Synthesis of microspheres with 'hairy–ball' structures from poly(styrene-*b*-2-vinyl pyridine) diblock copolymers

Reiko Saito*, Hidefumi Kotsubo and Koji Ishizu
Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12, O-okayama, Meguro-ku, Tokyo 152, Japan

(*Received 17 September 1990; revised 7 March 1991; accepted 25 March 1991*)

Monodispersed microspheres with 'hairy–ball' structures were synthesized by crosslinking poly(2-vinyl pyridine) spherical microdomains in poly(styrene-*b*-2-vinyl pyridine) [P(S-*b*-2Vp), $\bar{M}_n = 3.2 \times 10^5$, 2Vp = 15.5 mol%] diblock copolymer film cast from 1,1,2-trichloroethane solution. The yield of the microspheres increased to 80.8 wt% with increasing reaction time. The number-average external diameter of the microspheres was 50 nm and the microspheres were stiff and truly spherical. After crosslinking, the number-average diameter of the P2Vp ball ($\bar{D}_n$) decreased to 24 nm from the $\bar{D}_n$ of the starting block copolymer film (30.3 nm). This was due to the removal of the uncrosslinked block copolymer chains by purification of the crosslinked products. From the g.p.c. measurement with refractive index and u.v. double detected at 254 nm, the surface property of the microspheres was found to be very similar to that of PS. PS chains were expanded on the P2Vp ball, and the observed and theoretical degrees of stretching of the microsphere (1.13 and 1.12, respectively) were in good agreement.

(**Keywords: microsphere; synthesis; diblock copolymer; crosslinking; microseparated film**)

INTRODUCTION

An AB diblock copolymer with incompatible sequences shows a microseparated structure in solution and in the solid state[1]. When the morphological structure of the microseparated film in the solid state is a sphere in the matrix, microspheres with 'hairy–ball' structures can be synthesized by crosslinking the spherical microdomains in the solid state films.

Based on this suggestion, poly(styrene-*b*-isoprene) [P(S-*b*-Ip)] diblock copolymer film with PIp spherical microdomains and poly(S-*b*-4-vinyl pyridine [4Vp]) diblock copolymer film with P4Vp spherical microdomains were crosslinked, and the microgels with PIp cores[2] and P4Vp cores[3–5] were prepared. The core–shell morphology of microspheres of P(S-*b*-4Vp) was confirmed by transmission electron microscopy (TEM) and angular-dependent X-ray photoelectron spectroscopy (X.p.s.)[5].

The aims of this paper are to synthesize the poly-2-vinyl pyridine (P2Vp) ball–PS hair microspheres from P(S-*b*-2Vp) diblock copolymer films, and to characterize the properties of the microspheres.

The most important considerations for the synthesis of microspheres by crosslinking microseparated films were as follows:

1. The morphological structure of the P(S-*b*-2Vp) film must be P2Vp spheres in a PS matrix;
2. The domain size of the P2Vp spherical microdomains in the film must be monodispersed;
3. The morphological structure of the film must not be changed during the crosslinking of P2Vp chains.

Based on the first two considerations, P(S-*b*-2Vp) diblock copolymers were prepared using a standard sequential anionic addition polymerization[6]. The 2Vp content was set between 10 mol% and 30 mol% because the A content of the AB diblock copolymer for an A spherical microdomain structure in a B matrix was generally lower than 35 mol%[7].

To conform with the third consideration, the P2Vp chains in the segregated microdomain were crosslinked with 1,4-diiodobutane (DIB) vapour at room temperature. The synthesis of the microspheres was confirmed by g.p.c. and TEM, and the properties (size, shape, yield and crosslinking density) of the microgels were investigated.

EXPERIMENTAL

Synthesis and characterization of P(S-b-2Vp)

The well-defined P(S-*b*-2Vp) diblock copolymers were prepared by standard sequential anionic addition polymerization using n-butyllithium as an initiator in tetrahydrofuran (THF) at −78°C[6].

