Preparation and characterization of cationic copolymer latex. 1. Emulsion copolymerization of styrene with 4-vinylpyridine in the presence of non-ionic emulsifier

Yasuji Ohtsuka, Haruma Kawaguchi and Shuichi Watanabe
Department of Applied Chemistry, Keio University, Hiyoshi, Yokohama 223, Japan

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A study was made of the effect of 4-vinylpyridine (VP) on the kinetics of the emulsion polymerization of styrene (St) and on the distribution of polymeric VP in the cationic latex. Bimodal distribution of particle diameter was obtained in the polymerization under the conditions of low emulsifier concentration and high VP fraction in monomer feed. This would be caused by insufficient stabilization of resulting particles and by some changes in the character of growing radicals in aqueous phase with conversion. Polymerization under acidic conditions was affected by the amphiphilicity of VP-rich radicals which depended on VP fraction in monomer feed. On the surface of the latex particles prepared at pH 2 polymeric VP located preferentially whereas the latex particles prepared at pH 11 had a nearly statistical distribution of VP on their surface.

INTRODUCTION

Despite the considerable interest in cationic latices and although some have been developed industrially, only few academic investigations have been done on them. Sakota *et al.*[1] studied cationic polystyrene latices prepared by a cationic initiator or a cationic comonomer of which the latter was more effective in giving a stable latex. Liu and Krieger[2] also tried similar procedures for monodisperse cationic latices. Preparation of cationic polystyrene latex by use of a redox initiation system of cationic emulsifier and ceric ion was studied previously by us[3] but the product was not fully characterized.

There are some papers on the emulsion copolymerization of hydrophobic monomer with non-cationic hydrophilic comonomer. Yeliseyeva *et al.*[4] used some acrylates as comonomer with styrene and from the order of their reactivity pointed out that the higher degree of hydrophilization of particle/water interface layer caused by more polar monomer brings a greater decrease in the interfacial tension, leading to a rise in the rate of copolymerization. This is supposed to be a common phenomenon observed in similar copolymerization systems.

The relation between the hydrophilicity of comonomers and the number of latex particles was discussed by Ceska[5] who polymerized acrylic acid, methacrylic acid, and itaconic acid with styrene in an aqueous medium. The hydrophilicity of weak acid monomer or weak base monomer can be variable by changing pH. Sakota *et al.*[6,7] carried out the emulsion copolymerization of styrene with acrylic acid at different pH values and found that the increase in dissociated acrylic acid results in increases in the number of latex particles and in the surface density of polymeric acrylic acid on the particles.

It is the purpose of this work to analyse the characteristic phenomena in the emulsion copolymerization of styrene with 4-vinylpyridine under acidic or basic conditions and clarify the effect of the polar monomer on these phemomena. Some properties of resulting cationic latices will be discussed in relation to the polymerization conditions.

EXPERIMENTAL

Materials

Distilled water was used in all polymerizations. Styrene (St) (Kashima Kagaku Yakuhin Co.) was distilled at 40°C/14.5 mmHg and stored at 4°C. 4-Vinylpyridine (VP) (Tokyo Chemical Industry Co.) was distilled at 51°C/12 mmHg before use. Potassium persulphate (KPS) was recrystallized from the aqueous solution and dried in vacuum. Poly(oxyethylene octylphenyl ether) (E) (Nippon Oils & Fats Co.) was desalted with mixed-bed ion-exchange resin of Amberlite IR 120-B and IRA 410 (Rohm & Haas Co.). The number of oxyethylene units in E was 19.6 as determined from the area ratio of oxyethylene proton peak to alkyl proton peak on the n.m.r. spectrum of E. Hydrochloric acid (Kanto Chemical Co.) and sodium carbonate (Kanto Chemical Co.) were of specially pure grade, and were used without further purification.

Determination of critical micelle concentration of emulsifier in the presence of 4-vinylpyridine

Soap titration of the aqueous solution of VP at pH 2 and at pH 11 was carried out to determine the effect of VP on the critical micelle concentration (*CMC*) of E by using a Shimazu Surface Tensometer ST-1 at 20°C.

