Preparation and Chemical Fixation of Poly(4-vinylpyridine) Microgel Film with Ordered Structure

G. H. Ma* and T. Fukutomi

Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan

Received November 20, 1991

ABSTRACT: Poly(4-vinylpyridine) (P4VP) microgel films with ordered structure were prepared by casting the deionized aqueous solutions of monodispersed microgel followed by a drying process at 60 °C; the microgels then were fixed chemically by a number of methods using dihalobutane or *p*-(chloromethyl)styrene as the cross-linking agent. Besides the scanning electron microscopic (SEM) observation and the spectrophotometric measurement, a special method, by which the bond angles composed of three particles can be calculated from two SEM micrographs of the same place at different angles around one rotating axis, was devised to determine the arrangement of the microgels in films. A film showing beautiful iridescence where the pores between microgels were conserved was obtained for the solid microgel, while semitransparent films in which the pores between microgels vanished were obtained for the soft microgels. The arrangement of particles in these films almost showed face-centered cubic (a few parts in films maybe showed simple hexagonal packing). The films after chemical fixation became insoluble in methanol and water and other good solvents for quaternized or nonquaternized P4VP. The films in which the pores between microgels were conserved or vanished were obtained dependent on the different methods of fixation. The scanning electron microscopic observation confirmed that the ordered arrangement was not destroyed even after fixation by the chemical treatment of microgels.

Introduction

In recent years, keen attention has been paid to the extraordinary suspension properties of "deionized" microspheres (or microgels); that is, a phase separation[1-11] (sedimentary phase[12-16] and dilute phase) occurs when the solution of a monodispersed microsphere is concentrated to above a certain concentration. The sedimentary phase shows iridescence because of the Brag diffraction of visible light due to the ordered structure of particles, while the dilute phase shows random structure. The detailed structure [face-centered cubic (FCC), body-centered cubic (BCC)] in sedimentary phase has been predicted by a light scattering technique and other methods.[17-29] Further, Hachisu et al. have successfully carried out a direct observation of the ordered structure of the particle in sedimentary phase by using a metallurgical microscope,[11] and FCC and BCC structures were proposed. This phase separation phenomenon has been explained self-consistently by Kirkwood–Alder transition theory.[30-32] On the basis of this Kirkwood–Alder transition phenomenon, an idea that a film composed of microgels with ordered arrangement in sedimentary phase probably can be obtained if one dries this microgel solution completely was certainly made. Whether the ordered structure in aqueous solution was maintained in the dried film is very interesting.

In a previous study, we have established the preparative methods of positive charged monoingredient (not stained by surfactant) poly(4-vinylpyridine) (P4VP) microgel of 70–700-nm diameter with a narrow size dispersion.[36] In addition, the iridescence of the deionized microsphere solution and the dried film due to the ordered arrangement of microgels was observed. Therefore, in this study we have tried to prepare the films of ordered structures composed of positive charged poly(4-vinylpyridine) microgels by simply drying the microgel solutions and to devise a number of methods to fix such ordered structures chemically and control the pore sizes between microgels. These films with ordered structures and different pore size are considered to have more expansive applications.[34,35]

Poly(4-vinylpyridine) microgel was selected in this study because its chemical properties, for example, acidity, basicity, and hydrophilic and hydrophobic properties, can be modified, and it also can be cross-linked inside and among microgels easily. So the characteristics of the films can be designed easily for actual applications.[33-35]

As described above, the ordered structures in film or in solution usually were determined by direct microscopic observation or Brag diffraction of visible light. Even if they can provide much information about structures, it is not easy to know real structures by these methods if the structures are relatively complicated. In this study, we also devised a method to calculate the bond angles composed of three nearest-neighboring particles to confirm exactly that the structure proposed is the real one, by using two SEM micrographs of the same place but at different angles around one rotating axis.

Experimental Section

Materials. P4VP microgel was prepared according to a special emulsion polymerization method where the reactive polymer emulsifier was used. The detailed methods for preparation and characterization were described elsewhere.[36] Three kinds of P4VP microgels with different diameters and swelling degrees were employed in the preparations of films (Table I) to investigate the effects of different microgels on the properties of films. The soft microgel sample VCM2-2Q was prepared by quaternizing the VCM2-2 microgel further with the iodomethane, VCM2-2; VCM5-1 samples were used without further quaternization.