The number-average molecular weight ($\bar{M}_n$) of the precursor PS was determined with a Tosoh HLC-802A GPC with THF as an eluent at 38°C, a TSK-gel GMH column and a flow rate of 0.9 ml min^{-1}.

The weight-average molecular weight ($\bar{M}_w$) of the diblock copolymers was determined by combining the g.p.c. data and the viscometric data in THF at 38°C. The 2Vp content in the diblock copolymer was determined by ^{1}H n.m.r. (Hitachi, R-24B), and calculated from $\bar{M}_w$ values of the diblock copolymer and its precursor PS.

---

* To whom correspondence should be addressed

0032–3861/92/051073–05
© 1992 Butterworth–Heinemann Ltd.

Preparation and crosslinking of the film

The diblock copolymer films (120 μm thick) were cast from 1,1,2-trichloroethane (TCE, 0.05 g ml^{-1}) solution on a Teflon sheet. The cast film was gradually dried for 4 days at room temperature.

The crosslinking of the segregated 2Vp chains in the core was carried out by quaternization with DIB vapour. The film and DIB liquid were set in a 500 ml separable flask. The flask was cooled to 0°C, the air in the system was vacuumed and the system was closed. The flask was then heated to 25°C and crosslinking was carried out for 4 and 8 h at 25°C.

Morphological observation

The ultra-thin film specimens of the starting diblock copolymers were prepared for TEM by placing a drop of a 1 wt% TCE solution on a copper grid coated with a carbon substrate, and then evaporating the solvent as gradually as possible at room temperature.

The specimens were stained with methyl iodide vapour for 4 days at room temperature.

The crosslinked products were prepared by using a drop of 0.05 wt% TCE solution, and drying and staining using the same conditions as for the starting block copolymers. For the observation of the external shape of the products, the specimens cast from 0.05 wt% TCE solution were shadowed with Pt at an angle of 45°. The morphological results were obtained using a Hitachi H-500 TEM at 100 kV.

Characterization of the crosslinked products

The synthesis of the crosslinked products (the microgels) was confirmed and the yield of the products was measured using g.p.c. with refractive index (RI) and u.v. absorbance double detected at 254 nm (Tosoh UV-8 model-II spectrophotometer).

The degree of quaternization of P2Vp chains was measured by Volhard's titration. The film was dissolved in benzene and the I^- ion in the system was titrated with aqueous $AgNO_3$ and KCNS. For the measurement of pendant I^-, Volhard's titration was carried out for a benzene and triethylamine (TEA) mixture.

RESULTS AND DISCUSSION

Block copolymer and its crosslinking

The characteristics of P(S-*b*-2Vp) diblock copolymers are given in *Table 1*. The molecular weight distributions of the block copolymers were narrow, and the 2Vp contents were <35 mol%. Thus, preparation of microseparated films with P2Vp spherical domains in a PS matrix was expected.

Table 1 Characteristics of poly(styrene-*b*-2-vinyl pyridine) diblock copolymers and domain spacing

	$\bar{M}_n$ ($\times 10^{-5}$)				
	Block[a]	PS	2Vp content[b] (mol%)	2Vp (vol%)	Domain spacing[c] (nm)
SV1	3.2	2.7	15.5	18	30.3
SV2	1.5	0.9	38.0	46	80.0

[a] Determined from g.p.c. and viscometric data

[b] Estimated by ^{1}H n.m.r.

