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Architecture of polymeric superstructures with polypyrrole spherical lattices

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Polymer microspheres were synthesized by oxidation polymerization of pyrrole (Py) with functional poly(vinyl alcohol) having pendant Py groups as an emulsifier in water. Polypyrrole (PPy) microspheres had a very narrow particle size distribution ($\bar{D}_w/\bar{D}_n = 1.02$). Structural ordering of these microspheres was investigated through small-angle X-ray scattering measurements in *N*-vinylpyrrolidone (VP) monomer. The microspheres formed a lattice with a body-centred cubic structure near the overlap concentration. The polymeric superstructure was constructed by free radical polymerization of the monomer solution. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Nanoscopic conducting materials have been attracting considerable interest in recent years. We have reported the preparation of anisotropic conducting materials via the oxidation polymerization of pyrrole (Py) on microphase-separated block copolymer films (lamellar morphology) as a template[1]. These materials had a supramolecular structure composed of horizontally oriented lamellar microdomains of polypyrrole (PPy)/insulator layers (each domain was 20 nm in size). If the self-assemblies of such block copolymers can be fixed by crosslinking of the spherical microdomains, the crosslinked products should form the core-shell type microspheres. According to this concept, we prepared a new colloidal form of PPy core using microphase-separated spherical domains instead of lamellar structure as a micellar reaction vessel[2]. However, the film cast from such microspheres showed no sign of an electrically conducting nature (10^{-13} S cm^{-1}). The PPy cores (diameter, 46 nm) were not arranged continuously with each other but were located at a 10^2 nm order of magnitude. This morphology was the same as that shown in the original block copolymer film.

It is well known that submicrometre periodic ordered structures called crystalline colloidal arrays self-assemble from monodisperse colloidal spheres containing surface functional groups that ionize in solution[3–12]. If these spheres are dispersed in a polar medium such as water, the surface groups ionize to form spherical macroions which are surrounded by a diffuse counterion cloud. For high particle concentrations, significant interparticle repulsion occurs at the average interparticle spacing; the minimum energy configuration for the assembly of spherical macroions is a body-centred cubic (BCC) or face-centred cubic (FCC) crystal structure[13].

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More recently, Asher *et al.*[14] have developed an approach to permanently lock the crystalline colloidal array ordering in a solid matrix. They introduced into the crystalline colloidal array highly purified nonionic polymerizable monomers that can form a hydrogel network around the spherical particles. This approach is superior for the design of a variety of polymeric superstructures.

In this article, we report the architecture of polymeric superstructures with PPy spherical lattices. The PPy microspheres were synthesized by emulsion–oxidation copolymerization of Py monomer with functional poly(vinyl alcohol) in water. After these microspheres were arranged to form a BCC structure in *N*-vinylpyrrolidone (VP) monomer, the polymeric superstructure was constructed by free radical polymerization of VP monomer as a matrix. This concept can be developed for new electronic devices such as a tunnel-current device.

EXPERIMENTAL

Oxidation copolymerization

Functional poly(vinyl alcohol) (PVA-P) was prepared from the reaction of poly(vinyl alcohol) (PVA; $\bar{M}_n = 8.8 \times 10^4$ g mol^{-1}, degree of saponification = 78–82 mol%) with 4-(1H-pyrrole-1-yl)benzoic acid (PBA) in dimethyl sulfoxide in the presence of dicyclohexylcarbodiimide as a catalyst. The content of PBA was determined to be 15 per molecule by element analysis. Details concerning the synthesis and characterization have been given elsewhere[15].

Oxidation copolymerizations were carried out at 20°C under a nitrogen atmosphere in a glass vessel. Initially the mixture of PVA-P (0.120 g) and ferric chloride ($FeCl_3 \cdot 6H_2O$, 1.352 g) was dissolved in water (40 ml). To this solution was added purified Py monomer (0.8 ml),

and the mixture was maintained in a thermostatted bath with shaking (150 shakes min^{-1}) for 24 h. The resulting product was dialysed through a cellulose tube for 1 week. The polymer microsphere was removed by separation using a centrifugation technique.