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Table 1 Typical recipe for copolymer latex of styrene and 4-vinylpyridine

Ingredient	Quantity
Emulsifier solution (10 or 20 mmol/l)	180 ml
Buffer solution	10 ml
St + VP	20 g
KPS solution (4 mmol/l)	10 ml

Temperature, 40.0 ± 0.2°C; speed of stirrer, 300 rev/min; pH, 2 or 11

Latex preparation and determination of conversion

A typical recipe for St–VP copolymer latex is shown in *Table* 1. The polymerization temperature was fixed at 40°C because a moderate rate of polymerization was necessary to determine the dependence of polymerization behaviour on the polymerization conditions. Two levels of pH were chosen to clarify the influence of free base of cationic VP on the polymerization kinetics and on the latex properties. The reaction system was kept at pH 2 or 11 by adding proper amounts of 1 N HCl or sodium carbonate, respectively. The ratio of monomer to water was set to be 1/10 and VP fraction in monomer feed, f_{VP}, was varied from 0 to 0.25 above which no stable latex was obtained.

All the ingredients except KPS solution were placed in a 300 ml four-neck round-bottom flask equipped with stirrer, condenser, thermometer, serum stopper for sampling, and nitrogen inlet tube. After passing nitrogen gas through the emulsion for 1 h KPS solution was added with a syringe. Portions of the reaction sytem were expelled periodically and dried in vacuum. Total conversion was determined gravimetrically. Another method to determine the conversion was used for the samples polymerized at pH 2 because the monomeric pyridinium salt is non-volatile; the water-insoluble copolymer was neutralized, coagulated with hot water, filtered and dried in vacuum. The composition of copolymer was calculated from its elemental analysis data.

Determination of latex particle size and number of particles

Transmission electron micrographs at 10 000 × magnification were obtained with a Hitachi electron microscope HU-12AF by conventional procedures without shadowing the latex particles. Surface–volume average diameter (D), $\Sigma n_i d_i^3/\Sigma n_i d_i^2$ was calculated where n_i was the number of particles with diameter d_i. The number of latex particles in unit volume of aqueous medium was calculated from D, the conversion, and the average density of copolymer.

Determination of the amount of VP units on particle surface

Water-soluble oligomer, ions and most of emulsifier were removed by dialysis with Seamless Cellulose Tubing (Visking Co.) followed by ion-exchange treatment as described below: latex was diluted with the same amount of water, treated with cation exchange resin Amberlyst 15 (Rohm & Haas Co.), and then passed through a mixed-bed ion-exchnage resin column composed of 1:2 Amberlyst 15/Amberlyst A-29 (anion exchange resin, Rohm & Haas Co.). After this treatment the specific conductivity of the latex was lower than 5 $\mu\Omega$/cm. About 100 ml of purified latex (solid content 1%) was titrated with 0.1 N HCl under nitrogen. The amount of polymeric VP units exposed on the surface of latex particles was calculated from the point of intersection on the conductometric titration curve which was obtained by using a Yokogawa-Hewlett-Packard Ltd. 4255A Universal bridge equipped with a dip-type conductance cell. Homola's method[8] was employed to analyse the titration data.

RESULTS AND DISCUSSION

Emulsion copolymerization under basic conditions

Some time–conversion curves for the emulsion copolymerization of St with VP at pH 11 are shown in *Figure* 1. Two pseudo-linear parts were observed in a few time–conversion curves for the polymerization carried out at [E] = 10 mmol/l. In these cases two kinds of rate of polymerization, R_1 and R_2, were defined as shown in *Figure* 1. R_2 increased with VP fraction in monomer feed, f_{VP}, whereas the dependence of R_1 on f_{VP} was anomalous at [E] = 10 mmol/l (*Figure* 2). The ratio of R_2 to R_1 changed from 1 at $f_{VP} \leqslant 0.10$ up to 4 at $f_{VP} = 0.25$. On the other hand, in the polymerization at [E] = 20 mmol/l both R_1 and R_2 increased with increasing f_{VP}. As the rate of polymerization depends on the number of polymer particles, N, in general emulsion polymerization owing to its mechanism[9], the above-mentioned results on the rate of polymerization can be discussed in relation to N. Micelles of emulsifier play an important role in nucleation of polymer particles. In a typical emulsion polymerization of St N is proportional to $([E] - CMC)^{0.6}$ (generally [E] $> CMC$, so $N \propto E^{0.6}$). The CMC of emulsifier in 1% aqueous solution of VP at pH 11 was measured and the results are shown in *Table* 2. It is likely that the addition of VP results in an increase in the number of micelles at pH

