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Crystallization of ladderlike polyphenylsilsesquioxane (PPSQ)/isotactic polystyrene (i-PS) blends

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Abstract

The crystals of polyphenylsilsesquioxane (PPSQ) and isotactic polystyrene (i-PS) blends prepared from their toluene solutions had been studied by optical polarized microscope and DSC. Some big bright regular parallelogram-like single crystals from PPSQ with coarse surface are observed (PPSQ $\geq$ 90%) and no regular crystals could be formed (PPSQ $\leq$ 70%), however, at PPSQ $\leq$ 10%, this blend formed irregular continuous crystals from i-PS similar with pure i-PS. Crystallinity of rich-i-PS phase in the blend is higher than the corresponding percent of i-PS (i-PS $\geq$ 30%) while its crystallinity is less than the percent of i-PS (i-PS $\leq$ 10%). Effect of miscibility and solvent on their crystallization has also been discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: PPSQ/i-PS blend; Crystallization; Morphology of crystals

1. Introduction

Polyphenylsilsesquioxane (PPSQ), one kind of ladderlike polymers, is composed of two Si–O main chains bridged by oxygen. This polymer contains phenylsilsesquioxane (i.e. phenyl-T or $C_6H_5O_{1.5}$) units joined together to form syndio-tactic chains while maintaining tetrahedral bond angles on the silicones and the preferred bond angles of ca. 155° on the oxygen [1].

Because of its double chains, PPSQ has outstanding thermal and oxidative stability. In addition, PPSQ has good electric insulating property, selective permeability to gases and good solubility in many mild solvents. Therefore, in the past few years, much attention has been paid to application of PPSQ [2].

Because PPSQ has many good properties, we had studied a few binary blends of PPSQ with other linear polymers or copolymers, such as PPSQ/PET [3], PPSQ/PS [4–6], PPSQ/P(MMA-*co*-MAA) [7] and PPSQ/PVC [8]. Especially, we had investigated the miscibility of PPSQ/PS blend prepared by solution casting and in situ polymerization. PPSQ and PS in their casting film are miscible on several thousand nanometers while PPSQ and PS in their in situ blend are partially miscible. Besides these researches, we had found that PPSQ could form perfect regular single crystals at the special crystallization conditions [9,10]. So, in this paper, we study the crystallization of ladderlike PPSQ/isotactic PS blend.

2. Experimental

PPSQ with weight-average molecular weight of 4.09×10^4 had been synthesized by ourselves [11,12]. PS (90% isotactic, $M_w = 4 \times 10^5$, specific gravity = 1.047) was purchased from Scientific Polymer Products, USA. PPSQ and i-PS with a series of compositions, including 100/0, 99/1, 97/3, 95/5, 93/7, 90/10, 70/30, 50/50, 30/70, 10/90, 5/95 and 0/100, had been dissolved in toluene, respectively, and their all solutions are transparent. PPSQ/i-PS blend films had been prepared at 75°C as all solvent vaporized slowly. Morphology of these blends was observed by Nikon Y2S polarized optical microscope. Their melting behaviors were studied by Rigaku DSC8230 at a rate of 10°C/min from room temperature to 260°C.