Cross-linking agents 1,4-diiodobutane, 1,4-dibromobutane, and *p*-(chloromethyl)styrene (CMS) were purchased from Tokyo Chemical Industries Co., Ltd. They were used as received.

Preparation of Film with Ordered Structure. The microgel solution was purified as follows: the microgel solution was dialyzed by closing the microgel solution into a seamless cellulose tube, and then the tube was further immersed in a large amount of water for over 2 weeks at room temperature. Water was changed every day. The deionized microgel solution (2 wt %, 20 mL) was cast on a Teflon dish (6 cm × 6 cm), and then it was dried at 60 °C in the constant temperature oven to prepare a film.

Fixation of Ordered Structure. The films obtained were treated according to three methods. The chemical reactions are shown schematically in Figure 1.

0024-9297/92/2225-1870$03.00/0

Table I
Character of P4VP Microgel

sample code	diameter,[a] nm	quaternized degree, mol %	swelling degree[b]
VCM2-2	250	0.03	1.52
VCM5-1	700	0	1.70
VCM2-2Q	250	40.0	3.05

[a] Number-average diameter measured by transmission electron micrographs. [b] One dimension: refer to text.

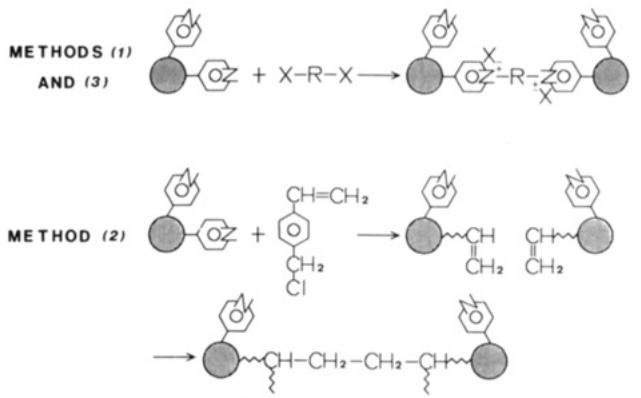

Figure 1. Reaction schemes for the cross-linking reactions between microgels. X–R–X, dihalobutane.

(1) Fixation with 1,4-Diiodobutane in Liquid Phase. The film was immersed in the 1,4-diiodobutane/acetone solution (2/100 v/v) for 24 h. Then the solution was decanted, and the wet film was heated at 60 °C to cross-link microgels for 24 h. Because the quaternization reaction of pyridine ring with alkyl iodite proceeds easily even at room temperature,[37] it can be considered that the cross-linking was carried out steadily.

(2) Fixation with *p*-(Chloromethyl)styrene (CMS) in Liquid Phase. First, CMS was added in the microgel solution (CMS/4VP unit; 10 mol %) to introduce the double bonds on the microgel, and the reaction was continued for 24 h under stirring; then this solution was cast on a Teflon plate followed by a drying process at 60 °C as before. The cross-linking reaction between double bonds would take place simultaneously in the drying process.

(3) Fixation with 1,4-Dibromobutane in Gas Phase. A vessel filled with 1,4-dibromobutane was put beside the film in a sealed container which was heated in a water bath at 60 °C for 24 h. Thus, 1,4-dibromobutane would evaporate into the microgel film to cross-link the microgels. This process was performed for both dried and wet films. The wet film was prepared by putting a vessel filled with water beside the film in the sealed container at room temperature for 24 h before the cross-linking process to make the microgel swollen.

The above cross-linking reactions (Figure 1) were confirmed by measuring the quaternized degrees of microgels and the swelling degrees of films. The quaternized degree was determined by measuring the potential due to halogenic ion released in the aqueous solution with halogenic ion electrode (I-125, Cl-125B, Br-125). The swelling degree was measured as follows: the corresponding lengths of the film in the dried state (d_d) and wet state (d_s) were measured before and after the immersion in water for 48 h. The linear (one-dimensional) swelling degree was determined as d_s/d_d.

Electron Microscopic Observation. The surfaces and cross sections of films before and after fixation were observed by JSM-5200 scanning electron microscope. The SEM sample was prepared by spattering and coating a thin Pd–Pt film (about 60 Å in thickness) on the sample under reduced pressure of below 0.05 Torr with a Hitachi E 102 ion sputter. To prepare the sample for cross-sectional observations, the film was cracked after it was immersed in liquid nitrogen for several seconds.

