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Microsphere synthesis of polypyrrole by oxidation polymerization

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Polymer microspheres were synthesized by oxidation polymerization of pyrrole (Py) with functional poly(vinyl alcohol) having pendent Py groups (PVA-P) or poly(vinyl alcohol) (PVA) as an emulsifier in various solvent media. In this polymerization system, PVA-P acted not only as a comonomer but also as a stabilizer. The diameter (submicrometre range) of the polymer microspheres decreased with increasing PVA concentration in the medium. Polypyrrole (PPy) microspheres had a very narrow particle size distribution ($\bar{D}_w/\bar{D}_n <\sim 1.05$). The particles stabilized with PVA-P were smaller than the corresponding particles stabilized with PVA. The use of PVA-P as an emulsifier was favourable to the formation of micelles with Py monomers. The electrical conductivity of the PPy particles was in the range $10^{-5}-10^{-1}$ S cm^{-1}, depending on the amount of dopant.

(Keywords: microsphere; pyrrole; oxidation polymerization)

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 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).

On the other hand, there have been reports on the preparation of monodisperse polymer microspheres in the micrometre-submicrometre range, these microspheres having potential applications in areas such as the biomedical field, the information industry and microelectronics. These studies have been almost exclusively concerned with synthesis by means of emulsion and soap-free polymerizations. In emulsion polymerization, the emulsifier stabilizes the water-insoluble monomer particles.

More recently, attempts have been made to synthesize polymer microspheres by dispersion copolymerization using hydrophilic macromonomers, such as poly(vinylpyrrolidone)[2,3], poly(2-alkyl-2-oxazoline)[4,5], poly(ethylene oxide)[6-8] and poly(methacrylic acid)[9], instead of a homopolymer as a stabilizer. The macromonomer acted not only as a stabilizer but also as a comonomer. Armes and co-workers[10] have prepared stable, aqueous dispersions of PPy latex particles by a dispersion polymerization technique using ferric chloride as the initiator and partially hydrolysed poly(vinyl acetate) as the emulsifier. They obtained monodisperse particles (100-150 nm diameter) as a function of the feed concentration of emulsifier. However, the effects on particle formation of the molecular weight of the emulsifier and the polarity in the reaction medium have not been resolved.

In this work, we prepared functional poly(vinyl alcohol) having pendent Py groups (PVA-P). The polymer microspheres were synthesized by emulsion-oxidation copolymerization of Py monomer with PVA-P or poly(vinyl alcohol) (PVA) in various solvent media. We studied the control of particle size and size distribution as functions of the solvent composition, the molecular weight and the feed amount of emulsifier.

EXPERIMENTAL

Synthesis and characterization of functional poly(vinyl alcohol)

A mixture of PVA (Tokyo Kasei #2000; $\bar{M}_n = 8.8 \times 10^4$ g mol^{-1}, degree of sponification = 78-82 mol%) and 4-(1H-pyrrole-1-yl)benzoic acid (PBA; Aldrich Chemicals) was stirred in dimethyl sulfoxide (DMSO) at 40°C for 7 days in the presence of dicyclohexylcarbodiimide (DCCI) as a catalyst. The resulting mixture was poured into tetrahydrofuran (THF). Purification was repeated three times from the water-THF system. The content of PBA was determined by Fourier transform infra-red

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(*FT*i.r.) spectroscopy (Shimadzu FTIR-8500 spectrometer) and elemental analysis.

Oxidation copolymerization

Oxidation polymerizations were carried out at 20°C under a nitrogen atmosphere in a glass vessel. Initially the mixture of PVA-P or PVA and ferric chloride ($FeCl_3 \cdot 6H_2O$) was dissolved in the solvent medium. To this solution was added purified Py monomer, and the mixture was maintained in a thermostated bath with shaking (150 shakes min^{-1}). 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, and resulting products were dialysed through a cellulose tube for 1 week. The polymer microspheres were removed by separation using a centrifugation technique.

