

# Flower type microgels: 1. Synthesis of the microgels

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Poly(2-vinyl pyridine-*b*-styrene-*b*-2-vinyl pyridine) BAB type block copolymers were synthesized by anionic living polymerization. The micelle formation of these BAB type triblock copolymers was carried out in toluene and toluene/cyclohexane mixture, and estimated with dynamic light scattering for the polymer solutions. Poly(2-vinyl pyridine) sequences in core part of the polymer micelles of the BAB type block copolymers were crosslinked with 1,4-diiodobutane. Upon crosslinking, no macrogelation was observed and the poly(2-vinyl pyridine) core–polystyrene shell type spherical microgels were synthesized. Copyright © 1996 Elsevier Science Ltd.

(Keywords: flower micelle; microgels; BAB block copolymer)

## INTRODUCTION

It is well known that block and graft copolymers with incompatible sequences form the microphase separation structures in solid state and in solution. When the volume fraction of microdomains of B sequence of AB diblock copolymer is less than 30 vol% in the polymer volume, A sequences form a spherical domain<sup>1</sup>. Upon crosslinking, the spherical domain chemically, B core–A shell type polymer microgels can be obtained. Based on this concept, we have synthesized the core–shell type polymer microgels from AB type block copolymers and graft copolymers in solution<sup>2–4</sup> and in the solid state<sup>5–8</sup>.

The diameter distribution of those core–shell type polymer microgels was narrow. The packing structure of these microgels was face-centered cubic (fcc), instead of body-centered cubic (bcc) for original AB diblock copolymers<sup>9,10</sup>. It was also found that the novel ordered micro-separated structures, for example the honeycomb structure, appeared by blending the microgels with other AB type diblock copolymers<sup>11,12</sup>. These microgels can be used as carriers of silver nano-clusters in the good solvents for shell sequences<sup>13–15</sup>. For all the above cases, the one end of shell sequence was attached to core and another end was free in the solvent, because AB diblock copolymers were used as the original materials for the microgels.

BAB block copolymers also form micelles in the selective solvent which is good for A and not for B sequences<sup>16–21</sup>. In such a system, three types of micelles shown in *Figure 1* are formed<sup>21</sup>. Among them, the flower type micelles, whose shells form a loop structure (*Figure 1a*), show the interesting properties such as low viscosity at high polymer concentration, low entanglement, etc. By fixing the structure of flower micelle upon crosslinking, the flower microgels will be obtained.

*Figure 2* shows the schematic synthetic process for flower microgels. First, flower micelles are formed with a BAB type triblock copolymer in the selective solvent which is good for the A sequence and non for B sequence. Then, in order to fix the flower micelle structure, the B core part is crosslinked in the solvent. However, the bridging between flowers (*Figure 1b*) will result in the macrogelation of the system by crosslinking. The main purpose of this paper is to hinder the macrogelation of the system and synthesize the flower microgels by crosslinking the core part of the flower micelles in the solvents.

Based on this consideration, poly(2-vinyl pyridine-*b*-styrene-2-vinyl pyridine) [P(2VP-*b*-S-*b*-2VP)] triblock copolymer was synthesized by anionic living polymerization with sodium  $\alpha$ -methyl styrene tetramer as an initiator. For forming the flower micelles, toluene and toluene/cyclohexane mixture are chosen as the selective solvent for the block copolymer. For crosslinking of the P2VP sequences, 1,4-diiodobutane was used. Micelle and microgel formation were investigated by viscosity measurement and dynamic light scattering.

## EXPERIMENTAL

### Synthesis of block copolymers

P(2VP-*b*-S-*b*-2VP) triblock copolymers were synthesized by an anionic living polymerization<sup>22</sup> with ( $\alpha$ -methyl styrene)<sub>4</sub>Na<sub>2</sub> anion as an initiator in THF at –78°C. Number-average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of the precursor polystyrene were measured with a Tosoh H-8020 g.p.c. with THF as an eluent at 38°C, a TSK-gel GMHXL column and a flow rate of 1.0 ml min<sup>-1</sup>. Poly(2-vinyl pyridine) contents of the block copolymers were determined with FTi.r. (Shimazu, FTIR-8500) using

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the peaks at 1500 and 1470  $\text{cm}^{-1}$  due to the styryl and the pyridyl group, respectively. The  $M_n$  of block copolymer was obtained by combining the  $M_n$  of the precursor polystyrene and P2VP content.

