Preparation and characterization of cationic copolymer latex. 2. Copolymerization of styrene with 4-vinylpyridine in an emulsifier-free aqueous medium

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A study was made of the effect of 4-vinylpyridine (VP) on the polymerization of styrene (St) in an emulsifier-free aqueous medium and on the property of the resulting cationic latex. Under basic conditions instantaneous copolymer composition was almost the same as the monomer composition in feed throughout the polymerization. Under acidic conditions, on the other hand, VP polymerized in preference to St and the reaction course was divided into two stages in terms of the main polymerization loci. Latex particles prepared under acidic conditions have unevenly-distributed polymeric VP on their surface which contributes to the stabilization of cationic latex at low pH. The latex behaves as an anionic one at high pH due to the presence of SO_4^- end groups on the polymer chains.

INTRODUCTION

The effect of polar comonomer on the emulsion copolymerization of styrene with 4-vinylpyridine was discussed in the previous paper[1]. It was found that the addition of a small amount of nonionic emulsifier caused a bimodal distribution of particle size because of the insufficient dispersion-stabilizing force of emulsifier and the change in the hydrophilicity of nuclei of particles. In the case of emulsifier-free polymerization the nuclei would come from the precipitate of growing radicals exclusively[2,3]. Krieger *et al.*[4] divided the course of aqueous copolymerization of styrene with styrenesulphonate into four stages, emphasizing the difference with the conventional emulsion polymerization in the presence of emulsifier. Sakota *et al.*[5] calculated the composition of growing radicals of styrene and dissociated and undissociated acrylic acid in aqueous phase by using their Q and e values and tried to determine the relation between the hydrophilicity of growing radicals and the number of latex particles. Recently Vijayendran[6] made a study on the effect of carboxylic monomers on the relative distribution of acid in latices.

In this paper the copolymerization of styrene with 4-vinylpyridine in an emulsifier-free aqueous medium is investigated. The mechanism of particle nucleation is discussed on the basis of the data from instantaneous polymer composition in addition to those from the rate of polymerization and the number of latex particles. The relation between the polymerization mechanism and the distribution of poly(4-vinylpyridine) is also studied.

EXPERIMENTAL

Materials

Distilled water was used in all polymerizations. Styrene (St) (Kashima Kagaku Yakuhin Co.) and 4-vinylpyridine (VP) (Tokyo Chemical Industry Co.) were distilled under reduced pressure. Potassium persulphate (KPS) (Taisei Kagaku Co.) was recrystallized from the aqueous solution. Hydrochloric acid and sodium carbonate (Kanto Chemical Co.) were used to buffer the polymerization system to pH 2 and 11, respectively.

Preparation of latices

The reaction system used was as follows: (St + VP) 20 g, buffer solution 190 ml, 4 mmol/l KPS solution 10 ml. The reaction system was purged with nitrogen for one hour prior to the addition of KPS solution. Polymerization was carried out at 70°C where the reaction proceeded in a moderate and reproducible rate. Further details were described in the previous paper[1].

Characterization of latices

Total conversion was determined gravimetrically. The composition of copolymer was calculated from elemental analysis data. The diameter of latex particles was measured by transmission electron micrography. The surface density of VP units on the latex particles was determined by conductometric titration of the latices purified with the method described in the previous paper[1]. Electrophoretic mobility (μ: cm^2/V sec) of the latex particles was determined with a modified Tiselius apparatus (Tsukasa Kogyo Co.) at ionic strength 0.02. The latices (solid content 0.3%) were dialysed to equilibrium against buffer solution before the electrophoresis. Zeta potential (ζ) was calculated from the following equation:

$$\zeta(V) = 3.6 \times 10^5 \ \pi\eta\mu/\varepsilon \qquad (1)$$

where η and ε are the viscosity and the relative dielectric constant of dispersion medium, respectively.

