

Surface Characterization of Styrene/2-Hydroxyethyl Methacrylate Copolymer Latex

HIROYUKI SHIRAHAMA and TOSHIRO SUZAWA, *Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Shitami, Saijo-cho, Higashi-hiroshima, 724, Japan*

Synopsis

Styrene/2-hydroxyethyl methacrylate copolymer (PS/PHEMA) latex was prepared without soap. From an electron micrograph, this latex was found to be highly monodisperse. The surface characterization of PS/PHEMA latex was compared with that of polystyrene (PS) latex. Conductometric titration curves of these latexes revealed that both strong and weak acid groups existed on the latex surface. It was found that pH dependence of surface charges for these latexes was not very pronounced whereas negative values of ζ -potentials for PS/PHEMA latex were smaller than that for PS latex over the whole range of measured pH. This was interpreted on the basis of the difference in the structure of the electrical double layer for these latexes. Methylene Blue adsorption onto PS and PS/PHEMA latexes was measured as a function of pH, too. The pH dependence of the dye adsorption onto these latexes was hardly discernible. However, the amount of Methylene Blue adsorbed was somewhat greater onto PS latex than onto PS/PHEMA latex. This result might be attributed to the strength of hydrophobic interaction between dye and latex. It was suggested that PS/PHEMA latex was more hydrophilic than PS latex in spite of having about the same surface charge as PS latex.

INTRODUCTION

Soap-free polymer latexes, especially polystyrene (PS) latexes, are widely used as a model of colloidal dispersions. That is because these latexes are monodisperse and their surface charged groups are derived from the initiator only. Recently, beginning with PS latex, many studies on surface characterization of polymer latexes¹⁻⁸ have appeared and revealed the kinds and quantities of these surface groups. Considering that their uses are extending to the fields of medicine,⁹ biology,¹⁰ information,¹¹ and so on, it may become increasingly important to characterize the surfaces of these latexes.

The purposes of the current work are to prepare styrene/2-hydroxyethyl methacrylate (HEMA) copolymer latexes (PS/PHEMA), and to compare the surface characterization with that of PS latex. Poly-HEMA is a typical hydrogel and widely used as a material of soft contact lenses. Moreover, this is a notable material for antithrombogenic polymer at the present time. Up to the present, there is little investigation on the surface characterization of PS/PHEMA latex. Since HEMA has no ionized group, it is possible to change the hydrophobicity of the latex surface in proportion to the amount of HEMA without changing its surface charge. Therefore, PS/PHEMA latexes can be expected to be used as the multiphase biomaterials such as an adsorbent for serum proteins etc.

EXPERIMENTAL

Materials

Styrene and HEMA used in this work were purified by vacuum distillation under a nitrogen atmosphere. Potassium persulfate (KPS), which was used as the initiator, was recrystallized twice from water. Cation- and anion-exchange resins, PK-212 and PA-312 (porous ion-exchange resin, obtained from Mitsubishi Chemical Industries, Ltd.), were purified by reference to the method of van den Hul and Vanderhoff.¹² Methylene Blue (obtained from Wako Pure Chemical Industries, Ltd.) was purified by recrystallization from water twice. Sodium hydroxide solution was prepared from "Sørensen liquid" not to contain carbonate ion. All other chemicals were analytical grade. Distilled-deionized water was used in all experiments.

Methods

Preparation and Purification of Latexes

PS/PHEMA latexes were prepared by the seed polymerization method with successive addition of monomer as described previously.¹³ PS latex was prepared by the usual heterogeneous polymerization. All these latexes were prepared without soap in a nitrogen atmosphere. The polymerization procedure is given in Table I. The ratio of KPS to total monomer for each latex was adjusted almost the same value.

The latexes obtained were first dialyzed against water with well-boiled Visking tube. Subsequently, the latex dispersions were purified by a mixed bed of cation- and anion-exchange resins using a batch procedure. The volumetric ratios of latex dispersion to ion-exchange resin for PS and PS/PHEMA latexes were 4:1 and 3:1, respectively.

