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# Effects of different core densities on the diffusibility of microspheres

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

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Various amounts of silver nano-clusters were introduced into the core of poly(2-vinyl pyridine) core–polystyrene shell type polymer microspheres. The density of the microsphere increased linearly from 1.08 to 1.44 with increasing feed amounts of silver ions. The diffusibility and diffusion coefficients of the microspheres in a good solvent for polystyrene were measured by dynamic light scattering. © 1997 Elsevier Science Ltd.

**(Keywords: core–shell microspheres; silver clusters; density)**

## INTRODUCTION

Core–shell polymer microspheres are potentially good composite materials for controlling the microphase separation of the polymers. We have already reported novel morphologies, such as a honeycomb structure, by blending poly(2-vinyl pyridine) [P2VP] core–polystyrene [PS] shell type polymer microspheres and PS–polyisoprene [PI] diblock copolymers[1,2]. The most interesting feature of such a morphology formed with the core–shell microspheres is not only novelty but also its high regularity. The high regularity of the morphology results in the superlattice formation of the core–shell microspheres in the dispersion and in the solid state due to the structure proposed by Daoud and Cotton[3]. In previous investigations[4,5], we succeeded in controlling the regular superlattice structure of the core–shell microspheres by blending homopolymers.

On the other hand, it is possible to introduce metal nano-clusters into the selected microdomains using the microphase separation of the block copolymers[6–8]. We also introduced silver nano-clusters into the P2VP microdomains of the P2VP–PS microphase separated films[9–12]. In particular, using the microphase separated films with P2VP spheres in PS matrices, P2VP core–PS shell microspheres with silver nano-clusters could be obtained[11,12]. By an improved method[12], the amount of introduced silver nano-clusters can be controlled when the molar ratio of feed silver ion to pyridine, $[Ag^+]/[Py]$, is less than 2.0. Therefore, these core–shell microspheres containing silver nano-clusters would be very interesting materials by combining the technique of superlattice formation. However, the density of the core–shell microspheres should be higher than those without silver nano-clusters, since the diameter of the microspheres would not change by introduction of the silver nano-clusters.

Based on these considerations, in this paper, we describe the synthesis of P2VP core–PS shell polymer microspheres containing different amounts of silver nano-clusters and our investigation into:

(1) whether the density of the core–shell microsphere can be controlled by changing the amount of silver nano-clusters introduced;
(2) whether the existence of the silver nano-clusters affects the diffusibility of the microspheres in the dispersion.

For the introduction of the silver nano-clusters into the microspheres, the improved method was chosen, because the amount of silver nano-clusters can be quantitatively controlled. For the investigation of the diffusibility of the microspheres, dynamic light scattering (DLS) measurements were carried out for the microsphere dispersions.

## EXPERIMENTAL

### *Materials*

PS–P2VP block copolymer, the raw material of the microspheres, was synthesized and analyzed previously elsewhere[13]. The number-average molecular weight of the PS precursor and the P2VP content were $3.22 \times 10^5$ and 19.9 mol%, respectively[13].

### *Synthesis of P2VP core–PS shell microspheres containing silver nano-clusters*

The synthesis and basic characterization of the microspheres were carried out based on the previous improved method[12] as follows: the block copolymer and silver nitrate were dissolved in a dioxane water mixture (water 3.2 vol%). The solution was then cast onto a flat Teflon sheet and allowed to dry gradually at room temperature. The poly(2-vinyl pyridine) sequences were then crosslinked with 1,4-diiodobutane gas. After crosslinking, the film was exposed to light, soaked in a hydroquinone–water–1,4-dioxane mixture and an aqueous solid bisulphite. The conditions are shown in *Table 1*.

### *Density measurement*

The purified microspheres were cast from the benzene

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* To whom correspondence should be addressed.

