Polymer Vol. 37 No. 17, pp. 3965–3970, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00+0.00

S0032-3861(96)00225-X

Synthesis of polymer microspheres with polypyrrole core

Koji Ishizu*, Kazuhisa Honda and Reiko Saito
Department of Polymer Science, Tokyo Institute of Technology, 2-12, Ookayama, Meguro-ku, Tokyo 152, Japan
(Received 22 September 1995; revised 5 January 1996)

The poly(styrene-*b*-2-vinylpyridine) diblock copolymer [poly(2-vinylpyridine) (P2VP), 22 mol%] was prepared by sequential anionic addition polymerization. This specimen showed thermal equilibrium morphology of dispersed P2VP spherical microdomains in a polystyrene (PS) matrix. After the introduction of Cu^{2+} (oxidant) into the P2VP spherical domains, oxidation polymerization was performed by exposing the ionic complex films as a template to a mixture of pyrrole and water vapour. The films obtained were dissolved in organic solvents such as benzene, tetrahydrofuran and chloroform. These oxidation products exhibited the structure of polypyrrole core/PS shell type microspheres with narrow particle size distribution. Copyright © 1996 Elsevier Science Ltd.

(Keywords: diblock copolymer; spherical microdomain; core-shell type microsphere)

INTRODUCTION

We have previously indicated that poly[styrene(S)-*b*-2-vinylpyridine (2VP)] diblock copolymers form horizontally oriented lamellar microdomains by virtue of air–copolymer and substrate–copolymer interactions[1]. Subsequently, semiconducting materials were obtained by exposing the film to alkyl dihalide vapour[2]. The film displayed anisotropic conductivity with the ratio of conductivity parallel to the film plane to conductivity perpendicular to the film plane being about eight. Colloidal silver was also introduced into quaternized poly(2-vinylpyridine) (P2VP) layers by reduction of silver iodide[3]. More recently, Cu^{2+} (oxidant) was introduced into P2VP layers by complexation based on the pyridine nitrogen interacting with metal ions. Electrically conducting composite films were synthesized by exposure of the diblock copolymer complexed with such an oxidizing agent to a mixture of pyrrole and water vapour[4].

If assemblies of these block copolymers can be fixed by crosslinking the spherical parts (the spherical microdomains in the solid state and the core in solution), the crosslinked products should form core-shell type polymer microspheres (see *Figure 1*). Several groups have obtained core-shell polymer microspheres by crosslinking of core domains in micelles formed in solvents selective for block and graft copolymers[5–14].

The microphase-separated structures in bulk film are more stable than the micelle in solution. Therefore, crosslinking spherical microdomains in a film is likely to be a superior preparation method for core-shell type microspheres. According to this concept, we have prepared core-shell microspheres composed of various chemical components[15–19]. Thus, we expected to be able to prepare a new colloidal form of polypyrrole (PPy) (PPy core) using microphase-separated spherical domains as the micellar reaction vehicle.

Since Bjorklund and Liedberg prepared PPy latex, many researchers have reported the synthesis of sterically stabilized colloidal dispersions of air-stable intrinsically conducting polymers such as PPy and polyaniline via dispersion polymerization in both aqueous and nonaqueous media using polymeric stabilizers[20–38]. Thin conductive films can be easily fabricated from such dispersions. This is one of the most important methods for improving processability.

More recently, Armes and coworkers[39,40] have synthesized PPy-silica nanocomposite particles which are colloidally stable in aqueous media. Miksa and Slomkowski[41] have indicated that PPy core/polyacrolein shell latex is suitable for immobilization of proteins and can be used as elements of various diagnostic systems. In this case the PPy latex was used as a seed for the radical polymerization of acrolein.

