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Effect of crystallization conditions on single crystals of ladderlike polyphenylsilsesquioxane (PPSQ)

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Abstract

For the first time, formation of single crystals of ladderlike polyphenylsilsesquioxane (PPSQ) is found from three kinds of solution (benzene, toluene or *p*-xylene) at different temperatures (room temperature, 55, 65, 75, 80, 85 or 100°C) for some time (from 10 min to 257 h). Crystallization conditions, such as temperature, time and solvent, have a great effect on number, size and shapes of PPSQ single crystals. The black crystals with shapes of square or rectangle have been prepared from benzene solution at 55°C for not less than 51 h. The single crystals with the shape of a parallelogram, whose acute angles are 70 and 60°, have also been obtained from benzene solution, however, at 65 or 75°C, while those parallelogram-like single crystals with acute angles of 39 and 26° have been obtained from toluene or *p*-xylene solution at 75 or 80°C. When PPSQ was crystallized at room temperature (about 20°C) or as high as 85°C ($\geq$ 85°C), only small irregular crystals are observed. The largest parallelogram-like single crystal with the size of $200 \times 75\ \mu m^2$ was formed from toluene solution at 75°C for 199 h. The size or number of PPSQ single crystals increases with an increase in the crystallization time.

Keywords: Ladderlike polyphenylsilsesquioxane; Single crystals; Crystallization condition

1. Introduction

Polyphenylsilsesquioxane (PPSQ) is a kind of ladderlike polymer. Since the synthesis of PPSQ using KOH as the catalyst by Brown [1,2], Hata obtained this polymer by using alkaline-earth metals and their fluorides as catalysts [3]. We studied the effect of polymerization condition on molecular weight and ladderlike structure of PPSQ [4,5]. From X-ray diffraction data [1,2], repeating distance of PPSQ is 5.0 ± 0.5 Å and its mean interchain spacing is about 12.5 Å. This double chain structure renders PPSQ the characteristics of resisting decreases in molecular weight since it requires at least two cleavages in a single ring to result in a significant drop in molecular weight [6]. Hence, PPSQ has excellent thermal and oxidative stability. In addition, PPSQ has good electric insulating property, selective permeability to gases and excellent solubility in some mild solvents such as acetone, benzene, tetrahydrofaran and toluene etc. Therefore, in the past few years, much more attention has been paid to the application of PPSQ [7]. Until the present time, however, nobody has reported the crystallization behaviors of PPSQ.

For the first time we find that PPSQ can form some perfect single crystals by carefully choosing the crystallization conditions. In this paper, we study in detail the effect of crystallization conditions, including temperature, time and solvent, on number, size and shapes of PPSQ single crystals.

2. Experimental results and discussion

The weight-average molecular weight of PPSQ synthesized by us is 4.09×10^4 [4]. Its ^{29}Si NMR and IR spectra indicated that it had a correct chemical structure as expected [5] (shown in Fig. 1). At first, PPSQ was dissolved in benzene, toluene or *p*-xylene with 2–4% (w/w) concentration. Then, single crystals were prepared from the above solution at different temperatures, such as room temperature (about 20°C), 55, 65, 75, 80, 85 or 100°C, for enough time until all the solvent in the dilute solution vaporized. The morphology of the single crystals was measured by Nikon

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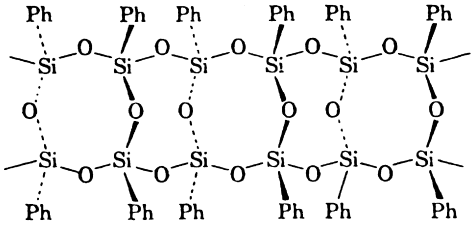

Fig. 1. PPSQ double chains.

Y2S Polarized Optical Microscope. X-ray diffraction photograph of one large PPSQ single crystal (not shown here) showed some diffraction spots and two rings. The diffraction spots were found to be related with the crystal inner structure while the two rings corresponded to the repeating distance and its mean interchain distance. These results indicated that the crystal was composed of PPSQ molecules.