Calculation of Bond Angles of Particles. Here, the bond angle was determined as the angle composed of three nearest-neighboring particles.

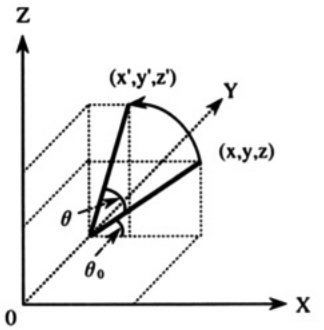

Figure 2. Calculation method of bond angles composed of three particles.

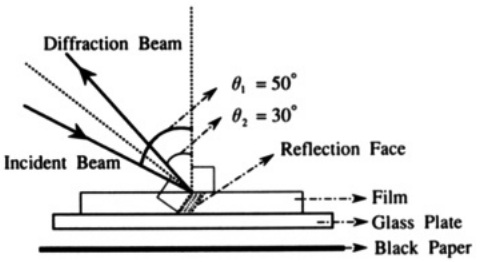

Figure 3. Optical setup for the spectrophotometric measurement.

First, two SEM micrographs of the same place, were taken at different angles around one rotating axis (here the *Y* axis) (Figure 2). Supposing the centric coordinates of a particle on SEM micrographs before and after rotation (rotating angle is θ) are x,y,x and x',y',z', respectively, (x,y and x',y' can be obtained directly from SEM micrographs), the equations

$$\tan \theta_0 = z/x$$

$$x' = \sqrt{x^2 + z^2} \cos (\theta + \theta_0)$$

$$y' = y$$

$$z' = \sqrt{x^2 + z^2} \sin (\theta + \theta_0)$$

can be obtained, where θ_0 is the angle of the samples with the level surface before rotation. z and z' can be expressed as follows:

$$z = (x \cos \theta - x')/\sin \theta$$

$$z' = (x - x' \cos \theta)/\sin \theta$$

If the coordinates of three particles are A_1 (x_1, y_1, z_1), A_2 (x_2, y_2, z_2), and A_3 (x_3, y_3, z_3), the bond angle ($\angle A_1A_2A_3$) can be obtained from the equation

$$\cos \angle A_1A_2A_3 = (d_{12}^2 + d_{23}^2 - d_{13}^2)/2d_{12}d_{23}$$

where d_{ij} is the distance between particles A_i and A_j. Therefore, the structure can be determined securely from the bond angles.

The coordinates of the particles before and after rotation were obtained from the SEM micrographs by using the A4-25 digitizer (PHOTRON) and the PC-9801 personal computer (NEC, Co., Ltd.).

Spectrophotometric Measurement. The GCMS-3 spectrophotometer was used for the measurement of Brag diffraction of the ordered structures in the films. The thin film for the spectrophotometric measurement was made as before but was cast on a transparent glass plate (4 cm × 4 cm) for the convenience of measurement. The optical system is shown in Figure 3. The angle of incident beam (θ_1) was fixed at 50°, and the diffraction beam was picked up at an angle (θ_2) of 30° from the perpendicular line (see Figure 3). A black paper was put behind the sample to remove the scattering and transmitted light which would disturb the measurement.