*Micelle formation of the block copolymers*

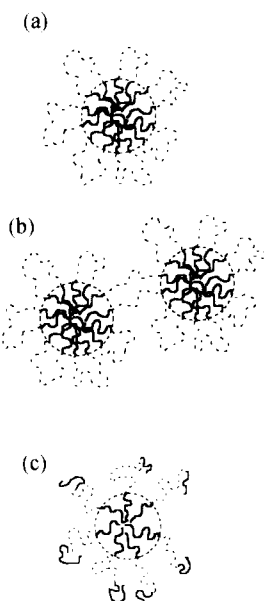
VSV-1 and VSV-2 block copolymers were dissolved in toluene at 1 and 2.5 wt% polymer concentration, respectively. Then, VSV-2 solution was diluted with cyclohexane until the polymer concentration was 1 wt%. Block copolymer solutions were heated to 60°C for 2 h and cooled down gradually till 25°C.

*Crosslinking of the core part of micelles*

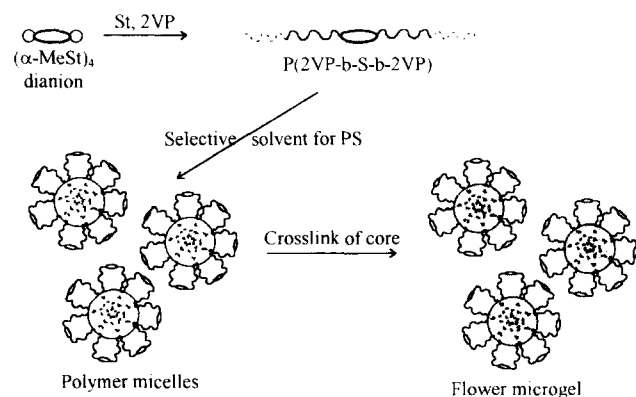
10 mol% 1,4-diiodobutane for pyridyl group was added to the micelle solution. The crosslinking of P2VP was carried out with 1,4-diiodobutane for 48 h at 25°C.

*Dynamic light scattering*

The diameter and distribution of the micelle and microgel were measured with DLS (Photal, DLS-7000) for solutions of  $c = 0.005\text{--}2.5$  wt% at an angle of 90°.



**Figure 1** The micelle structures of the triblock copolymers: (a) flower type; (b) bridged flowers; (c) dangling type



**Figure 2** The schematic synthetic process of the flower microgels

*Morphological observation by transmission electron microscopy (TEM)*

The crosslinked produces solution was cast on a copper microgrid covered with carbon substrate. The solvent was evaporated quickly without heating. The sample specimen was stained with methyl iodide gas overnight at room temperature. The inner texture of the crosslinked products was observed with a transmission electron microscope (Hitachi, H-500) with 75 kV.

**RESULTS AND DISCUSSION**

*Block copolymers and their micelle formation*

The characteristics of the block copolymers are given in Table 1. Since the molecular weights of both block copolymers were much larger than the  $\alpha$ -methyl styrene tetramer, the influence of the  $\alpha$ -methyl styrene sequence in the block copolymers was neglected.

In order to form flower polymer micelles, the block copolymers were dissolved into the selective solvents which were good for PS and not for P2VP. Toluene is good solvent for PS and non for P2VP. The toluene solution of VSV-1 showed a bluish tint above 0.5% polymer concentration. Balsara *et al.*<sup>21</sup> and Tang *et al.*<sup>20</sup> reported the micellization of P(2VP-*b*-S-*b*-2VP) triblock copolymer in toluene. Therefore, the presence of large aggregates of the VSV1 was expected in these solutions. When the polymer concentration of VSV1 was larger than 3.3%, the system was macrogelated.