Fig. 2 shows micrographs of PPSQ crystals prepared from benzene solution at room temperature (about 20°C), 55, 65 and 75°C. When crystallized at room temperature, a lot of small irregular PPSQ crystals (the largest one: $14 \times 7\ \mu m^2$) are observed (Fig. 2(a)). When crystallized at 55°C for 119 h, many regular black single crystals and much more bright small irregular crystals were formed (Fig. 2(b)). The regular crystals are so black under polarized optical microscope that they were difficult to be distinguished from the dim background. Hence, non-polarized optical micrograph of these crystals is given in Fig. 2(c). It is easily noted that the shapes of the regular black crystals are square or rectangle and the size of the largest crystal is about $50 \times 39\ \mu m^2$. As PPSQ was crystallized at 65 and 75°C, some single crystals with the shape of a parallelogram (the largest one: $65 \times 60\ \mu m^2$) are observed (Fig. 2(d)–(f)). Acute angles of the parallelograms are different, some are 70°, and the others are about 60°. Fig. 3 represents the polarized optical micrographs of the single crystals obtained from toluene solution at 75, 80, 85 and 100°C. These regular single crystals from toluene solution (Fig. 3(a)–(d)) also look like parallelogram and are similar with those crystals from the benzene solution (Fig. 2(d)–(f)). However, the acute angles of the parallelogram are about 39° (shown in Fig. 3(a)–(c)) and 26° (shown in Fig. 3(a), (b) and (d)) and are smaller than those from benzene solution. The largest single crystal with a size of $200 \times 75\ \mu m^2$ (in Fig. 3(b)) was prepared from toluene solution at 75°C for 199 h. When PPSQ was crystallized at 85 or 100°C, only few small irregular crystals are observed (Fig. 3(e)–(f)). Micrographs of PPSQ single crystals, which have been formed from *p*-xylene solution at 75 and 100°C are shown in Fig. 4. The morphology of the single crystals seemed to be unclear and their shapes are parallelogram with an acute angle of 39° (Fig. 4(a) and (b)). The size of the largest PPSQ single crystals is about $89 \times 33\ \mu m^2$ (shown in Fig. 4(b)) and is smaller than that of the largest crystal prepared from toluene solution. When the crystals were prepared at 100°C, only few irregular PPSQ crystals are observed (Fig.4(c)). From the above discussion, PPSQ single crystals with different shapes have been formed from three kinds of solution. The

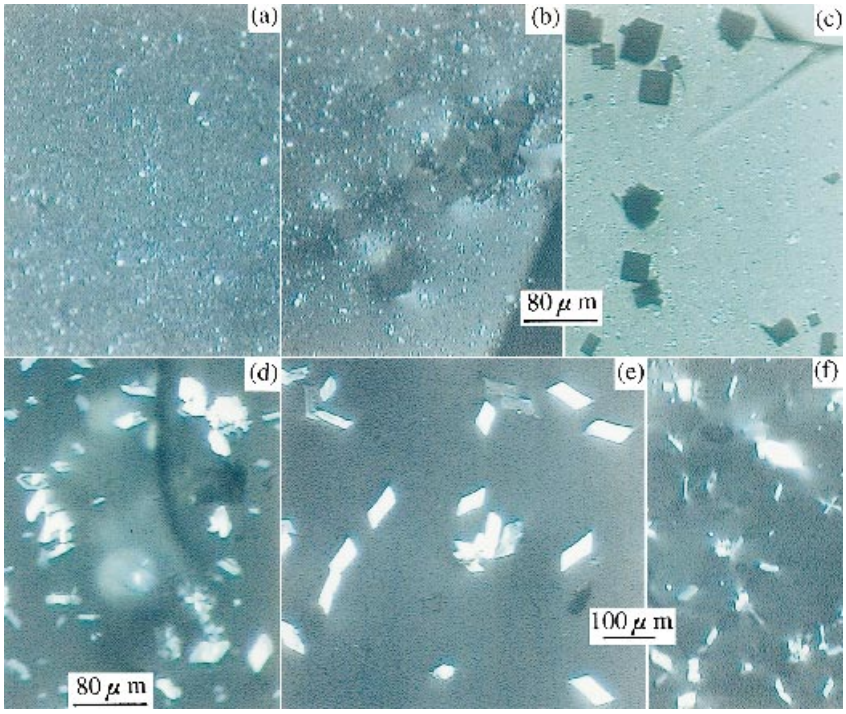

Fig. 2. Micrographs of PPSQ single crystals from benzene solution (1) RT/58 h ((a) 180×), (2) 55°C/119 h ((b) 180× and (c) 180×), (3) 65°C/40 h ((d) 180×), (4) 75°C/28 h ((e) 100×) and (5) 75°C/39 h ((f) 100×), in which (c) is non-polarized optical micrograph.