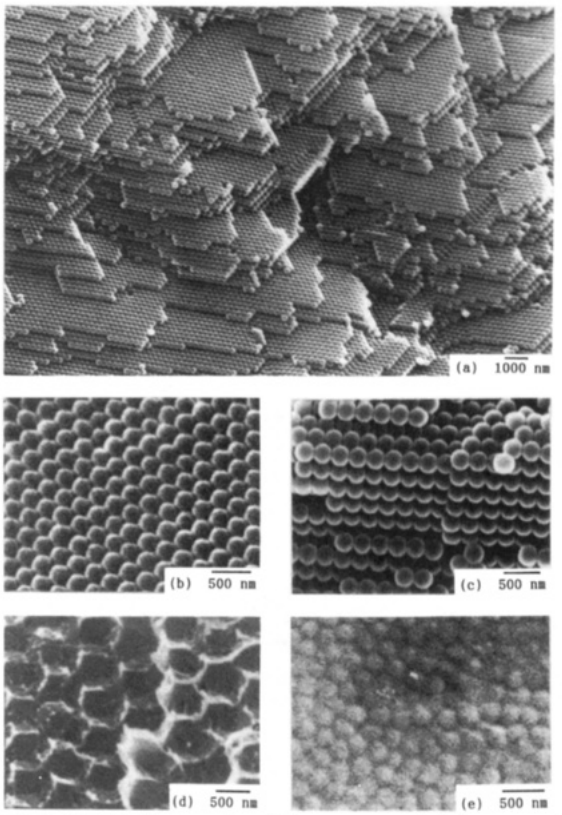

Figure 4. SEM micrographs of films prepared: (a) cross section of VCM2-2 sample; (b) surface of VCM2-2 sample; (c) cross section of VCM2-2 sample; (d) cross section of VCM5-1 sample; (e) surface of VCM2-2Q sample.

The ordered structure can be considered to be a multimicrocrystal, so the principle of the calculation for Brag distance is the same as that in the X-ray diffraction of crystal powder

$$2d \sin \theta = \lambda/n$$

$$\theta = (180 - \theta_1 + \theta_2)/2$$

where d is the Brag distance, λ the wavelength at the diffraction peak, and n the refraction index of the film.

Results and Discussion

Result of Preparation of Microgel Film. A film (6 cm × 6 cm) with beautiful iridescence was obtained for the solid microgel VCM2-2 which had small swelling degree. The deionized microgel solution of 2 wt % before drying was milky, but the surface of solution has already begun to show beautiful iridescence after 1 h of drying. Further, after complete evaporation of water, more beautiful iridescence appeared. This result suggested that the structure in this film should be ordered in a wide range. On the other hand, the semitransparent films, where iridescence was not observed, were obtained for the soft microgels VCM5-1 and VCM2-2Q which had large swelling degrees. To determine substantive arrangements of the microgels in these films, the SEM observations, the calculations of bond angles, and the spectrophotometric measurements were carried out.

The SEM micrographs of surface and cross sections of VCM2-2 are shown in parts a, b, and c of Figure 4, respectively. Those of VCM5-1 and VCM2-2Q samples are shown in parts d and e of Figure 4. From Figure 4a–c it can be seen that the film of solid microgel VCM2-2 also showed ordered structure as observed in the sedimentary phase of microsphere solution and that the pores between microgels were conserved. From the cross section (Figure 4c), two different arrangements in two dimensions can be observed. One seemed to be "hexagonal packing", another "square packing". The former would be determined naturally as (1,1,1) of FCC or (1,1,0) of BCC and the latter as (2,0,0) of FCC or BCC, if it is remembered that only FCC and BCC have been found in the microspheres solutions. Because the real angle in square and hexagonal packing and the angle between these two faces cannot be known only from one SEM micrograph, the real structure cannot be identified.

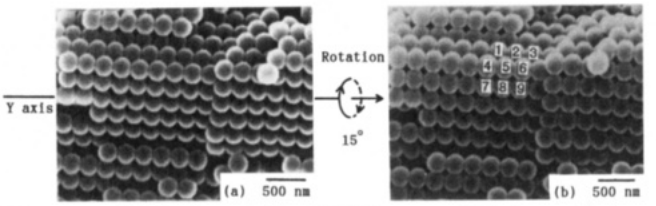

Figure 5. SEM micrographs of VCM2-2 sample before and after rotation: (a) before rotation (0° with the level surface); (b) after rotation (15° with the level surface).

Table II
Bond Angles Composed of Three Microgels Determined by Rotating Method of SEM

particle no.	bond angle	corresponding faces of FCC
1–4–5	58	(1,1,1)
1–5–4	61	(1,1,1)
2–5–6	61	(1,1,1)
1–4–7	122	(1,1,1)
2–5–8	122	(1,1,1)
1–5–8	117	(1,1,1)
4–7–8	93	(1,0,0)
4–5–8	87	(1,0,0)
7–4–5	88	(1,0,0)

To define the real structures in VCM2-2 film and to prevent the conclusions from an optical illusion, the bond angles were calculated from two SEM micrographs as shown in Figure 5. Parts a and b of Figure 5 were the SEM micrographs at 0° and 15° with the level surface, respectively. The calculation of bond angles was carried out on numbered particles, and the results are shown in Table II. From Table II, it was confirmed that the bond angles of particles in the faces of square packing and hexagonal packing were really about 90° (±3°) and 60° (±2°), and the particles of 1–4–7, 2–5–8, 1–5–8 formed the angles of about 120° (±3°). Apparently, this structure corresponded to the FCC structure but not the BCC structure or other structures.