Morphology and particle size of the polymer microspheres were obtained by scanning electron microscopy (SEM; JEOL JSM-T220) with a tilt angle of 30°C. The particle size distribution was determined from SEM micrographs. The hydrodynamic diameter (D_h) of the polymer microspheres was determined using dynamic light scattering (DLS: scattering angle = 90°, Otsuka Electric Co. Ltd Photal TMLS-6000HL) in 0.01 wt% water ($\eta = 0.890$ cp, $n_D = 1.33$) solution at 25°C.

SAXS measurements

The SAXS intensity distribution was measured with a rotating-anode X-ray generator (Rigaku Denki Rotaflex RTP 300RC) operated at 40 kV and 100 mA. The X-ray source was monochromatized to Cu Kα ($\lambda = 1.54$ Å) radiation. In the measurement of the *N*-vinylpyrrolidone (VP) solution of the sample, we used glass capillary ($\phi = 2.0$ mm, Mark-Röhrchen Ltd) as holder vessel.

Immobilization of superlattice

The reaction vessel was a 100 ml flask with a flat flange, lid and stopcock. The prescribed VP solution of PPy microspheres in a Petri dish was mounted inside the reaction vessel. Free radical polymerization was carried out in the presence of 2,2′-azobisisobutyronitrile (AIBN; initiator) and *N*,*N*′-methylenebis (acrylamide) (BAA; crosslinker) at 60°C in vacuum for 6 h. After polymerization, a SAXS measurement was taken for the film in order to check the immobilization of the PPy lattices.

RESULTS AND DISCUSSION

In a previous work[15], we studied the effects of the solvent medium and PVA-P concentration on PPy microsphere formation. Within a few seconds of adding Py to the reaction mixture the colour changed from orange to brown-black, indicative of the onset of polymerization. After 15 h of polymerization, > 90% conversion of monomer was achieved. We employed the optimum conditions of oxidation polymerization to obtain a relatively small diameter of the PPy particle size. This was because the three-dimensional ordering structure formed by PPy particles of small diameter can be made clear by means of SAXS measurements.

Table 1 lists the oxidation polymerization conditions and results for experiment OP-11. A typical SEM micrograph of the polymerization product OP-11 is shown in *Figure 1*. The product OP-11 comprises spherical particles of PPy; moreover, it is found from this micrograph that the particle size distribution ($\bar{D}_w/\bar{D}_n = 1.03$) of these microspheres is very narrow. The value of particle diameter ($\bar{D}_n$) in the solid state is 94 nm. On the hypothesis that all amounts of the feed stabilizer (PVA-P) are grafted quantitatively on the PPy microspheres (the feed amount of PVP-P being 15 wt for Py monomer), the core diameter of the PPy particle can be estimated to be *ca* 90 nm. *Figure 2* shows the DLS result of particle size distribution for the OP-11 microsphere in water. A single clear peak for the diameter ($\bar{D}_h$) can be observed at 122.2 nm. Therefore, the PPy cores are stabilized stereoscopically by stretched PVA graft chains in water.

These microspheres are expected to form the ordered structure near the overlap concentration (C^*). We calculated the C^* of the PPy microspheres as follows. The overlap concentration C^* is given by

$$C^* = 3M_w/(4\pi R_h^3 N_A) \quad (1)$$

where R_h is the hydrodynamic radius of the PPy microspheres and is therefore equal to $(1/2)\bar{D}_h$. M_w and N_A are the molecular weight of PPy microspheres and the Avogadro number, respectively. This equation can be reduced to the following equation using D_n (particle diameter of PPy microspheres in the solid state), D_h and d_M (density of PPy microsphere):

$$C^* = d_M(D_n/D_h)^3 \quad (2)$$

The values of D_n (94 nm) and d_M (1.42 g ml^{-1}) were taken from a SEM micrograph and the density measurement. C^* was estimated to be 0.281 g ml^{-1} in water.