In this paper we describe the preparation of polymer microspheres with PPy cores. The poly(S-*b*-2VP) diblock copolymer was prepared by sequential anionic addition polymerization. This specimen showed the thermal equilibrium morphology of dispersed P2VP spherical microdomains in a polystyrene (PS) matrix. We have recently shown that silver nanoclusters were introduced quantitatively into the P2VP phases of poly(S-*b*-2VP) diblock copolymers[42]. Analogously, the introduction of Cu^{2+} (oxidant) into P2VP spherical domains was performed by the following two methods. (1) Cu^{2+} was introduced into P2VP domains by complexation based on the pyridine nitrogen interacting with metal ions, after the domain fixing of P2VP spherical parts. (2) Diblock copolymer films exhibiting P2VP spherical domains complexed with Cu^{2+} were obtained by the direct casting from the diblock copolymer–$CuCl_2$/

---

*To whom correspondence should be addressed

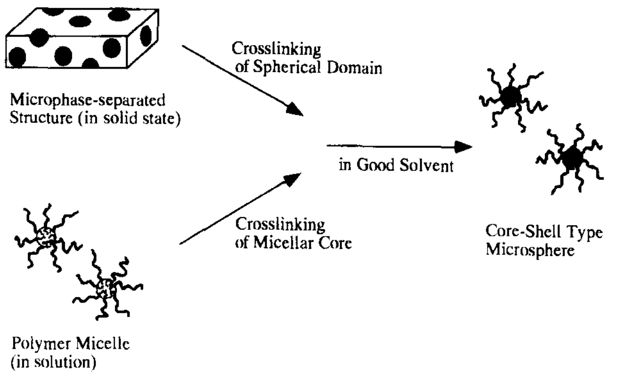

Figure 1 Schematic presentation of core-shell polymer microspheres synthesized by crosslinking of self-assemblies

dioxane–water solutions. Oxidation polymerizations were performed by exposing these ionic complex films to a mixture of pyrrole and water vapour. Characterization of the composite films was carried out by energy dispersive X-ray spectrometry (EDX), electron microscopy, Fourier transform infra-red (*FT*i.r.) spectroscopy and element analysis. Several samples of the composite films were dissolved in organic solvents such as benzene, tetrahydrofuran (THF) and chloroform. These oxidation products exhibited the structure of PPy core-PS shell type microspheres with narrow particle size distribution.

EXPERIMENTAL

Polymer characterization and morphology

The well defined poly(S-*b*-2VP) diblock copolymer was prepared by the usual sequential anionic addition. The details concerning the synthesis and characterization of these block copolymers have been given elsewhere[1–3]. *Table 1* lists the characteristics of the 'monodisperse' diblock copolymer, which exhibited the equilibrium morphology of dispersed P2VP spherical microdomains in a PS matrix. The film was embedded in an epoxy resin and cut perpendicularly to the film surface into ultrathin sections (~70–100 nm thick) using an ultramicrotome (Reichert-Nissei Co., Ultracut N). Morphological results were obtained on a Hitachi H-500 at 75 kV.

Introduction of oxidant to P2VP phases

The introduction of Cu^{2+} (oxidant) to P2VP phases was performed by the following two methods. *Figure 2* shows the schematic illustration of these methods. (1) The diblock copolymer films (*ca* 60 μm thick) with P2VP spherical domains were obtained by casting from 1,1,2-trichloroethane (TCE) solution. These films were exposed to 1,4-diiodobutane (DIB) vapour at 70°C under reduced pressure for 6 h. This reagent leads to not only quaternization but also to crosslinking of P2VP microdomains. Subsequently, several films were quaternized with methyl iodide vapour at room temperature for 24 h, in order to increase the hydrophilicity of P2VP phases. The determination methods of the degree of quaternization (Q_1) and the crosslink density (CD) were described in a previous paper[4]. Crosslinked films were soaked in dioxane/water (1:9–5:5, v/v) mixture of $CuCl_2$ (0.1 mol l^{-1}) for 8 h. The film was washed with water and was dried at 30°C. The Cu^{2+} content introduced was determined by the following titration[43]. After soaking the film, the residual $CuCl_2$ solution was reacted with an excess amount of potassium iodide (KI). The I_2 produced was titrated with aqueous sodium thiosulfate ($Na_2S_2O_3$) solution using 0.2 wt% of starch as an indicator. (2) The block copolymer was dissolved in a dioxane–water mixture. The polymer concentration and the water content in the mixture were 4.5 wt% and 4.0 v%, respectively. $CuCl_2$ was dissolved in the mixture. The solution was then cast onto a Teflon sheet and allowed to dry gradually at room temperature. Thus the ionic complex films were prepared by one-step method, where Cu^{2+} was introduced directly to P2VP phases.