The calculations were carried out in the same way for a number of other parts of the same sample, and the same results were obtained. Therefore, it can be concluded that the arrangement of particles in VCM2-2 almost showed FCC structure.

The spectrophotometric result of the VCM2-2 sample is shown in Figure 6, where double peaks were found at wavelengths of 535 and 467 nm. The ratio of wavelengths of these two peaks [λ(535 nm)/λ(467 nm)] was 1.14. On the basis of the above results, these two peaks would be expected to be ascribed to the diffraction of (1,1,1) and (2,0,0) faces in FCC structures. For these two faces, the Brag distances ($d_{(1,1,1)}$ or $d_{(2,0,0)}$) can be calculated from

$$d_{(1,1,1)} = \frac{\lambda_1}{2n \sin \theta} = \frac{\sqrt{2}}{\sqrt{3}} D \quad (1)$$

$$d_{(2,0,0)} = \frac{\lambda_2}{2n \sin \theta} = \frac{\sqrt{2}}{2} D \quad (2)$$

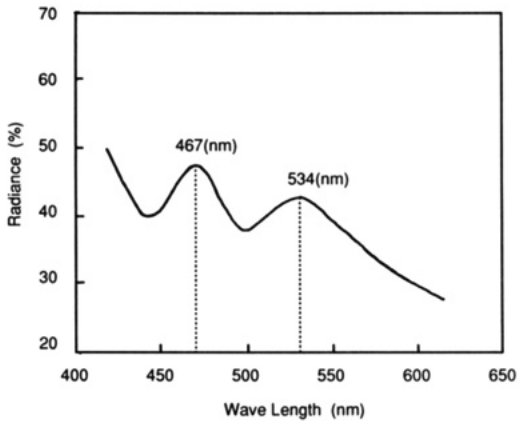

Figure 6. Diffraction light spectrum of VCM2-2 films.

where D is the diameter of particles, that is, the distance between nearest-neighboring particles.

From eqs 1 and 2, eq 3 can be obtained:

$$\frac{\lambda_1}{\lambda_2} = \frac{2}{\sqrt{3}} = 1.15 \tag{3}$$

This value is very close to the result of the diffraction light spectrum shown in Figure 6. It confirmed further that the arrangement of the particles in VCM2-2 film almost showed FCC structure.

For the soft microgel VCM5-1, same as for the solid microgel of VCM2-2, the arrangement of microgels in the film also showed FCC structure by the SEM observation (Figure 4d) and the calculations of bond angles. But, different from the VCM2-2 film, the shape of spherical VCM5-1 microgel changed to polyhedron (hexagon in two dimensions of SEM micrograph) and the pore vanished as shown in Figure 4d. This is because VCM5-1 had a larger swelling degree, and the fusion between microgels proceeded faster and earlier than the evaporation of the water inside microgels. From Figure 4e (for convenience, we showed the micrograph of the surface), the similar result that the pores vanished was observed for VCM2-2Q microgel with a much larger swelling degree. The arrangement of particles also showed FCC structure but less ordered. This is probably because the surfaces of microgels with the larger swelling degrees penetrated each other and the penetration impeded the movement for arrangement of microgels. As a result, less ordered structure was obtained.

In the spectrophotometric measurement, no peak was found for VCM5-1 and VCM2-2Q films, which were semitransparent. This is because the Brag plane was not clear or vanished because the particles touched each other in the closely packed arrangement. This result was consistent with the electron microscopic observations.

On the whole, FCC structure of the microgel and the deformation of the soft spherical microgel to polyhedron are not so singular. The former is due to the conservation of the structure in the solution during evaporation. The latter is caused inevitably by the packing of soft microgels containing solvent. Contrary to these results, it is mysterious if BCC structure, which has always been found in the microsphere solutions, and other packing existed or not in the films of microgels. In this study, because the range of SEM observations was limited and the result that the diffraction peaks of the film were relatively broader was obtained, we only can say the arrangement almost showed FCC structure.

The experiments are continued to analyze the structure in these films.

