Studies on the Preparation and Characterization of Poly(4-vinylpyridine) Microgel. I. Preparation with Polymer Emulsifier

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SYNOPSIS

Poly(4-vinylpyridine) (P4VP) microgels with a narrow size distribution have been prepared by a special emulsion polymerization method. This is to say that P4VP, to which cation and double-bond were introduced with iodomethane and chloromethylstyrene, by quarternization reaction, was used as a polymer emulsifier. Divinylbenzene was used as a crosslinking agent. It was found that the microgel became larger with the increase in monomer concentration, and became smaller and softer with the enhancing emulsifier/monomer ratio. Microgels, with the diameter of between 70–700 nm, were obtained by varying the monomer concentration from 1.0 wt % to 5.0 wt %, and by varying the emulsifier/monomer (unit/unit) ratio from 0–10.0 mol %. Compared with conventional emulsion polymerization with surfactant or hydrophilic monomer, this method provides an advantage in that monoingredient microgels can be obtained.

INTRODUCTION

Polymer latices, whose sizes are submicron (10–1000 nm) and which are crosslinked inside, are named microgels. The studies of the preparation,[1-19] characterization,[20-26] and application[27-34] of polymer microgels have become more and more attractive because of the microgels' special, interesting characters. For example, the globularity, various sizes, large surface areas, various swelling degrees, and various inside and outside characters among other things have caused microgels to be of special interest. In the application area, the character of the large surface area of the microgel has been utilized most extensively and for the longest time. Examples of some such uses are as a coating agent[27-30] and as an adhesive agent.[31] In recent years, the applications in medical science have come into prominence. Examples of this use include drugs,[32-34] fixed chemically or physically on the surface of microgels and then carried to a particular part of the body and released with the appropriate speed (polymer drugs); diagnostic medicine,[15] where antibodies (or antigens) are fixed on a microgel and the antibody–antigen reaction can be confirmed with the naked eye by observing the aggregation of microgels. Some uses require monoingredient microgels because another ingredient would spoil the microgel's properties.

In the preparation area of microgels, emulsion[1-11] or soap-free[12-16] polymerizations are the most popular, because the monodispersed microgel can be synthesized easily with the polymerization. Especially with soap-free polymerization method, one can take advantage of the fact that the different microgel, with various inside and outside characters, can be obtained by selecting properly the hydrophilic and hydrophobic monomer. This method, however, can not satisfy the demand of the monoingredient microgel (not to be stained by emulsifier or hydrophilic monomer) in application. It is thus necessary to establish the preparative methods of the monoingredient microgels. We will study the preparative method of the poly(4-vinylpyridine) (P4VP) monoingredient microgel in this study.

P4VP was selected for this study because its chemical properties, such as acidity, basicity, and hydrophilic and hydrophobic properties, can be modified. P4VP also can be crosslinked both within

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and among microgels easily. Its character can thus be designed for actual application. The preparative method that is often used for styrene microgel (acrylamide and N'N-dimethylaminopropylacrylamide were used as an hydrophilic monomer in a soap-free polymerization) cannot be applied to the case of 4VP. Unexpectedly, macrogels generated in both cases. This is probably due to the fact that the micelle nucleus cannot be formed as the polymerization progresses. We thus surmised that the partially quarternized, reactive P4VP could perhaps have been used as an emulsifier because it has interesting characteristics in an aqueous solution. For example, P4VP behaves like a polysoap, which forms an inside microdomain and can dissolve monomer oil. The place of polymerization can thus be exhibited as in Figure 1. Furthermore, the quarternized, monoingredient P4VP microgel can be obtained if we quarternize this microgel completely.

In this study, the value of the partially quarternized, reactive P4VP emulsifier for the preparation of microgels was confirmed, and the variations of size and characteristics of microgels with monomer concentrations, emulsifier/monomer ratios, were made clear.

EXPERIMENTAL

Materials and Apparatus

4-vinylpyridine (4VP), iodomethane (CH_3I), chloromethylstyrene (CMS), 1,4-diiodobutane, and divinylbenzene (DVB) were purchased from Tokyo Chemical Industries Co., Ltd. Water soluble azo-initiator 2,2-Azobis(2-methylpropionamidine) dihydrochloride (V50) and oil-soluble azo-initiator 2,2-Azobis(2-methylpropanenitrile) (AIBN) were offered by Wako Pure Chemicals Industries, Ltd. The 4VP, DVB, CMS, and methanol were distilled under reduced pressure of *ca.* 10^{-3}–10^{-4} mmHg before use. The 1,4-diiodobuthane, V50, and AIBN were used without further purification.