Below C^*, the microspheres remain isolated, as any arrangements of microspheres in VP monomer are expected to appear near or above C^*. We therefore studied the possibility of structural ordering of OP-11 microspheres in VP monomer by means of SAXS measurements, varying the microsphere concentrations with reference to the C^* value in water. *Figure 3* shows typical SAXS intensity distributions for the microsphere solutions (15, 20 and 25 wt% microsphere concentrations) in the small-angle region. The arrows show the scattering angles. Values in parentheses indicate the interplanar spacings (d_1/d_n) of cubic lattices. *Table 2* lists the interplanar spacings for three types of cubic lattice according to Bragg's equation: $2d \sin\theta = n\lambda$ (where θ is one-half the scattering angle, $\lambda = 1.5418$ Å). As the OP-11 microspheres had a relatively large particle size, the scattering peaks appeared at the side of low angular position. The first scattering peak could therefore not be detected in the SAXS profiles. In this work, we inferred the position of the first peak by fitting from high-order scattering peaks.

Table 1 Oxidation polymerization conditions and results of PPy microspheres[a]

	Feed				PPy microsphere			
	Py	PVP-P	$FeCl_3 \cdot 6H_2O$	water	in solid[b]		in water[c]	
Code	(ml)	(g)	(g)	(ml)	D_n (nm)	D_w/D_n	D_h (nm)	$\bar{D}_w/\bar{D}_n$
OP-11	0.8	0.120	1.352	40	94	1.03	122.2	1.02

[a] Polymerized at 20°C for 24 h
[b] Particle diameter ($\bar{D}_n$) in the solid state determined by SEM micrographs
[c] Particle diameter in water determined by DLS

Figure 1 SEM micrograph of PPy microsphere OP-11

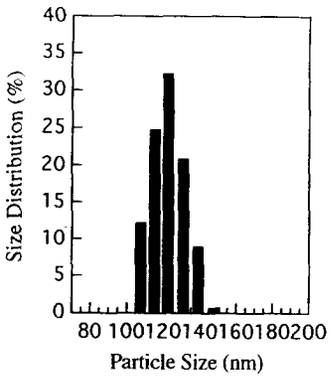

Figure 2 Particle size distribution for PPy microsphere OP-11 in water

We measured first the SAXS of the OP-11 microsphere at 15 wt% VP monomer solution (*Figure 3a*). Although several scattering peaks appeared at this concentration, regular interplanar spacings (d_1/d_n) corresponding to a packing pattern of cubic structures were not obtained from the SAXS intensity distribution. We therefore judged this particle solution to be disordering. At 20 wt% VP monomer solution (*Figure 3b*), the first eight peaks appear closely at the relative angular position of $\sqrt{5} : \sqrt{6} : \sqrt{7} : \sqrt{8} : \cdots$ on the basis of the first scattering angle ($2\theta = 0.107$) as shown by the arrows. This packing pattern is identical to the interplanar spacings of the BCC structure (see *Table 2*). At 25 wt% VP monomer solution (*Figure 3c*), the first six peaks appear closely at the relative angular positions on the basis of the first scattering angle ($2\theta = 0.110$). In these interplanar spacings, the relative angular positions of $\sqrt{3} : \sqrt{12}$ correspond to a packing pattern of a BCC structure. On the other hand, the relative angular positions of $\sqrt{16/3} : \sqrt{20/3} : \sqrt{8} : \sqrt{43/3}$ correspond to a packing pattern of an FCC structure. Therefore, it is concluded that the microspheres at 25 wt% VP monomer are packed in a mixed lattice of BCC and FCC structures.

We consider spatial packing of the cubic lattice in solution. The measured Bragg spacing d_1 is related to the cell edge a of the cubic lattice and the nearest-neighbour distance of the spheres D_s (see *Figure 4* for a BCC lattice):

$$D_s = (\sqrt{3}/2)a = (\sqrt{3/2})d_1 \qquad \text{for BCC} \qquad (3)$$

By using these relations, the radius R_s (equal to $D_s/2$) of spheres in solution was estimated as listed in *Table 3* (code OP-11-20).