Table 1 Characteristics and domain size of poly(S-*b*-2VP) diblock copolymer

Code	$\bar{M}_n$[a] ($\times 10^{-5}$)	P2VP block content (mol%)	$\bar{M}_w/\bar{M}_n$[a]	Domain size[b] (nm) $\bar{D}_{P2VP}$
SV20	1.97	22.0	1.15	46.0

[a] Determined by gel permeation chromatography using universal calibration

[b] $\bar{D}_{P2VP}$, average domain diameter of P2VP spheres. $\bar{D}_{P2VP}$ was determined by TEM micrograph of specimen cast from TCE

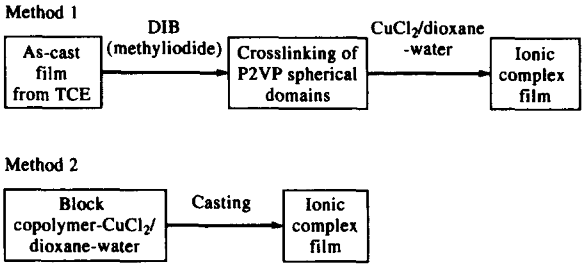

Figure 2 Schematic presentation for the preparation of ionic complex films

The element (Cu, I and Cl atoms) distributions on a vertical section of the ionic complex films were measured by EDX (Philips EDAX 9900I). The *K* intensity was fitted with a Zn atom ($K_\alpha = 8.628$ and $L_\alpha = 1.019$ keV). The concentration of the elements was estimated using a correction [stopping power, absorption and fluorescence corrections: RT-11 SJ(S) V5.01C] on a computer (LSI-11/23). The ultrathin sections were observed directly on a transmission electron microscope (TEM) without staining treatment.

Oxidation polymerization by pyrrole

The oxidation polymerizations of pyrrole were performed by exposing the ionic complex films to a mixture of pyrrole/water (1:1, v/v) vapour at 60°C under reduced pressure. The apparatus used for oxidation polymerization of pyrrole has been given elsewhere[4].

In order to determine whether or not PPy was formed in the P2VP spherical microdomains, ultrathin vertical sections were observed on a TEM after staining with osmium tetraoxide (OsO_4) vapour and thin film was observed by *FT*i.r. spectroscopy (Shimadzu FTIR-8500). The amount of polymerization of PPy on the ionic complex films was estimated by element analysis (C and N).

Core-shell type microspheres

If the oxidation polymerization of pyrrole is performed within P2VP spherical domains, oxidation products such as multi-molecular micelle should behave as microspheres of a PS shell and PPy core in solution. Several samples of the composite films were dissolved in organic solvents.

The particle size distribution of core-shell type microspheres was determined using dynamic light scattering (d.l.s.; scattering angle = 90°, Otsuka Electronics Ltd, Photal DLS-600) in 0.1 wt% benzene ($\eta = 0.654$ cp, $n_D = 1.501$) at 20°C.

RESULTS AND DISCUSSION

Morphology of diblock copolymer films

Figure 3 shows a cross-sectional TEM micrograph of the SV20 film cast from TCE. The dark portions are the P2VP blocks selectively stained with OsO_4. The SV20 specimen shows the thermal equilibrium morphology of dispersed P2VP spherical microdomains in a PS matrix. From the diameter (46.0 nm) of the P2VP sphere, the segregation number of the block copolymer (f) can be calculated by using the following equation:

$$f = (4\pi/3)R_c^3\rho_{P2VP}N_A/M_{P2VP} \qquad (1)$$

where R_c, ρ_{P2VP}, N_A and M_{P2VP} are the radius of the sphere, the density of P2VP ($11.4 \times 10^3\,mol\,m^{-3}$)[44], the Avogadro number, and the molecular weight of the P2VP sequence, respectively. f is calculated to be 840 using equation (1).