**Table 1** Synthetic conditions and properties of the microspheres

| Run number | $[Ag^+]/[Py]^a$ | $[Ag]/[Py]^b$ | Crosslink density (mol%)$^c$ | Density (g/cm$^3$) Found | Calcd.$^d$ |
|---|---|---|---|---|---|
| SV2-0 | 0 | 0 | 9.6 | 1.08 | 1.077 |
| SV2-1 | 0.196 | 0.174 | 12.1 | 1.118 | 1.12 |
| SV2-2 | 0.382 | 0.397 | 23.4 | 1.199 | 1.16 |
| SV2-3 | 0.648 | 0.583 | 10.5 | 1.32 | 1.21 |
| SV2-4 | 0.827 | 0.728 | 10.9 | 1.36 | 1.24 |
| SV2-5 | 1.011 | 0.910 | 12.0 | 1.44 | 1.28 |

$^a$Molar ratio of feed silver nitrate to pyridine group.
$^b$Molar ratio of introduced silver nano-clusters to the pyridine group.
$^c$Crosslink density of P2VP sequences.
$^d$Calculated density of the microspheres.

dispersion. The density of the microsphere films was measured using a picnometer with KI/water dispersion.

*Dynamic light scattering measurement*

The microspheres were dispersed in benzene (polymer concentration 0.05 wt/vol%). DLS measurement (Photal DLS-7000) was carried out for the microsphere/benzene dispersion at an angle of 90° at 20°C. The diffusion coefficient of the product was calculated from the slope of the decay curve of correlation function (log $G1(\tau)$ *versus* $\tau$).

## RESULTS AND DISCUSSION

### *Synthesis of the microspheres*

For the microsphere synthesis, PS–P2VP diblock copolymer SV2, which was previously synthesized and characterized[13], was used. According to a previous investigation[13], the morphology of the microphase separation of SV2 was P2VP spheres in a PS matrix, and the number-average diameter of P2VP spherical domains was 66 nm.

As described in Section 1, the P2VP core–PS shell microspheres containing the silver nano-clusters in the P2VP cores were synthesized by our improved method[12]. Conditions, introduced amounts of silver nano-clusters and crosslink densities are listed in *Table 1*. The final products were freely dispersed in benzene. Thus, no macrogelation of the systems occurred. The P2VP chains in the P2VP microdomains were strongly crosslinked to retain the core–shell structure even in good solvents for both PS and P2VP, since all crosslink densities of these products were higher than 9 mol%.

The greatest advantage of our improved method for the synthesis of core–shell microspheres containing silver nano-clusters is that the silver nano-clusters are quantitatively introduced into the P2VP core, i.e. the yield of the introduced silver nano-clusters is high. This is due to the fact that the silver salt and the diblock copolymer are cast together from a mixture. In this study, the molar ratios of introduced silver nano-clusters to pyridine groups, [Ag]/[Py], showed fair agreement with the feed molar ratios of silver ions to pyridine groups, $[Ag^+]/[Py]$. It was confirmed that the silver nano-clusters were quantitatively introduced into the P2VP cores in this study. Consequently, P2VP core–PS shell microspheres with various amounts of silver nano-clusters were obtained.

### *Densities of the microspheres*

Densities of the microsphere films are shown in *Figure 1* and *Table 1*. A linear relationship was observed between the [Ag]/[Py] ratio and the density of the film. Thus, it was found that the density of the microsphere film could be controlled by changing the amount of silver nano-clusters introduced. Then, the theoretical densities of the microsphere films in the solid state were calculated and are listed in *Table 1*. For these calculations, it was assumed that (1) the size of the microsphere did not change in any case; and (2) silver compounds existing in the films are only pure silver.

When the [Ag]/[Py] ratio was less than 0.2, the experimental and calculated values agreed well. However, the experimental data were clearly greater than the calculated values over a [Ag]/[Py] ratio of 0.382. From TEM observation, the clear change in the diameters of the P2VP cores was not observed. Thus, the former assumption was appropriate.