3. Results and discussion

3.1. Morphology of PPSQ/i-PS blend crystals

Polarized optical micrographs of PPSQ/i-PS blend

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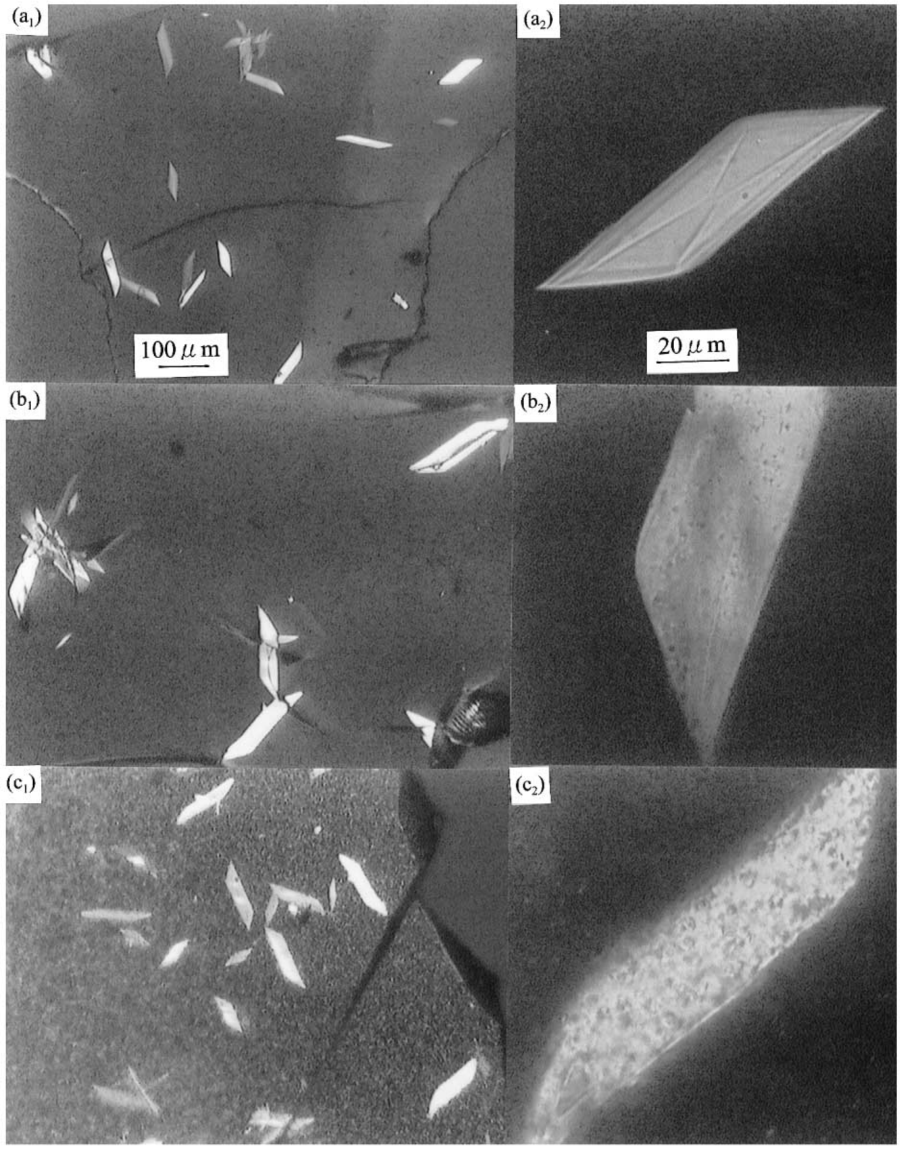

Fig. 1. Polarized optical micrographs of PPSQ/i-PS blend (1) 100/0 ((a_1) × 100 and (a_2) × 720), (2) 99/1 ((b_1) × 100 and (b_2) × 720) and (3) 97/3 ((c_1) × 100 and (c_2) × 720).

crystals at a series of compositions prepared from toluene solution at 75°C for a few days are shown in Figs. 1–4, respectively. From Fig. 1(a_1), several big bright PPSQ single crystals with shape of parallelogram are observed and the largest crystal is about 90 μm × 30 μm. From the micrograph at high magnification times, the surface of PPSQ single crystal seems to be smooth and two diagonal lines across the center divide the parallelogram into four triangles (Fig. 1(a_2)). However, as PPSQ blend with i-PS, there is much difference on their morphology. When the composition of PPSQ/i-PS is 99/1, although Fig. 1(b_1) shows a few regular PPSQ single crystals (the largest one: 150 μm × 60 μm), Fig. 1(b_2) shows some dim dots on the surface of PPSQ regular single crystal for the irregular i-PS crystals were formed on its surface and as a result its surface became coarse. As the percentage of i-PS is up to 3%, many small irregular bright crystals are observed on the blend except of some regular PPSQ single crystals with size of about 120 μm × 50 μm (Fig. 1(c_1)), in which many irregular crystals were formed on the whole surface of PPSQ regular crystals and its surface seemed to be more coarse (Fig. 1(c_2)).