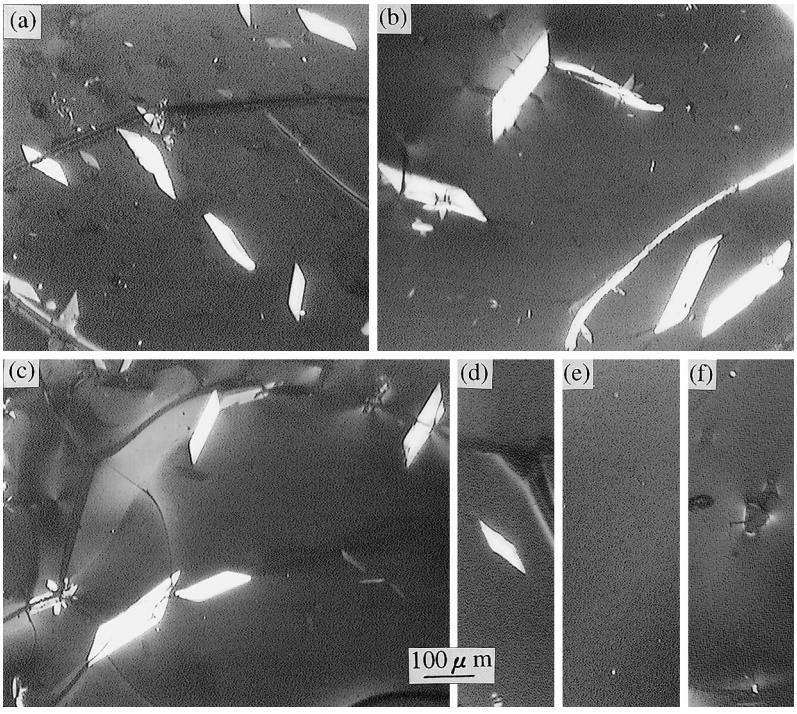

Fig. 3. Polarized optical micrographs of PPSQ single crystals prepared from toluene solution (1) 75°C/105 h ((a) 100 ×), (2) 75°C/199 h ((b) 100 ×), (3) 75°C/207 h ((c) 100 ×), (4) 80°C/89 h ((d) 100 ×), (5) 85°C/44 h ((e) 100 ×) and (6) 100°C/30 h ((f) 100 ×).

PPSQ single crystals with shapes of square, rectangle or parallelogram (acute angles: 70 and 60°) have been obtained from benzene solution. Those PPSQ single crystals with shapes of parallelogram (acute angles: 39 and 26°) have been obtained from toluene or *p*-xylene solution and the largest PPSQ single crystal was formed from toluene solution at 75°C.

All the data about PPSQ crystals prepared at different temperatures for different time from three kinds of solution are summed up in Table 1. When crystallized at room temperature (about 20°C) or higher than 85°C, only some small irregular crystals were formed. This result means that the regular single crystals are difficult to form if crystallization temperature is too low or too high. Regular single crystals with different shapes were formed at 55, 65, 75 or 80°C. The black single crystals with shapes of square or rectangle were obtained from benzene solution at 55°C for not less than 51 h. These parallelogram-like PPSQ single crystals with acute angles of 70 or 60° have been prepared at 65 or 75°C from benzene solution while those parallelogram single crystals with acute angles of 39 or 26° have been obtained from toluene or *p*-xylene solution at 75 or 80°C. Both number and size of the crystals increase with an increase in the crystallization time when crystallization temperature is room temperature or 55°C. As PPSQ crystallized at 65 or 75°C from the same solution, size or number of PPSQ single crystals increases with an increase in the crystallization time. When crystallization temperature is about 80, 85 or 100°C, crystallization time has little influence on the number or size of the PPSQ crystals.

