The weight-average molecular weight ($\bar{M}_w$) was determined by GPC at room temperature with tetrahydrofuran (THF) as eluent. These experiments were carried out with a Waters-244 GPC system using differential refractometer as a detector. High performance columns of μ -Styragel 10²nm,

10^3nm and 10^4nm three columns set were employed for PPSQ. Monodispersed standard polystyrene samples with molecular weights from 3600 to 5×10^5 were used to calibrate the columns. The following Mark-Houwink equations of PPSQ and PS in THF at 25°C were used in $\bar{M}_w$ calculation of PPSQ^[9,10] by means of universal treatment:

$$[\eta]_{\text{THF}} = 2.26 \times 10^{-4} \times M^{1.03} \quad (\text{PPSQ})$$

$$[\eta]_{\text{THF}} = 0.016 \times M^{0.706} \quad (\text{PS})$$

RESULTS AND DISCUSSION

In order to reduce the experiments and study the effect of reaction conditions on $\bar{M}_w$ of PPSQ, we predetermined different polymerization conditions (Table 1) according to an orthogonal design $L_9(3^4)$. Four factors are the reaction temperature, catalyst, solvent and reaction time. There are three levels for every factor. CaF_2 and MgF_2 were separately used as the main catalyst in system 1 and 2. $\bar{M}_w$ of all PPSQ and calculation results treated on the orthogonal design^[11] are given in Table 2. I, II and III in one column are the sum of all $\bar{M}_w$ of PPSQ that had been synthesized at level

Table 1 Polymerization conditions of PPSQ determined by orthogonal design

No	Temperature ($^\circ\text{C}$)	Catalyst(mg)		Solvent(ml)			Time (hr)
		CaF_2 or MgF_2	DCC	Toluene	Diphenylether	Xylene	
1	180	10	50	20	10	$10^{\text{a)}$	5
2	180	1	50	50	5		3
3	180	1		20	5	20	$1^{\text{b)}$
4	210	10	50	50	5		$1^{\text{b)}$
5	210	1	50	20	5	20	5
6	210	1		20	10	$10^{\text{a)}$	3
7	250	10	50	20	5	20	3
8	250	1	50	20	10	$10^{\text{a)}$	$1^{\text{b)}$
9	250	1		50	5		5

a) The volume of benzene is 10 ml.

b) The reaction time is changed into 7 hours in system 2 using MgF_2 as the main catalyst.

1, 2 and 3 of the factor in the corresponding column, respectively. To system 1, I in column A (reaction temperature) named I_A are the sum of all $\overline{M}_w$ of PPSQ synthesized at the first level (180°C). In column B (quantity of catalysts), II_B are the sum of all $\overline{M}_w$ of PPSQ whose quantity of catalysts is the second level (DCC 50mg and CaF_2 1mg).

$I_A = 1.72 + 4.09 + 1.59 = 7.4$ (system 1)

$II_B = 4.09 + 2.57 + 2.01 = 8.67$ (system 1)

All results were calculated as described above.

$R = \max(I, II, III) - \min(I, II, III)$

Table 2 $\overline{M}_w$ of PPSQ and results of orthogonal calculation

No		A Temperature	B Catalyst	C Solvent	D Time	$\overline{M}_w (\times 10^{-4})$ (CaF_2)	$\overline{M}_w (\times 10^{-4})$ (MgF_2)
1		1	1	1	1	1.72	5.04
2		1	2	2	2	4.09	3.38
3		1	3	3	3	1.59	0.92
4		2	1	2	3	0.99	2.75
5		2	2	3	1	2.57	1.91
6		2	3	1	2	0.84	1.08
7		3	1	3	2	2.08	3.28
8		3	2	1	3	2.01	2.78
9		3	3	2	1	1.47	1.24
1*	I	7.40	4.79	4.57	5.76		
	II	4.40	8.67	6.55	7.01		
	III	5.56	3.90	6.24	4.59		
	R	3.00	4.77	1.98	2.42		
2*	I	9.34	11.07	8.90	8.19		
	II	5.74	8.07	7.37	7.74		
	III	7.30	3.59	6.11	6.45		
	R	3.60	7.48	2.75	1.74		

* CaF_2 and MgF_2 are used as the main catalyst in system 1 and 2 respectively.