When the composition of PPSQ/i-PS blend is 95/5, a lot of big and much bright irregular crystals are observed except of several small parallelogram-like PPSQ single crystals with size of about 60 μm × 30 μm (Fig. 2(a_1)) and some dots aggregated and formed bigger irregular crystals on the surface of regular crystals (Fig. 2(a_2)) and the regular single crystals look much more coarse. The morphology of PPSQ/i-PS blend 97/3 with the regular crystal of about 70 μm × 60 μm (Fig. 2(b_1) and (b_2)) is similar with PPSQ/i-PS 95/5. As the percentage of i-PS increases to

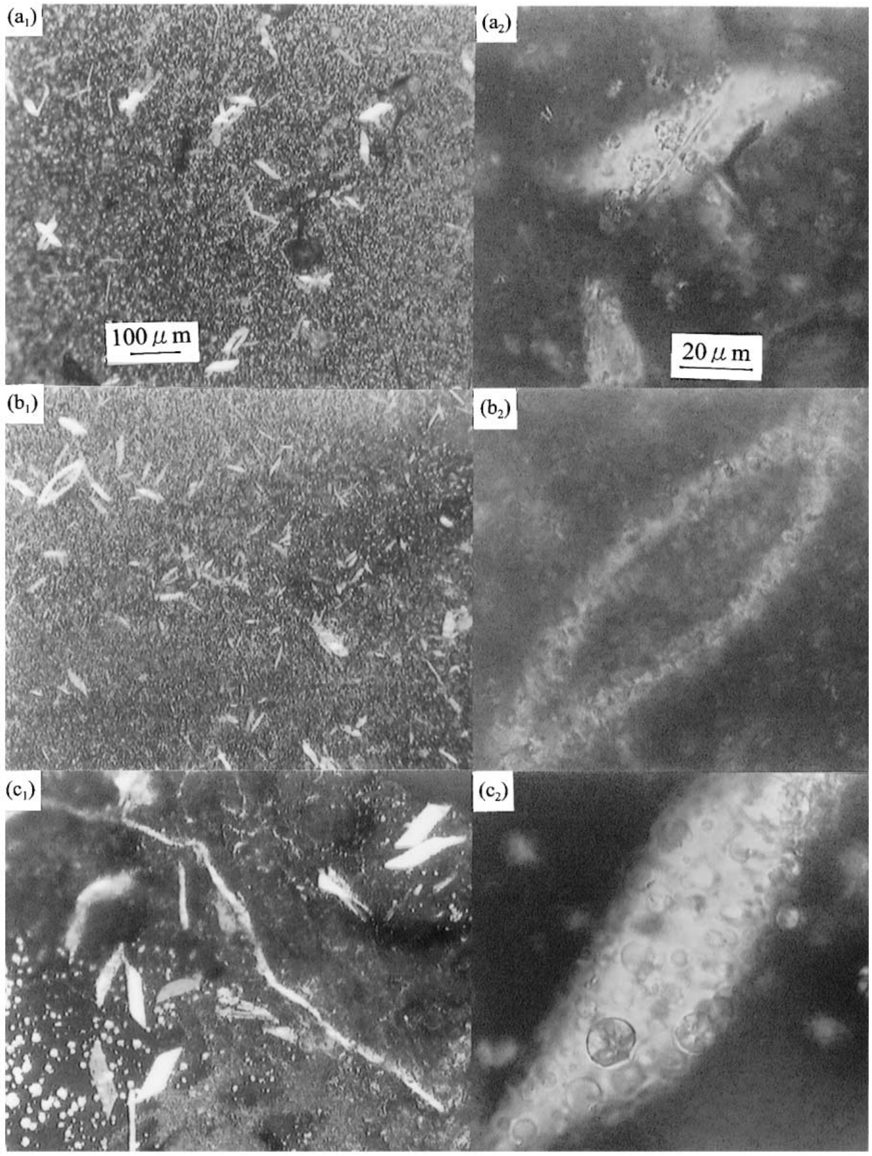

Fig. 2. Polarized optical micrographs of PPSQ/i-PS blend (1) 95/5 ((a_1) ×100 and (a_2) ×720), (2) 93/7 ((b_1) ×100 and (b_2) ×720) and (3) 90/10 ((c_1) ×100 and (c_2) ×720).