Water was purified by ion exchange resin.

A transmission electron microscope HITACHI H-50 was used.

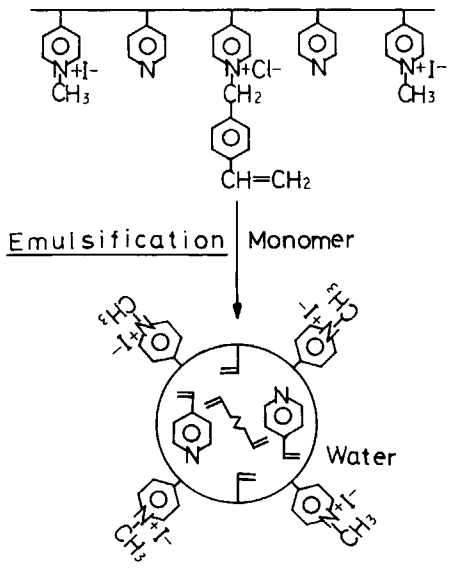


Figure 1 The role of partially quarternized and double bond-introduced P4VP emulsifier.

Preparation of Polymer Emulsifier

P4VP was synthesized by radical polymerization. A standard recipe for polymerization is given as: 4VP 100 g, solvent methanol 100 g, and initiator AIBN 0.5 g. The polymerization was carried out in a vacuum sealed 300 mL ampoule at 60°C for *ca.* 24 h. The resulting polymer was precipitated in large quantity of water to remove the residual monomer and other impurities. The dissolution of the polymer into methanol and precipitation cycles was repeated several times, then the polymer was dried in vacuum. The molecular weight of the polymer was calculated as follows,[35] with intrinsic viscosity determined in ethanol at 25°C using an Uelbuld viscosimeter:

$$[\eta] = 25 \times 10^{-3}\, M^{0.68}\ (\mathrm{mL/g}).$$

After 10 g of P4VP was dissolved in 50 mL methanol, 3.5 mL of CMS (26.5 mol %/4VP units) was added to it to react with the polymer while stirring for 24 h at room temperature to introduce a double-bond into the polymer. Then 3 mL (50.8 mol %/4VP units) of iodomethane was added in solution to partially quarternized P4VP, and the reaction was continued further for 24 h at room temperature. This solution was diluted with water to 200 mL and was stored in a refrigerator at 4°C to await use. The fractions quarternized by CMS and CH_3I were measured by an IR spectrometer. After quarternization, each solution was cast on a teflon plate to make a thin film for the IR spectrometer. The degree of quarternization ratio was next calculated from the IR spectrum using 1600 cm^{-1} (nonquarternized pyridine rings) and 1640 cm^{-1} (quarternized pyridine rings) absorbance with calibration as shown in Figure 2; Abs(1640)/[Abs(1640) + Abs(1600)] was plotted against the molar fraction of the quarternized 4VP unit, where Abs(n) was the absorbance at n cm^{-1}. The molar fraction of the quarternized

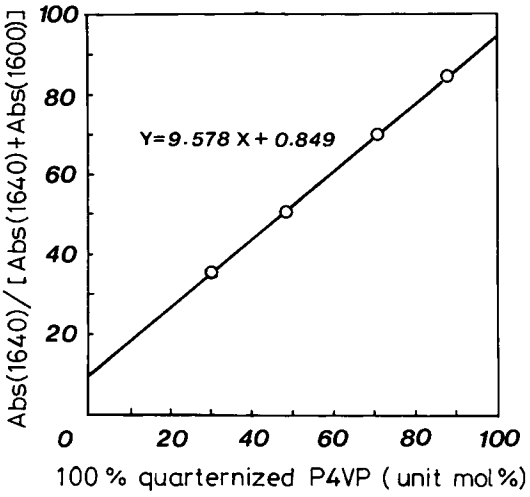


Figure 2 Calibration for the determination of quarternized fraction in P4VP.

4VP unit was determined by the mixing fraction of 100% quarternized P4VP in 100% quarternized P4VP and nonquarternized P4VP.

Synthesis of the Microgel

Emulsion polymerization was carried out in a 500-mL, three-neck, round-bottomed flask equipped with a nitrogen inlet and condenser. The standard recipe for polymerization was as follows: (4VP + emulsifier) 3–15 g, V50/4VP (wt/wt) 0.02, DVB/4VP (mol/mol) 0.05. Distilled water was added to bring all solutions to 300 mL. The 4VP unit ratio of polymer emulsifier to 4VP monomer (emulsifier/4VP) varied from 0 to 10.0 mol %. The detail feed composition in polymerization was summarized in Table I. The polymerization was carried out at 70°C for 12 h.