TABLE I
Preparation of Polymer Latexes (Atmosphere N₂)

Conditions	PS/PHEMA ₅ ^a	PS/PHEMA ₁₀ ^a	PS
Styrene (g)	70.37	65.85	45.34
HEMA (g)	4.63	9.15	—
KPS (g)	0.3750	0.3750	0.2473
Water (mL)	425	425	450
Seed monomer (g)	15	7.5	—
Speed of agitation (rpm)	350	350	350
Seed polymerization (°C, h)	70, 0.5	70, 0.5	—
Successive addition of monomer (°C, h)	70, 1.0	70, 2.0	—
After polymerization (°C, h)	70, 5.5	70, 4.5	70, 11.0 ^b
Solid content ^c (g/mL)	0.149	0.149	0.091

^a Subscripts of 5 and 10 represent the mol % of HEMA.

^b This time corresponds to the polymerization time.

^c Theoretical values.

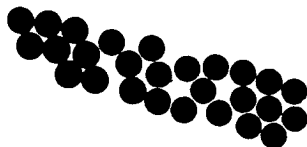


Fig. 1. Electron micrograph of PS/PHEMA₅ latex ($\times 10,000$).

Measurements of Particle Size

The particle sizes of latexes were determined by electron microscopy (using JEM-100V transmission electron microscope, JEOL, Ltd.). All latexes were highly monodisperse, e.g., an electron micrograph of PS/PHEMA₅ latex is shown in Figure 1. The average diameters, the specific surface areas, and the uniformity ratios (U) for latexes are given in Table II. U is described as follows¹⁴:

$$U = \bar{D}_w / \bar{D}_n$$

where \bar{D}_w is the weight average diameter of latex particles and \bar{D}_n is the number average diameter. In the case of $U \leq 1.01$, latex would be considered as monodisperse.

IR Spectra for PS/PHEMA Latexes

To confirm that HEMA had been introduced into the latex particles, the IR absorption spectra for PS/PHEMA latexes were measured using the IR spectrometer (Hitachi, Type-215). The latex dispersions were first centrifuged; then the precipitate was dried in vacuum. This dried sample was made into a tablet with KBr powder. For example, the IR spectrum for PS/PHEMA₁₀ latex is shown in Figure 2. As observed in this figure, in addition to the characteristic absorption of styrene, it can be seen that HEMA absorbs at about 1730 and 3500 cm^{-1} (these peaks correspond to the stretching vibrations of $-\text{C}=\text{O}$ and $-\text{OH}$, respectively).

Conductometric and Potentiometric Titrations

Titrations were carried out at 25°C under a nitrogen atmosphere. Conductometric titrations were carried out with $5 \times 10^{-3}N$ NaOH aqueous solution as a titrant. Conductivities were measured using a Toa digital conductivity meter CM-30ET. The particle volume fraction (ϕ) was about 1.25%. During the titrations, the latex dispersions were stirred with a magnetic stirrer.

TABLE II
Particle Diameters, Specific Surface Areas, and Uniformity Ratios of Polymer Latexes

Latex	Particle diameter (nm)	Specific surface area (m^2/g)	Uniformity ratio
PS/PHEMA ₅	510	11.13	1.0003
PS/PHEMA ₁₀	491	11.48	1.0006
PS	526	10.86	1.0003

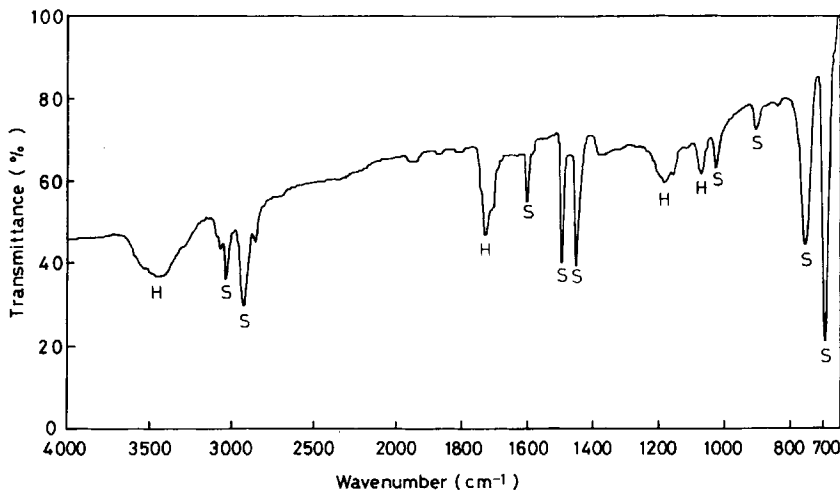


Fig. 2. The IR spectrum of PS/PHEMA₁₀ latex. S and H represent polystyrene and poly-HEMA absorption, respectively.