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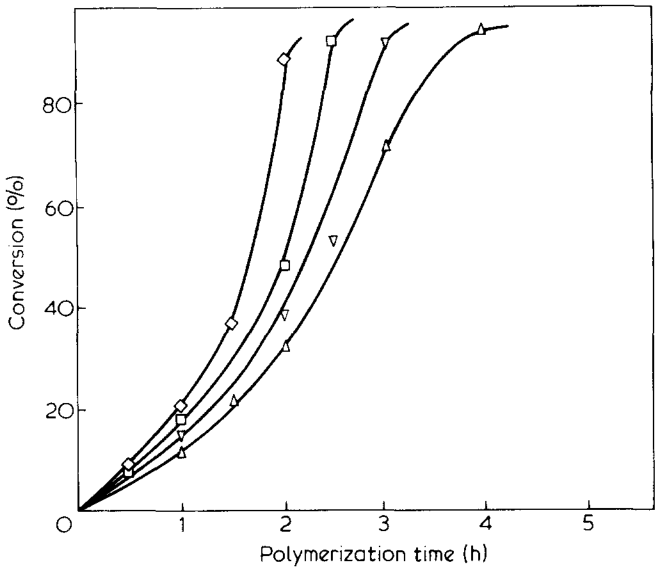

Figure 1 Time–conversion curves for the polymerization of St with VP in an emulsifier-free aqueous medium at pH 11. VP fraction in monomer feed (f_{VP}): △, 0.10; ▽, 0.15; □, 0.20; ◇, 0.30. (KPS), 4 mmol/l; temp., 70°C

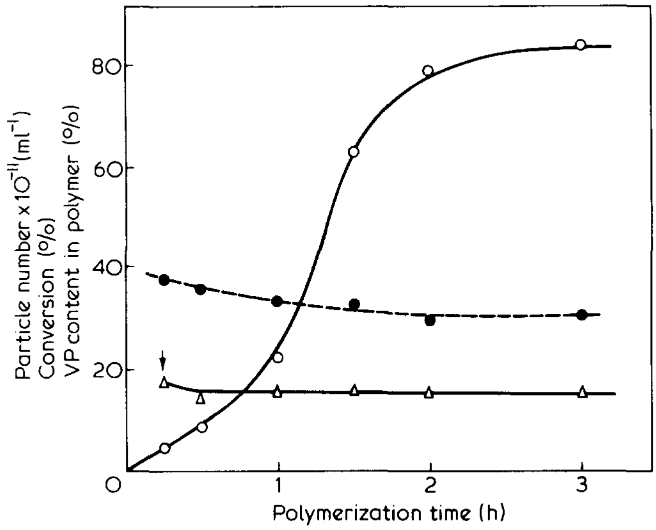

Figure 2 Change in conversion, polymer composition and particle number with polymerization time at pH 11 and f_{VP} = 0.30. ○, Conversion (%); ●, VP content in polymer (%); △, particle number x 10^{-11} (ml^{-1}); ↓, point where particles were detected on their electron micrograms for the first time

RESULTS AND DISCUSSION

Copolymerization of St and VP in a basic aqueous medium

Time–conversion curves for the copolymerization of St with VP at various monomer ratio and at pH 11 are shown in *Figure* 1. The slope of all curves increased gradually with conversion up to more than 80% conversion. The rate of polymerization increased as the VP fraction in monomer feed, f_{VP}, increased, whereas the number of polymer particles, N, depended little on f_{VP} (N = ~2×10^{12} particles/ml). This little dependence of N on f_{VP} would imply that VP does not contribute to the increase in the surface area of latex particles as do almost polar monomers. Some results for the polymerization at pH 11 and f_{VP}=0.30 are shown in *Figure* 2. It indicates that VP fraction in copolymer decreases slightly with time and polymer particles are discernible on electron micrograms of the latex at conversions lower than 5%. These results imply that the growing radicals and polymer molecules formed in the aqueous phase at the initial stage of polymerization precipitate promptly to give the nuclei of latex particles; preferential conversion of VP in the aqueous phase is not important in these reaction systems.

