Synthesis and Characterization of Polystyrene Latex with an Amphoteric Emulsifier

K. KATO, H. KONDO, K. YOKOTA, K. ESUMI, and K. MEGURO,
*Department of Applied Chemistry and Institute of Colloid and
Interface Science, Science University of Tokyo, Kagurazaka,
Shinjuku-ku, Tokyo 162, Japan*

Synopsis

An emulsion polymerization of styrene in the presence of an amphoteric emulsifier of amino-acid type, N-lauroyl-N,N-dimethyllysine (DMLL), has been studied at pH 7.0. The polymerization rate increased exponentially with the concentration of DMLL. The concentration of latex particles was proportional to the DMLL concentration to the 0.6 power. The latex particle size decreased with increasing concentration of DMLL. The molecular weight of polystyrene latexes increased with an increase in DMLL concentration. Furthermore, the zeta potentials of latex particles were significantly dependent on the pH, and showed the existence of an isoelectric point at about pH 4.0.

INTRODUCTION

In the process of emulsion polymerization for preparing the latex, emulsifiers play important roles; the polymerization progresses in emulsifier micelles containing the solubilized water-insoluble monomer.[1-5] Further, the emulsifiers considerably affect the colloidal characteristics of the synthesized latex, such as stability, particle size, molecular weight, and electrokinetic behavior of its surface.[6-9]

Amphoteric surfactants have characteristic properties to change their ionic forms with pH, and they are used in various fields depending on their superior properties: biodegradation, antibacterial, antistatic activity, and safety *in vivo*. Therefore, there are many reports on the fundamental properties of various amphoteric surfactant aqueous solutions, e.g., micellization, surface tension, critical micelle concentration (CMC), aggregation number, and Krafft point.[10-13]

However, there are only a few reports relating to the emulsion polymerization using amphoteric emulsifiers,[14] compared with using ionic or nonionic ones. We have previously reported the emulsion polymerization of styrene using N,N-dimethyl-n-laurylbetaine (LNB) as an amphoteric emulsifier of betaine type at pH 7.0, and have found that the surface charge of the synthesized latex is considerably dependent on pH of its suspended solution.[15]

In this work, the emulsion polymerization of styrene in the presence of DMLL as an amino-acid type amphoteric emulsifier was carried out and characterized by measuring the stability, the polymerization rate, the particle size, the molecular weight of polystyrene latex, and the zeta potential of latex particles.

EXPERIMENTAL

Materials

N-lauroyl-N,N-dimethyllysine [$C_{11}H_{23}CONH(CH_2)_4CH[N(CH_3)_2]COOH$] (DMLL) supplied from Ajinomoto Co. was purified by repeated recrystallization from the mixture of n-hexane and 2-propanol (7:3) and carefully dried *in vacuo* before use. The purity of the sample was confirmed by the lack of a minimum in its surface tension vs. the concentration curve.

Styrene monomer (Wako Pure Industries) was distilled under dried nitrogen atmosphere and was stored in a refrigerator under nitrogen before use. Potassium peroxodisulfate used for an initiator was an analytical grade (Wako Pure Industries) Water used in all experiments was purified by passing through the Milli-Q Water Purification System.

## PROCEDURE

Appraisal of the Isoelectric Region of DMLL

In estimation of an isoelectric region of DMLL, Michaelis's or Sakakibara et al.'s method was adopted.[16,17] At first, several couples of buffer solutions with different known pH were prepared. Into one of each several couple of buffer solution, 10 cm^3 of DMLL (10 mmol dm^{-3}) dissolved in ethanol–water mixture (50:50) was poured. Otherwise, 10 cm^3 of only mixed solution of water–ethanol (50:50) was added into the other solution, and this solution was kept as a blank sample. The pH of each solution was measured with a pH meter (Model-COM-8, Denki Kagaku Keiki Co.) at 25°C under nitrogen atmosphere. The pH of the former solution dissolved DMLL is expressed as pHs, and the pH of the latter is expressed as pHi. The absolute value of a difference between pHs and pHi can be expressed as ΔpH:

$$\Delta pH = |pHs - pHi|$$

This ΔpH is plotted as a function of pHi, and the results are shown in Figure 1. The pHi region, where the pH is satisfied within $0.01 > \Delta pH > 0$, was regarded as an isoelectric one. In the measurement of pH, acetic acid–sodium acetic buffer solution in the pH range 2.0–5.2, phosphate buffer solution in the pH range 5.2–8.6, and glycine–sodium hydroxide in the range of 8.6–13.0 were used, respectively. The difference in pH of each buffer solution was neglected.