On the other hand, silver is easily contaminated with halides. In this study, aqueous potassium iodide was used for the density measurement. The molecular weight of silver iodide is higher than that of silver. Thus, part of the silver could convert to silver iodide during the density measurement. However, in this study, further analysis of the silver compounds after the density measurement was not carried out since the density of these films could be controlled linearly by changing the introduced amount of

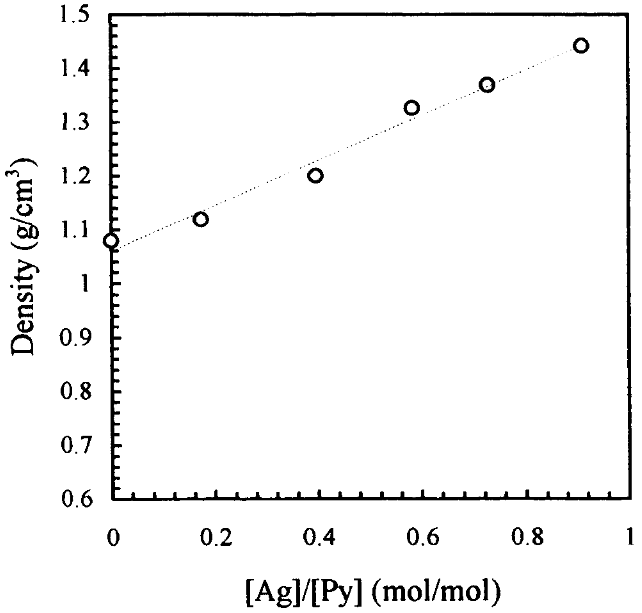

**Figure 1** The film density of the microspheres containing the silver nano-clusters

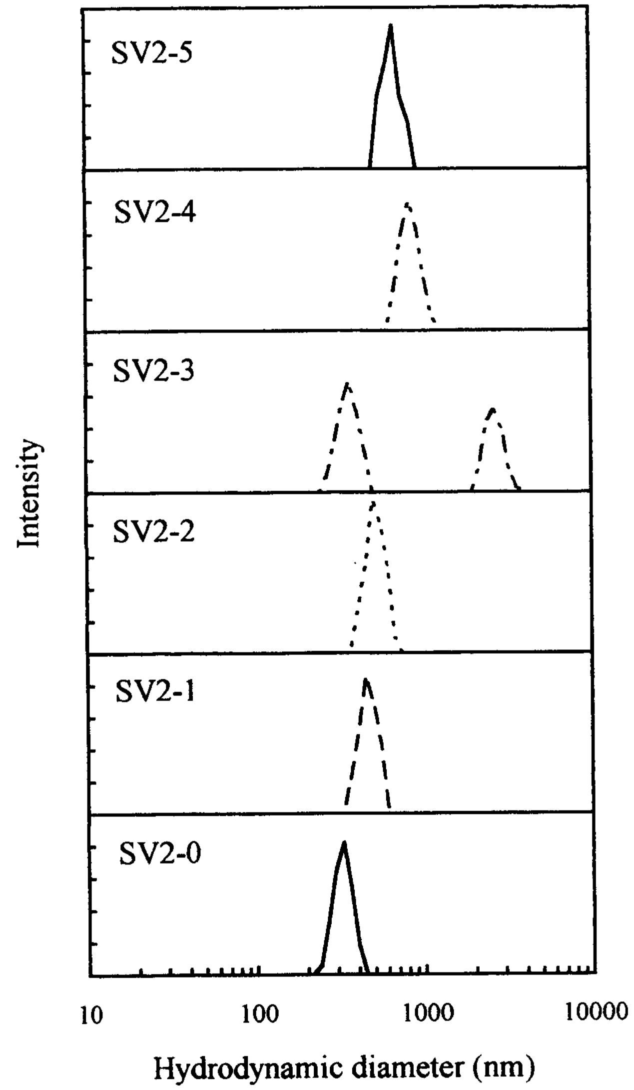

**Figure 2** Distribution of hydrodynamic diameters of the microspheres in benzene at 20°C

silver nano-clusters. Consequently, P2VP core–PS shell microspheres with various densities were obtained.

*Density effect on the diffusibility of the microsphere*

Next, in order to investigate the effect of density on the diffusibility of the microspheres in the dispersion, dynamic light scattering (DLS) measurements were carried out for the microsphere–benzene dispersion. *Figure 2* shows the hydrodynamic diameter distributions of the microspheres. For SV2-3, two peaks were observed. This suggests that the products were partially macrogelated during the cross-linking. However, apart from SV2-3, the diameters of the microspheres were monodispersed and their distribution indices were less than 1.1. Thus, it was concluded that the microspheres could disperse well in the good solvent even though their densities were higher than that of the original diblock copolymer.