Copolymerization of St and VP in an acidic aqueous medium

The results obtained from the copolymerization at pH 2 were quite different from those under basic conditions. The time–conversion curves were found to be very characteristic as shown in *Figure* 3. Judging from their shape, the polymerization process can be divided into the following two stages: (1), from the start to the time when the time–conversion curves level off at the conversion (10 ~40%) which varies with f_{VP} (0.05 ~ 0.25); (2), from the time when re-acceleration of polymerization is observed to the end. *Figure* 4 gives some information on the reason why these phenomena were observed. VP is not a free base but a cation in the aqueous medium at pH 2 and its high solubility results in the preferential reaction of VP with

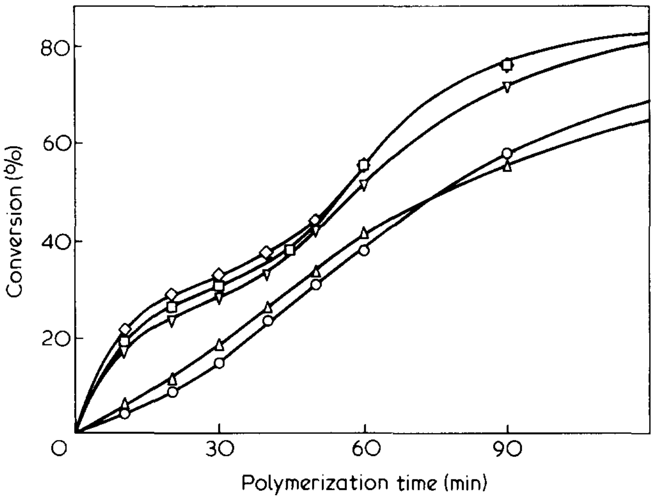

Figure 3 Time–conversion curves for the polymerization of St with VP in an emulsifier-free aqueous medium at pH 2. f_{VP}: ○, 0.05; △, 0.10; ▽, 0.15; □, 0.25; ◇, 0.30. (KPS), 4 mmol/l; temp. 70°C

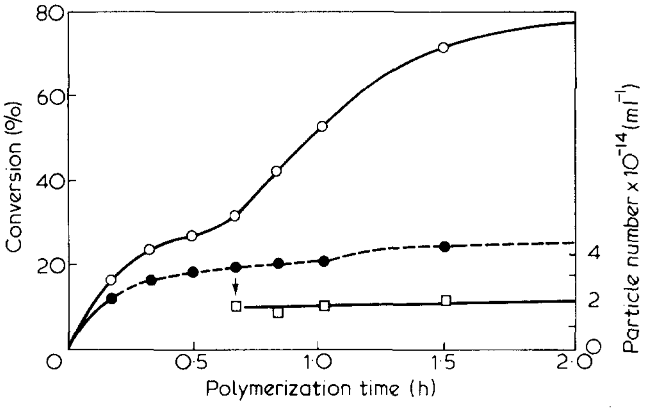

Figure 4 Change in conversion, polymer composition and particle number with polymerization time at pH 2 and f_{VP} = 0.25. ○, Total conversion (%); ●, VP conversion (per total monomer); □, particle number x10^{-14} (ml^{-1}); ↓, the same as that in *Figure 2*