10%, some big bright irregular crystals are dispersed in the whole film (Fig. 2(c_1)) and the sphere crystals were formed on the surface or side of the regular PPSQ single crystals (Fig. 2(c_2)). From above discussion, it is clear that the inclusion of a small amount of i-PS in the blend induces the coarse surface of regular single crystals from PPSQ and this coarseness increases with the percentage of i-PS. Because the blend crystals were formed in their toluene solution, we should take into account the effect of solvent toluene on the crystallization of PPSQ and i-PS. As the blend contains much PPSQ (≥90%), the concentration of PPSQ in the blend solution is much higher than i-PS. In this case, the regular single crystals of PPSQ could be formed earlier than formation of i-PS irregular crystals. That means some i-PS irregular crystals could be formed on the surface of PPSQ regular crystals and this may be the reason why the regular single crystals in the blend have coarse surface. More and more irregular crystals from i-PS could be formed with an increase of i-PS content. As a result, some irregular crystals could aggregate and form bigger crystal and some sphere i-PS crystals could also be formed in PPSQ/i-PS 90/10. In other words, some parallelogram-like PPSQ single crystals with coarse surface in the blend film could be formed as if it contains much PPSQ (≥90%).

As the composition of PPSQ/i-PS blend is 70/30, no any regular PPSQ single crystal is observed and only some big irregular bright crystals are dispersed unevenly on the whole film and some area looks black (Fig. 3(a_1)). From the micrograph with high magnification times (Fig. 3(a_2)), the big irregular crystals were formed by aggregating of many small crystals. As the composition is 50/50, only a few bright irregular crystals were formed on some area and the

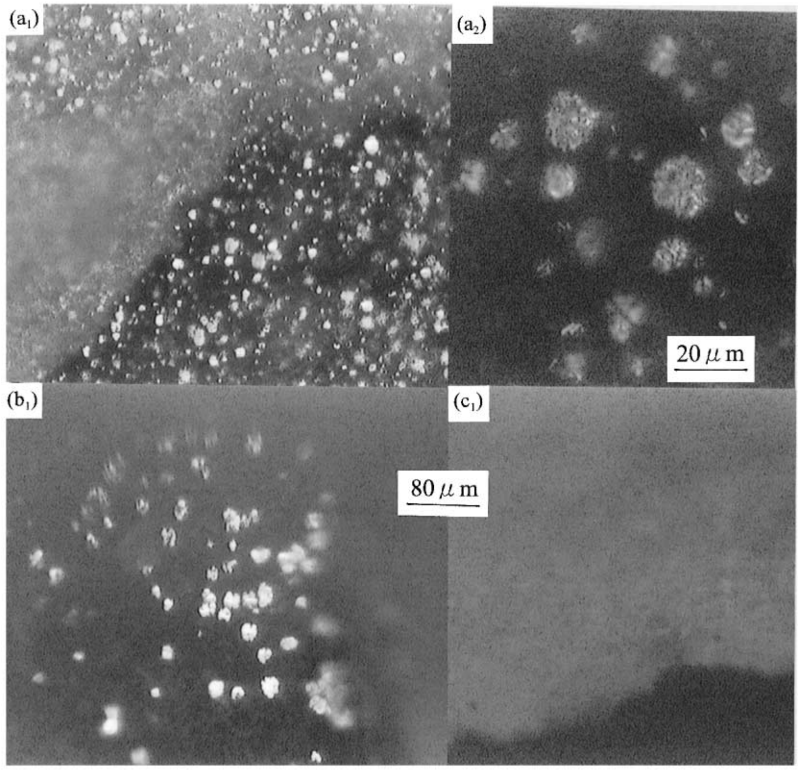

Fig. 3. Polarized optical micrographs of PPSQ/i-PS blend (1) 70/30 ((a_1) × 180 and (a_2) × 720), (2) 50/50 ((b_1) × 180) and (3) 30/70 ((c_1) × 180).