Potentiometric titrations using a Hitachi-Horiba pH meter F-7ss were carried out with $2 \times 10^{-2}N$ NaOH solution as a titrant. Before the titrations, the latex dispersions were adjusted to pH about 3 and ionic strength 0.01 by adding 0.01N HCl and 0.1M NaCl. The particle volume fraction was about 2.3%. In the same way, the latex dispersions were stirred except at reading the pH values. To determine the surface charge densities (σ) of latexes as a function of pH, an equal volume of blank solution (containing only 0.01N HCl and 0.1M NaCl) was titrated in the same conditions as the latex dispersions.

Zeta (ζ)-Potentials of Latexes

To clarify better the surface characterization of latexes, ζ -potentials of the latexes were measured using a microelectrophoresis apparatus (Mitsumura Riken Co., Ltd.) at 25°C. First the electrophoretic mobilities of latexes were measured, and then mobility values were converted into ζ -potentials according to the treatment of Wiersema et al.¹⁵ ζ -potentials were measured as a function of pH or electrolyte concentration. The pH and ionic strength were adjusted with HCl, NaOH, and NaCl solutions.

Methylene Blue Adsorption onto Latexes

In order to compare the results of titration curves and ζ -potential measurements, Methylene Blue (basic dye) adsorption onto latexes was measured at 25°C. After mixing Methylene Blue solution with latex dispersion, the sample solution was centrifuged using a high-speed centrifuge (Kubota, KH-180). The amount adsorbed was determined from the difference between the initial concentration and equilibrium one by spectrophotometry (at $\lambda = 670$ nm). From the results of preliminary experiments, 2 h was chosen for the equilibration time of adsorption. The pH and ionic strength of the solutions for measurement were adjusted with HCl, NaOH, and NaCl solutions.

RESULTS AND DISCUSSION

Conductometric Titrations of Latexes

The conductometric titration curves for PS and PS/PHEMA latexes are shown in Figure 3. The shapes of these titration curves are similar to one another. Two distinct inflection points (i.e., end points of titration) are shown for each latex. The first end point corresponds to the equivalence point of strong acid derived from the decomposed initiator fragment ($-\text{OSO}_3^-$). The second end point may correspond to that of weak acid ($-\text{COO}^-$). It seems that carboxyl groups come from an oxidation of hydroxyl groups.^{16,17} Hydroxyl groups can be formed by the Kolthoff reaction,¹⁸ and oxidation of this groups can be performed even in a nitrogen atmosphere.^{18,19} From this figure, there seems to be little difference in surface charges of these latexes.

Potentiometric Titrations of Latexes

Figure 4 shows the potentiometric titration curves of PS and PS/PHEMA latexes. In the alkaline pH region, the titrant volume at the same pH value is somewhat greater for PS/PHEMA latex than for PS latex.

On the basis of the results of potentiometric titrations, assuming that the difference in titration volume between blank and latex dispersion systems corresponds to the volume of NaOH aqueous solution which is used for titrating surface groups of the latex particles at some pH value, we may be able to determine the surface charge densities (σ) of latexes as a function of pH. The results are shown in Figure 5. For each latex, $-\sigma$ somewhat increases from a neutral pH value (pH about 6). This may arise from the dissociation of weak acid groups of latex surface. This tendency is greater for PS/PHEMA latex than for PS latex. For this result, the following explanations are possible: (i) As HEMA is more hydrophilic than styrene,

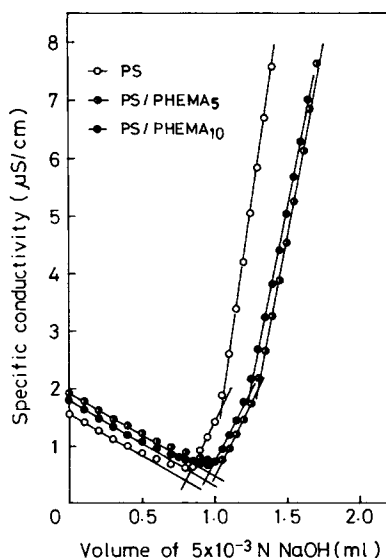


Fig. 3. Conductometric titration curves of PS and PS/PHEMA latexes at 25°C.