[c] The number-average diameter of the 2Vp microdomain for SV1. The lamella thickness for SV2

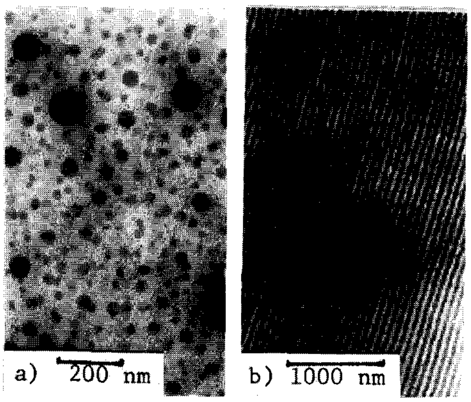

Figure 1 Transmission electron micrographs of (a) SV1 and (b) SV2 diblock copolymer films cast from TCE and stained with methyl iodide

Figure 1 shows the TEM micrographs of diblock copolymer specimens (SV1 and SV2) cast from TCE. The dark regions are the selectively stained 2Vp chains. The microdomain structure in SV1 is P2Vp spheres in a PS matrix. The number-average diameter ($\bar{D}_n$) of the P2Vp domains was 30.3 nm for SV1, and the P2Vp domains were monodispersed. The microdomain structure in SV2 was lamellar with a domain spacing of 80 nm.

The films (120 μm thick) were crosslinked with DIB at room temperature. After crosslinking, the SV2 film was macrogelated. SV1-M1 and SV1-M2 were the SV1 films crosslinked for 4 and 8 h, respectively. All crosslinked products of SV1, SV1-M1 and SV1-M2, were dissolved in TCE, THF and benzene. After crosslinking, the 2Vp chains became insoluble in hydrophobic solvents. Thus, the crosslinked SV2 with a large 2Vp content was insoluble in hydrophobic solvents. Similar phenomena were observed in the crosslinking of amino groups of poly(acrylic acid-*g*-*N*,*N*′-dimethylamino-n-propyl acrylamide) by quaternization[8]. Thus, a soluble crosslinked product (the microsphere) was expected.

To confirm the synthesis of crosslinked products, the g.p.c. profiles of the products were measured. *Figures 2a* and *b* show the g.p.c. profiles of the SV1 series detected with u.v. (254 nm) and RI equipment, respectively. After crosslinking, the peak of the starting block copolymer at an elution count of 27.5 (hydrodynamic radius $R =$ 50 nm) decreased and the new peaks appeared at an elution count of 26.5 ($R = 70$ nm). From these new peaks, the presence of crosslinked products (the microgels) in the films was confirmed.

The g.p.c. profiles of the crosslinked products in *Figures 2a* and *b* were different. This can be easily explained. The peak height in *Figure 2a* detected with u.v. equipment at 254 nm was a function of the benzoyl group concentration. On the other hand, the peak height detected with RI equipment was obtained as a function of polymer concentration and the difference of the RI between the eluent (THF) and the polymer surface. When the RI values of the polymer surface change, g.p.c. peaks with different heights are obtained for the same polymer concentrations.

According to Yeung and Frank[9], the RI values for poly(styrene-*b*-ethylene propylene) in heptane changed drastically at the critical micelle concentration. Based on their result, it was possible to estimate the surface properties of the microgel from the change in height of the g.p.c. peak.