Introduction of Cu^{2+} to P2VP phases

Table 2 Reaction conditions and results of introducing Cu^{2+} ions into P2VP spheres[a]

Expt. no.	Q_1[b] (mol%)	cd[c] (mol%)	Solvent dioxane/water (v/v)	$Cu^{2+}/2VP$[d] (mol mol^{-1})
SV20-H11	53	36	1/9	0.005
SV20-H12	53	36	2/8	0.045
SV20-H13	53	36	5/5	0.082
SV20-H21	61	36	5/5	0.093

[a] Film weight, *ca* 80 mg; concentration of $CuCl_2$ [$CuCl_2$], 0.1 mol l^{-1}
[b] Degree of quaternization
[c] Crosslink density
[d] Determined by oxidation–reduction titration

First, Cu^{2+} (oxidant) was introduced into P2VP phases, after converting the P2VP phases to hydrophilic domains. P2VP domains of the SV20 film were not only quaternized but also crosslinked with DIB and methyl iodide [Q_1, 53–61 mol%; crosslink density (CD), 36 mol%]. *Table 2* lists the reaction conditions and the results of introducing Cu^{2+} into P2VP spheres, varying the solvent composition. The Cu^{2+} loading within the P2VP microspheres was estimated by the oxidation–reduction titration of residual $CuCl_2$ solution. It is found from these results that the ionic complex increases with increasing dioxane fraction (SV20-H11–SV20-H13). The $CuCl_2$ salts are able to permeate into the bulk with a large diffusion rate in the swollen state of the films. The amount of introduced ionic complex in the crosslinked film SV20-H21 is slightly larger than that in the SV20-H13 film. It seems that the hydrophilic character of P2VP spheres is advantageous for the incorporation of Cu^{2+} ions. The cross-sectional TEM micrograph of the SV20-H13 specimen was observed directly. In this micrograph, the TEM image was constructed by electrons scattered from Cu atoms, as shown in *Figure 3*. Cu^{2+} ions were distributed only in the quaternized P2VP spherical domains.

Figure 3 Cross-sectional TEM micrograph of SV20 film cast from TCE

Figure 4 shows typical spot analysis of the vertical section SV20-H13 for Cu, I and Cl atoms at the centre. *Table 3* summarizes the results of spot analyses on SV20-H12 and SV20-H13 ionic complex films. It is found from these results that the observed values of Cu at the centre are almost the same as those at both edges for SV20-H12 and SV20-H13 fragments. Moreover, the amount of ionic complex introduced for SV20-H13 increases in comparison with that for SV20-H12 film. This phenomenon supports the result obtained from the oxidation–reduction titration (*Table 2*). Moreover, it is also found from the Cu and Cl data that the ionic complexes do not exist completely as complexed $CuCl_2$ oxidant within P2VP spherical microdomains. It seems that the ion exchange reaction between Cl^- and I^- occurs in the local area within the spherical microdomains.

The results for the one-step method concerning the introduction of Cu^{2+} into P2VP phases are as follows.

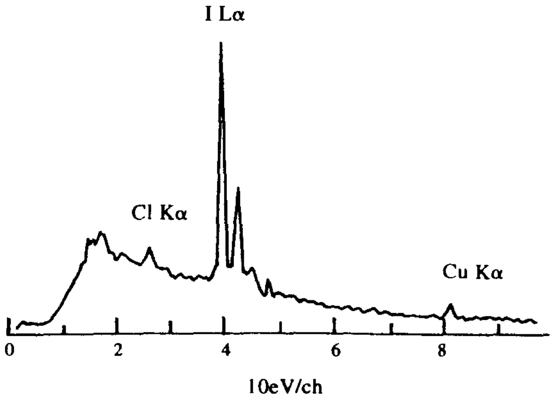

Figure 4 EDX spot analysis of vertical section SV20-H13 at centre

Table 3 Spot analyses of SV20-H12 and SV20-H13 films by means of EDX

Code	Position	Element (atom %)		
		Cu	I	Cl
SV20-H12	Left	7.88	86.25	5.87
	Right	6.59	83.93	9.48
	Centre	7.05	85.51	7.44
SV20-H13	Left	12.81	76.92	10.27
	Right	10.69	79.52	9.79
	Centre	13.26	77.73	9.02