In contrast to the VSV-1 solution, the toluene solution of VSV-2 was clear below 3 wt% toluene at 25°C. The P2VP content of VSV-2 was 19.1 mol% and less than VSV-1 (67.6 mol%). According to the theoretical calculations of the micellization of triblock copolymers, the cmc increases with increasing molecular ratio of the middle block<sup>23,24</sup>. It was suggested that the cmc of VSV-2 is higher than 3 wt% in toluene at 25°C, because the solubility of the polystyrene middle block was too large to form micelles. In order to decrease the solubility of the polystyrene sequence to the solvent, cyclohexane which was a theta solvent for PS at 35°C and non-solvent for P2VP was added till a bluish tint appeared. The toluene content and polymer concentration in the VSV-2 solution were 25 vol% and 1 wt/vol%, respectively. For VSV2, the macrogelation was observed above 3.0% in this solution.

In order to investigate the micelle formation of the triblock copolymers in the solution, which showed the bluish tint, the DLS measurement was carried out at 25°C. Figure 3 showed the specific DLS result of the VSV-1/toluene solution at 1% of polymer concentration at 25°C. Only one peak with 1.035 of the size distribution appeared at 91.5 nm in a hydrodynamic radius ( $R_h$ ). The

**Table 1** Characteristics of the triblock copolymers

	$M_n$		
	Precursor PS <sup>a</sup>	Block <sup>b</sup>	2VP content <sup>c</sup> (mol%)
VSV-1	$4.57 \times 10^4$	$1.40 \times 10^5$	67.6
VSV-2	$4.10 \times 10^4$	$5.07 \times 10^5$	19.1

<sup>a</sup> Determined with g.p.c.

<sup>b</sup> Calculated by combining  $M_n$  of precursor PS and P2VP content

<sup>c</sup> Determined by FTi.r.

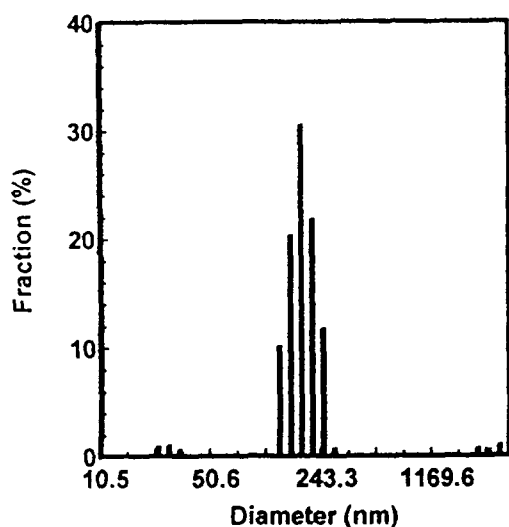


Figure 3 Hydrodynamic radius of aggregates of VSV-1 in toluene at 1 wt%

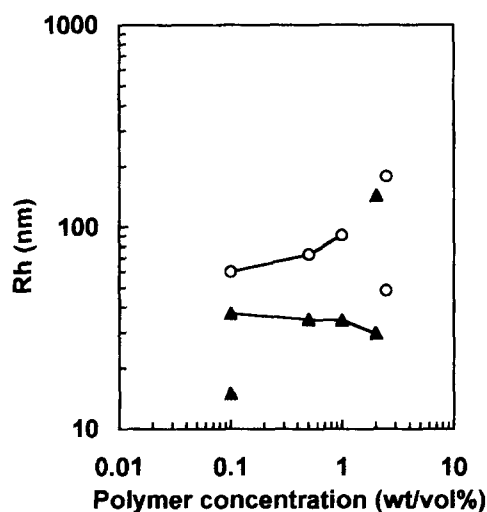


Figure 4 Hydrodynamic radii of polymer micelles of VSV1 and VSV2: (O) VSV1 series, (▲) VSV2 series

dependence of  $R_h$  of VSV1 and VSV2 on the polymer concentration is shown in Figure 4.