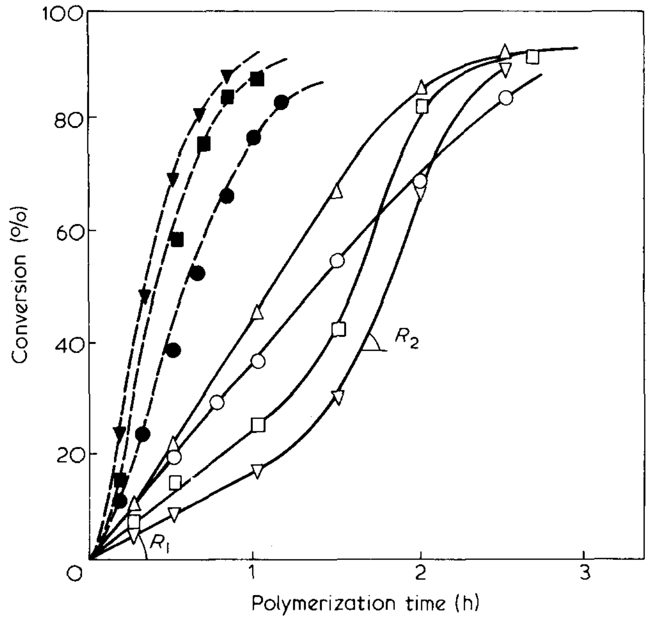

Figure 1 Time–conversion curves for the emulsion copolymerization of St with VP under basic conditions

VP fraction in monomer feed (f_{VP})	[E] (mmol/l) 10	20
0.05	○	●
0.10	△	▲
0.20	□	■
0.25	▽	▲

Conditions: [KPS] = 4 mmol/l, pH 11, 40°C

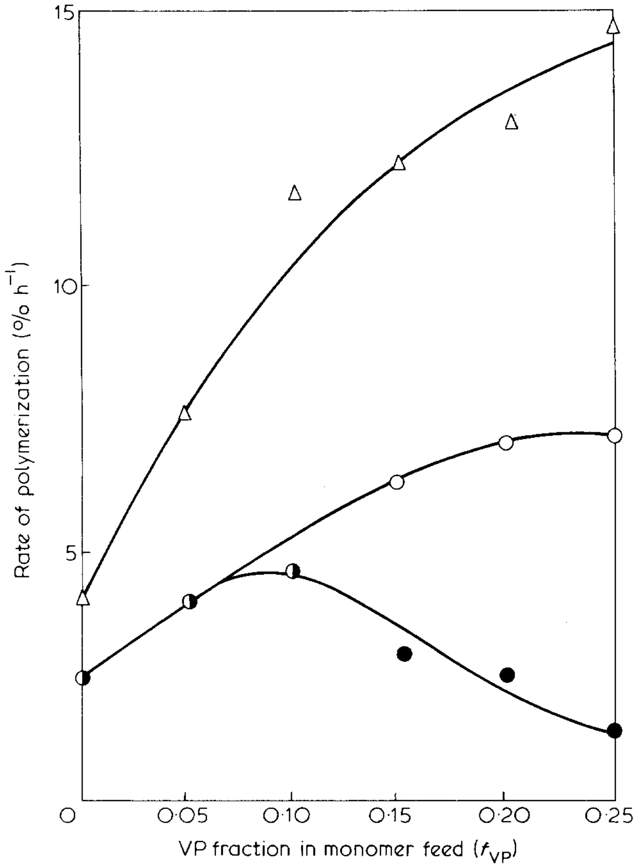

Figure 2 Dependence of rate of polymerization on monomer composition in the emulsion polymerization under basic conditions

	[E] (mmol/l)	Rate of polymerization
●	10	R_1*
○		R_2*
△	20	R_2

*See Fig. 1

11, but in general a decrease in *CMC* is accompanied by an increase in the number of emulsifier molecules in each micelle which compensates a significant change in the number of micelles[10]. Moreover [E] is much higher than *CMC* and it was concluded that the change in the number of micelles would have little, if any, effect upon the polymerization behaviour.