The hydrodynamic diameters appear to increase with increasing density of the microspheres. However, it should be noted that the diameters of the core–shell microspheres synthesized in this study should be the same in the dispersion. As described above, the diameters of the P2VP cores did not change by introducing the silver nano-clusters. The hydrodynamic diameter of the microsphere does not indicate the true diameter of the microsphere in the dispersion. The hydrodynamic radius, $R_h$, is calculated by following equation:$R_h = k_B T/(6D\eta)$where $k_B$ is the Boltzmann constant, $T$ the dispersion temperature, $\eta$ the solvent viscosity and $D$ the translational diffusion coefficient at infinite dilution. In order to make clear the effect of the existence of the silver nano-clusters on microsphere diffusibility, the $D$ values were obtained.

*Figure 3* shows the change in the $D$ values of the microspheres. Two $D$ values at a density of 1.326 were due to the double peaks observed for the SV2-3 dispersion. Apart from SV2-3, the $D$ values clearly decreased with increasing density of the microspheres. This indicates that the diffusibility of the microspheres in the dispersion decreased with increasing density of the microspheres. When the diameters of the microspheres are constant in the dispersion, this can be explained as follows. For the core–shell polymer microspheres investigated in this study, the

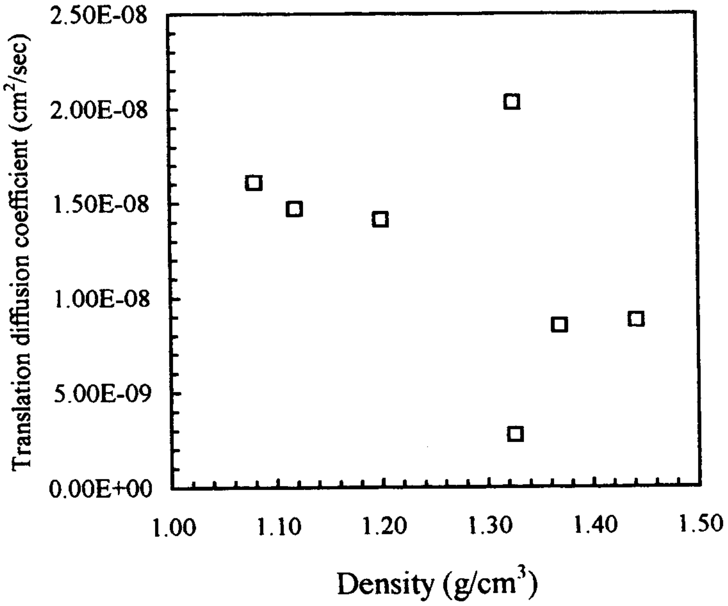

**Figure 3** Translation diffusion coefficient of the microspheres in benzene at 20°C

diffusibility of the microspheres in the dispersion is driven by the solubility of the shell chains. By introducing the silver nano-clusters, only the core part becomes heavier, despite the constant solubility of the shell. As a result, total diffusibility of the microsphere decreases with increasing amounts of the silver nano-clusters introduced. Thus, it was concluded that the increase in the apparent hydrodynamic diameter of the microspheres resulted from the decrease in diffusibility of the microspheres. Consequently, it was found that the microsopic decrease in the diffusibility of the microsphere could be quantitatively observed by DLS.

## CONCLUSIONS

Six types of P2VP core–PS shell polymer microspheres containing silver nano-clusters were synthesized with different feed amounts of silver nitrate. The silver nano-clusters were quantitatively introduced into the microspheres. The density of the microsphere film showed a linear relationship with the amount of silver nano-clusters introduced. It was found that the density of the microspheres could be controlled by changing the feed amount of the silver nitrate. However, from theoretical calculations of the density, the contamination of the silver nano-clusters was pointed out. From the DLS results, an increase in the hydrodynamic diameter of the microspheres in the dispersion was observed with increasing density of the microspheres. This increase was concluded to be due to the decrease in the diffusibility of the microspheres due to the heavy core containing the silver nano-clusters.

## ACKNOWLEDGEMENTS

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