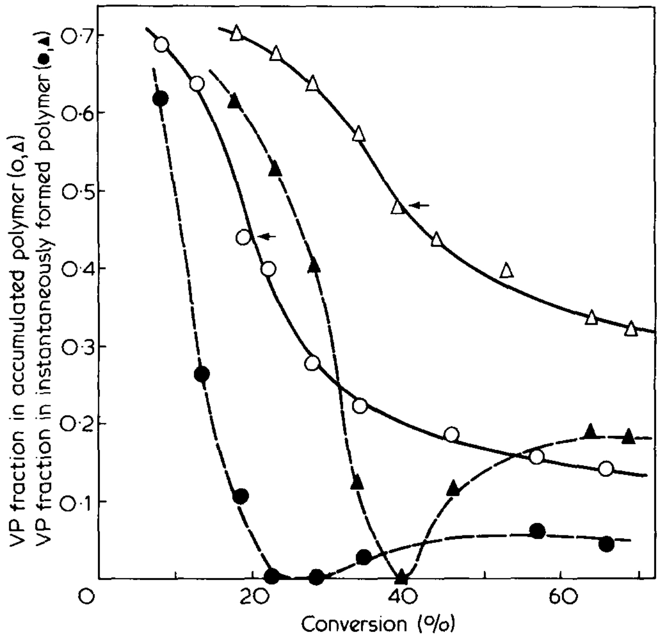

Figure 5 Dependence of polymer composition on conversion f_{VP}: ○, ●, 0.10; △, ▲, 0.25. ←: VP fraction at which particles were detected on their electron micrograms for the first time

initiator radicals or growing radicals soluble in the aqueous phase. As the result of this the growing radicals retain their solubility much longer than those under basic conditions. At this stage almost all the St would exist as monomer droplets which serve to supply St exhausted by copolymerization with VP in the aqueous phase. Levelling-off of the conversion at the first stage results from the exhaustion of most of VP. Polymerized St fraction in growing radicals increases as the VP concentration in the aqueous phase decreases and this change may accelerate the polymerization of St because the decrease in hydrophilic–hydrophobic balance of growing radicals causes an increase in their affinity with St even though they could still stay in the aqueous phase. When the hydrophilic–hydrophobic balance of growing radicals decreases up to a critical level they precipitate to nucleate latex particles. Results in *Figures* 4 and 5 in which the polymerized VP fraction in the copolymer is plotted against the conversion shows that the critical polymer composition (PVP/(PSt + PVP)) at which growing radicals commence to precipitate would be about 0.5.

Formation of particles induces a drastic change in the rate of polymerization of St. Particles can be favourite loci for St to exist in the concentrated state and now the polymerization of St accelerates as shown in *Figure* 4 where St conversion corresponds to the difference between total conversion and VP conversion. In this manner the main locus of polymerization alters from aqueous phase to particles. As St polymerized much more quickly than VP at this stage, PVP fraction in copolymer formed at each instant falls to almost zero (*Figure 5*) and after St supply from droplets ceases polymer composition changes in response to monomer composition in the particles. The polymerization behaviour at this stage seems to be similar to that of a typical emulsion polymerization except that the surface of polymerizing particles is occupied by cationic VP-rich polymer. Number of particles, N, changed from 10^{13} ml^{-1} at $f_{VP}=0.02$ to 1.5×10^{14} ml^{-1} at $f_{VP}=0.30$ and is proportional to about 1.1 powers of f_{VP}.

Some investigators[2,3] mention that growing radicals precipitate from the aqueous phase and nucleate latex particles in the polymerization of St in emulsifier-free media. The rapid increase in the volume of the nuclei leads to their aggregation and, consequently, to a decrease in the number of particles in course of polymerization. According to the measurement by Goodall *et al.*[3] 5×10^{12} nuclei (ml^{-1}) decreased to $10^{11}\sim10^{12}$ particles (ml^{-1}) due to their aggregation. Similar phenomena were observed in some of present cases, especially in the system with low f_{VP}.

Ceska[7] used ionic comonomers (methacrylic acid, acrylic acid, and itaconic acid) with St and found that the copolymerization of St with more hydrophobic carboxylic monomer resulted in a larger number of particles. This was attributed to the more rapid supply of hydrophobic carboxylic monomer to the newly formed unstable particles, that is, to a more rapid increase in the surface concentration of carboxylic groups on the particles. According to this deduction, it might be supposed that the number of particles is larger in the latex prepared at pH 11 than in that prepared at pH 2 because of the difference in the hydrophilicity of VP. This was the case in the copolymerization system of St with VP containing emulsifier at 40°C, but not in the present system, the one carried out in the absence of emulsifier at 70°C. In the present case free base VP must diffuse more quickly to newly formed particles than cationic VP but it is not supposed to act as a stabilizing group on the particles, that is, hydrated layer of free base VP units on the particle surface must be less effective to prevent the aggregation at 70°C than at 40°C.