In conclusion, PPSQ single crystals with different shapes and sizes have been prepared from its three kinds of solution for the first time. Crystallization conditions, such as temperature, time and solvent have a great effect on the number, size and shape of the PPSQ crystals. Only some small irregular crystals were obtained at room temperature

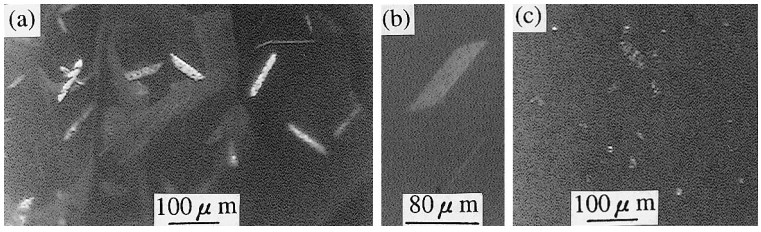

Fig. 4. Polarized optical micrographs of PPSQ single crystals prepared from *p*-xylene solution (1) 75°C/257 h ((a) 100 × and (b) 180 ×) and (2) 100°C/89 h ((c) 100 ×).

Table 1
Shapes, size and number of PPSQ crystals

Temperature (°C)	Solvent	Time (h)	Main shapes of crystals[a]	Size of largest crystal (μm^2)	Number of crystals[a]
20	Benzene	0.17	Irregular	8 × 6	A few
20	Benzene	22	Irregular	11 × 7	Some
20	Benzene	58	Irregular	14 × 7	Many
55	Benzene	35	Irregular	11 × 8	Some
55	Benzene	51	Irregular, ①	27 × 27	Many
55	Benzene	93	Irregular, ①	28 × 47	Many
55	Benzene	119	①, Irregular	50 × 39	Many
65	Benzene	19	②, ③	33 × 12	Many
65	Benzene	40	②, ③	39 × 30	Some
75	Benzene	6	②, ③	25 × 10	A few
75	Benzene	24	②, ③	50 × 25	Many
75	Benzene	28	②, ③	75 × 45	Some
75	Benzene	39	②, ③	65 × 60	Many
75	Toluene	55	④	90 × 65	Few
75	Toluene	79	④	140 × 60	Some
75	Toluene	105	④, ⑤	100 × 50	Some
75	Toluene	167	④, ⑤	120 × 75	Many
75	Toluene	199	④, ⑤	200 × 75	A few
75	Toluene	207	④	170 × 80	A few
75	*p*-xylene	257	④	89 × 33	Some
80	Toluene	89	⑤	80 × 60	Few
85	Toluene	44	Irregular	5 × 5	Few
100	Toluene	30	Irregular	20 × 10	Few
100	*p*-xylene	60	Irregular	5 × 5	Few
100	*p*-xylene	89	Irregular	5 × 5	Few

[a] Number of PPSQ crystals is few < a few < some < many. Shape 1 is square or rectangle and shapes 2–5 are parallelograms with acute angles of 70, 60, 39 and 26°.

or at temperatures higher than 85°C. Regular single crystals with shapes of square, rectangle and parallelogram (acute angle: 70 and 60°) have been prepared from benzene solution at 55, 65 or 75°C, while those parallelogram-like single crystals with acute angles of 39 and 26° have been got from toluene or *p*-xylene solution at 75 or 80°C. The largest PPSQ single crystal was formed from toluene solution at 75°C for 199 h. The size or the number of crystals increases with an increase in the crystallization time.

References

[1] Brown Jr JF. J Am Chem Soc 1960;82:6194.
[2] Brown Jr JF. J Polym Sci, Part C 1963;1:83.
[3] Hata, Japan Patent (A) 59–129 230, 1984.
[4] Li GZ, Ye ML, Shi LH. Chin J Polym Sci 1994;12(4):331.
[5] Li GZ, Shi LH, Ye ML. Chin J Polym Sci 1996;14(1):41.
[6] Critchley JP, Knight GJ, Wright WW. Heat resistant polymers, technologically, useful materials, New York: Plenum Press, 1983. pp. 425.
[7] Baney RH, Itoh M, Sakakibara A, Suzuki T. Chem Rev 1995;95:1409.