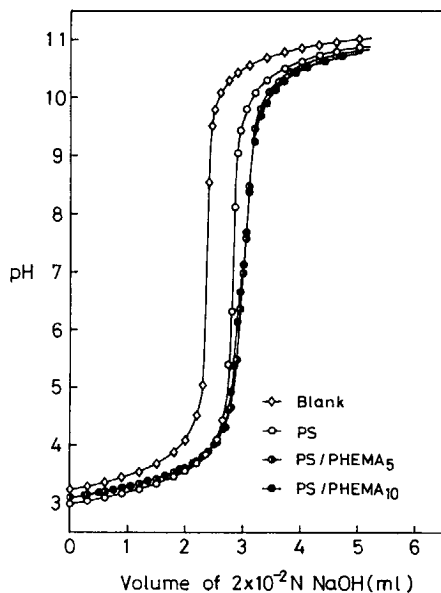


Fig. 4. Potentiometric titration curves of PS and PS/PHEMA latexes (25°C, ionic strength 0.01).

water-soluble initiator fragments may be incorporated more into PS/PHEMA latex than into PS latex. Therefore, it seems that weak acid groups exist more on PS/PHEMA latex than on PS latex. (ii) Weak acid groups may be formed by hydrolysis of HEMA during the polymerization. But, as HEMA is stable to hydrolysis except at high alkalinity,²⁰ this effect seems to be not so large. However, in general, pH dependence of surface charges for these latexes is relatively small. Hence, it appears that PS/PHEMA latexes are more hydrophilic than PS latex in spite of their having about the same surface charges as PS latex.

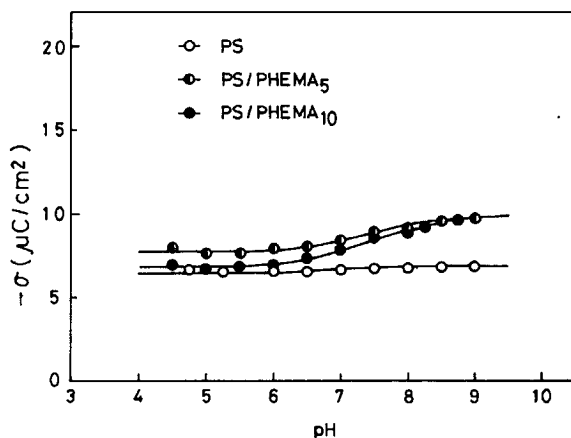


Fig. 5. Surface charges for PS and PS/PHEMA latexes as a function of pH (25°C, ionic strength 0.01).

ζ -Potentials of Latexes

Figure 6 shows ζ -potentials of PS and PS/PHEMA latexes as a function of pH. From this figure, it can be seen that all these latexes have negative charges derived from the initiator fragment. Negative values of ζ -potentials for PS/PHEMA latexes are smaller than that for PS latex over the whole range of measured pH, and this tendency is proportional to the quantity of copolymerized HEMA. Considering that the differences in surface charge between these latexes are not so large (strictly speaking, $-\sigma$ of PS/PHEMA latexes is somewhat greater than that of PS latex), it is difficult to understand this trend in ζ -potentials (cf. Figs. 5 and 6). The differences in tendency between surface charges and ζ -potentials may be attributed to the structure of the electrical double layer for these latexes. That is to say, surface charge represents the quantities of all ionized groups existing on the latex surface, while the ζ -potential is the potential at the plane of shear of the electrical double layer. These differences will be discussed in the following section.

Position of the Plane of Shear and ζ -Potential

As described above, the difference in ζ -potential between PS and PS/PHEMA latexes is very great. Its difference may be attributed to the structure of the electrical double layer. To clarify this, we made an attempt to estimate the position of the plane of shear on the basis of the Gouy-Chapman-Stern model of the double layer.