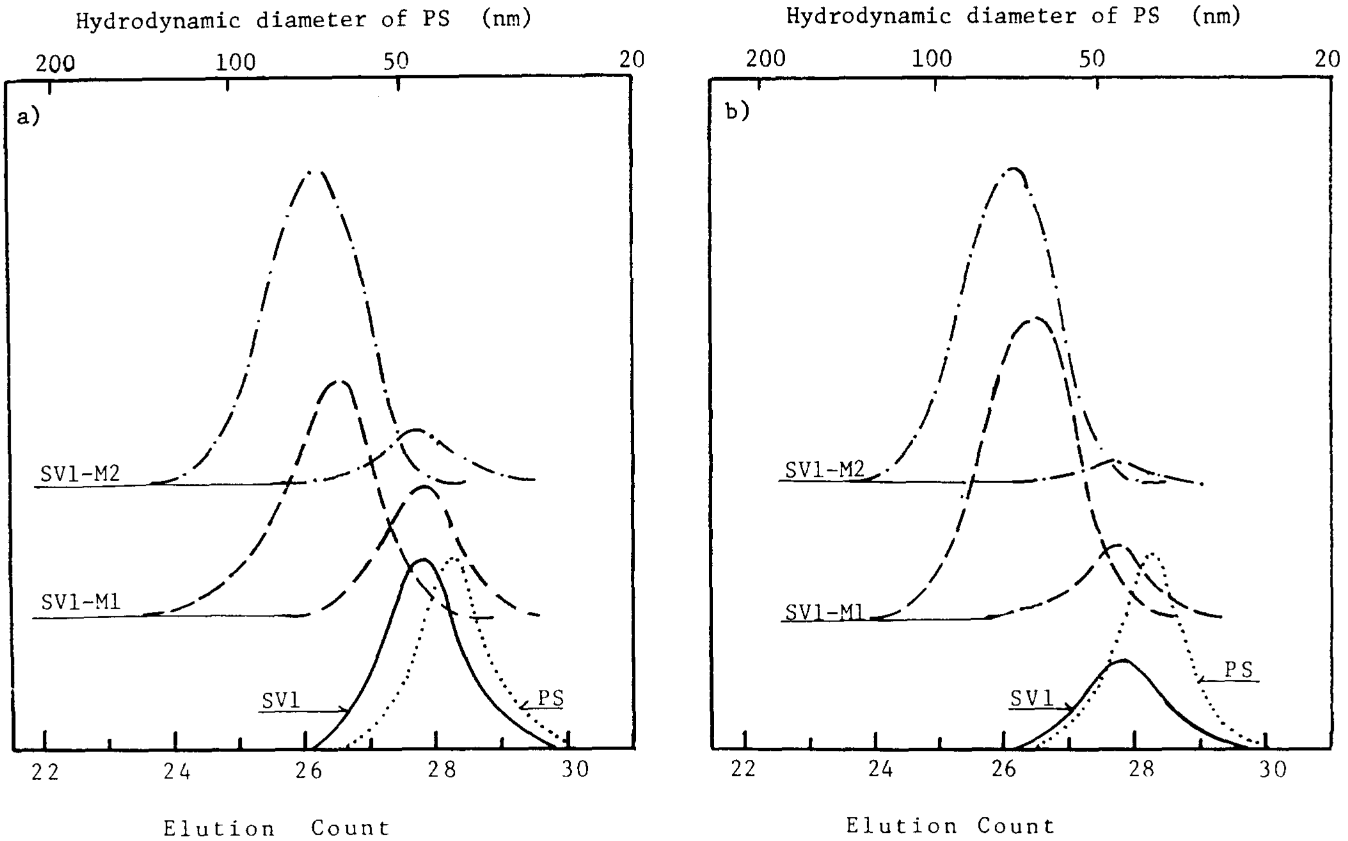

Figure 2 G.p.c. profiles of the SV1 diblock copolymer and the crosslinked products SV1-M1 and SV1-M2 detected (a) by the u.v. method and (b) by the RI method

Table 2 Ratios of the peak heights detected by RI and u.v. for the diblock copolymer (H_B) and the microgels (H_M)

	Reaction time (h)	H_B	H_M
SV1	0	0.5	–
SV1-M1	4	0.48	0.88
SV1-M2	8	0.5	0.97

The ratio (H) of the peak height detected by RI and u.v. was calculated for each peak (*Table 2*). (The suffixes S, B and M correspond to PS, the diblock copolymer and the microgel.) The value of H_S was 0.96 and the H_B values of all samples were constant (0.5). On the other hand, the H_M values increased to 0.97 with the onset of crosslinking. These H_M values were close to the H_S value (0.96). This shows that the surface of the crosslinked products was covered with PS.

To obtain the yield of the crosslinked products, the peak area ratio of the microgel to the whole peak area in *Figure 2a* was calculated. As described above, the peak height in *Figure 2a* indicated the benzoyl group concentration in the sample solution. The microgel yields were 63 and 81% for SV1-1M and SV1-2M, respectively. The microgel yield increased with reaction time. This is unexpected. A possible explanation is that the crosslinking time might not govern the yield but the crosslinking density in this study, because crosslinking was carried out on a very thin film.