Measurements

Morphology and particle size of the polymer microspheres were obtained by scanning electron microscopy (SEM; JEOL JSM-T220) with a tilt angle of 30°. The particle size distribution was determined from SEM micrographs.

Conductivity measurements were made on films cast from particle dispersions. The method and instrument used to measure conductivities are given in a previous report[11].

RESULTS AND DISCUSSION

The functional PVA having pendent Py groups (PVA-P) was synthesized by the reaction of PVA and PBA in the presence of DCCI as a catalyst. *Table 1* lists the reaction conditions and characteristics of PVA-P1 and PVA-P2. The rate of ester exchange reactions was very slow due to poor solubility of PVA in DMSO. A typical *FT*i.r. spectrum of PVA-P1 is shown in *Figure 1*, along with the spectra of PVA and a PVA/PBA blend to judge the introduction of Py groups by the ester exchange reaction. In the spectrum of PVA-P1, the characteristic absorptions due to secondary hydroxyl groups of PVA are observed at 3630 cm^{-1}. Bands are also observed at 1540 and 1680 cm^{-1} (as indicated by arrows) that are attributable to the 1,4-substituted phenyl group of PBA. It is found qualitatively that PBA groups are introduced into pendent positions of PVA molecules. The content of PBA was determined by element analysis. The Py contents of PVA-P1 and PVA-P2 are 15 and 102 (number/1-polymer), respectively.

In order to determine the yield of PPy microspheres, we examined first the relationship between conversion of the monomer and time for oxidation polymerization. Initially, 0.15 g of PVA ($\bar{M}_n = 8.8 \times 10^4$ g mol^{-1}; 15 wt% for Py monomer) plus 0.004 mol of $FeCl_3$ were dissolved in 50 ml water. To this solution was added 1 ml (0.014 mol) of Py monomer, and the mixture was stirred at 20°C for 1–24 h. *Figure 2* shows the time–conversion curve of Py monomer by oxidation polymerization. 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 1 h of polymerization, ~ 80% conversion of monomer was achieved; and it is shown that > 90% conversion of monomer is achieved after 15 h. So, we set 24 h as the oxidation polymerization time in the following experiments.

We studied the effect of the solvent medium [tetrahydrofuran (THF)/water and ethanol/water] on microsphere formation by varying the solvent composition. *Table 2* lists the oxidation polymerization conditions and the results for experiments Op-10–Op-14 (THF/water medium) and OP-20 (ethanol/water). Typical SEM micrographs of the polymerization products OP-12,

Table 1 Synthetic conditions and characteristics of functional PVA having pendent pyrrole groups (PVA-P)[a]

Expt	PVA[b] (g)	PBA[c] (g)	DCCI[d] (g)	DMSO (ml)	Py content[e] (number/1-polymer)
PVA-P1	0.56	0.10	0.33	10	15
PVA-P2	0.56	0.20	0.66	10	102

[a] Stirred at 40°C for 7 days
[b] $\bar{M}_n = 8.8 \times 10^4$ g mol^{-1}
[c] 4-(1H-Pyrrole-1-yl)benzoic acid
[d] Dicyclohexylcarbodiimide
[e] Determined by elemental analysis