R_A, R_B, R_C and R_D to system 1 and 2 are respectively arranged in the following orders: $R_B > R_A > R_D > R_C$ (in system 1), $R_B > R_A > R_C > R_D$ (in

system 2). These results indicate that the composition of the dual catalysts is the most important factor that affects $\bar{M}_w$ of PPSQ and reaction temperature is the second important one. The other factors, such as mixture of solvents and reaction time, have the least influence on the molecular weight of PPSQ. Effect of different factors on $\bar{M}_w$ of PPSQ are discussed in detail as follows:

(1). Catalyst The amount of catalysts in system 1 (CaF_2 1mg and DCC 50mg) to get PPSQ with the highest $\bar{M}_w$ is smaller than that in system 2 (MgF_2 10mg and DCC 50mg) because CaF_2 has the higher activity. Either in system 1 or 2, $\bar{M}_w$ of PPSQ is low while it is prepared without addition of DCC. It seems to us that is due to the fact that DCC can react with H_2O produced in the process of condensation polymerization and thus raise the molecular weight of PPSQ^[12]. Shi and his coworkers had demonstrated that $\bar{M}_w$ of PPSQ synthesized using DCC as the only one catalyst is low. So, MgF_2 or CaF_2 is more important than DCC in the two systems.

(2). Reaction temperature From Fig. 1, it is easily noted that PPSQ with the highest $\bar{M}_w$ can be obtained at the lowest temperature (180°C) in the two systems. The possible reason is that high reaction temperature may cause the degradation of PPSQ. Because the solvents and H_2O are more easily evaporated at higher reaction temperature (250°C), the sum of $\bar{M}_w$ of PPSQ obtained at 250°C is larger than that at 210°C .

(3) Reaction time Fig. 2 shows that the appropriate reaction time (3hrs) to get PPSQ with the highest $\bar{M}_w$ in system 1 is shorter than that (5hrs) in system 2. So, the reaction time can be reduced by using CaF_2 as the main catalyst which has the high activity.

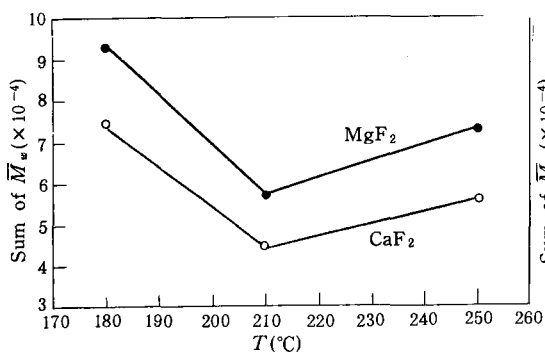


Fig. 1 Relation between the sum of $\bar{M}_w$ of PPSQ and reaction temperature

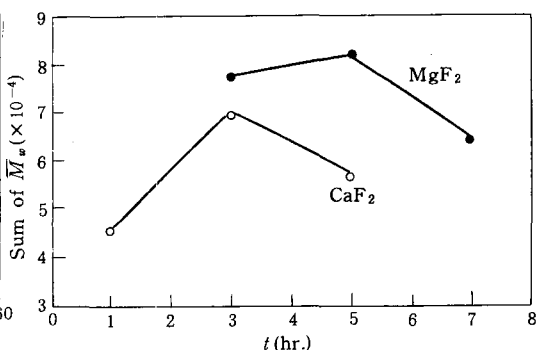


Fig. 2 Relation between the sum of $\bar{M}_w$ of PPSQ and reaction time

(4) Mixture of solvents To two systems, when the mixture of solvents is the second level (toluene 50ml and diphenol ether 5ml), PPSQ with high $\overline{M}_w$ can be synthesized. Boiling points of the two solvents are 110.6°C and 258°C which correspond with the progressively increased reaction temperature. Thus, mixture of solvents with different boiling points is very useful for obtaining PPSQ with high $\overline{M}_w$.

CONCLUSIONS

In the system using CaF_2 or MgF_2 as the main catalyst, the quantity of catalysts is the most important factor that affects the molecular weight of PPSQ and the reaction temperature is the second most important. Adding DCC can inhibit crosslinking and raise $\overline{M}_w$ of PPSQ. The reaction time and quantity of catalysts can be reduced by using CaF_2 as the main catalyst which has the higher activity. PPSQ with high $\overline{M}_w$ can be obtained at a low temperature (180°C) and in a suitable mixture of solvents.

Keywords:

Polyphenylsilsesquioxane; Polymerization conditions; Molecular weight

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