Shape and size of the microgel

The morphological structure of the microgel was investigated. Typical photographs of the crosslinked products are shown in *Figure 3*.

First, the external shape and the size of the microgel were investigated. *Figure 3a* shows SV1-M2 particles cast from 0.05% TCE solution and shadowed with Pt at an angle of 45°. The spheres were well dispersed on the carbon substrate. The SV1-M2 particle was spherical, and its $\bar{D}_n$ was 50 nm. The number-average shadow length ($\bar{S}_n$) of the microsphere was 60 nm. The height (h) of the microgel could be calculated from the shadow length (S) as follows:

$$h = 2S \times \tan 22.5^\circ$$

The number-average height ($\bar{h}_n$) of the microsphere was calculated as 50 nm. The $\bar{h}_n$ and the $\bar{D}_n$ of the microsphere were in good agreement. Thus, it was concluded that the crosslinked product was a hard microsphere and was not flattened on the carbon substrate.

Next the inner texture of the microspheres was investigated. *Figures 3b, c* and *d* are the TEM micrographs of the SV1-M2 ultra-thin films cast from 0.05% TCE solution, 5% TCE solution and 5% TCE/acetone (v/v) solution, respectively. The dark regions are the P2Vp microdomains selectively stained with methyl iodide.

From *Figure 3b*, it was found that the P2Vp domains were dispersed on the carbon substrate. The $\bar{D}_n$ value of the P2Vp spheres was 24 nm. The diameter distribution of the P2Vp microdomains of SV1-M2 was 1.05. From *Figure 3c*, the $\bar{D}_n$ of the P2Vp ball was found to be 24 nm and the distance between the centre of the P2Vp spheres was 50 nm. This latter value showed good agreement with the external diameter (50 nm) of the microspheres. From the results of g.p.c. measurements, the microgel was found to be covered with PS. Therefore, from the external diameter of the microspheres (50 nm) and the $\bar{D}_n$ of the P2Vp ball (24 nm), the PS hair thickness was calculated as 13 [=(50–24)/2] nm. It was concluded that monodispersed microspheres with a P2Vp 'ball' and PS 'hair' structure were synthesized.

The $\bar{D}_n$ of the P2Vp spheres cast from the TCE/acetone mixture (*Figure 3d*) was also 24 nm; the distance between the centre of the P2Vp balls was 35–60 nm. This showed that the structure of the microspheres was stabilized by crosslinking and the $\bar{D}_n$ of the P2Vp ball was constant in any solvent. However, the PS hair thickness could be varied by changing the solvent. Next, we discuss the P2Vp ball state and the conformation of the PS hair.

P2Vp ball state

The 2Vp ball diameter shrank from the domain spacing (30.3 nm) of the starting diblock copolymer SV1 to 24 nm. The shrinkage of the ball by crosslinking was also reported for the crosslinking of P(S-*b*-4Vp)[4]. Two reasons are proposed for the shrinkage: one is that the chemical properties of the 2Vp balls were changed by crosslinking; the other is that the aggregation number of the block copolymer chains in the 2Vp balls was changed.