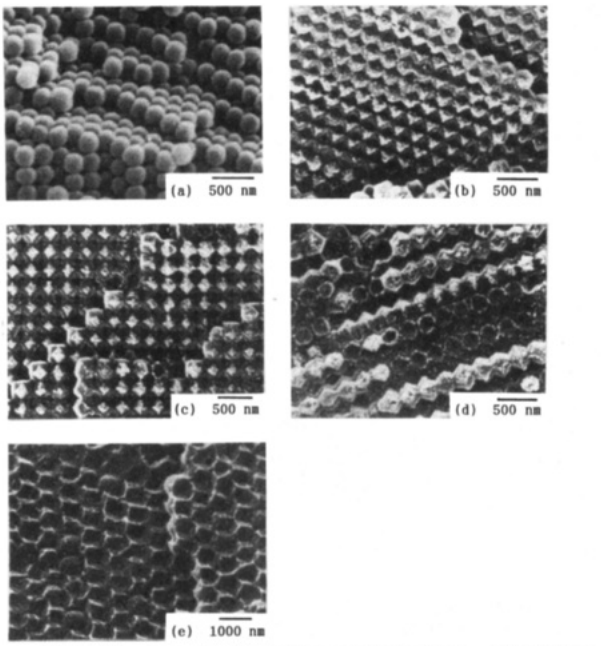

Figure 7. SEM micrographs of films after fixation. (a) VCM2-2 film cross-linked by 1,4-diiodobutane in liquid phase; (b–d) VCM2-2 film cross-linked by 1,4-dibromobutane in gas phase for wet film; (e) VCM5-1 film cross-linked by CMS in liquid phase.

Result of Fixation of Ordered Structure in Films. After the films were fixed by 1,4-diiodobutane, CMS, or 1,4-dibromobutane, the ordered structures were conserved as shown in Figure 7. Furthermore, the pores between solid microgels in VCM2-2 film were conserved even after it was fixed by method 1 or 2 and method 3 for dried films. The typical SEM micrograph is shown in Figure 7a. On the other hand, when it was cross-linked by method 3 for wet film, the shape of spherical microgel changed to hexagon or square in the two dimensions and the pores vanished as shown in Figure 7b,c. This is because the microgels in film were swollen with water; the shape of it then changed to hexagon or square [(1,1,1,) and (2,0,0) faces of FCC] in two dimensions. Because it was cross-linked at swollen state, the shape of hexagon or square was fixed. In addition, in the former case where the pores were conserved, the film still showed iridescence, although it was very weak even after fixation, while the iridescence vanished and the semitransparent film was obtained in the latter case where the pores vanished.

Furthermore, from Figure 7b–d, information about the overlapping methods of the upper particles can be obtained. In Figure 7b, for example, because four faces (one was bright, the others were dark) of one particle were discovered, it can be known that three particles had overlapped on it. On the other hand, five faces (one bright, the others dark) of one particle can be found in Figure 7c; that is, four particles had overlapped on it. Apparently, (b) and (c) correspond to (1,1,1) and (2,0,0) faces. But in Figure 7d, overlapping method was different from that of parts b and c. The particle showed dark except the circumference. This suggested that the upper layer of hexagonal packing had piled up right on the under layer of hexagonal packing. That is, the simple hexagonal packing (HP) existed somewhere in this film, although the quantity of it maybe was very small. Due to this structure or other structure, the diffraction peak became broader.

Figure 7e showed the result of VCM5-1 films fixed by *p*-(chloromethyl)styrene. In it, the microgel still showed

Table III
Quaternized Degrees and Swelling Degrees of the Cross-Linked Films

cross-linking method[a]	cross-linking agent	quaternized degree, mol %	swelling degree	
			methanol	water
1	1,4-diiodobutane	21.2[b]	1.16	1.12
2	p-(chloromethyl)styrene	8.3	1.39	1.08
3	1,4-dibromobutane	7.4[b]	1.04	1.04
		6.7	soluble	soluble
	p-ethylbenzyl chloride	18.9	soluble	soluble
	(monofunctional	45.5	soluble	soluble
	quaternizing agent)	67.7	soluble	soluble

[a] Refer to text. [b] The value was calculated by supposing both ends of the cross-linking agents had reacted with microgels.

ordered FCC structure and the pores between microgels were closed as before fixation. The same result was also observed when it was cross-linked by 1,4-diiodobutane and 1,4-dibromobutane.