We formed a solid superlattice film by introducing purified BAA (3 wt% for VP monomer) and AIBN

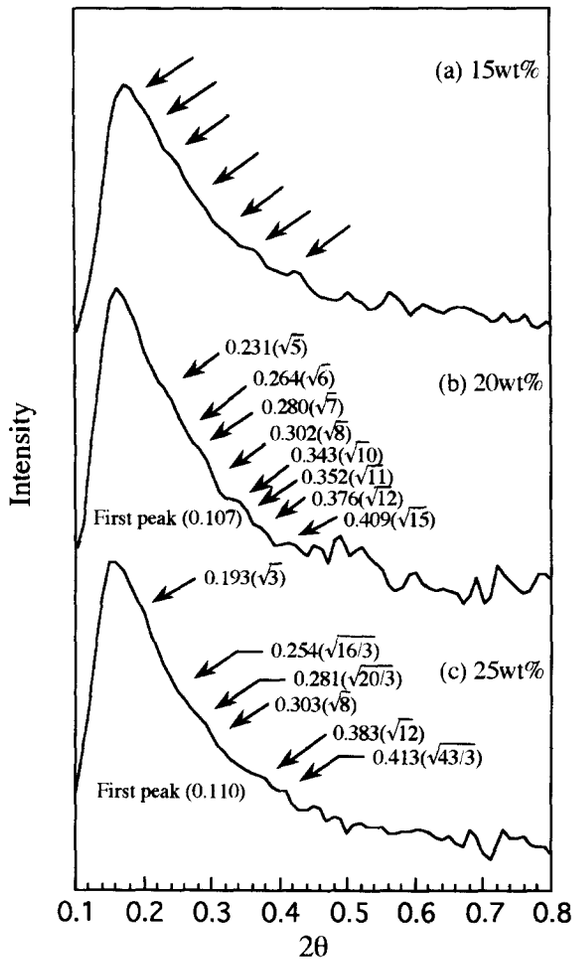

Figure 3 SAXS intensity distributions for *N*-vinylpyrrolidone solutions of microsphere OP-11. The arrows show the scattering maxima. The values in parentheses indicate the cubic packing (d_1/d_i): (a), 15 wt% PPy concentration; (b), 20 wt% PPy concentration; (c), 25 wt% PPy concentration

Table 2 Interplanar spacings for three types of cubic lattice

	SC[a]	BCC	FCC
d_1/d_1	1	1	1
d_1/d_2	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{4/3}$
d_1/d_3	$\sqrt{3}$	$\sqrt{3}$	$\sqrt{8/3}$
d_1/d_4	2	2	$\sqrt{11/3}$
d_1/d_5	$\sqrt{5}$	$\sqrt{5}$	2
d_1/d_6	$\sqrt{6}$	$\sqrt{6}$	$\sqrt{16/3}$
d_1/d_7	$\sqrt{8}$	$\sqrt{7}$	$\sqrt{19/3}$
d_1/d_8	3	$\sqrt{8}$	$\sqrt{20/3}$
d_1/d_9	$\sqrt{10}$	3	$\sqrt{8}$
d_1/d_{10}	$\sqrt{11}$	$\sqrt{10}$	3

[a] Simple cubic

(5 wt% for monomer) into the OP-11-20 solution, and polymerized it at 60°C to decompose AIBN in vacuum for 6 h. By this procedure, the VP monomers can be expected to form a network around the superlattice of PPy microspheres. We tried first to excite benzoin methyl ether (photosensitizer) to initiate the polymerization using u.v. light. However, photopolymerization proceeded scarcely, perhaps due to extremely low transmission of the u.v. beam through the monomer solution containing the black particles of PPy.