Table 4 Preparation conditions of ionic complex films[a]

Expt no.	Feed amount ratio of $Cu^{2+}/2VP$ units (mol mol^{-1})
SV20-C31	0.40
SV20-C32	0.56
SV20-C33	1.0
SV20-C34	1.8

[a] Composite films were obtained by casting from a mixture of 96 v% dioxane solution of SV20 and 4 v% aqueous $CuCl_2$ solution

The ionic complex films were prepared by the casting method, varying the feed amount ratio of $Cu^{2+}/2VP$ units. The preparation conditions of ionic complex films are listed in *Table 4*. *Figure 5a* shows the cross-sectional TEM micrograph of the SV20-C32 specimen ($Cu^{2+}/2VP$ units = 0.56 mol mol^{-1}), where the TEM image is constructed by electrons scattered from Cu atoms. This texture is the same as that shown in *Figure 3*. It is found that Cu^{2+} ions are predominantly incorporated in P2VP spherical microdomains. The cross-sectional TEM micrograph of the SV20-C34 specimen ($Cu^{2+}/2VP$ units = 1.8 mol mol^{-1}) is shown in *Figure 5b*. In this specimen, the P2VP spherical microdomains are dispersed heterogeneously in a PS matrix. The fusion among P2VP spherical domains and the $CuCl_2$ crystallized in a PS matrix can also be observed from this texture. Similar results were also observed on the SV20-C33 specimen ($Cu^{2+}/2VP$ units = 1.0 mol mol^{-1}). The direct casting method has the advantage that the amount of introduced $CuCl_2$ ions can be controlled quantitatively by changing the amount of $CuCl_2$ in the feed ($Cu^{2+}/2VP$ units = less than *ca* 0.6 mol mol^{-1}). Subsequently, P2VP domains of SV20-C31–SV20-C34 films were not only quaternized but also crosslinked with DIB vapour. It was also recognized from the TEM observation that morphologies of these ionic complex films were not disturbed during crosslinking reactions.

Oxidation polymerization of pyrrole

In the oxidation polymerization of pyrrole, the SV20-H and SV20-C films were employed as an ionic complex film. The brown colour of the ionic complex film changed slightly black on exposure to pyrrole vapour. A typical *FT*i.r. spectrum of the SV20-C32 oxidation polymerization film (composite film, SV20-C32M is shown in *Figure 6*. The *FT*i.r. spectrum of the ionic complex SV20-C32 is also shown in this figure to gauge the oxidation polymerization of pyrrole. In the spectra of the ionic complex SV20-C32 and composite SV20-C32M, the characteristic absorptions due to the phenyl and quaternized pyridinium groups are observed at 750 and 1600, and 1640 cm^{-1}, respectively. In the spectrum of the composite film SV20-C32M, the bands are observed near 1167 and 1430 cm^{-1} as indicated by arrows, attributable to PPy. The PPy loadings within P2VP spherical microdomains could not be calculated from a correlation between the *FT*i.r. spectra of the ionic complex and the composite films. Because a reasonable calibration could not be obtained from the mixture of the ionic complex film and PPy homopolymer.