Location of VP units in St–VP copolymer latex particles

After 2½ hours polymerization, polymer latices were dialysed and ion-exchanged. The viscosity of some latices decreased slightly (within 5%) during these procedures. In this manner water-soluble ingredients were removed and at the same time all of the VP units were changed to free base typed one because a mixture of strongly acidic cation exchangers and strongly basic anion exchangers were used. The amount of VP units on the surface of particles was determined by conductometric titration and compared with the amount of PVP in the latex particles as calculated from elemental analysis data. Their ratio was defined as PVP fraction existing on surface, S_{PVP}, the dependence of which on f_{VP} is shown in *Figure* 6. The ionization of VP during the polymerization results in an increase in S_{PVP} by about 20 times. S_{PVP} values shown here are larger than those for the polymer latices prepared in the presence of non-ionic emulsifier[1] either at pH 2 or pH 11. This is deduced to be due to the absence of the surface area occupied by emulsifier and at least partly due to the difference in the solubility of VP units in water owing to the difference in the polymerization temperatures. A gradual decrease in S_{PVP} with an increase in f_{VP} would be caused by the closeness to the saturation of VP units on the surface and by burying of excess VP units into particles with increasing f_{VP}. The closeness to the saturation of VP units on the surface can be checked from the dependence of the surface density of VP units, D_{VP}, on f_{VP} (*Figure* 7). D_{VP} increases as f_{VP} increases but the extent of increment in D_{VP} gets smaller gradually with f_{VP}. D_{VP} for the latex prepared at pH 2 and $f_{VP}=0.30$ is 0.25 VP unit/Å^2 surface which is the maximum value and cor-

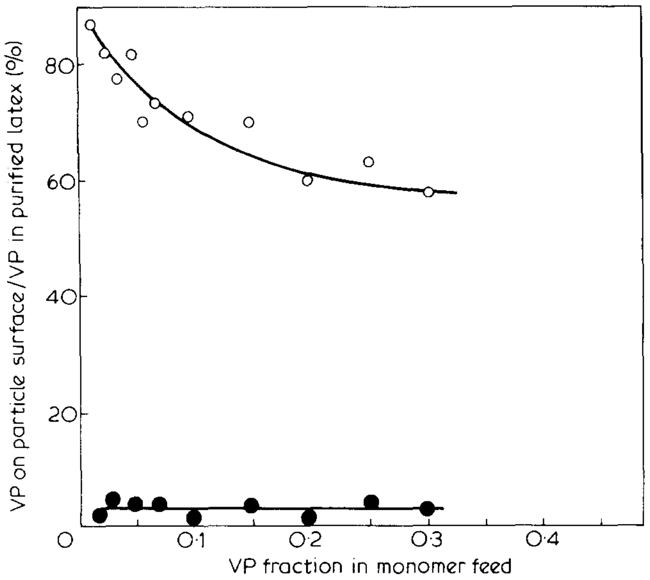

Figure 6 Dependence of distribution of polymeric VP on VP fraction in monomer feed. pH at which latices were prepared: ○, 2; ●, 11