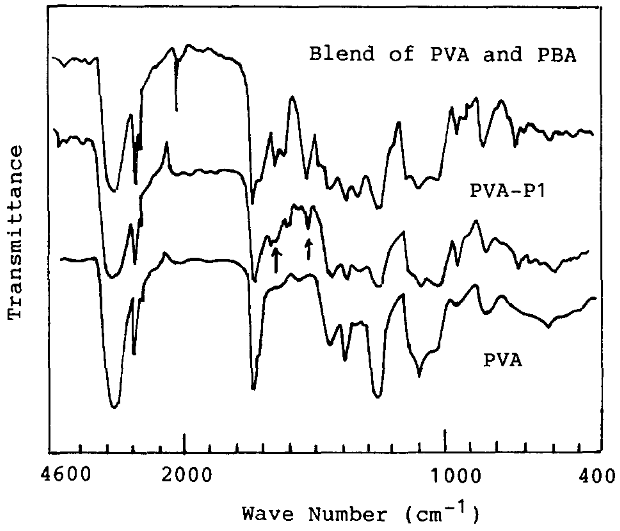


Figure 1 Typical *FT*i.r. spectra of PVA-P1, PVA and the blend of PVA and PBA

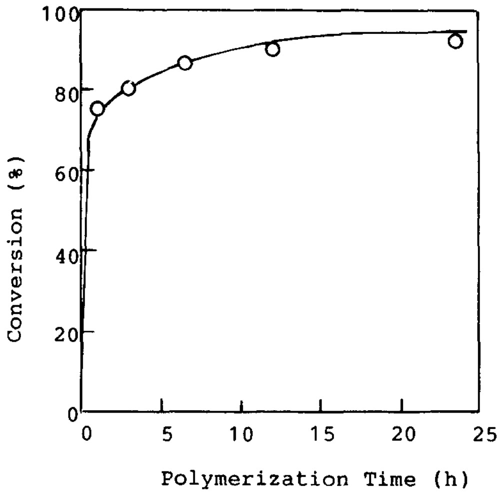


Figure 2 Time–conversion curve of Py monomer by oxidation polymerization

Table 2 Oxidation polymerization conditions and results for experiments OP-10–OP-14 and OP-20, varying solvent composition[a]

Expt	THF/water (v/v)	$\bar{D}_n$[b] (μm)	$\bar{D}_w/\bar{D}_n$[b]
OP-10	0/10	0.13	1.05
OP-11	2/8	0.17	1.08
OP-12	4/6	0.36	1.04
OP-13	5/5	0.40	1.07
OP-14	6/4	0.38	1.11
OP-20[c]	5/5	0.41	1.01

[a] Polymerized at 20°C for 24 h: PVA ($\bar{M}_n = 8.8 \times 10^4\,\mathrm{g\,mol^{-1}}$) = 15 wt% for Py monomer. Py = $0.28\,\mathrm{mol\,l^{-1}}$, $FeCl_3 = 0.08\,\mathrm{mol\,l^{-1}}$

[b] Determined from SEM micrographs

[c] Solvent medium: ethanol/water

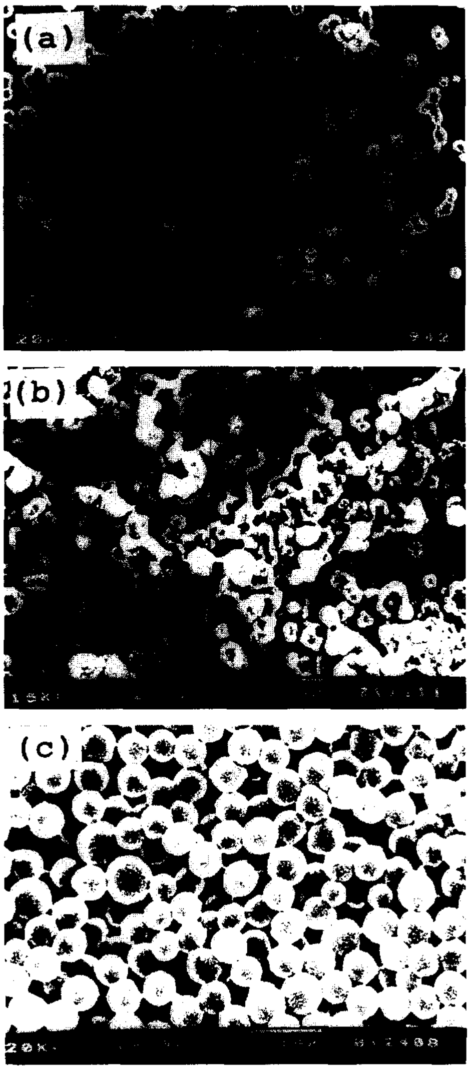


Figure 3 SEM micrographs of polymerization products OP-12 (a), OP-13 (b) and OP-20 (c)