Thus, the PPy loadings within P2VP spherical microdomains were estimated using the data from element analyses (the increase of C and N atom values for the composite film against those for corresponding complex film). *Figure 7* shows the relationship between the amount of PPy formed (PPy/composite film) and the ratio of the introduced Cu^{2+} to 2VP units ($Cu^{2+}/2VP$ units). It is found from this correlation that the growth of PPy increases with an increase in the amount of $Cu^{2+}/$ 2VP units. An oxidant amount of less than $Cu^{2+}/2VP$

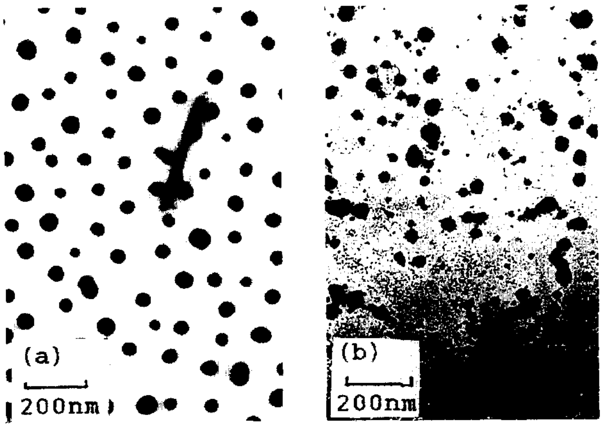

Figure 5 Cross-sectional TEM micrographs of ionic complex films: (a) SV20-C32; (b) SV20-C34

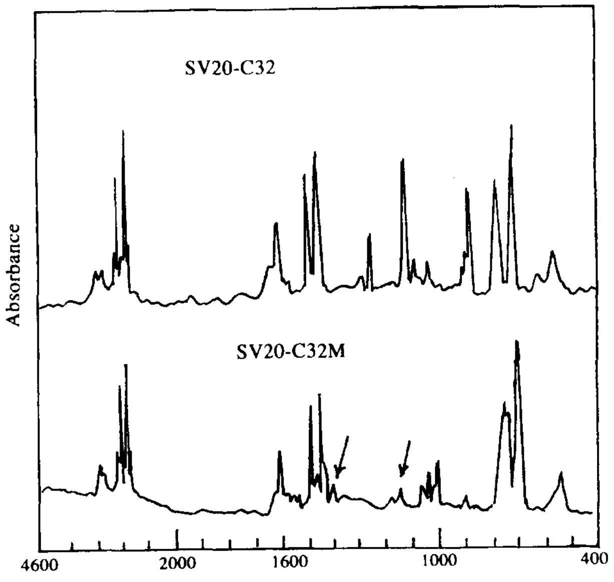

Figure 6 *FT*i.r. spectra of composite film SV20-C32M and ionic complex film SV20-C32

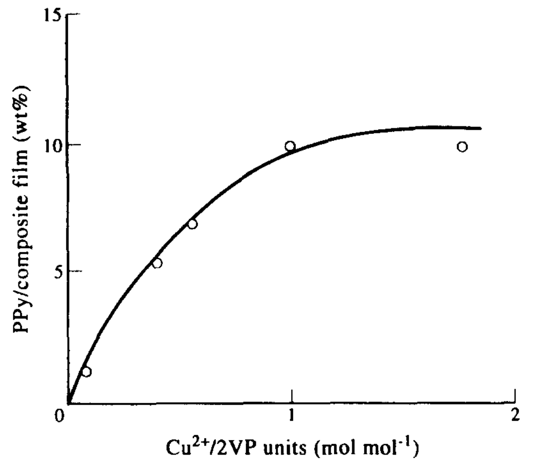

Figure 7 Plot of amount of PPy (PPy/composite film) against ratio of introduced ionic complex to 2VP units (Cu^{2+}/2VP units)

Figure 8 Cross-sectional TEM micrograph of composite film SV20-C32M

units = *ca* 1.0 (mol mol^{-1}) is enough for complete diffusion of pyrrole vapour through the matrix polymer. The composite films (less than Cu^{2+}/2VP units = 0.56 mol mol^{-1}) were dissolved in organic solvents such as benzene, THF and chloroform. Neither SV20-C33M nor SV20-C34M films were dissolved in such solvents.