The cross-linking reactions were confirmed by the measurements of quaternized degrees and swelling degrees. The results are shown in Table III. In Table III, the quaternized degree was calculated by supposing both ends of dihalogen had reacted with microgels for the samples fixed by dihalogen. The quaternized degrees after the microgels had reacted with 1,4-diiodobutane, p-(chloromethyl)-styrene, and 1,4-dibromobutane for dried films were 21.2%, 8.3%, and 7.4%, respectively. These results suggested at least that the cross-linking agents were introduced into the microgels. But it was unknown if both ends of dihalogen had reacted with microgels and if the reaction between the double bonds had occurred or not for the sample fixed by p-(chloromethyl)styrene.

From Table III it can be known that the films obtained became insoluble, but only swelled even in water and methanol, good solvents for nonquaternized and quaternized P4VP microgels, after the fixations by all three methods. This result suggested that the cross-linking reactions between microgels probably had occurred, although there was concern that this insolubility may be ascribed to the quaternization of microgels where hydrophobic alkyl groups of 1,4-diiodobutane, 1,4-dibromobutane, and p-(chloromethyl)styrene might have decreased the solubility in methanol or water. As a reference, the microgels were also allowed to react with p-ethylbenzyl chloride, which has a hydrophobic group similar to the p-(chloromethyl)styrene and is more hydrophobic than the end groups of the other cross-linking agents. The results of quaternized degrees and swelling degrees of films after they had reacted with the p-ethylbenzyl chloride are also shown in Table III. The film treated by p-ethylbenzyl chloride was soluble in both water and methanol even if the quaternized degree was very large. This is because the quaternization of microgels increased its hydrophilic character, although the alkyl group increased its hydrophobic character; these two factors would cancel each other. Therefore, the film was always soluble in water or methanol if it had reacted only at one end of the dihalogen or the double bond had not been coupled. This result confirmed that the cross-linking between microgels had been successfully performed.

Furthermore, all cross-linked products became perfectly insoluble in methanol, ethanol, and 1,1,2-trichloroethane, good solvents for P4VP or partially quaternized P4VP. These strongly fixed films with ordered structure and different pore size are expected to have many applications, although there remain many problems to be investigated, such as the relations between the strength of films and the defects of the ordered structures and the cross-linking conditions.

Conclusions. The film showing ordered structure of poly(4-vinylpyridine) microgel can be prepared by casting the deionized monodispersed microgel followed by a drying process at 60 °C. The SEM micrographs, spectrophotometric measurements, and especially the calculation of bond angles of the particles revealed that the films of microgel almost showed FCC structure, although a few HP structures maybe coexisted. The method of calculation of bond angles composed of three particles provided a good means for the analysis and identification of complicated structures. The ordered structures can be fixed by suitable cross-linking agents such as 1,4-diiodobutane or p-(chloromethyl)styrene in liquid phase or 1,4-dibromobutane in gas phase. The films where the iridescence and the pores were conserved can be obtained by fixing the films composed of solid microgel with all of the cross-linking agents for the dried films. On the other hand, the films where the pores vanished can be obtained by fixing the film composed of soft microgel by all three methods or by fixing the wet film composed of solid microgel with 1,4-dibromobutane in gas phase.

Acknowledgment. We thank Mr. R. Oki, Mr. T. Tiba (Tokyo Institute of Technology), and Prof. O. Fukunaga (Tokyo Institute of Technology, Department of Inorganic Material) for kindly helping us take some of the SEM micrographs and Mr. M. Takizawa, S. Matuzaki, M. Tukano (Dainichi Seika Co., Ltd.) for kindly helping us carry out spectrophotometric measurements.