The position (t) of the plane of shear was estimated using the treatment of Eversole and Boardman.²¹ They considered the dependence of ζ -potentials on the concentration of indifferent electrolyte in the form:

$$\ln \tanh(ze\zeta/4kT) = \ln \tanh(ze\psi_s/4kT) - \kappa t \quad (1)$$

where z is the valence of ions, e is the unit charge of electron, k is the Boltzman constant, T is the absolute temperature, ψ_s is the Stern potential,

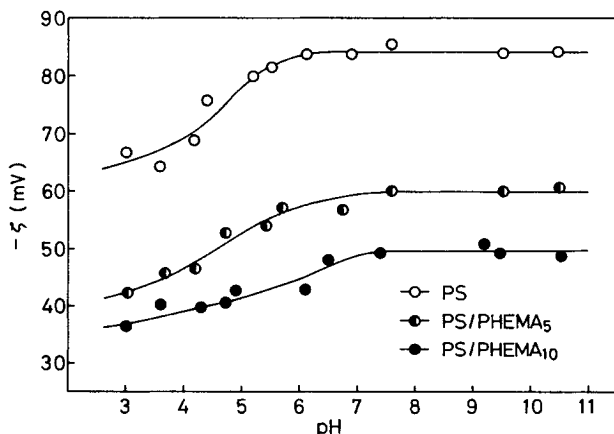


Fig. 6. ζ -potentials of PS and PS/PHEMA latexes as a function of pH (25°C, ionic strength 0.01).

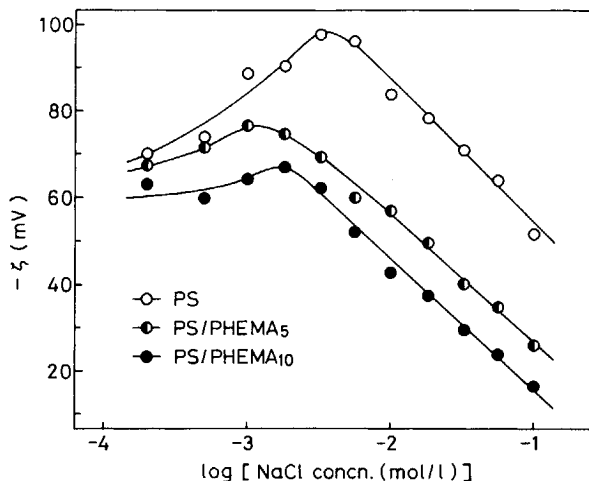


Fig. 7. ζ -potentials of PS and PS/PHEMA latexes as a function of NaCl concentration at 25°C.

and κ is the Debye-Hückel parameter. In the case of 1-1 electrolyte, eq. (1) can be written for water solutions at 25°C:

$$\ln \tanh(9.727 \times 10^{-3} \zeta) = \ln \tanh(9.727 \times 10^{-3} \psi_\delta) - 0.3285 c^{1/2} t \quad (2)$$

where ζ , c (electrolyte concentration), and t are in mV, mol/L, and Å, respectively. Thus, the position (t) of the plane of shear can be estimated from the linear slope of eq. (2).

First of all, ζ -potentials of PS and PS/PHEMA latexes are measured as a function of NaCl concentration. As observed in Figure 7, ζ -potentials of these latexes exhibit maxima at about 2×10^{-3} mol/L of NaCl concentration. A reasonable explanation for the increase in ζ -potential up to this NaCl concentration is the adsorption of negative chloride ion from solution to the surface of latex particle.²² The rapid decrease in ζ -potential above

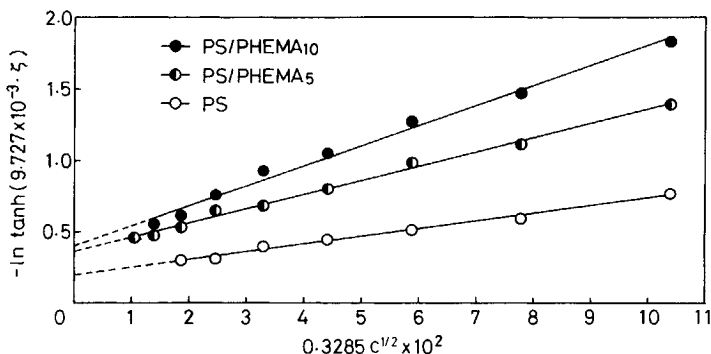


Fig. 8. Plots of $-\ln \tanh(z e \zeta / 4 k T)$ as a function of NaCl concentration (the Eversole-Boardman plot) at 25°C.

ca. 2×10^{-3} mol/L of NaCl concentration may be attributed to the compression of the electrical double layer.