Figure 8 shows the cross-sectional TEM micrograph of the SV20-C32M specimen stained with OsO_4. The dark portions indicate the P2VP/PPy phases. The pyrrole monomers were polymerized inside the area of P2VP spherical microdomains. This film had never shown an electrically conducting nature (10^{-13} S cm^{-1}). As indicated in the TEM micrograph, the P2VP/PPy composite spheres were not arranged continuously with each other, but located at 100 nm order of magnitude. Thus, this conductivity corresponds to that of PS film. Such electrical property is very different from the usual colloidal PPy particles synthesized via dispersion polymerizations. These composite films are expected to behave as a microsphere composed of PPy core-PS shell in solution. The formation of microspheres depends strongly on the morphology of the ionic complex films.

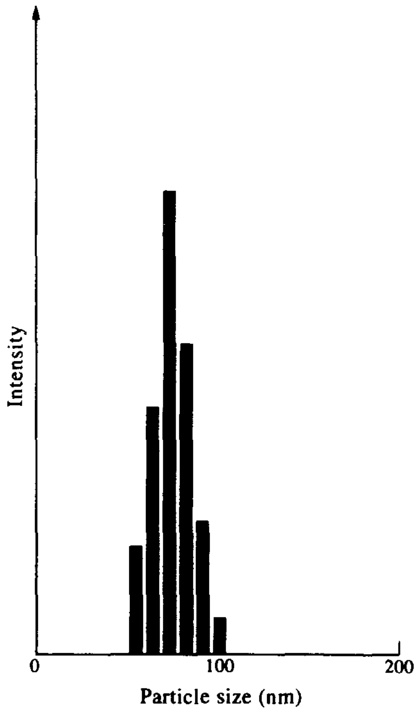

Figure 9 Particle size distribution of SV20-C32M microsphere in benzene

Core-shell type microspheres

The particle size distribution of SV20-C32M was determined in benzene by means of d.l.s. *Figure 9* shows the particle size distribution of the SV20-C32M specimen. A single clear peak for the particle diameter can be observed at 74 nm. Thus, SV20-C32M has the primary structure of PPy core-PS shell microsphere in solution. As the PPy core is stabilized by highly branched PS arms (arm number, $f = 840$), the core/shell microsphere moved in benzene as the pseudolatex. We are investigating technological applications for these microspheres composed of a conducting core. The results will be reported shortly.

ACKNOWLEDGEMENTS

We acknowledge Mr R. Ooki and Mr T. Chiba, Faculty of Engineering, Tokyo Institute of Technology, for taking the EDX data and the electron microscopic cross-section of block copolymer films, respectively.

REFERENCES

1 Ishizu, K., Yamada, Y. and Fukutomi, T. *Polymer* 1990, **31**, 2047
2 Ishizu, K., Yamada, Y., Saito, R., Kanbara, T. and Yamamoto, T. *Polymer* 1992, **33**, 1816
3 Ishizu, K., Yamada, Y., Saito, R., Kanbara, T. and Yamamoto, T. *Polymer* 1993, **34**, 2256
4 Ishizu, K., Honda, K., Kanbara, T. and Yamamoto, T. *Polymer* 1994, **34**, 4901
5 Procházka, A., Baloch, M. K. and Tuzar, Z. *Makromol. Chem.* 1979, **180**, 2521
6 Tuzar, Z., Bednář, B., Koňák, C., Kubín, M., Svobodová, S. and Procházka, K. *Makromol. Chem.* 1982, **183**, 399
7 Bednář, B., Devátý, J., Koupalová, B and Králiček, J. *Polymer* 1984, **25**, 1178
8 Park, M. H., Ishizu, K. and Fukutomi, T. *Polymer* 1989, **30**, 202