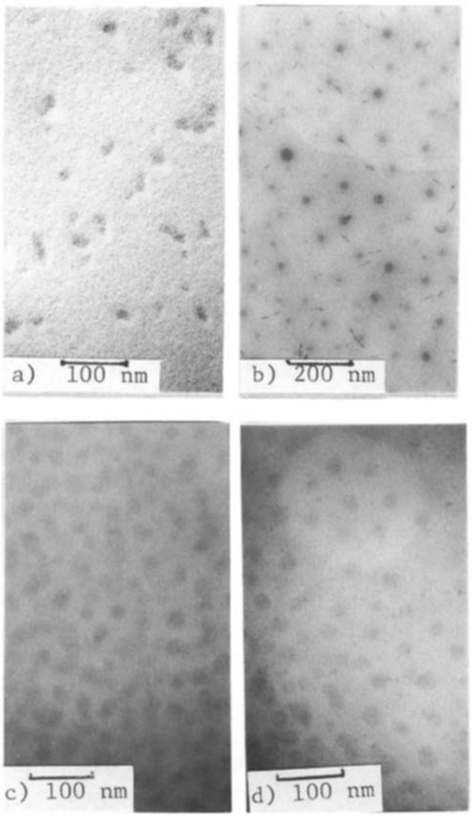

Figure 3 Transmission electron micrographs of SV1-M2: (a) cast from TCE (0.05 wt%) and shadowed with Pt at an angle of 45°; (b) cast from TCE (0.05 wt%) and stained with methyl iodide; (c) cast from TCE (5 wt%) and stained with methyl iodide; (d) cast from TCE/acetone (v/v) (5 wt%) and stained with methyl iodide

To check the first proposal, properties [the degree of quaternization (Q_n) and the crosslinking density] of the P2Vp ball were measured by Volhard's titration.

The crosslinking of P2Vp microdomains with DIB is a two-step reaction. First, one I^- group from DIB reacts with 2Vp to form a pendant I^- group in the 2Vp chains. Second, the pendant I^- group reacts with more 2Vp and the 2Vp chains are crosslinked. To obtain the crosslinking density, the degree of the pendant I^- groups (Q_p) must be measured. The pendant I^- groups in microspheres can be quaternized with TEA in benzene. The crosslinking density can be calculated from $2Q_n - Q_w$, where Q_w is the degree of quaternization of microspheres containing the quaternized pendant I^- with TEA, and $Q_p = Q_w - Q_m$. For SV1-M1 and SV1-M2, Q_m and Q_w were measured by Volhard's titration and are given in *Table 3*.

The Q_m reached 73 mol% for SV1-M2. The crosslinking density of the P2Vp ball increased from 23 (SV1-M1) to 66% (SV1-M2) with the crosslinking time. It was concluded that the properties of the 2Vp balls changed with an increase in the crosslinking time. If the decrease in the $\bar{D}_n$ of the P2Vp ball was due to change in the ball properties, the $\bar{D}_n$ of the P2Vp ball of SV1-M1 must be nearer to the value of the block copolymer than that of SV1-M2. However, the $\bar{D}_n$ of the crosslinked 2Vp ball approached the $\bar{D}_n$ of the P2Vp microdomain of the starting block copolymer (30.3 nm) when crosslinking occurred. Hence, it was difficult to relate the decrease in $\bar{D}_n$ of the P2Vp ball of the microgel to the change in the crosslinking density.

To check the second proposal, the $\bar{D}_n$ of the P2Vp balls was estimated again from the viewpoint of microgel yield. As described above, the yield values were not 100%. All films crosslinked in this study were very thin (120 μm), and the size distribution of the crosslinked products was narrow.

It was supposed that the crosslinking occurred in all P2Vp microdomains uniformly, but in each microdomain some block copolymer chains remained uncrosslinked. During the preparation of TEM samples, the uncrosslinked block copolymer chains were removed from the crosslinked products. (The TEM sample solution was prepared after purification of the samples.) The $\bar{D}_n$ of the crosslinked P2Vp ball observed by TEM might decrease by removal of the uncrosslinked block copolymer.