Characterization of Microgel

The conversion of the polymer was determined by gravimetry. 50 mL of the sample was sucked up, filtrated to remove the monomer by microfilter, and then dried and weighed. The size and shape of the dry microgel was observed by transmission electron microscope (TEM). The TEM sample for shadowing was prepared as follows: after the copper mesh was coated with a thin carbon film, one drop of dilute microgel solution (5×10^{-4} g/mL) was cast on it; after the sample was dried at room temperature for 24 h, it was coated with a thin Platinum–Palladium (Pt–Pd) film was at an angle of 45° to shadow the microgel. The swelling degree was measured as follows: the dried film of microgel was immersed in 2 V % 1,4-diiodobutane of acetone solution for 24 h, then the solution was decanted and the film was heated at 60°C in a constant temperature oven in order to crosslink microgels; the corresponding lengths of this film in dry state (d_d) and wet state (d_s) were then measured before and after their immersion in each solvent for 48 h. The liner (one dimensional) swelling degree was determined as d_s/d_d.

RESULTS AND DISCUSSION

P4VP with a molecular weight of 2.4×10^5 (g/mol) was obtained. The fractions of quarternized 4VP units in polymer emulsifier by CMS and CH_3I were shown in Table I with the quantity of CMS, CH_3I added. The emulsifier with 25 mol % CMS and 44 mol % CH_3I on it was obtained. The total conversion of emulsion polymerization and the diameter of the product were summarized in Table II, along with the conditions of polymerization.

Table I The Conditions and Results of the Introduction of CH_3I CMS on P4VP

Conditions			Results			
P4VP Concn. (wt %)	CMS[a]	CH_3I[b]	r_{CMS}[c] (mol %)	CMS	r_{CH_3I}[d] (mol %)	CH_3I
10.0	26.5	50.8	30.4	25.0	37.7	44.4

[a] CMS: Chloromethylstyrene.
[b] CH_3I: Iodomethane.
[c] r_{CMS}: $\{Abs(1640)/[Abs(1640) + Abs(1600)]\}_{CMS}$.
[d] r_{CH_3I}: $\{Abs(1640)/[Abs(1640) + Abs(1600)]\}_{CH_3I+CMS} - \{Abs(1640)/[Abs(1640) + Abs(1600)]\}_{CMS}$.

Table II Preparative Conditions[a] and Results of Microgel

Sample Code	4VP Concn. (wt %)	Emulsifier/4VP (unit mol/mol × 100%)	Conversion (%)	d(TEM)[b] (nm)
VCM1-1	1.0	0	90.3	400
VCM1-2	1.0	0.03	87.9	190
VCM1-3	1.0	0.10	87.9	190
VCM1-4	1.0	0.30	84.1	200
VCM1-5	1.0	1.00	85.9	160
VCM1-6	1.0	2.50	87.5	70
VCM1-7	1.0	10.00	86.2	80
VCM2-1	2.0	0	98.6	550
VCM2-2	2.0	0.03	99.9	250
VCM2-3	2.0	0.10	90.0	250
VCM2-4	2.0	0.30	88.3	200
VCM2-5	2.0	0.50	99.9	190
VCM2-6	2.0	1.00	98.6	110
VCM2-7	2.0	2.50	99.2	70
VCM2-8	2.0	10.00	95.3	70
VCM5-1	5.0	0	99.8	700
VCM5-2	5.0	0.30	95.0	300
VCM5-3	5.0	1.00	89.5	130
VCM5-4	5.0	2.5	93.1	100
VCM5-5	5.0	5.0	94.4	100

[a] Crosslinking agent: Divinylbenzene (DVB), DVB/4VP (mol/mol); 0.05. Initiator: V50 (2,2'-Azobis(2-methylpropionamidine)dihydrochloride), V50/4VP (wt/wt); 0.02.

[b] d(TEM): Number of the average diameter measured by transmission electron micrograph.

Effect of Monomer Concentration

The diameter of the microgel increased with monomer concentration as shown in Figure 3. When the emulsifier/monomer ratio was zero, the diameter of microgel varied very widely with the monomer concentration, for example from 400 nm to 700 nm with the variance in monomer concentration of 1.0 wt % to 5.0 wt %. The diameter of microgel, however, changed only from 200 nm to 300 nm at same monomer concentration range when the emulsifier/monomer ratio was increased only to 0.30 mol %. This dependency of the diameter on the monomer concentration decreased (70–100 nm) when the emulsifier/monomer ratio increased further to 2.50 mol %.