other area looks black (Fig. 3(b_1)). From Fig. 3(c_1) of PPSQ/i-PS 30/70, no any bright crystals could be observed. Because PPSQ and PS are partially miscible and there are some entanglements among molecules of PPSQ and i-PS, it is very difficult to form any regular PPSQ crystals as the percentage of PPSQ in the blend decreases to 70%. The irregular crystals shown in Fig. 3(a_1) and (b_1) are different from the i-PS irregular crystals in Figs. 1 and 2 (i-PS < 10%) and also different from the pure i-PS crystals (Fig. 4(d_1) and (d_2)) and their number decreases with a decrease of PPSQ content. So, it can de deduced that the bright irregular crystals in Fig. 3 should be formed from PPSQ molecules. The crystallization ability of PPSQ decreases quickly with an increase of i-PS content while i-PS is much more easily crystallized in the blend solution even if its percentage is 1% (shown in Fig. 1(b_2)). Therefore, as the percentage of PPSQ decreases to 70%, no any regular single crystals could be formed and only some irregular crystals from PPSQ with big size were formed. On the other hand, i-PS crystals may be formed before the formation of PPSQ irregular crystal as the percent of i-PS is up to 30% (PPSQ 70%) because i-PS is more easily crystallized from toluene solution than PPSQ. Therefore, we can observe some bright irregular crystals from PPSQ in Fig. 3(a_1) and (b_1). Because the concentration of PPSQ is quite high and a lot of PPSQ irregular crystals were formed, some of its irregular crystals could aggregate and form big crystals. In contrast to the i-PS irregular crystals, PPSQ irregular crystals are unevenly dispersed in the whole film. Due to the much decrease of PPSQ crystallization, only some PPSQ irregular crystals were formed in some area and amorphous phase of PPSQ were formed on the other area when the composition of PPSQ/i-PS is 50/50. As the percentage of PPSQ decreases to 30%, neither regular nor irregular crystals could be formed from PPSQ. Because i-PS irregular crystals could be formed first at this composition, some amorphous PPSQ phase was formed late and covered the i-PS crystals. Due to this coverage, we could not observe any bright crystals in PPSQ/i-PS 30/70 (Fig. 3(c_1)).

As the percent of PPSQ in this blend reduce further to 10%, only some area show continuous bright crystal and most area look dim (Fig. 4(a_1)) due to partial coverage of PPSQ amorphous phase. As the composition of PPSQ/i-PS blend is 5/95, there is a continuous bright phase in the whole film (Fig. 4(b_1)). When the percentage of i-PS increases to 99% (Fig. 4(c_1) and (c_2)), the same morphology as PPSQ/i-PS 95/5 is observed. These results are similar with the pure i-PS (Fig. 4(d_1) and (d_2)). No any regular single crystals could be formed in the pure i-PS film. Therefore, if the percentage of i-PS is more than 90%, the continuous bright irregular crystal from i-PS could be formed.

From above discussion, the change on bimodal morphology of PPSQ/i-PS blend crystals depends on their compositions. When the blend contains much PPSQ (≥90%), some regular parallelogram-like single crystals from PPSQ could be formed before the formation of i-PS irregular crystals and as a result these regular single crystals have coarse surface.