On the basis of the results in Figure 7, the data are plotted in Figure 8 (the Eversole-Boardman plot) in accordance with eq. (2). For each latex, the plot of $-\ln \tanh(9.727 \times 10^{-3}\zeta)$ vs. $0.3285c^{1/2} \times 10^2$ shows a good linearity. The position (t) of the plane of shear is estimated from the slope of this straight line, where the slopes are determined by the least-squares method. The values of t are given in Table III. As shown in Table III, the values of t for PS/PHEMA latexes are about two times greater than that for PS latex. Moreover, t increases with increasing the quantity of copolymerized HEMA. From these results, it seems that a schematic representation of the electrical double layer for polymer latex surfaces is given in Figure 9. That is to say, in the case of PS/PHEMA latex, hydrous poly-HEMA layer exists on its surface, and this layer may shift the position of the plane of shear away from the particle surface. Therefore, in the case of having much the same surface potential, the potential at the plane of shear (i.e., ζ -potential) for PS/PHEMA latex is smaller than that for PS latex (see Fig. 9). Thus, the differences between surface charges and ζ -potentials for these latexes can be explained by considering the existence of poly-HEMA layer.

Methylene Blue Adsorption onto Latexes

On the basis of the above results of surface characterization, Methylene Blue adsorption onto polymer latexes was investigated. Figure 10 shows pH dependence of Methylene Blue adsorption onto PS and PS/PHEMA latexes. It can be seen that pH dependence of Methylene Blue adsorption is relatively small. Comparing this figure with the results of surface charges (σ) and ζ -potentials for these latexes (cf. Figs. 5, 6, and 10), the overall tendency of Methylene Blue adsorption is similar to rather σ -pH curves (Fig. 5) than ζ -pH curves (Fig. 6). That is because these latexes and Methylene Blue molecules have the opposite charges each other, dye molecules may adsorb electrostatically on the sites of surface charge groups regardless of ζ -potential values. However, contrary to σ -pH curves (Fig. 5), Methylene Blue adsorption onto PS latex is somewhat greater than that onto PS/PHEMA latex. This may indicate that Methylene Blue adsorption is affected by hydrophobic interaction between dye and latex, too.

To better understand this result, the ratio (r) of the number of adsorbed Methylene Blue molecules (n_1) to the number of surface charged groups (n_2) was calculated as a function of pH, where n_1 and n_2 are obtained from

TABLE III
Values of t for PS and PS/PHEMA Latexes

Latex	t (Å)
PS	5.4
PS/PHEMA ₅	10.0
PS/PHEMA ₁₀	14.0

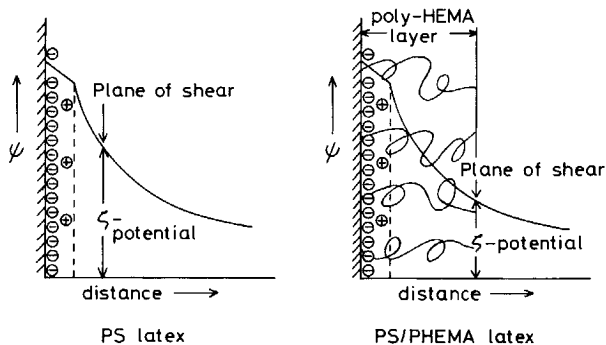


Fig. 9. Schematic representation of the electrical double layer for polymer latex surfaces.

the amount of Methylene Blue adsorbed and surface charge density of latexes, respectively. As a result, r for PS, PS/PHEMA₅ and PS/PHEMA₁₀ latexes were about 1.09, 0.71, and 0.74, respectively, regardless of pH. The value of r may be considered as an indication of electrostatic interactions between dye and latex. Namely, in the case of $r = 1$, each dye molecule adsorbs on the individual site of surface charge groups of latex particle. From the fact that pH dependence of r for each latex is hardly discernible, it appears that Methylene Blue adsorption onto these latexes mainly occurs electrostatically. However, r for PS latex [$r(\text{PS})$] are greater than that for PS/PHEMA latexes [$r(\text{PS/PHEMA})$]. Further, $r(\text{PS})$ are greater than 1.0 and $r(\text{PS/PHEMA})$ are less than 1.0. As described above, this fact may be attributed to hydrophobic interaction between Methylene Blue molecules and these latexes. Namely, when Methylene Blue molecules adsorb onto polymer latexes, this dye must displace the hydrated layer of latex surface. Therefore, the more hydrophilic the latex surface is, the more difficult Methylene Blue adsorbs. This tendency is also observed in the adsorption of sodium dodecyl sulfate onto these latexes.²³