Effect of Emulsifier/Monomer Ratio

The change of diameter with emulsifier/monomer ratio at various monomer concentrations was summarized in Figure 4, and the typical transmission electron micrographs (TEM) at 2.0 wt % monomer concentration were shown in Figure 5. It can be seen that the diameter of the microgel decreased dramatically when emulsifier was added even if the quantity of emulsifier is very small. For example, at 2.0 wt % monomer concentration, the microgel of 550 nm diameter was obtained when emulsifier was not used, whereas the diameter decreased to 250 nm with only 0.03 mol % emulsifier. But, when the quantity of emulsifier was further increased, the decrease of the diameter with the emulsifier/monomer ratio became less marked. In addition, there was almost no variation in the diameter when the emulsifier/monomer ratio increased to above 2.50 mol %. From the TEMs shown in Figure 5, the microgel seems to become harder, and the surface to become smoother, when the emulsifier/monomer ratio was lower, but the inverse could be observed with the increase in emulsifier/monomer ratio, and in this case the spherical microgel was not observed any longer. This result may be due to the different swelling degree of the microgel. In order to confirm this conclusion, the swelling degree was measured.

The swelling degree of VCM2 series (monomer concentration is 2.0 wt %) is shown in Table III. Both the swelling degree in water or methanol increased with the quantity of emulsifier. The value in water was relatively small (1.15) when the emul-

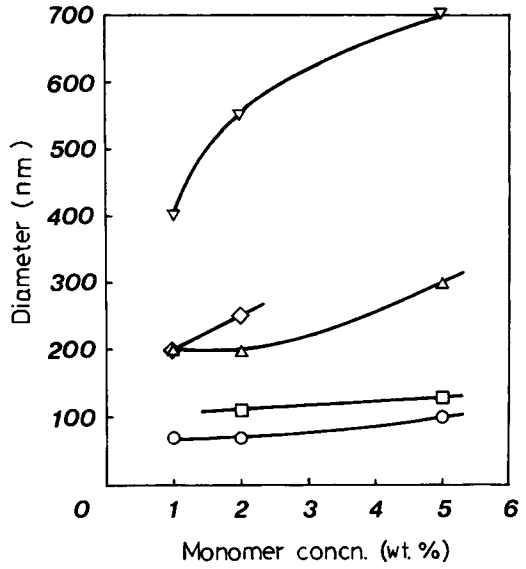


Figure 3 The variation of diameter of microgel as a function of the 4VP monomer concentration. Emulsifier/monomer (unit mol/mol × 100%): (▽) 0; (◇) 0.03; (△) 0.30; (□) 1.00; (○) 2.50. Temperature of polymerization: 70°C.

sifier was not used, but the value became larger (1.42) when the emulsifier/monomer ratio was enhanced to only 0.30 mol %. The swelling degree reached a very large value (2.18) when the emulsifier/monomer ratio was enhanced to 10.0 mol %. In methanol, the same tendency for the swelling degree

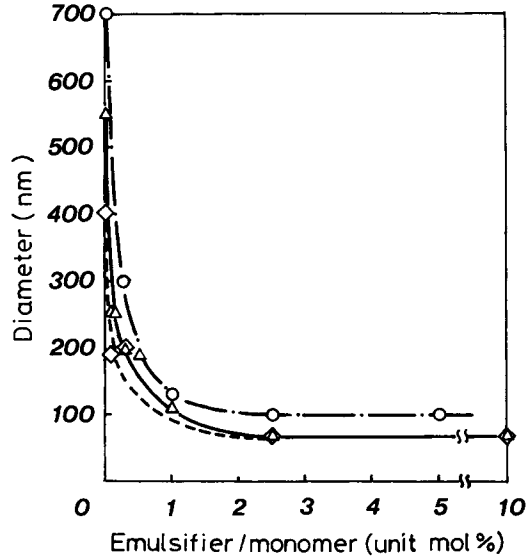
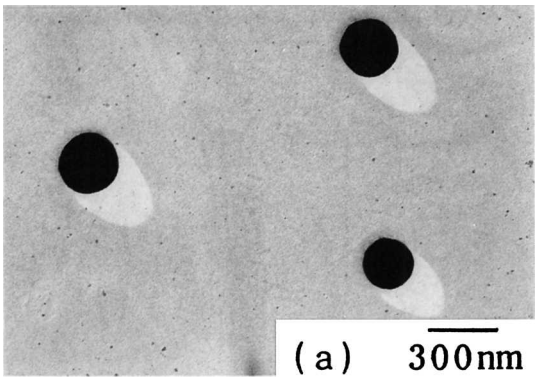


Figure 4 The variation of the diameter of the microgel as a function of the emulsifier/monomer ratio. Concentration of monomer (wt %): (-·-○-·-) 5.0; (— △ —) 2.0; (---◇---) 1.0. Temperature of polymerization: 70°C.