The fraction of micelles to become the nuclei of polymer particles is dependent on the rate of radical penetration into micelles and the rate of micelle destruction due to the diffusion of emulsifier molecules from micelles onto polymerizing particles. Growing radicals in the aqueous phase are possibly another source of particles as proposed in some studies on the emulsion polymerization of various monomers[11-13]. The rate of particle nucleation from growing radicals and the rate of flocculation also determine the number of polymer particles.

Free base VP is soluble in water to some extent and reacts with an initiator radical in the aqueous phase to become a growing radical. It would diffuse into a micelle, precipitate as a nucleus, or aggregate with an existing particle. It is suggested by Yeleseyeva *et al.*[14], in the study on the emulsion polymerization of polar monomers, that an increase in hydrophilicity of the particle surface decreases emulsifier adsorption on the polymer particles as well as stability of the particle surface and particle flocculation occurs. So the increase in f_{VP} is likely to result in a smaller number of particles at low [E].

Particle diameter in some latices prepared at pH 11 and [E] = 10 mmol/l had a bimodal distribution as shown in *Figure* 3. The number of larger particles decreased but their size increased with increasing f_{VP} above 0.15. This would be attributed to the above-mentioned flocculation mechanism. Namely it is concluded that larger particles are formed by the flocculation of easily aggregable VP-rich copolymer at the initial stage of polymerization. The nucleation of particles from growing radicals in aqueous

Table 2 Critical micelle concentration of emulsifier in aqueous solution of VP at various pH

Additives	pH	*CMC* (mmol/l)
None	6.5	0.46
VP 2.5%, KPS 4 mmol/l, HCl	2.0	0.74
VP 0.5%, KPS 4 mmol/l, Na_2CO_3	11.0	0.39

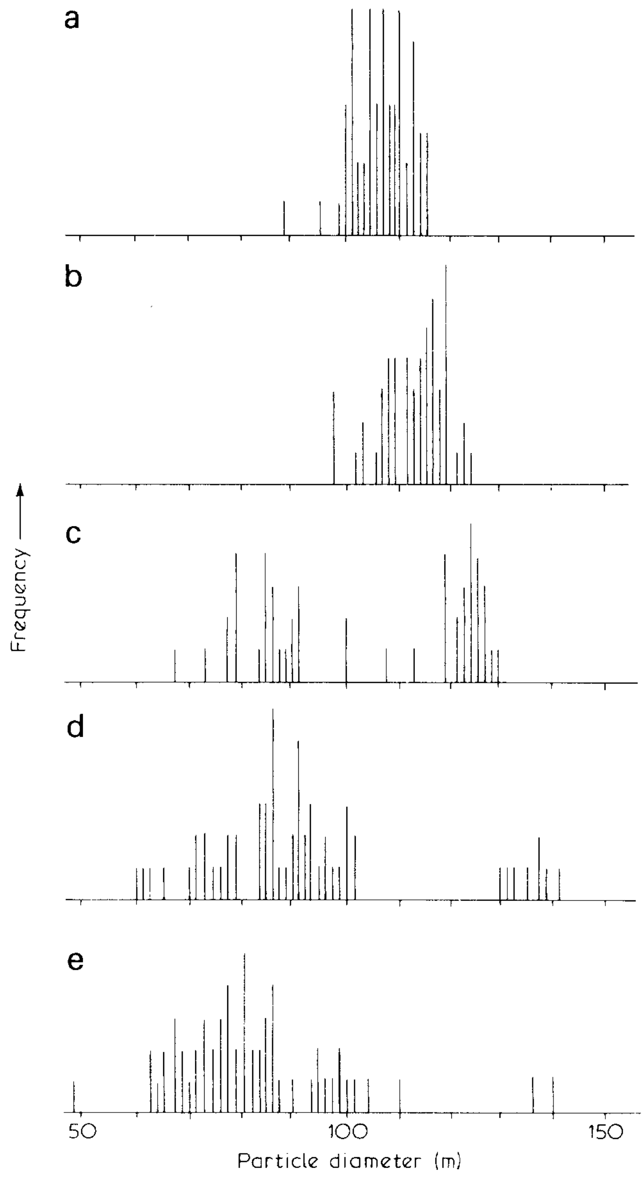

Figure 3 Size distribution of polymer particles prepared at pH 11 and [E] = 10 mmol/l