To confirm this point, the calculated diameter (D_{calc}) of the P2Vp ball was estimated from the yield of the

Table 3 Characteristics of the microspheres SV1-M1 and SV1-M2

	Reaction time (h)	Yield[a] (wt%)	$\bar{D}_n$ of the microsphere[b] (nm)	$\bar{D}_n$ of 2Vp ball[c] (nm)	$\bar{D}_w/\bar{D}_n$ of 2Vp ball	Q_m[d] (%)	Q_w[e] (%)	Crosslinking density (%)
SV1-M1	4	63.0	–	23	1.10	38	53	23
SV1-M2	8	80.8	50	24	1.05	73	80	66

[a] Calculated from g.p.c. data detected by u.v.
[b] Determined from the TEM specimen shadowed with Pt at an angle of 45°
[c] Determined by TEM
[d] Degree of quaternization of the microsphere determined by Volhard's method in benzene
[e] Total degree of quaternization of the microsphere and the pendant I^- group determined by Volhard's method in benzene and TEA

crosslinked products as follows:

$$D_{\text{calc}} = (\text{yield})^{1/3} \times 30.3\ \text{nm}$$

where 30.3 nm was the $\bar{D}_n$ of the P2Vp microdomain of the starting block copolymer films. The D_{calc} values of SV1-M1 and SV1-M2 were 26 and 28 nm, respectively. The observed diameter values were 23 and 24 nm, respectively. The $\bar{D}_n$ and D_{calc} values showed good agreement. Thus, it was concluded that the decrease in $\bar{D}_n$ of the 2Vp ball with crosslinking was due to the removal of the uncrosslinked block copolymer chains from the crosslinked products by purification.

From these considerations, it was also concluded that the P2Vp balls of these crosslinked products were hard true spheres (so-called stiff) in the solid state. The aggregation numbers of the P2Vp chains in the crosslinked P2Vp ball could be calculated from the density of the P2Vp and $\bar{D}_n$ of the P2Vp ball. The density of P2Vp[10] was $11.4 \times 10^3\ \text{mol m}^{-3}$. The number-average aggregation numbers of the P2Vp chains per P2Vp ball were calculated as 90 and 94 for SV1-M1 and SV1-M2, respectively.

Conformation of PS hairs

As described above, the P2Vp ball was stiff, and the PS hair thickness varied with the solvent (*Figures 3c* and *d*). The conformation of the PS hair on the P2Vp ball surface of SV1-M2 was investigated.

From the aggregation number of 2Vp chains in the ball, the shell volume of closely packed PS was calculated from:

$$V_{\text{shell.calc.}} = A \times DP \times b$$

where A, DP and b are the aggregation number of 2Vp chains in the ball, the degree of polymerization of PS and the molar volume of the closely packed PS, respectively. For SV1-M2, $V_{\text{shell,calc}}$ was calculated to be $94 \times 2596 \times 0.165 = 4.0 \times 10^4\ \text{nm}^3$.

The shell volume observed, $V_{\text{shell,obsd}}$, from TEM results was $4[(12 + 13)^3 - 12^3]/3 = 5.82 \times 10^4\ \text{nm}^3$. The values of $V_{\text{shell,obsd}}$ and $V_{\text{shell,calc.}}$ did not agree. It was suggested that the PS chains were expanded on the P2Vp ball surface.

As a consequence of the geometric factors involved, the conformation of the hair chains of the hairy–ball microspheres generally changes with the ball radius, degree of grafting, the chain length of the hair chain and the solvent. The ball radius, degree of grafting and the chain length of the hair chain can be related to the composition of the block copolymer. According to Zhulina and Birshtein[11,12], when the block copolymer composition was in the order $N_B > N_A > N_B^{(1+2\tau)/6}$, the degree of external chain stretching could be calculated from $N_A^{1-\tau} N_B^{(\tau-1)/6}$, where N_A, N_B and τ were the volume fraction of the external block, the volume fraction of the inner block and the exponent in the molecular mass dependence of the mean dimensions of the isolated external coil in the solution. For SV1, $N_A = 0.82$ and $N_B = 0.18$. The solvents used in this study for TEM sample preparation and g.p.c. measurement were TCE and THF, and were both good solvents for PS. Thus, $\tau = 0.6$. Though the composition of SV1 corresponded to the order $0.84(=0.18^{0.6}) > 0.82 > (0.18^{0.37} =)0.53$, the theoretical degree of PS stretching was $0.84^{0.4} \times 0.18^{-0.11} = 1.12$. The degree of the PS chain stretching was $1.13 = [V_{\text{shell,obsd}}/V_{\text{shell,calc.}}]^{1/3}$. The theoretical (1.12) and observed (1.13) values agreed well.