Emulsion Polymerization

Each run of the emulsion polymerizations were performed by using a batch process in a 1-L glass reactor, fitted with a metal screw, thermometer, and
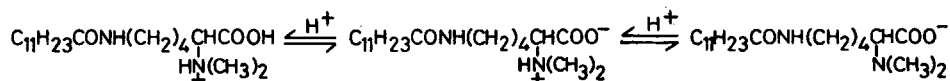
a) Cationic form   b) Zwitterionic form   c) Anionic form

Fig. 1. The change of ionic forms of DMLL molecule with pH of its aqueous solutions.

TABLE I
Emulsion Polymerization Recipe

Ingredients	(g)
Styrene	50
Water	250
Potassium Peroxodisulfate	0.2
N^{ϵ}-lauroyl-N^{α},N^{α}-dimethyllysine (DMLL)	2–7

facilities for charging and sampling. A typical polymerization recipe is shown in Table I. At first, water and emulsifier were added to the reactor at room temperature. Then, the pH of this mixture was adjusted to be about 6.8, and further styrene monomer was added to them. The reactor was immersed in a constant temperature bath being adjusted to be $60 \pm 1°C$ under nitrogen atmosphere, and the mixture was stirred at 250 rpm. After the temperature rose up to 60°C, the aqueous solution of potassium peroxodisulfate (0.2 g/50 cm^3) was added to the contents in the reactor for beginning the polymerization.

The samples for determination of the conversion, the particle size, the molecular weight distribution, and the zeta potential were withdrawn with pipettes at fixed intervals. The procedure for the determination of the conversion was as follows: 5 cm^3 samples which had taken with pipettes were poured into 5 cm^3 of p-benzoquinone methanol solution (0.015 g dm^{-3}) as an inhibitor to terminate the polymerization reaction. Then, the unreacted styrene monomer, methanol, and water were evaporated at 70°C. The percent conversions of styrene to polystyrene were estimated by measuring the weight of dried samples on the assumption that the (monomer + polymer)/water was constant throughout the reaction.

MEASUREMENT

In order to determine the particle size, the molecular weight, and the zeta potential of the latex particle after 90 min of reaction time, the samples were cooled rapidly in cold water (0°C). The particle sizes and size distributions were determined by transmission electron microscopy (TEM) and by submicron particle sizer (Malvern Autosizer Model-700), which was carried out under following conditions: The temperature was 25.0°C, the refractive index of its solution was 1.33, and the viscosity was 0.8909 cP.

The molecular weight distributions of the polystyrene latex samples were measured by using gel permeation chromatograph (GPC) fitted with packed column (Showa Denko K.K. A-80M). The weight-average molecular weights (M_w) and their molecular weight distributions (M_w/M_n) were calculated by Shimadzu Chromatopac C-R2AX.