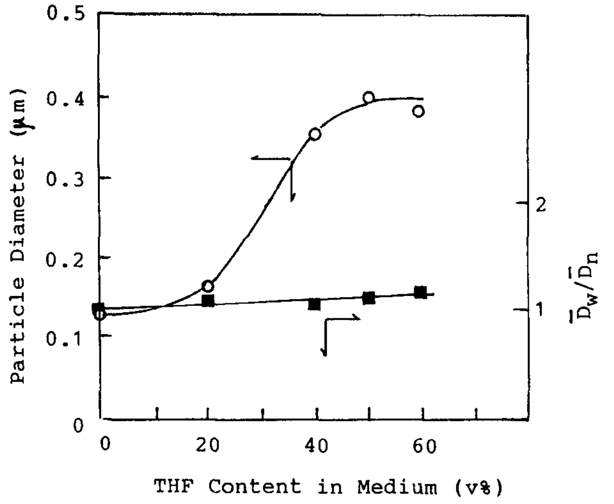


Figure 4 Dependence of particle diameter and particle size distribution on solvent composition (THF/water medium)

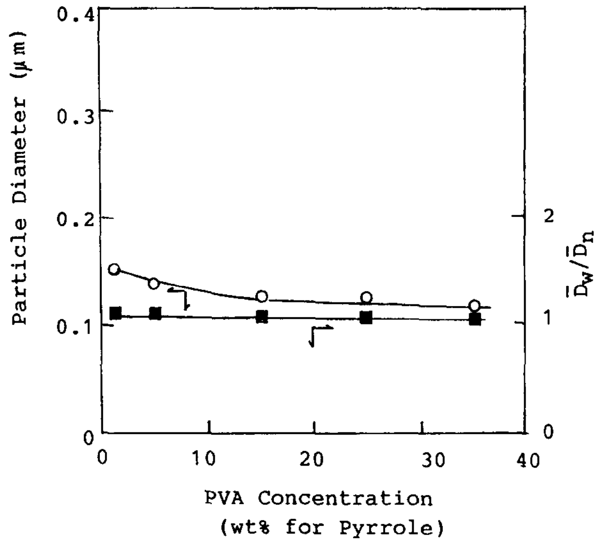


Figure 5 Dependence of particle size and particle size distribution on PVA concentration

OP-13 and OP-20 are shown in *Figures 3a–c*, respectively. The product OP-12 comprises spherical particles of PPY; moreover, it is found from this micrograph that the particle size distribution ($\bar{D}_w/\bar{D}_n$) of these microspheres is very narrow. On the other hand, the product OP-13 shows a morphology of partially aggregated PPy particles. The values of particle diameter ($\bar{D}_n$) and $\bar{D}_w/\bar{D}_n$ are collected in *Table 2*. *Figure 4* shows the dependence of particle diameter and particle size distribution on solvent composition (THF/water medium). The diameter of the microspheres increases gradually with increasing THF content in the medium. Submicrometre-sized polymer microspheres have a relatively narrow size distribution ($\bar{D}_w/\bar{D}_n = 1.04$–$1.11$). Thus, we observed a tendency in which the more hydrophilic the solvent medium became, the smaller the particle size of PPy. *Figure 3c* shows the SEM micrograph of OP-20 (ethanol/water = 5/5 (v/v) medium); in this solvent, submicrometre-sized PPy microspheres also have a very narrow size distribution ($\bar{D}_w/\bar{D}_n = 1.01$).

We examined the influence of PVA concentration on microsphere formation (PVA; $\bar{M}_n = 8.8 \times 10^4\,\mathrm{g\,mol^{-1}}$; Py = $0.28\,\mathrm{mol\,l^{-1}}$; $FeCl_3 = 0.08\,\mathrm{mol\,l^{-1}}$ in water). *Figure 5* shows the dependence of particle size and particle size distribution on PVA concentration: the diameter (0.10–0.15 μm) of the microspheres decreases gradually with increasing PVA concentration. However, the microspheres obtained under the conditions < 5 wt% PVA concentration for Py monomer, indicated partial aggregation behaviour. It is seen that PPy particles are