9 Saito, R., Ishizu, K., Nose, T. and Fukutomi, T. *J. Polym. Sci., Polym. Chem. Ed.* 1990, **28,** 1793
10 Saito, R., Ishizu, K. and Fukutomi, T. *Polymer* 1990, **31,** 679
11 Saito, R., Ishizu, K. and Fukutomi, T. *Polymer* 1991, **32,** 531
12 Saito, R., Ishizu, K. and Fukutomi, T. *Polymer* 1991, **32,** 2258
13 Saito, R., Ishizu, K. and Fukutomi, T. *J. Appl. Polym. Sci.* 1991, **43,** 1103
14 Saito, R., Ishizu, K. and Fukutomi, T. *Polymer* 1992, **33,** 1712
15 Ishizu, K. and Fukutomi, T. *J. Polym. Sci., Polym. Lett. Ed.* 1988, **26,** 281
16 Ishizu, K. *Polymer* 1989, **30,** 793
17 Saito, R., Kotsubo, H. and Ishizu, K. *Polymer* 1992, **33,** 1073
18 Ishizu, K. and Önen, A. *J. Polym. Sci., Polym. Chem. Ed.* 1989, **27,** 3721
19 Saito, R., Kotsubo, H. and Ishizu, K. *Eur. Polym. J.* 1991, **27,** 1153
20 Bjorklund, R. B. and Liedberg, B. *J. Chem. Soc., Chem. Commun.* 1986, 1293
21 Armes, S. P. and Vincent, B. *J. Chem. Soc., Chem. Commun.* 1987, 288
22 Armes, S. P. and Aldissi, M. *Polymer* 1990, **31,** 569
23 Cawdery, N., Obey, T. M. and Vincent, B. *J. Chem. Soc., Chem. Commun.* 1988, 1189
24 Epron, F., Henry, F. and Sagnes, O. *Makromol. Chem., Macromol. Symp.* 1990, **35/36,** 527
25 Odegard, R., Skotheim, T. A. and Lee, H. S. *J. Electrochem. Soc.* 1991, **138,** 2930
26 Digar, M. L., Bhattacharyya, S. N. and Mandal, B. M. *J. Chem. Soc., Chem. Commun.* 1992, 18
27 Armes, S. P. and Aldissi, M. *Synth. Met.* 1990, **37,** 137
28 Beaman, M. and Armes, S. P. *Colloid Polym. Sci.* 1993, **271,** 70
29 Armes, S. P. and Aldissi, M. *J. Chem. Soc., Chem. Commun.* 1989, 88
30 Vincent, B. and Waterson, J. W. *J. Chem. Soc., Chem. Commun.* 1990, 683
31 Liu, J.-M. and Yang, C. *J. Chem. Soc., Chem. Commun.* 1991, 1529
32 Gospodinova, N., Mokreva, P. and Terlemezyan, L. *J. Chem. Soc., Chem. Commun.* 1992, 923
33 Armes, S. P., Aldissi, M., Agnew, S. F. and Gottesfeld, S. *Langmuir* 1990, **6,** 1745
34 Armes, S. P., Aldissi, M., Agnew, S. F. and Gottesfeld, S. *Mol. Cryst.* 1990, **190,** 63
35 Tadros, P., Luk. S. Y. and Armes, S. P. *J. Mater. Chem.* 1992, **2,** 125
36 DeArmitt, C. and Armes, S. P. *J. Colloid Interface Sci.* 1992, **150,** 134
37 Lui, C.-F., Moon, D.-K., Maruyama, T. and Yamamoto, T. *Polym. J.* 1993, **25,** 775
38 Maeda, S., Corradi, R. and Armes, S. P. *Macromolecules* 1995, **28,** 2905
39 Maeda, S., Gill, M. and Armes, S. P. *Langmuir* 1995, **11,** 1899
40 Flitton, R., Johal, J., Maeda, S. and Armes, S. P. *J. Colloid Interface Sci.* 1995, **173,** 135
41 Miksa, B. and Slomkowski, S. *Colloid Polym. Sci.* 1995, **273,** 47
42 Saito, R. and Ishizu, K. *Polymer* 1995, **36,** 4119
43 JIS M 8121, 1977 in 'Bunseki Kagaku Binran (Handbook of Analytical Chemistry)', Maruzen, Tokyo, 1991, p. 206
44 Berkowitz, J. B., Yamin, M. and Fuoss, R. M. *J. Polym. Sci.* 1958, **28,** 69