For VSV1, no aggregates were observed for the solution at 0.05%. In the range of polymer concentration of VSV1 from 0.1 to 1%, the  $R_h$  values of the micelles were constant (ca 86 nm). At 2.5% not only the micelles with 48 nm of radius but also the large aggregates with 150 nm of the radius are observed. According to theoretical investigations<sup>23,24</sup>, the BAB type block copolymer tends to form the bridges between micelles at high polymer concentration. These bridges are assumed to be a sort of the physical crosslinking of the micelles and they cause the macrogelation of the system upon crosslinking of the P2VP sequences. Since the macrogelation occurred in the VSV1/toluene system above 3.3% of the polymer concentration, the larger aggregates observed at 2.5% were concluded to be the bridge micelles of VSV1. Consequently, it was found that there was no bridge between the micelles below 1 wt% in this system. These results agreed well with the results of Balsara *et al.*<sup>21</sup> that neither branching nor network-like

Table 2 The hydrodynamic radii of the micelles of triblock copolymers and their products

Sample <sup>a</sup>	$R_h^b$ (nm)	$R_{hw}/R_{hn}^c$	$R_{h,fs}^d$ (nm)	$R_{h,random}^d$
VSV-1	91.5	1.035		
VSV-1M	72.1	1.038	471	18.1
VSV-2	34.0	1.04		
VSV-2M	36.6	1.18	1706	34.6

<sup>a</sup> VSV-1M and VSV-2M are crosslinked products

<sup>b</sup> Hydrodynamic radius measured by DLS in toluene at 25°C

<sup>c</sup>  $R_{hw}/R_{hn}$ : the polydispersity of the radius

<sup>d</sup>  $R_{h,fs}$  and  $R_{h,random}$  are the calculated hydrodynamic radii of the microspheres under the fully stretched state and random coil, respectively, using the half values of the  $M_n$  of block copolymers

structure appeared for the P(2VP-*b*-S-*b*-2VP) triblock copolymers in toluene at lower polymer concentration.

For VSV2 solution, the  $R_h$  value was constant (36 nm) in the range of polymer concentration from 0.5 to 1%. In the 0.1 and 2% solutions, two different  $R_h$  values were obtained. For the 0.1% solution, new micelles of radii smaller than 36 nm were observed. In addition, the intensity of the solution was very low. Thus, it is suggested that the aggregation of the VSV2 was insufficient at 0.1%. In contrast to the 0.1% solution, large aggregates with radius of 142 nm were observed for the 2% solution. As described above, the macrogelation was confirmed for 3% solution of this system. Therefore, as for VSV1, the large aggregates in 2% solution were due to the bridging of the micelles. From these results, the formation of isolated micelle of VSV2 was confirmed between 0.5 and 1%. The size of the micelles and their distributions of VSV-1 and VSV-2 at 1% are listed in Table 2.

Based on the structure of flower micelle, the hydrodynamic radii of the polymer micelles should be smaller than the halves of the fully stretched length of the block copolymers. In Table 2, the fully stretched lengths ( $R_{h,fs}$ ) and the radii of the random coils ( $R_{h,random}$ ) of the halves of the block copolymers are also shown. As shown in Table 2, the  $R_h$  values of the micelles were in between the  $R_{h,fs}$  and  $R_{h,random}$ . These results also support the formation of flower micelles in solutions.

#### Synthesis of microgels

In order to synthesize the flower microgels, the P2VP sequences in the core part of the polymer micelles were crosslinked with 1,4-diiodobutane. The size distribution of the micelles increases with increasing polymer concentration even in the range between cmc and cmc\*. Thus, the polymer concentration was set to 1 wt/vol%, which was slightly larger than cmc. The molar ratio of the iodide group to the pyridyl group in the feed was set to 20 mol%.

After crosslinking, no macrogelation was observed. The crosslink density of the products measured by Volhard's titration was 16.8 mol%. As the crosslink density of the P2VP was closed to the feed, it was found that the 1,4-diiodobutane completely reacted with P2VP sequences. Figure 5 is the DLS result of the toluene solution of crosslinked VSV-1 at 0.005 wt% of polymer concentration. For the crosslinked products, one clear peak appeared at  $R_h = 72.1$  nm, no larger peaks above 10 nm were observed for the VSV-1 triblock copolymer at 0.005 wt%. This indicates that

the large products with 72.1 nm diameter were synthesized by crosslinking. The  $R_h$  of the crosslinked products was slightly smaller than that of the polymer micelle of VSV-1 formed in the toluene at 1 wt% of polymer concentration. However, the size distribution of the crosslinked products was still less than 1.04. The  $R_h$  values and the size distribution of the crosslinked product of VSV-2 are listed in Table 2. For VSV-2, the  $R_h$  values of the crosslinked products and polymer micelle also agreed well. Therefore, it is suggested that the polymer micelles in selective solvents were successfully crosslinked and neither macrogelation nor inter-micelle crosslinking occurred.