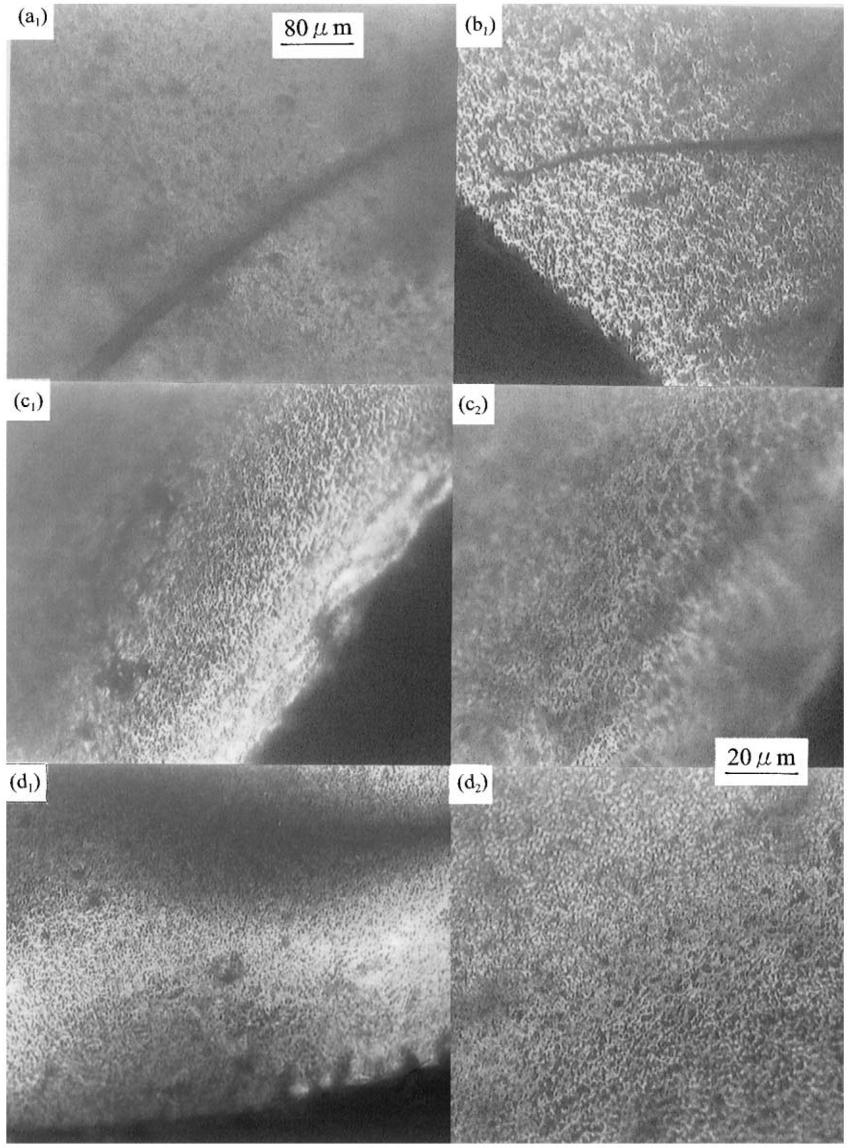

Fig. 4. Polarized optical micrographs of PPSQ/i-PS blend (1) 10/90 ((a_1) × 180), (2) 5/95 ((b_1) × 180), (3) 1/99 ((c_1) × 180 and (c_2) × 720) and (4) 0/100 ((d_1) × 180 and (d_2) × 720).

As the blend contains much i-PS (≥90%), one continuous bright irregular crystal similar with pure i-PS is observed. As if compositions of PPSQ/i-PS blend vary from 70/30 to 50/50, only some bright irregular crystals could be obtained from PPSQ while some area looks black. Due to the coverage of PPSQ amorphous phase on the surface of i-PS crystals, no any bright crystals could be observed in PPSQ/i-PS 30/70. Therefore, there are much inter-influence on the morphology of PPSQ/i-PS blend crystals due to the miscibility between PPSQ and i-PS and the effect of solvent. So, the morphology of PPSQ/i-PS blend crystals is determined by their compositions.