Table 3 Oxidation polymerization conditions and results for experiments OP-30–OP-32 and OP-40–OP-42[a]

	Emulsifier[b]				
Expt.	Code	Py content (number/1-polymer)	Conc. (wt% for Py monomer)	$\bar{D}_n$[c] (μm)	$\bar{D}_w/\bar{D}_n$[c]
OP-30			2	0.12	1.05
OP-31	PVA-P1	15	5	0.11	1.05
OP-32			15	0.09	1.01
OP-40			2	0.11	1.03
OP-41	PVA-P2	102	5	0.08	1.01
OP-42			15	0.06	1.02

[a] Polymerized at 20°C for 24 h: Py = 0.28 mol l^{-1}, $FeCl_3$ = 0.08 mol l^{-1} in water
[b] $\bar{M}_n$ of PVA-P1 and PVA-P2 = 8.8×10^4 g mol^{-1}
[c] Determined from SEM micrographs

stabilized by >~ 10 wt% PVA concentration for Py monomer as an emulsifier.

We studied the dependence of particle size and particle size distribution on molecular weight of PVA. Oxidation polymerization was carried out under similar conditions to experiment OP-10: PVA ($\bar{M}_n = 2.2 \times 10^4$ g mol^{-1}) concentration = 15 wt% for Py monomer, Py = 0.28 mol l^{-1}, $FeCl_3$ = 0.08 mol l^{-1} in water. As a result, the particle size ($\bar{D}_n$) and particle size distribution ($\bar{D}_w/\bar{D}_n$) were 0.20 μm and 1.17, respectively. The particle diameter seemed to decrease gradually with increasing molecular weight of PVA. High-molecular-weight emulsifier is favourable to steric stability of PPy microspheres formed by oxidation polymerization.

Next, we studied the effect of functional PVA having pendent Py groups (PVA-P) as an emulsifier on microsphere formation. *Table 3* lists the oxidation polymerization conditions and results for experiments OP-30–OP-32 and OP-40–OP-42. It was found from SEM micrographs that the products were spherical PPy microspheres and their particle size distributions were very narrow ($\bar{D}_w/\bar{D}_n$ <~ 1.05). It was mentioned previously that the PPy microspheres obtained under the conditions < 5 wt% PVA ($\bar{M}_n = 8.8 \times 10^4$ g mol^{-1}) concentration for Py monomer, indicated partial aggregation behaviour.

The observed values of particle diameters are plotted against PVA-P1 or PVA-P2 concentration in *Figure 6*, where the data concerning oxidation polymerizations using PVA as an emulsifier are also plotted. It is indicated from these plots that the particle diameter (0.12–0.06 μm) decreases with increasing content of pendent Py groups at the same PVA concentration. The mechanism of adsorption of PVA on the PPy particles is related to the interaction between hydrophobic acetate groups in the PVA and the PPy surface[10]. There may well be hydrogen bonding between the > C=O group of the acetate moieties and the H–N < group of the Py moieties. On the other hand, the PPy particles are stabilized by even 2 wt% of PVA-P1 or PVA-P2 concentration for Py monomer as an emulsifier. Both PVA-P1 and PVA-P2 acted not only as stabilizer but also as a comonomer. Pendent chains of functional PVA contain hydrophobic structures such as pyrrole *N*-substituted phenyl groups. The stronger the hydrophobic nature of the pendent groups of PVA becomes (corresponding to increasing content of pendent Py), the smaller the size of the Py monomer droplets (micelles) stabilized by the emulsifier. This may be because the critical degree of polymerization, at which the oligomers form the nuclei, decreases in the more hydrophobic nature of the pendent Py groups, and the number of nuclei increases. However, the solubility of PVA-P in water decreases with the introduction of greater amounts of pendent Py groups. This results in poor steric stability of PPy particles by grafted chains. So, the content of pendent Py groups on the PVA backbone may have to be an optimum amount to play a role in effective stabilization.