References and Notes

(1) Krieger, I. M.; Hiltner, P. A.; Papir, Y. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1970**, *11*, 690.
(2) Wadati, M.; Toda, M. *J. Phys. Soc. Jpn.* **1972**, *32*, 1147.
(3) Vanderhoff, J. W.; Van den Hul, H. J. *J. Macromol. Sci., Chem.* **1973**, *A7*, 677.
(4) Kose, A.; Hachisu, S. *J. Colloid Interface Sci.* **1974**, *46*, 460.
(5) Hachisu, S.; Kobayashi, Y. *J. Colloid Interface Sci.* **1974**, *46*, 470.
(6) Ise, N.; Okubo, T. *Acc. Chem. Res.* **1980**, *13*, 303.
(7) Ise, N.; Okubo, T.; Sugimura, M.; Ito, K.; Nolte, H. J. *J. Chem. Phys.* **1983**, *78*, 536.
(8) Ise, N.; Okubo, T.; Ito, K.; Dosho, S.; Sogami, I. *J. Colloid Interface Sci.* **1985**, *103*, 292.
(9) Ise, N.; Ito, K.; Okubo, T.; Dosho, S.; Sogami, I. *J. Am. Chem. Soc.* **1985**, *107*, 8074.
(10) Ise, N.; Okubo, T.; Ito, K.; Dosho, S.; Sogami, I. *Langmuir* **1985**, *1*, 176.
(11) Kose, A.; Ozaki, M.; Takano, K.; Kobayashi, Y.; Hachisu, S. *J. Colloid Interface Sci.* **1973**, *44*, 330.
(12) Luck, W.; Klier, M.; Wesslau, H. *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 75.
(13) Luck, W.; Klier, M.; Wesslau, H. *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 84.
(14) Luck, W.; Klier, M.; Wesslau, H. *Naturwissenschaften* **1963**, *50*, 483.
(15) Luck, W.; Klier, M.; Wesslau, H. *Naturwissenschaften* **1963**, *50*, 485.
(16) Vanderhoff, W.; van de Hul, H. J.; Tausk, R. J. M.; Overbeek, T. Th. G. *Clean Surfaces: Their Preparation and Characterization for Interfacial Studies*; Goldfinger, G. Ed.; Dekker: New York, 1970.
(17) Krieger, I. M.; O'Neill, F. M. *J. Am. Chem. Soc.* **1968**, *90*, 3114.
(18) Hiltner, P. A.; Krieger, I. M. *J. Phys. Chem.* **1969**, *73*, 2386.
(19) Hiltner, P. A.; Papir, Y. S.; Krieger, I. M. *J. Phys. Chem.* **1971**, *75*, 1881.
(20) Barclay, L.; Harrington, A.; Ottewill, R. H. *Kolloid Z. Z. Polym.* **1972**, *250*, 655.
(21) Willians, R.; Crandall, R. S. *Phys. Lett.* **1974**, *48A*, 225.
(22) Clark, N. A.; Hurd, A. J.; Ackerson, B. J. *Nature* **1979**, *281*, 57.
(23) Tomita, M.; Takano, K.; van de Ven, T. G. M. *J. Colloid Interface Sci.* **1983**, *92*, 367.
(24) Tomita, M.; van de Ven, T. G. M. *J. Colloid Interface Sci.* **1984**, *99*, 374.

(25) Tomita, M.; van de Ven, T. G. M. *J. Colloid Interface Sci.* **1984**, *100*, 112.
(26) Yoshiyama, T.; Sogami, I.; Ise, N. *Phys. Rev. Lett.* **1984**, *53*, 2153.
(27) Okubo, T. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 3163.
(28) Okubo, T. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 3175.
(29) Okubo, T. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 3185.
(30) Kirkwood, I. G. *J. Chem. Phys.* **1939**, *7*, 919.
(31) Alder, B. J.; Wainright, T. E. *Phys. Rev.* **1962**, *127*, 359.
(32) Alder, B. J.; Hoover, W. G.; Young, D. A. *J. Chem. Phys.* **1968**, *49*, 3688.
(33) Kawakuchi, H.; Muroi, S. *Polymer Colloid*; Kyoritu: Tokyo, 1989.
(34) Ma, G. H.; Saito, R.; Ishizu, K.; Fukutomi, T. *Polym. Prepr. Jpn.* **1989**, *38*, 390.
(35) Ma, G. H.; Fukutomi, T. *Polym. Prepr. Jpn.* **1991**, *40*, 4084.
(36) Ma, G. H.; Fukutomi, T. *J. Appl. Polym. Sci.* **1991**, *43*, 1451.
(37) Winkler, C. A.; Hinshelwood, C. N. *J. Chem. Soc.* **1935**, 1147.

Registry No. P4VP·MeI·CMS, 139276-35-0; (4VP)(DVB)(I_2Bu) (copolymer), 139276-36-1; (4VP)(DVB)(Br_2Bu) (copolymer), 139276-37-2; (4VP)(DVB)·*x*CMS (copolymer), 139276-38-3; (4VP)(DVB) (copolymer), 9017-40-7.