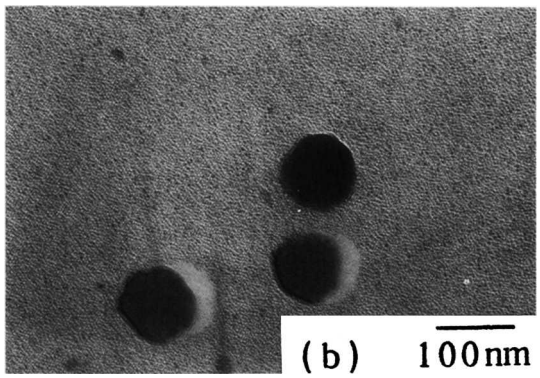


Figure 5 Typical transmission electron micrograph of microgels shadowed with Pt–Pd. Shadowing angle: 45°. Concentration of monomer (wt %): 2.0. Emulsifier/monomer (unit mol/mol × 100%): (a) 0.03, (b) 2.50.

to become larger with the increase in emulsifier/monomer ratio was found, even though the solubility of quarternized P4VP in methanol was not good. So the conclusion that the crosslinking density inside the microgel decreases with the increase of emulsifier can be obtained if we suppose that the crosslinking density inside the microgel is uniform.

The quantity of the DVB crosslinking agent was the same in all cases (DVB/4VP units = 1/20 mol/mol). Thus the average crosslinking density should be same, and be independent of the emulsifier concentration if we consider without preconception, contrary to the above observation. This discrepancy probably is a result of the fact that the crosslinking density inside the microgel is not uniform, due to the very large molecular weight of the polymer emulsifier. When a small quantity of emulsifier is

Table III Effect of the Quantity of Polymer Emulsifier on the Swelling Degree of the Microgel

Sample Code	Emulsifier/4VP (unit mol/mol × 100%)	Linear Swelling Degree ($S^{1/3}$)			
		Water	Methanol	Acetone	Benzene
VCM2-1	0	1.15	1.42	1.10	1.01
VCM2-4	0.30	1.42	1.49	1.01	1.00
VCM2-6	1.00	1.44	1.51	1.01	1.00
VCM2-7	2.50	1.56	1.67	1.01	1.00
VCM2-8	10.00	2.18	1.95	1.00	1.01

added, it will localize on surface of the emulsion in order to enhance the hydrophilicity and will emulsify all monomers inside it uniformly. As a result, a microgel of uniform crosslinking density can be obtained. On the other hand, when the quantity of emulsifier is high, it will penetrate into an emulsion and make many small monomer drops in the midst of an emulsion. Even if the crosslinking density of the monomer drop in the emulsion is high, the crosslinking density between monomer drops may be relatively low. As a result, nonhomogeneous crosslinking was formed. Furthermore, during drying, the phase separation was generated between the hydrophilic unit and the hydrophobic unit, so the surface of microgel became rough. The same observation was obtained once in the case of soap-free polymerization with hydrophilic monomer,[15] but the relationship between swelling degree and the quantity of emulsifier has not been discussed in detail.

Compared with conventional emulsion polymerization of microgels, where surfactant or hydrophilic monomer was used, this method provides an advantage in that the microgel is not stained by the emulsifier and hydrophilic monomer; consequently monoingredient microgel can be obtained by quarternizing the product completely with CH_3I. The order of diameter reached by this method, however, is the same (100–1000 nm) as that obtained by conventional methods. In order to obtain much smaller microgels, on the order of 10 nm, other methods must be devised. We will report in the next article the preparative method for such small P4VP microgels.

CONCLUSION

The microgel composed of partially quarternized poly(4-vinylpyridine) could be prepared by a special emulsion polymerization method by using polymer emulsifier. The size, swelling degree, and shape of the microgel was found to depend on the emulsifier/monomer ratio. The microgel became smaller and softer, and the surface of the microgel got rougher as the emulsifier/monomer ratio increased. Almost monodispersed microgel, with a diameter of 70–700 nm, could be prepared by this method.

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