The zeta potential of latex particles was measured by a microelectrophoresis apparatus at 25°C of Laser Zee TM Model 500 (PEN-KEM Inc.) The electrophoretic mobility values were converted into zeta potentials following by the Wiersema et al.[18] All of the suspended solutions for measuring the electrophoresis were prepared in 10^{-3} mol dm^{-3} potassium chloride to keep
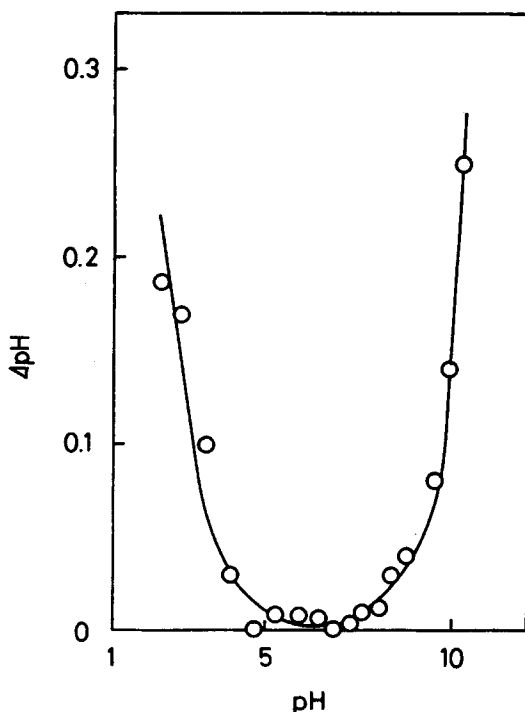
Fig. 2.   Isoelectric region of DMLL aqueous solution at 25°C.

the ionic strength as constant as possible. The pH of the solutions was adjusted by addition of potassium hydroxide or hydrochloric acid.

RESULTS AND DISCUSSION

Characterization of DMLL

DMLL as an amphoteric emulsifier has both acidic and basic groups in the same molecule, and its ionic forms change on the pH value of its aqueous solution. These three forms are shown in Figure 1.

The results for the measurement of isoelectric region of DMLL is shown in Figure 2. This figure indicates that DMLL aqueous solution has a wide isoelectric region ranging from pH 4.0 to 9.0. The cationic structure (a) is predominantly formed in acidic solutions below pH 4.0, the zwitterionic one (b) is in the range of pH 4.0–9.0, and the anionic one (c) is mainly in basic solutions above pH 9.0.

Emulsion Polymerization

In studying an emulsion polymerization, it is necessary to confirm the stabilities of formed latex because the occurrence of coagulum causes the degradation of polymerization rate and the properties of formed latex. In order to evaluate the stabilities of the latex particles, percent coagulum, which is the ratio of coagulum to total residue in definite volume of each emulsion polymerization reaction time, was used. In this emulsion polymerization of
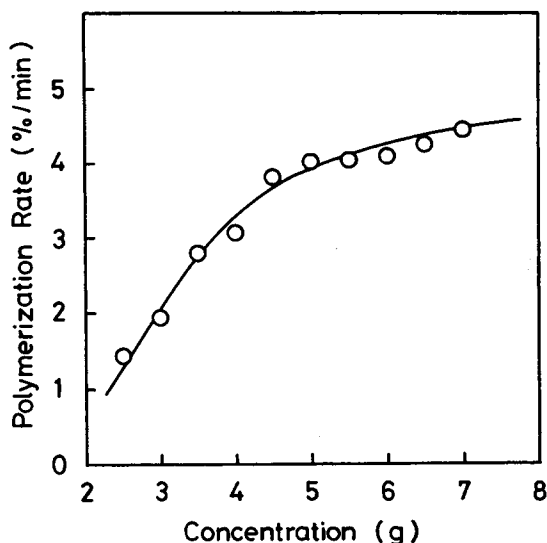
Fig. 3. The change of polymerization rate with the concentration of DMLL.

styrene in the presence of DMLL, only a few visible coagula were observed, and the coagulation ratios were below 1% in every time. Therefore, it is confirmed that the formed latex particles using DMLL are quite stable through the polymerization at pH 7.0.

In this experiment, emulsion polymerization containing the constant concentration of initiator, but various concentrations of emulsifiers was done in order to examine an effect of the emulsifier (DMLL). Each polymerization rate (% min^{-1}) with various DMLL concentrations was calculated from the initial slope on the time–conversion curve in the emulsion polymerization. Figure 3 shows the change in the polymerization rate with the concentration of DMLL. This figure describes an exponential increase in the polymerization rate with the concentration of DMLL. In fact, the relationship between the polymerization rate (R_p) and the concentration of DMLL [DMLL] was expressed as follows:

$$R_p \propto [\text{DMLL}]^{0.78}$$

The number of latex particles per cubic meter of aqueous phase (N) was calculated from the conversion and the number-average diameter at various DMLL concentrations. Figure 4 shows the relationship between the number of latex particles (N) and the DMLL concentration. It can be seen from this figure that N increases approximately in proportion to the 0.6 power of DMLL concentration, and N can be mathematically expressed as follows;

$$N \propto [\text{DMLL}]^{0.64}$$

The mechanisms of particle formation in emulsion polymerization have been investigated by many workers.[1-8] According to the micellar nucleation theory of Smith and Ewart,[1] the number of latex particles (N) and the
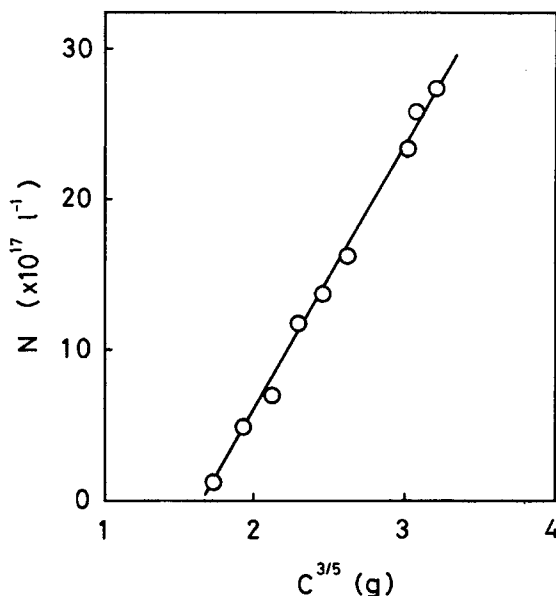
Fig. 4.   Number of latex particles (N) vs. DMLL concentration of 3/5 power.

polymerization rate (R_p) can be expressed as follows, when a homogeneous nucleation occurs in the emulsion polymerization of a water-insoluble monomer such as a styrene:

$$N \propto [I]^{2/5}[S]^{3/5}$$

$$R_p \propto (N/2)[M]$$

where [I] is the initiator concentration, [S] the emulsifier concentration, and [M] the monomer concentration. These expressions have been proven to be valid only for the emulsion polymerization using water-insoluble monomer in an anionic emulsifier aqueous solution above its CMC.

In this study, the change of the number of latex particles with DMLL concentration is in agreement with the Smith–Ewart theory, whereas R_p is proportional to the 0.78 power of DMLL concentration. The deviation observed between the theoretical and practical values in emulsifier concentration dependence seems to be attributed to the change of the monomer concentration [M] in growing particles through the reaction. Therefore, from these results, it is confirmed that the emulsion polymerization of styrene in the presence of DMLL as an amphoteric emulsifier at pH 7.0 is in good agreement with Smith–Ewart theory, indicating an ideal emulsion polymerization process.

The particle sizes and size distributions measured in two methods are shown in Table II. One is number-average particle diameter (D_n) and its polydispersity (D_w/D_n) by TEM, and the other is the z-average particle diameter (D_z) and its polydispersity index (Pusey's Q factor), giving an indication of the breadth of the size distribution by the light scattering.[19, 20]

TABLE II
Change of Particle Size and Size Distribution with Concentration of DMLL

DMLL concentration (g)	Electron micrography method		Light scattering method	
	D_n (nm)	D_w/D_n	D_z (nm)	Qf
7.0	46.6	1.07	56.0	0.07
6.5	47.1	1.07	56.7	0.05
6.0	48.4	1.07	59.9	0.05
5.5	54.7	1.07	62.5	0.11
5.0	54.8	1.06	84.7	0.23
4.5	56.7	1.05	92.3	0.22
4.0	61.3	1.05	170.8	0.39
3.5	65.5	1.06	178.7	0.38
3.0	70.5	1.05	213.6	0.39
2.5	89.5	1.21	217.1	0.30

There are many methods for measuring the particle size, and it is known that each average diameter provides a different value in size because of the difference of the measuring method.[21] In this work, D_z determined by the light scattering was larger than D_n by TEM. This is because the light scattering measurement would be capable of detecting the coalescing in the suspended state.