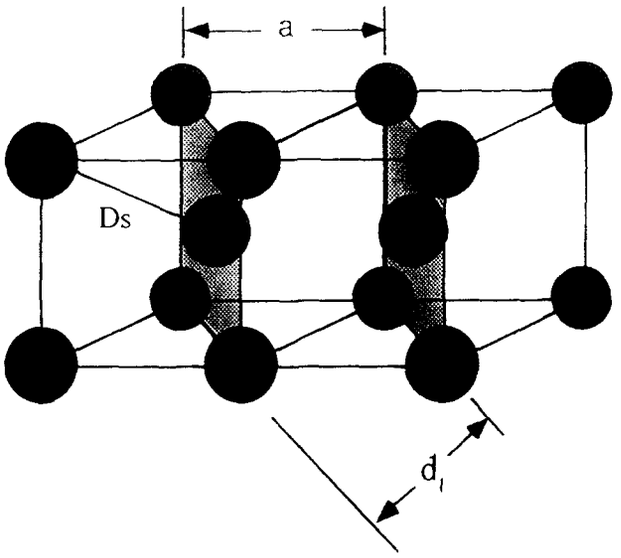

Figure 4 Schematic illustration of BCC lattice

Table 3 Space arrangement of PPy microspheres before and after immobilizing[a]

Code	d_1 (nm)	a (nm)	D_s (nm)	Lattice
OP-11-20	82.9	117.3	101.6	BCC
OP-11-20I[b]	79.9	113.0	97.9	BCC

[a] OP-11-20 [20-wt% VP solution of OP-11] (D_n = 94 nm) was polymerized with AIBN and BAA at 60°C in vacuum for 6 h
[b] Immobilized film of OP-11-20

The SAXS intensity distribution of the solid superlattice film after immobilization (OP-11-20I) is shown in *Figure 5*. It is found that the first eight peaks appear closely at the relative angular position of $\sqrt{3} : 2 : \sqrt{5} : \sqrt{6} : \cdots$ on the basis of the first scattering angle ($2\theta = 0.111$) as shown by the arrows. This packing pattern is identical to the interplanar spacings of a BCC structure. This monomer solution of PPy particles was locked with a BCC lattice into a poly(*N*-vinylpyrrolidone) (PVP) network by free radical polymerization. It is also noticed that the first peak ($2\theta = 0.111$) of a solid film shifts to the side of high angular position compared to that ($2\theta = 0.107$) of the OP-11-20 sample. This means that the d_1 of the solid film became shorter than that of OP-11-20, because the volume shrinkage of PVP occurred during polymerization of the VP monomer. The space arrangement of a solid film OP-11-20I is also given in *Table 3*.

It was mentioned previously that the core diameter $\bar{D}_{(core)}$ of PPy particles and the shell thickness of PVP-P grafted chains could be estimated as 90 and 2 nm, respectively, in the solid state. *Figure 6* shows the illustration of the space arrangement for the nearest-neighbour PPy microspheres in the solid state. Here $\bar{D}_{(insulator)}$ is the distance of the insulator part between the nearest-neighbour PPy particles. The stretched PVA-P graft chains therefore stabilized sterically the PPy microspheres in the VP monomer solution. After immobilization of the superlattice of PPy microspheres, the PVA-P thin layers (2 nm) seemed to enclose the surface of the PPy particle due to immiscibility between