3.2. Crystallinity of PPSQ/i-PS blends

Crystallinity of PPSQ/i-PS blends was characterized by DSC. Some DSC curves of PPSQ/i-PS blends are given in Figs. 5 and 6, respectively. A wide endothermic peak with two tops from 150 to 250°C is shown on the DSC curve of pure i-PS (PPSQ/i-PS, 0/100), but there is almost no peak in the whole measured temperature range for PPSQ (PPSQ/i-PS, 100/0). As the percentage of i-PS in the blend is more than 30%, each DSC curve of PPSQ/i-PS at a series of compositions (Figs. 5 and 6) exhibits a wide endothermic peak, which should be attributed to the crystals mainly composed of i-PS molecules. Although no bright crystals are observed from the polarized optical micrograph of PPSQ/i-PS 30/70, there is a distinct endothermic peak on its DSC curves (Fig. 6). So, some crystals had been formed in this sample. This result also indicates that we could not observe any bright crystals in PPSQ/i-PS 30/70 because the crystals of i-PS were covered by amorphous PPSQ phase.

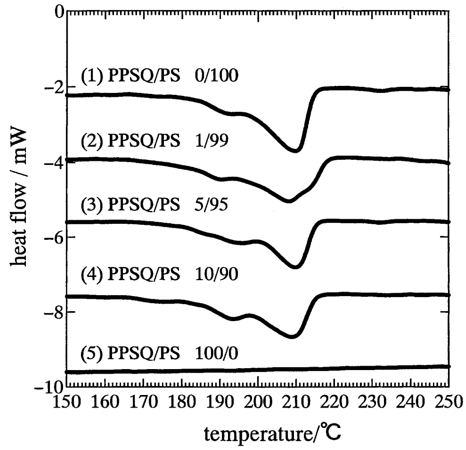

Fig. 5. DSC curves of PPSQ/i-PS blend (1) 0/100, (2) 1/99, (3) 5/95, (4) 10/90 and (5) 100/0.

Some information of PPSQ/i-PS blend crystals obtained from DSC curves is summed up in Table 1.

In Table 1, because the ΔH for endothermic peak is proportional to the crystallinity and the endothermic peak from 154 to 223°C is mainly determined by rich-i-PS phase, ΔH (blend)/ΔH (i-PS) can be used to characterize roughly the crystallinity of rich-i-PS phase in the PPSQ/i-PS blends. When the percentage of i-PS is less than 10% (≤10%), the crystallinities of PPSQ/i-PS, 97/3, 95/5, 93/7 and 90/10 are less than the corresponded percent of i-PS, 3, 5, 7 and 10%. That means i-PS molecules that are dispersed well in the continuous PPSQ is more difficult to be crystallized than pure i-PS. However, as the percentage of i-PS is more than 30% (≥30%), the crystallinities of rich-i-PS phase in the PPSQ/i-PS blends, such as 70/30, 50/50,30/70, 5/95 and 1/99, are higher than the corresponding percent of i-PS except of PPSQ/i-PS 10/90. This result indicates the existence of PPSQ molecules enhance the crystallization of i-PS and lead to high crystallinity of rich-i-PS phase. As the PPSQ/i-PS blends contain much i-PS (≥30%), the

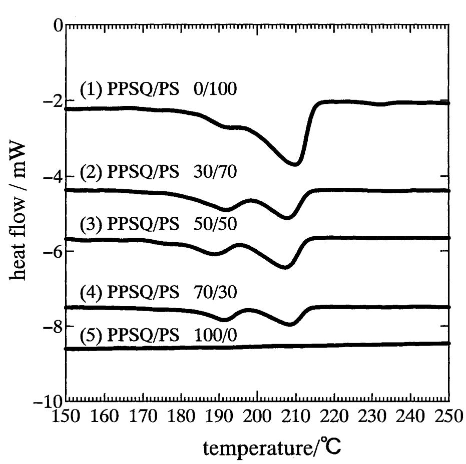

Fig. 6. DSC curves of PPSQ/i-PS blend (1) 0/100, (2) 30/70, (3) 50/50, (4) 70/30 and (5) 100/0.