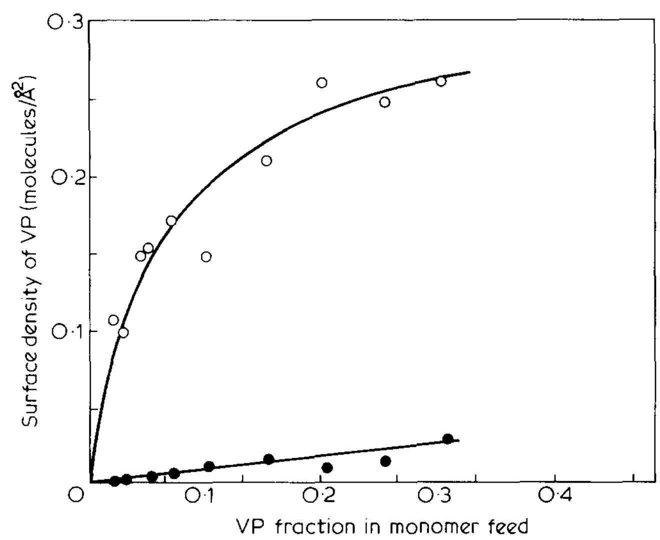

Figure 7 Dependence of surface density of polymeric VP on VP fraction in monomer feed. pH at which latices were prepared: ○, 2; ●, 11

responds to the surface area of 4 Å²/VP unit. Further discussion on the absolute value is abandoned as it is ambiguous whether titrated HCl reacts only with VP units on the particle surface or penetrates into the particle to react with VP units inside of the particle.

Zeta potential of two latices measured at several pH values is shown in *Figure* 8. Zeta potential as well as the potential at the outside of Stern layer is a hyperbolic function of surface charge density (σ). So even a significant difference in σ causes only a little difference in the potential when σ exceeds a critical value like in this case. The potential at the outside of Stern layer (φ) is estimated from Gouy–Chapman equation:

$$\varphi = \frac{2RT}{ZF}\sinh^{-1}\frac{\sigma}{(2RT\,\varepsilon C/\pi)^{0.5}} \qquad (2)$$

where Z, C and ε are the valence and the concentration of ions, and the dielectric constant of the medium, respectively, and T the temperature, and R and F the gas constant and Faraday's constant, respectively. Substituting numerical values in equation (2) yields

$$\varphi(\mathrm{V}) = 5.14\times10^{-2}\sinh^{-1}0.602\sigma(\mu\mathrm{C/cm^2}) \qquad (3)$$

$\varphi = 0.32$ V and 0.17 V are obtained for the latex particles ($f_{\mathrm{VP}} = 0.25$) prepared at pH 2 and pH 11, respectively, which show a reasonable correspondence to the obtained zeta potential.

The latices behave as anionic ones at pH above 7.5 because they contain appreciable amounts of sulphate ion end groups originating from the initiator fragment. The latex prepared at pH 11 has more sulphate groups than that prepared at pH 2. The homopolymerization of St in an aqueous medium at pH 2 and 11 shows no significant differences in the rate of polymerization with each other, which means that the rate of initiator decomposition is little dependent on pH. Kurt[8] showed that the rate of hydrolysis of alkyl sulphates increased with decreasing pH and it was found[9] that the number of hydroxyl groups produced in a persulphate initiated emulsion polymerization got less at higher pH. The above-mentioned phenomenon is consistent with these results. A difference in the location of sulphate groups as well as in the degree of hydrolysis between two systems may partly affect the anionic property of copolymer latices under basic conditions. It is suggested by Vanderhoff[10] that newly formed polymer molecules near the particle surface seldom interpenetrate with previously formed polymer molecules but force the latter away from the surface into the interior of the particle and even a part of their sulphate end groups suffers from this force. In a polymer particle prepared at pH 2 sulphate groups would be more permeable through a certain depth due to surrounding cationic PVP than in that prepared at pH 11. Electrophoresis under basic conditions would be affected mainly by on-surface sulphate groups but little by inner ones and cause an underestimation of the amount of sulphate groups in the latex prepared at pH 2.