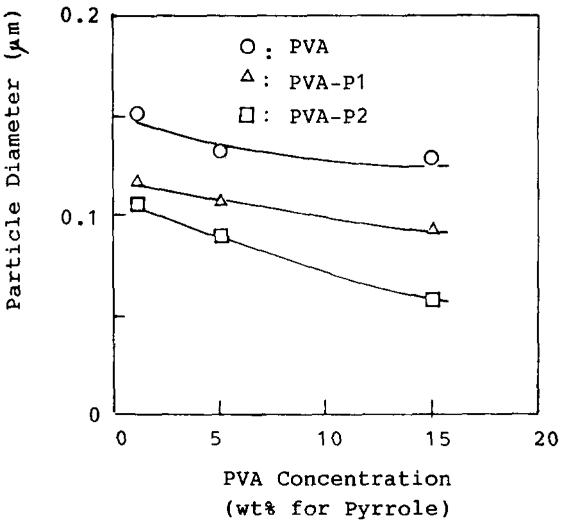


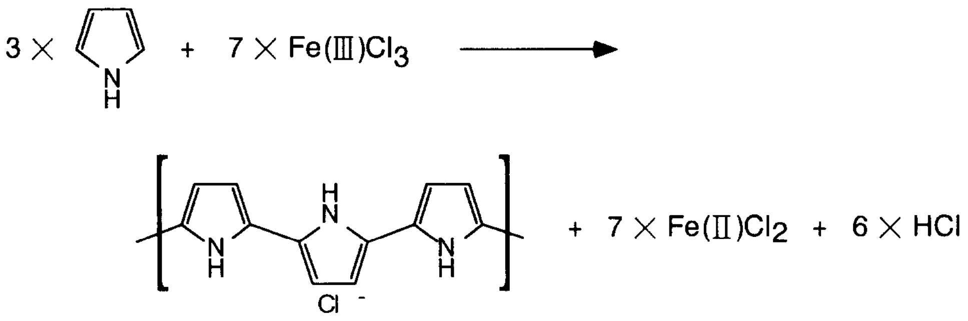
Figure 6 Plot of particle diameters against PVA-P1 or PVA-P2 concentration

Table 4 Conductivity of polypyrrole particles[a]

Expt	$FeCl_3$ (mol)	$\bar{D}_n$[b] (μm)	$\bar{D}_w/\bar{D}_n$[b]	σ[c] (S cm^{-1})
OP-50	0.004	0.13	1.01	8×10^{-6}
OP-51	0.008	0.12	1.03	2×10^{-5}
OP-52	0.017	0.16	1.03	7.78×10^{-2}
OP-53	0.033	0.17	1.05	9.7×10^{-3}

[a] Polymerized at 20°C for 24 h: Py = 1.0 ml (0.014 mol), PVA = 15 wt% for Py monomer ($\bar{M}_n = 8.8 \times 10^4$ g mol^{-1}) in 50 ml of water
[b] Determined from SEM micrographs
[c] Electrical conductivity

Table 4 lists the electrical conductivity of PPy particles obtained via oxidation polymerizations by varying the feed amounts of initiator. There appears to be a downward trend in conductivity with decreasing feed amounts of $FeCl_3$. Armes[12] has reported the optimum conditions for the polymerization of Py monomer in aqueous solution using $FeCl_3$ as the initiating/doping species. The approximate stoichiometric reaction is thought to proceed as shown in *Scheme 1*. There is one Cl ion associated with every three Py moieties in the polymer chains. In such optimum conditions, the feed amount of $FeCl_3$ to Py monomer becomes 2.33 (mol mol^{-1}). The polymerizaton OP-53 (*Table 4*) corresponds to this optimum condition. The PPy particles obtained in polymerization OP-52 show maximum conductivity (~ 0.1 S cm^{-1}). In addition, the decrease in conductivity is considered to be an effect of incorporation of the non-conducting PVA adsorbed in the PPy



Scheme 1

particles. Therefore, if high conductivity is desired, the ratio of stabilizer to monomer must be optimized.

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