Table 1
Some information of PPSQ/i-PS blend crystals obtained from DSC curves

Compositions of PPSQ/i-PS	ΔH (J/g)	ΔH (blend)/ΔH (i-PS) (%)
0/100	25.433	100.0
1/99	28.128	110.6
5/95	25.704	101.0
10/90	22.626	89.0
30/70	19.669	77.3
50/50	14.826	58.3
70/30	9.318	36.6
90/10	1.471	5.8
93/7	1.297	5.1
95/5	1.039	4.1
97/3	0.573	2.3
99/1	–	–
100/0	–	–

endothermic peaks' positions of the blends are quite similar with that of pure i-PS. From above discussion, PPSQ has much effect on the crystallinity of rich-i-PS phase in this blend.

Because it is very difficult for DSC to characterize the melting behavior of regular PPSQ single in the blend (PPSQ ≥ 90%), we used polarized optical microscopy to study the melting behavior of PPSQ/i-PS 95/5. The blend film on quartz substrate was heated from 20 to 260°C at a rate of 5°C/min. All bright irregular crystals had been melted from 185 to 220°C. However, even if the temperature increases to 260°C, some regular big crystals from PPSQ have little change. Therefore, the regular PPSQ single crystals can withstand much higher temperature than i-PS crystals.

4. Conclusions

Bimodal morphology of crystals in PPSQ/i-PS blends depends on their compositions due to their miscibility and the effect of solvent. When the blend contains much PPSQ (≥90%), some big regular parallelogram-like single crystals from PPSQ with coarse surface due to the formation of some irregular crystals on their surface from i-PS. As the blend contains much i-PS (≥90%), the morphology of their crystals is similar with that of pure i-PS, exhibiting continuous bright irregular crystal. When the compositions of PPSQ/i-PS are 70/30 and 50/50, no any regular single crystals were obtained and only some irregular crystals from PPSQ were formed and some area looks black. Due to the coverage of PPSQ amorphous phase on the surface of i-PS crystals, no any bright crystals are observed in PPSQ/i-PS 30/70. By DSC, crystallinity of rich-i-PS phase in the blend could be characterized roughly. Due to the miscibility between PPSQ and i-PS, the crystallinity of rich-i-PS phase in this blend is higher than the corresponding percent of i-PS if the percentage of i-PS is more than 30% (≥30%) while their crystallinity is less than the percent of i-PS (i-PS ≤ 10%). The regular PPSQ single crystals can withstand much higher temperature than i-PS crystals. Because there are some entanglement of PPSQ and i-PS molecules and some effect of solvent on crystallization of each component, both morphology and crystallinity of PPSQ/i-PS blends are determined by their compositions.

References

[1] Brown Jr JF, Vogt Jr LH, Katchman Jr A, Eustance JW. J Am Chem Soc 1960;82:6194.
[2] Banney RH, Itoh M, Sakakibara A, Suzuki T. Chem Rev 1995;95:1409.
[3] Li GZ, Shi LH, Ye ML. Chin J Polym Sci 1995;13(4):366.
[4] Li GZ, Jin Y, Shi LH, Ye ML. J Polym Sci, Part B: Polym Phys 1996;34:1079.
[5] Li GZ, Ye ML, Shi LH. J Appl Polym Sci 1996;60:1163.
[6] Li GZ, Shi LH, Ye ML, Yu WZ. Mater Sci Forum 1995;175–178:439.
[7] Li GZ, Ye ML, Shi LH. Gao Fen Zi Xue Bao 1998;2:160.
[8] Li GZ, Zhou CG. You Ji Gui Cai Liao Ji Ying Yong 1997;3:1.
[9] Li GZ, Yamamoto T, Nozaki K, Hikosaka M. Polymer 2000;41(8):2827.
[10] Li GZ, Yamamoto T, Nozaki K, Hikosaka M. Macromol Chem Phys 2000;201:1283.
[11] Li GZ, Ye ML, Shi LH. Chin J Polym Sci 1994;12(4):331.
[12] Li GZ, Ye ML, Shi LH. Chin J Polym Sci 1996;14(1):41.