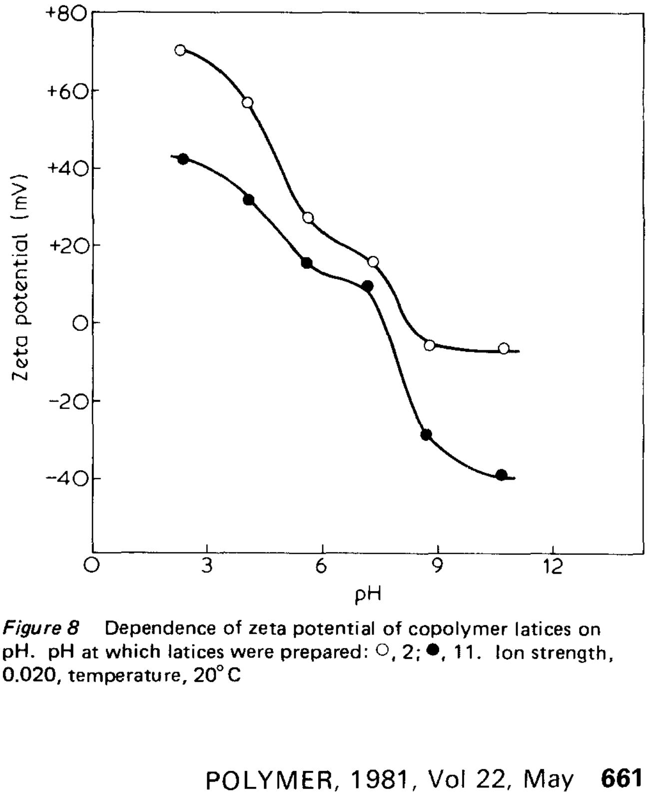

Figure 8 Dependence of zeta potential of copolymer latices on pH. pH at which latices were prepared: ○, 2; ●, 11. Ion strength, 0.020, temperature, 20° C

CONCLUSIONS

Copolymerization of St with VP was carried out in an emulsifier-free aqueous medium at various monomer ratio and at pH 2 or 11. The following results were obtained.

(1) Addition of cationic VP results in increases in the rate of polymerization and in the number of particles, whereas free base typed VP does not contribute to any increase in the number.

(2) The two-step scheme observed in the copolymerization at pH 2 was interpreted by the preferential polymerization of cationic VP in the aqueous phase followed by the polymerization of St in the latex particles.

(3) The distribution of polymerized VP in the polymer particle significantly depends on pH at which the polymerization is carried out. More than a half of polymerized VP was exposed on the particle surface in the latex prepared at pH 2 although a nearly statistical amount of VP was exposed on it in the latex prepared at pH 11.

(4) The apparent maximum surface density of VP on particles was 0.25 units/$Å^2$. Latices with such surface density of VP were stable cationic ones under acidic conditions.

REFERENCES

1 Ohtsuka, Y., Kawaguchi, H. and Watanabe, S. *Polymer* 1980, **21**, 1073

2 Goodwin, J. W., Hearn, J., Ho, C. C. and Ottewill, R. H. *Br. Polym. J.* 1973, **5**, 347

3 Goodall, A. R., Wilkinson, M. C. and Hearn, J. *J. Polym. Sci. (Polym. Chem. Edn.)* 1977, **15**, 2193

4 Juang, M. S. and Krieger, I. M. *J. Polym. Sci. (Polym. Chem. Edn.)* 1976, **14**, 2089

5 Sakota, K. and Okaya, T. *J. Appl. Polym. Sci.* 1976, **20**, 2583, 3265

6 Vijayendran, B. R. *ibid.* 1979, **23**, 893

7 Ceska, G. W. *ibid.* 1974, **18**, 427

8 Kurz, J. L. *J. Phys. Chem.* 1962, **66**, 2239

9 Van der Hull, H. J. and Vanderhoff, J. W. *Br. Polym. J.* 1970, **2**, 121

10 Vanderhoff, J. W. *Proc. Water-Borne Polym. Higher-Solids Coat. Symp.* 1976, **3**, paper No. 6