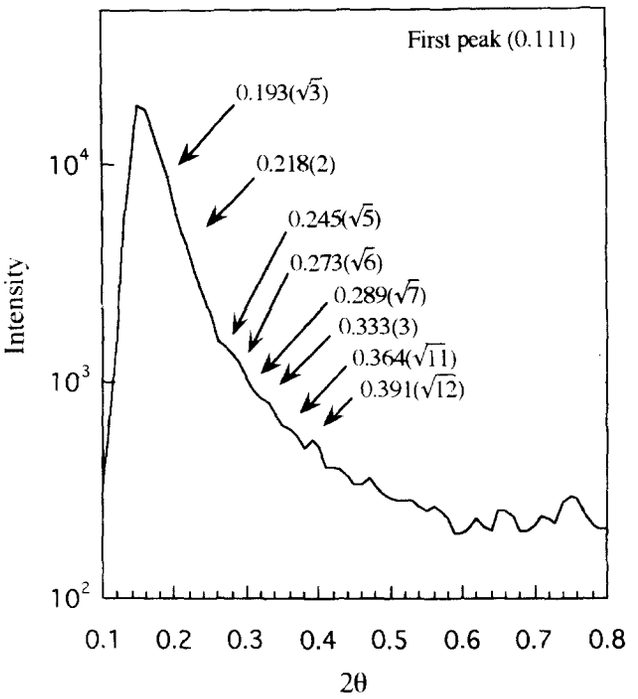

Figure 5 SAXS intensity distribution for solid superlattice film (OP-11-20I). The arrows show the scattering maxima. The values in parentheses indicate the cubic packing (d_1/d_i)

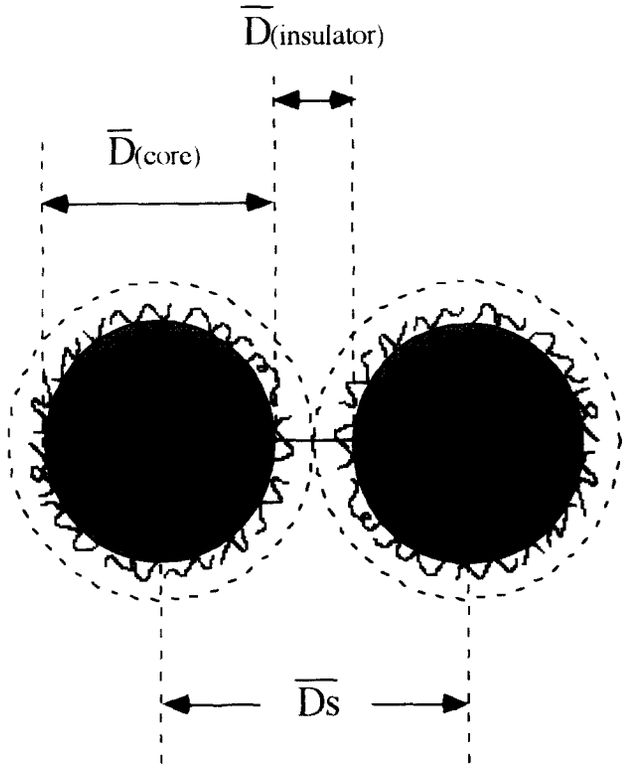

Figure 6 Illustration of space arrangement for the nearest-neighbour PPy microspheres in the solid state

PVA and PVP chains. *Table 4* lists the domain spacings of the nearest-neighbour PPy microspheres before and after radical polymerization, evaluated from the SAXS data. The value of $\bar{D}_{(insulator)}$ decreased from 11.6 to

Table 4 Domain spacings of nearest-neighbour PPy microspheres before and after radical polymerization

State	$\bar{D}_{(core)}$ (nm)	$\bar{D}_s$ (nm)	$\bar{D}_{(insulator)}$ (nm)
Monomer solution (OP-11-20)	90	101.6	11.6
Solid film (OP-11-20I)	90	97.9	7.9

7.9 nm due to the volume shrinkage during radical polymerization of the VP monomer. The interplanar spacings of superstructures can be controlled by changing the monomer concentration and the types of cubic lattice.

The work here demonstrates a design for preparing polymeric superstructures composed of nanoscopic cubic lattices. The PPy microspheres prepared in this work can be converted to colloidal dispersions in organic solvents by means of acetylation of PVA as a stabilizer. Therefore, hydrophilic monomer in the film can be replaced by other hydrophobic monomers without changing the cubic lattice of PPy particles. These systems will have numerous applications in electronic and optical devices.

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