Since the particle sizes of latex formed with DMLL have relatively narrow distributions in both polydispersities as shown in Table II, these latexes seem to be rather monodispersed microspheres. The particle sizes shown in Table II become smaller with increasing the concentration of DMLL. This can be owing to the increase of the particle concentration with increasing the DMLL concentration and to the decrease of the monomer per particle. In other words, the period which polymer particles and emulsion droplets coexist becomes longer as the polymerization is slower, since the polymerization of water-insoluble monomer is carried out in the monomer-solubilized micelles. As a result, the latex particle size continuously increases up to the depletion of monomer droplets.

The molecular weight of polystyrene latex was measured by GPC after being dissolved into tetrahydrofuran. In this case, the same samples were used for the particle size measurements. The weight-average molecular weights (M_w) and the molecular weight distributions (M_w/M_n) of several polystyrene latexes are shown in Table III. Table III indicates that the weight-average molecular weights increase with the DMLL concentration.

TABLE III
Change of Weight Average Molecular Weight (M_w) and
Molecular Weight Distribution (M_w/M_n) with Concentration of DMLL

DMLL (g)	M_w (10^6)	M_w/M_n
7.0	2.02	5.80
6.0	1.94	5.25
5.0	1.79	5.79
4.0	1.75	5.16
3.0	1.56	5.71
2.5	1.43	9.03

It is known that the molecular weight of polymer obtained from emulsion polymerization are closely related to the particle concentrations and the polymerization rates. Stockmayer and Vanderhoff have suggested that there is an ideal relationship between the degree of polymerization and the rate of polymerization:[22,23] If an ideal state is constantly maintained through the emulsion polymerization process, the degree of polymerization is proportional to the polymerization rate.

In this work, it is found that the increase of molecular weights of polystyrene in latex particles formed in the emulsion polymerization is attributed to the increase of the number of latex particles and the polymerization rate with the DMLL concentration. In practice, however, since various factors (the volume of particles, the average number of free radicals in the growing particles) change throughout the reaction, the relationship between the molecular weight of latex polymer and the polymerization rate deviates from an ideal state.

Further, it was found from M_w/M_n in Table III that the breadth of molecular weight distributions of polystyrene in latex prepared with DMLL was rather broadened compared with those with a normal emulsifier in emulsion polymerization. These results seem to demonstrate that the compositions of emulsions and micelles in DMLL emulsifier solutions have a much wider distributions, and it is considered that a chain transfer polymerization occurred.

Zeta Potential of Synthesized Latex

The zeta potentials (Z_p) of the latex particles formed with various DMLL concentrations are shown in Figure 5 as a function of the pH. All the curves have an extended S shape, and the Z_p are largely dependent on the pH. In fact, at the point of about pH 4, each latex particle has no charge, indicating an isoelectric point (IEP). In an acidic solution below pH 4, the latexes have positive charges, which decrease with the increase of the pH. On the other hand, in the solution above pH 4, the latexes have negative charges, which increase with increasing the pH. Although the negative charge in Z_p of each latex particle becomes small with increasing the DMLL concentration, there is little difference in the shape of all the curves. These variations in Z_p of latex particles with the change of pH in their solutions are considered to be attributed to DMLL molecules adsorbed onto the surface of latex particles. Since the DMLL molecules can exist in different forms depending on pH value, the surface property of a latex particle, which is dominated by the nature of DMLL molecules adsorbed onto it, would also change due to the pH as similar as the change of the ionic forms of DMLL. In fact, the zeta potential of latex particle had a break point about pH 9. This pH is in good agreement with the one which the structure of DMLL changes from zwitterionic to anionic form.