f_{VP}: A, 0.05; B, 0.10; C, 0.15; D, 0.20; E, 0.25

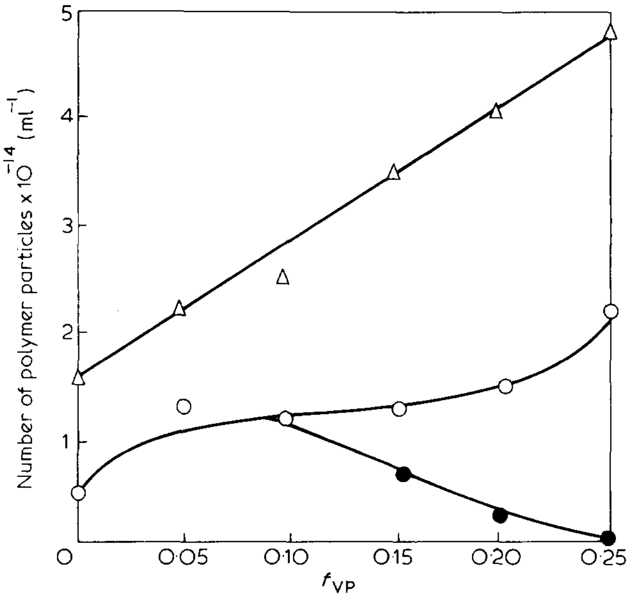

Figure 4 Dependence of number of particles on monomer composition in the emulsion polymerization under basic conditions

	[E] (mmol/l)	Particles
○	10	Total
●		Larger part
△	20	Total

phase would continue to occur at the subsequent stage of polymerization. If newly-formed nuclei obtain stability due to some change in their character or circumstance, it is possible that the number of smaller particles increases at this stage. For example, the hydrophilicity of newly-formed nuclei would decrease at the later stage of polymerization because of the gradual decrease in VP fraction in residual monomer and according to Yeleseyeva *et al.*[14] this change would be attended by some increase in the adsorption of emulsifier on them. In this manner the bimodal distribution of particle size would be obtained at higher f_{VP} and lower [E] at pH 11.

Smith–Ewart's theory is not effective in the emulsion polymerization of partially water-soluble monomer[11,12] and even then proportionality of the rate of polymerization with N is not observed in some cases[11]. But in St–VP copolymerization at pH 11 the rate of polymerization seems to depend on N as mentioned below. Comparison of *Figure* 2 with *Figure* 4 indicates that R_1 and R_2 are related to the number of larger particles and to that of total particles, respectively. This relation would also support the above-mentioned speculation about the formation of bimodal particle-size distribution.

The flocculation of particles is restricted in the emulsion copolymerization of St with VP at higher [E] ([E] = 20 mmol/l) and pH 11 and the slightly preferential conversion of VP leads to an increase in the rate of polymerization as well as an increase in N with increasing f_{VP} (*Figures* 2 and 4).

Emulsion copolymerization under acidic conditions

Time–conversion curves for the emulsion copolymerization of St with VP at pH 2 are shown in *Figure* 5. Most of them are sigmoidal curves and they have no obvious intersection between R_1 and R_2 as observed in the polymerization under the conditions of pH 11 and [E] = 10 mmol/l (*Figure* 1). The rate of polymerization at pH 2 decreased with an increase in f_{VP} irrespective of [E].

VP at pH 2 is soluble in water and insoluble in St. The *CMC* of emulsifier in the aqueous solution of VP at pH 2 was measured to estimate the dependence of the number of micelles on VP addition. The result shown in *Table* 2 might imply the possibility that VP addition causes an increase in *CMC* and consequently a decrease in the number of micelles. But the change in the number of micelles was judged not to affect the rate of polymerization significantly for the same reasons as mentioned previously.