It is well known that the micelles are formed under equilibrium between the unaggregated block copolymer chains and the micelles in the solution<sup>25,26</sup>. In previous studies<sup>27</sup>, it was found that the crosslinking of the core part of the polymer micelles should be finished before the break-up of the micelles; otherwise the inter-micelles crosslinking which causes the macrogelation and the increasing of the polydispersity of the microgels would occur. Again, as the size distribution of the crosslinked products was narrow and the hydrodynamic radii were constant through the crosslinking, it was also found that the reaction was completed before the micelles broke up. According to the crosslinking data of P2VP with 1,4-diodobutane in the solid state<sup>8</sup>, the reaction was completed in less than 8 h. Therefore, the life time of the micelles of this study was concluded to be longer than 8 h.

In order to investigate the inner texture of the crosslinked products, TEM observation was carried out of the triblock copolymers and crosslinked products cast from 1 and 0.005 wt% of the polymer concentration. Figure 6 showed the TEM micrographs of VSV-1 series. For all micrographs, the P2VP sequences were stained dark with methyl iodide.

The morphology of the VSV-1 triblock copolymer was the PS cylinders in P2VP matrix. The diameter of PS cylinder was 20 nm. Taking into account the P2VP content in VSV-1 (67.6 mol%), this morphology agreed well with Molau's law<sup>1</sup>. In contrast to VSV-1, the

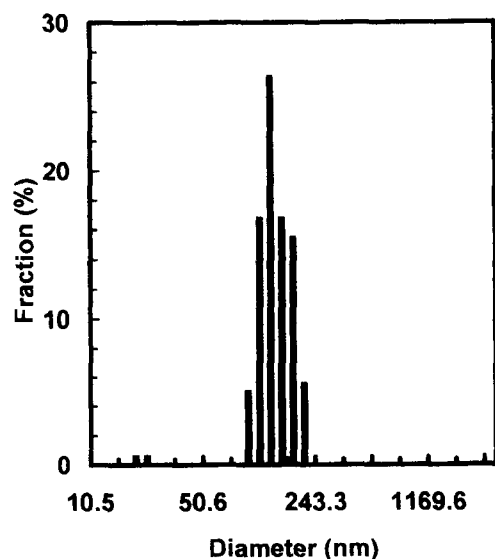


Figure 5 Hydrodynamic radius of crosslinked products of VSV-1 in toluene at 0.005 wt%

morphology of the crosslinked products of VSV-1 in the concentrated state was P2VP spheres in the PS matrix (Figure 6b). The diameter of the P2VP sphere and PS thickness were 104 and 16 nm, respectively.

Here, the existence of the bridged multi-cores in the microgels should be considered. If the P2VP core part was composed of the bridge multi-P2VP cores, the volume fraction of the core would differ with the volume fraction of the P2VP block in the block copolymer. The volume fraction of P2VP core part observed by TEM was calculated to be 0.65 ( $= R_{\text{core}} \rho_{\text{P2VP}} / R_{\text{total}} \rho_{\text{total}}$ ), where  $R_{\text{core}}$  and  $R_{\text{total}}$  are the radii of the P2VP core and the microsphere, respectively, and  $\rho_{\text{P2VP}}$  and  $\rho_{\text{total}}$  are the density of the P2VP and the block copolymer, respectively. This volume fraction 0.65 showed sufficient agreement with the P2VP content of the block copolymer 0.676. Consequently, the P2VP cores of the microspheres synthesized in this study were composed with only P2VP sequences. The results also indicate that no bridging occurred in the micelles and the microspheres.