The zeta potentials of latex particles formed with DMLL were compared with those of latex particles formed with sodium dodecyl sulfate (SDS) as an anionic emulsifier and polyoxyethylene hexadecyl ether (BC-10) as a nonionic one, which has examined in our previous paper.[15] The Z_p of latex formed with BC-10 had a small negative charge in the entire pH range, which was due to
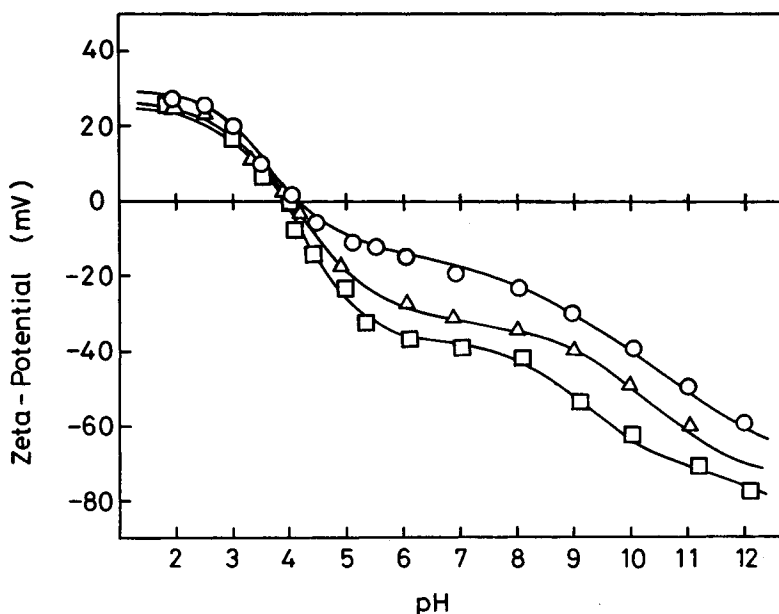
Fig. 5. Zeta-potential of latex particles formed with various concentrations (g) of DMLL [(○) 7; (△) 4; (□) 3] as a function of pH at a constant ionic strength (KCl 1.0 mmol dm^{-3}): (○) 7 g; (△) 4 g; (□) 3 g.

the end group ($-OSO_3^-$) of polystyrene latex resulting from the decomposition of the initiator. On the other hand, latex particles formed with SDS exhibited a large negative charge in Z_p all over the pH, which was due to the end group ($-OSO_3^-$) of SDS adsorbed onto the surface of the latex. Thus, the latex particles synthesized using SDS and BC-20 were independent on the pH of their suspended solutions. Accordingly, it is found that the surface properties of the latex particles formed with the amphoteric emulsifiers such as the DMLL are considerably dependent on pH, compared with the latexes formed with anionic emulsifiers or with nonionic ones.

Next, the removal of the unbound substances from the surface of latex particles was carried out by dialyzing with seamless cellulose tubing against distilled water. Their substances involve residual initiator, decomposition products, solute electrolyte, and, especially, free emulsifier. The dialysates were changed every day. The zeta potentials of the latex particles before and after the dialysis are shown in Figure 6 as a function of pH. The surface tension of water is 70.0 dyn. The zeta potential of the dialyzed latex changed day by day, compared with that of the latex before the dialysis. The negative charge in zeta potential of the latex decreased above pH 4, and IEP of the zeta potential shifted from pH 4.0 to 4.5 after the dialysis. This result can be explained from the removal of unbound DMLL molecules which are loosely adsorbed on the particle surface or dissolved in the aqueous phase. But, the zeta potential of the latex particles hardly changed after 7 days of the dialysis. These results support that the DMLL molecules still rather adsorb onto the surface of the latex particles, and the complete desorption of DMLL from the surface of the latex particles scarcely occurs.[24,25] The properties of the latex
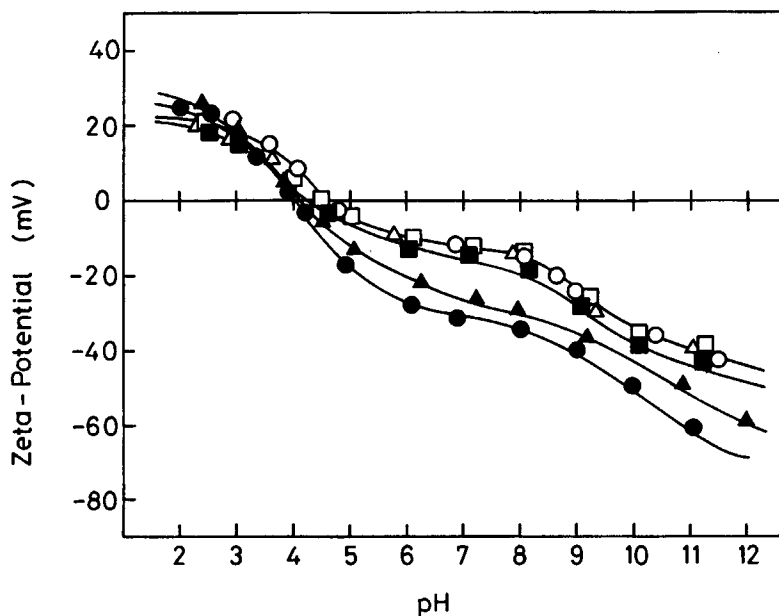
Fig. 6. Zeta-potential of the latex particles before and after the dialysis as a function of pH at a constant ionic strength KCl 1.0 mmol dm^{-3}): (●) before; (▲) 2; (■) 4; (○) 7; (□) 20; (△) 30.