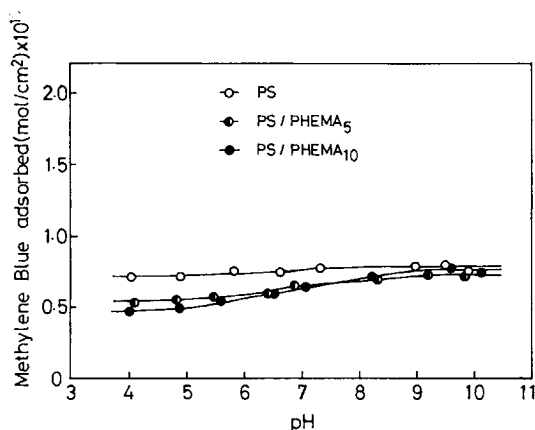


Fig. 10. Methylene Blue adsorption onto PS and PS/PHEMA latexes as a function of pH (25°C, ionic strength 0.01).

References

1. T. Matsumoto and A. Ochi, *Kobunshi Kagaku*, **22**, 481 (1965).
2. A. Kotera, K. Furusawa, and Y. Takeda, *Kolloid Z. Z. Polym.*, **239**, 677 (1970).
3. J. B. Smitham, D. V. Gibson, and D. H. Napper, *J. Colloid Interface Sci.*, **45**, 211 (1973).
4. J. W. Goodwin, J. Hearn, C. C. Ho, and R. H. Ottewill, *Brit. Polym. J.*, **5**, 347 (1973).
5. J. Stone-Masui and A. Watillon, *J. Colloid Interface Sci.*, **52**, 479 (1975).
6. D. E. Yates, R. H. Ottewill, and J. W. Goodwin, *J. Colloid Interface Sci.*, **62**, 356 (1977).
7. M. E. Labib and A. A. Robertson, *J. Colloid Interface Sci.*, **77**, 151 (1980).
8. H. Kawaguchi, H. Hoshino, and Y. Ohtsuka, *J. Appl. Polym. Sci.*, **26**, 2015 (1981).
9. A. Rembaum, S. P. S. Yen, and W. Volksen, *Chemtech, March* (1978), p. 182.
10. M. Okubo, T. Takeya, and T. Matsumoto, Fall Annual Meeting of the Chemical Society of Japan, 1980.
11. H. Fujita, *Kobunshi*, **29**, 118 (1980).
12. H. J. van den Hul and J. W. Vanderhoff, *J. Colloid Interface Sci.*, **28**, 336 (1968).
13. T. Suzawa, H. Shirahama, and T. Fujimoto, *J. Colloid Interface Sci.*, **86**, 144 (1982).
14. A. Homola and R. O. James, *J. Colloid Interface Sci.*, **59**, 123 (1977).
15. P. H. Wiersema, A. L. Loeb, and J. Th. G. Overbeek, *J. Colloid Interface Sci.*, **22**, 78 (1966).
16. R. H. Ottewill and J. N. Shaw, *Kolloid Z. Z. Polym.*, **218**, 34 (1967).
17. J. Hearn, R. H. Ottewill, and J. N. Shaw, *Br. Polym. J.*, **2**, 116 (1970).
18. I. M. Kolthoff and I. K. Miller, *J. Am. Chem. Soc.*, **73**, 3055 (1951).
19. J. W. Vanderhoff, in *Vinyl Polymerization*, G. E. Ham, Ed., Marcel Dekker, New York, 1969, Vol. 1, Part 2, Chap. 1.
20. E. Omori, in *Acrylic Esters and Their Polymers* [II], Shokodo (Japan), 1975, p. 70.
21. W. G. Eversole and W. W. Boardman, *J. Chem. Phys.*, **9**, 798 (1941).
22. C. M. Ma, F. J. Micale, M. S. El-Aasser, and J. W. Vanderhoff, in *Emulsion Polymers and Emulsion Polymerization*, D. R. Bassett and A. E. Hamielec, Eds., American Chemical Society, Washington, D. C., 1981, p. 251.
23. T. Suzawa, H. Shirahama, and S. Kawasaki, unpublished data.

Received November 9, 1983

Accepted February 29, 1984