When the crosslinked product was cast from diluted solution (Figure 6c), it was found that the crosslinked

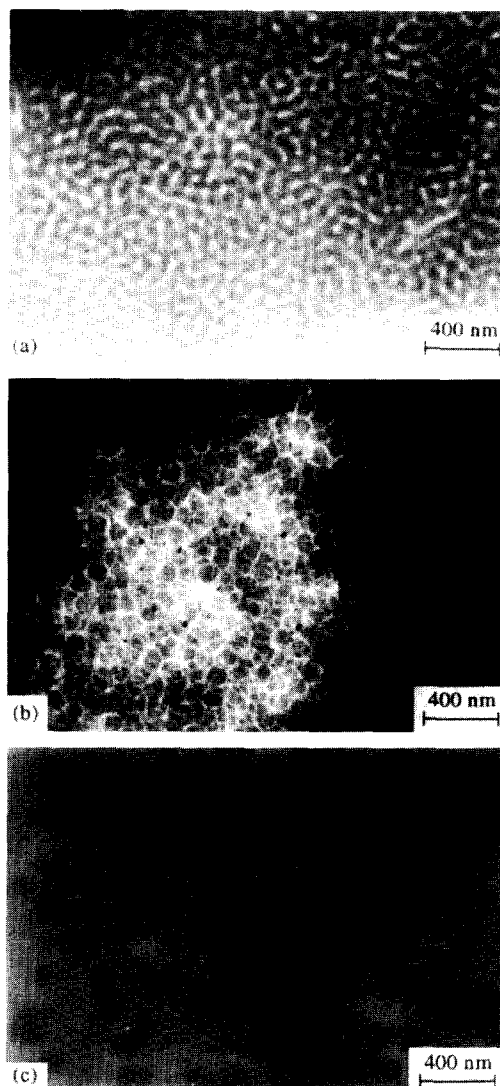


Figure 6 TEM micrograph of the VSV-1 series: (a) VSV-1 cast from 1 wt%; (b) the crosslinked VSV-1 cast from 1 wt%; (c) the crosslinked VSV-1 cast from 0.005 wt%

products had a spherical outlook and the diameter of the P2VP sphere was 110 nm. As PS was not stained with methyl iodide, the PS sequence could not be observed in this concentration (0.005 wt%). The morphology of Figure 6b was concluded as the aggregated state of these microspheres. For the VSV-2 series, the morphologies of the block copolymer and the crosslinked products were P2VP spheres in PS matrices. However, the diameters of P2VP spheres of the crosslinked products (20 nm) did not agree with that of the block copolymers (25 nm). Therefore, it was found that the crosslinked products had different structure from the block copolymer.

Consequently, the P2VP core-PS shell type polymer microgels were synthesized by crosslinking the polymer micelles of the triblock copolymers in the selective solvents, which were good for PS and non for P2VP. This is also indicated that the micelle structure in the solution was P2VP core-PS shell type sphere, shown in Figure 1a.

In addition, the  $\alpha$ -methyl styrene sequence at the centre of polystyrene sequence can be decomposed by u.v. Thus, the B core-A shell type polymer microgel with open shell chains will be obtainable by decomposition of the  $\alpha$ -methyl styrene sequence in the flower microgels. The hydrodynamic properties of the flower microgel and the open core-shell microgel will be compared elsewhere.

## CONCLUSIONS

Two types of the P(2VP-b-S-b-2VP) triblock copolymers were synthesized by additional living polymerization. These polymers formed the micelles in the toluene or toluene/cyclohexane mixture. By DLS measurements, it was found that the polymer micelles were mono-dispersed. The polymer micelles were crosslinked with 1,4-diiodobutane. After the crosslinking, no macrogelation was observed. The large products were observed by DLS in the very diluted solution, and the radii of the products were very close to those of the polymer micelles. Therefore, the fixing of the polymer micelles by crosslinking was confirmed. The inner texture and outlook of the crosslinked products were observed by TEM. The morphology of the crosslinked products did not

correspond to that of the original triblock copolymer. All products were polystyrene spheres and each of them had one P2VP core in its centre. Therefore, it was concluded that the P2VP core-PS shell type flower microgels were synthesized by crosslinking of the flower micelles in solution.

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