However, the theoretical and observed values were considered in solution and in the solid state, respectively. It was reported that the expanded states of the hairy chains on the ball in solution remained after drying the hairy–ball microspheres[13,14]. Consequently, it was concluded that the conformation of the PS chain was expanded by geometric factors, and this expanded state of the chain remained after drying the microspheres.

CONCLUSIONS

Hairy–ball microspheres are synthesized from microseparated films by crosslinking the microsegregated chains.

Well-defined P(S-*b*-2Vp) diblock copolymer SV1 ($\bar{M}_n = 3.2 \times 10^3$, 2Vp = 15.5 mol%) was synthesized by standard sequential anionic addition polymerization. The microseparated films with P2Vp spheres in a PS matrix were prepared from the SV1 diblock copolymer in TCE solutions and the crosslinking of the 2Vp microdomain in the films was carried out in DIB vapour.

The crosslinked SV1 film (SV1-M2) could be dissolved in benzene, TCE and THF, and the presence of the crosslinked products was confirmed by g.p.c. The yield of the crosslinked products was 80.8%.

Morphological observation of the products was carried out using TEM. The crosslinked products were true spheres with a 50 nm external diameter, and were not flattened on the carbon substrate. The microsphere had a hairy–ball structure (P2Vp ball). The $\bar{D}_n$ of the P2Vp ball shrank from 30.3 nm for the starting diblock copolymer SV1 to 24 nm. However, the microspheres had a narrow size distribution ($\bar{D}_w/\bar{D}_n = 1.05$). The reason for the decrease in the $\bar{D}_n$ of the crosslinked P2Vp ball was that uncrosslinked block copolymer remained in the P2Vp ball after crosslinking. These uncrosslinked block copolymers were removed from the crosslinked products during the preparation of TEM samples. The P2Vp ball was stiff. The PS chains were expanded on the P2Vp ball, and the degree of stretching of the PS chains showed good agreement with the theoretical value.

The Q_m and the pendant I^- group concentration were measured by Volhard's titration. The Q_m and the crosslinking density of SV1-M2 were 73 and 66%, respectively.

REFERENCES

1 Molau, G. E. 'Block Polymers' (Ed. S. L. Aggarwal), Plenum Press, New York, 1970, p. 79

2 Ishizu, K. and Onen, A. *J. Polym. Sci., Polym. Lett. Edn.* 1989, **27**, 3721

3 Ishizu, K. and Fukutomi, T. *J. Polym. Sci., Polym. Lett. Edn.* 1988, **26**, 281

4 Ishizu, K. *Polym. Commun.* 1989, **30**, 209

5 Ishizu, K. *Polymer* 1989, **30**, 793

6 Scindler, A. and Williams, J. L. *Am. Chem. Soc., Div. Polym. Chem. Polym. Prep.* 1969, **10**, 832

7 Helfand, E. and Wasserman, Z. R. *Macromolecules* 1978, **11**, 960

8 Saito, R., Ishizu, K. and Fukutomi, T. *Polym. Bull.* 1985, **14**, 541

9 Yeung, A. S. and Frank, C. W. *Polymer* 1990, **31**, 2089

10 Berkowitz, J. B., Yamin, M. and Fuoss, R. M. *J. Polym. Sci.* 1958, **28**, 69

11 Zhulina, Ye. B. *Vysokmol. Soyed.* 1983, **B25**, 834

12 Zhulina, Ye. B. and Birshtein, T. M. *Vysokmol. Soyed.* 1985, **A27**, 511

13 Birshtein, T. M. and Zhulina, E. B. *Polymer* 1986, **27**, 1078

14 Witten, T. A. and Pincus, P. A. *Macromolecules* 1986, **19**, 2509