particles synthesized in emulsion polymerization are found to be appreciably attributed to the nature of emulsifiers, which adsorb onto the surface of the formed latex particles. The zeta potential of the dialyzed latex is also considerably dependent on the pH of its suspended solution.

References

1. E. W. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).

2. C. P. Roe, *Ind. Eng. Chem.*, **60**, 20 (1968).

3. R. M. Fitch and C. H. Tsai, *Polymer Colloids*, R. M. Fitch, Ed., Pergamon, New York, p. 73.

4. J. Ugelstad, M. S. El-Asser, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 503 (1979).

5. F. K. Hansen and J. Ugelstad, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 3047 (1979).

6. S. S. Medvedev, I. A. Gritskova, A. V. Zuikov, L. I. Sedakova, and G. D. Berejnoi, *J. Macromol. Sci. Chem.*, **A7**, 715 (1973).

7. I. Piirma and M. Chang, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 489 (1982).

8. G. Lichti, R. G. Gilbert, and D. H. Napper, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 269 (1983).

9. A. A. Kamel, C. M. Ma, M. S. El-Asser, F. J. Micale, and J. W. Vanderhoff, *J. Disper. Sci. Technol.*, **2**, 315 (1981).

10. K. Tori and T. Nakagawa, *Kolloid Z. Z. Polym.*, **188**, 47 (1962).

11. K. W. Herrman, *J. Colloid Interface Sci.*, **22**, 352 (1966).

12. H. Hidaka, *JAOCS*, **56**, 914 (1979).

13. K. Tsujii, *Yukagaku*, **29**, 562 (1980).

14. J. L. Guillaume, *Polym. Mater. Sci. Eng.*, **52**, 309 (1985).

15. K. Kato, H. Kondo, A. Morita, E. Esumi, and K. Meguro, *Colloid Polym. Sci.*, **264**, 737 (1986).

16. L. Michaelis, *Z. Biochem.* **47**, 250 (1912).

17. S. Sakakibara, N. Kurata, and S. Komori, *Kougyo Kagaku*, **60**, 1294 (1975).

18. P. H. Wiersema, A. L. Loeb, and J. Th. G. Overbeek. *J. Colloid Interface Sci.*, **22**, 78 (1966).

19. P. N. Pusey, in *Industrial Polymer; Characterization by Molecular Weights*, Green and Dietz, Eds., Transcripta Books, London, 1973.

20. S. Provencher, *J. Chem. Phys.*, **69**, 4273 (1978).

21. S. H. Maron, C. Moore, and A. S. Powell, *J. Appl. Phys.*, **23**, 900 (1952).

22. W. H. Stockmayer, *J. Polym. Sci.*, **24**, 314 (1957).

23. R. M. E. Vanderhoff, *J. Polym. Sci.*, **33**, 487 (1958).

24. H. J. van den Hul and J. W. Vanderhoff, *Br. Polym. J.*, **2**, 121 (1970).

25. H. J. van den Hul and J. W. Vanderhoff, *J. Colloid Interface Sci.*, **28**, 336 (1968).