The polymer at 5% conversion prepared under the condition of $f_{VP}=0.25$ and [E] = 10 mmol/l contains more than 80% VP units (*Figure* 5) and the rate of polymerization of VP at the initial stage little depends on f_{VP}. The rate of polymerization of St, on the other hand, increased with a decrease in f_{VP} so drastically that it could not be attributed to the change in $(1-f_{VP})$. The following situation was considered to explain these results.

Initiator radicals react with ionic VP preferentially but not exclusively and VP-rich radicals grow in the aqueous phase, reacting with St on rare occasions. Then these radicals become amphiphilic and St can exist at higher concentration near the radicals than in bulk. This would occur more in the polymerization system with lower f_{VP} and result in a remarkable increase in the rate of polymerization of St with decreasing VP in residual monomer. After the polymer particles are formed the major loci of polymerization are the particles because data on polymer composition (*Figure* 5) shows that the conversion of St surpassed that of VP at this stage of polymerization. Rate of polymerization per particle decreased with increasing f_{VP}. This would be caused by previously formed VP-rich polymer which tends to remain near the surface of the polymer particle and might prevent the supplementation of St or decrease the concentration of St.

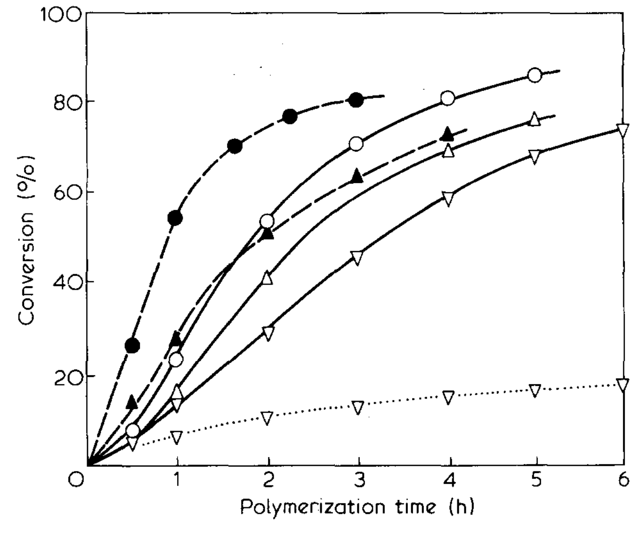

Figure 5 Time–conversion curves for the emulsion copolymerization of St with VP under acidic conditions. Symbols are the same as those in *Figure 1* except . . . ▽. . . , which shows the composition of the polymer formed at [E] = 10 mmol/l for f_{VP} = 0.25. (Conversion presented by dotted line)/total conversion indicates polymeric VP fraction in polymer

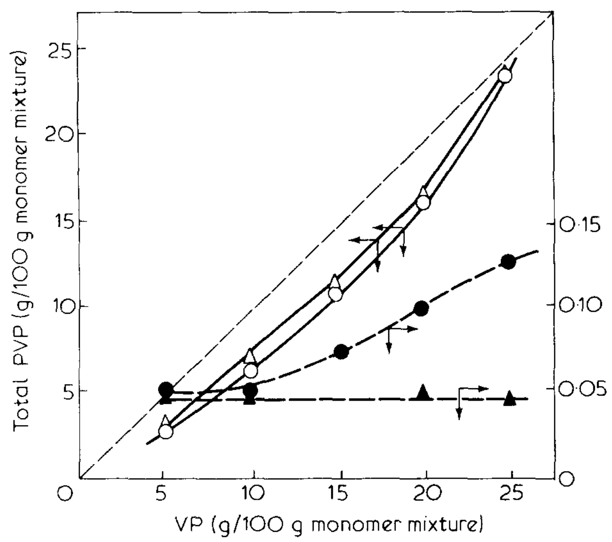

Figure 6 Population of VP units in the entire system copolymerized at pH 11

[E] (mmol/l): –○– –●–, 10; –△– –▲–, 20

Distribution of polymeric VP in latices

Polymerization was continued until the time–conversion curve levelled off for each run and final conversion of VP was determined from the total conversion and nitrogen content in the purified copolymer. The solid lines in *Figures* 6 and 7 show that there are no significant differences in the amount of unreacted VP for all the reaction systems. It was found from gravimetric analysis that the amount of polymeric VP (PVP) dissolved in water phase was negligible.

The amount of VP units on the surface of latex particles were determined by conductometric titration to examine the dependence of the distribuion of PVP in the latex particles on the polymerization conditions. The percentage of PVP on the surface of polymer particles prepared at pH 11 was less than 2.0% although for the latex prepared at pH 2 it was between 30 to 70%. The fraction of on-surface PVP increased with increasing f_{VP} up to 0.20, above which it levelled off.

The surface density of PVP on polymer particles was calculated from the data in *Figures* 6 and 7 assuming that only VP units on the particle surface would be detected by hydrochloric acid titration. The surface density also levelled off above $f_{VP}=0.20$. The apparent effective area of VP unit on the particle surface at the maximum point was calculated to be 6A^2/unit.

In contrast to the preferential localization of PVP on the particle surface in the latex prepared at pH 2, the surface density of PVP was very low in the latex under basic conditions. Assuming a statistical distribution of VP units in the particle, the ratio of on-surface PVP to total PVP was estimated. The total number of monomeric units constituting a particle (Ut) and that of units exposed on the surface of a particle (Us) are expressed as follows, supposing both St and VP units are isotropic and of the same size;

$$Ut=\frac{\pi D^3 d N_A}{6M} \qquad (1)$$

$$Us=0.350\,\pi^{5/3}\left(\frac{N_A d}{M}\right)^{2/3} D^2 \qquad (2)$$

where D and d are the diameter and density of the particle, respectively, M the molecular weight of monomeric unit, and N_A Avogadro's number. Substituting numerical values in equations (1) and (2), and dividing equation (2) by equation (1), yields:

$$Us/Ut=2.46/D \qquad (D{:}\mathrm{nm}) \qquad (3)$$

As $D=75$ to 120 nm, Us/Ut should be 0.020 to 0.033, which are of the same order as the values obtained (0.01 to 0.02). This implies that the composition of on-surface copolymer is almost the same as that of the copolymer in the core of particles.

CONCLUSION

Emulsion copolymerization of St with VP was carried out at different monomer ratios in the presence of non-ionic emulsifier at pH 2 or 11. The following results were obtained.

(1) A slight preferential polymerization of VP and little interaction between VP and emulsifier would cause the formation of large particles at the initial stage followed by the formation of small particles at the later stage in the polymerization at pH 11.

(2) Polymerization behaviour at pH 2 is interpreted in terms of the high solubility and amphiphilic property of the growing radicals.

(3) The amount of polymeric VP on the surface of latex particles prepared under basic conditions was less than 2% of that of total polymeric VP.

(4) The amount and the density of polymeric VP on the surface of latex particles prepared under acidic conditions were much more than those of polymeric VP prepared at pH 11. They increased with f_{VP} up to 0.20 and then levelled off.

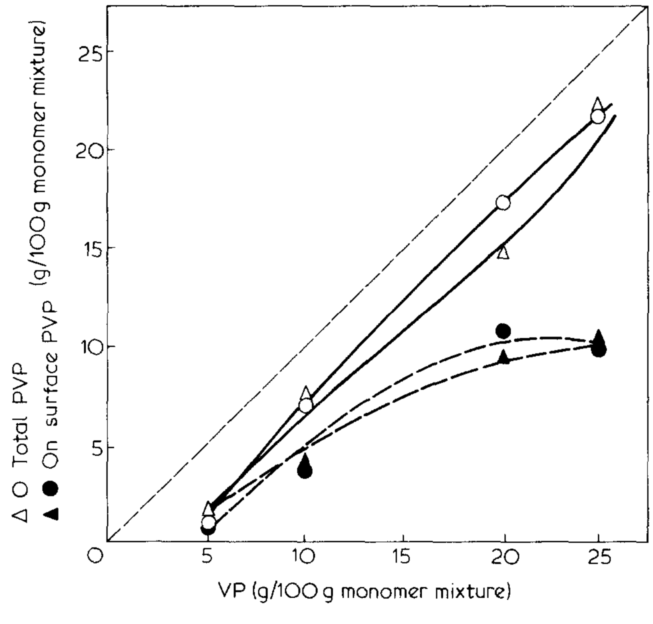

Figure 7 Population of VP Units in the entire system copolymerized at pH 2. Symbols are the same as those in *Figure 6*

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