Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Kato, Kazufumi , Kondo, Harumi , Esumi, Kunio and Meguro, Kenjiro(1987) 'The Effect of pH on Emulsion Polymerization of Styrene in the Presence of an Amphoteric Emulsifier', Journal of Macromolecular Science, Part A, 24: 12, 1391 — 1405

To link to this Article: DOI: 10.1080/00222338708078149

URL: http://dx.doi.org/10.1080/00222338708078149

J. MACROMOL. SCI.–CHEM., A24(12), pp. 1391-1405 (1987)

THE EFFECT OF pH ON EMULSION POLYMERIZATION OF STYRENE IN THE PRESENCE OF AN AMPHOTERIC EMULSIFIER

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ABSTRACT

The emulsion polymerization of styrene in the presence of an amphoteric emulsifier of the amino acid type, *N*-lauroyl-*N*,*N*-dimethyllysine (DMLL), has been studied at various pH values. The polymerization rate and the particle number concentration increased with increasing pH of the aqueous DMLL solution and these curves changed in slope at approximately pH 4 and pH 9. The physicochemical properties of the aqueous DMLL solution, such as CMC and the aggregation number, changed with the pH and similarly changed in slope at almost the same pH as the emulsion polymerization. These pH values were in good agreement with the pH at which the ionic form of the DMLL molecule changes. The number of latex particles formed changed in proportion to the number of DMLL micelles in the solution. The particle size and the molecular weight of the synthesized latex particles were also dependent on the physicochemical solution properties accompanying the change in the ionic forms of DMLL.

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INTRODUCTION

The ionic forms of amphoteric surfactants characteristically change with the pH of their aqueous solutions, and they have been used in various fields because of their superior properties such as resistance to biodegradation, antibacterial activity, antistatic activity, and *in vivo* safety. The properties of their aqueous solutions change largely with pH as their ionic forms change.

There have been many reports about the fundamental properties of their aqueous solutions as a function of pH, e.g., micellization, surface tension, critical micelle concentration (CMC), aggregation number, and Krafft point [1-8]. However, there are only few reports concerning emulsion polymerization using amphoteric surfactants as emulsifiers [9]. We recently reported the emulsion polymerization of styrene with various concentrations of an amino-acid type amphoteric emulsifier at a pH of about 7.0. It was confirmed that the surface charge of the synthesized latex particles depends considerably on the pH of their suspensions owing to the changes of the properties of the amphoteric emulsifier with the pH [10].

Since emulsion polymerization occurs in the micelles of the emulsifier solution, it is of substantial interest to correlate the pH-dependent properties of the aqueous amphoteric emulsifier solutions with the emulsion polymerization process and the latex particles synthesized.

In this work, emulsion polymerization of styrene was carried out at changing pH in the presence of an amphoteric emulsifier of the amino-acid type, *N*-lauroyl-*N*,*N*-dimethyllysine (DMLL), and the stability, the polymerization rate, the particle size, and the molecular weight of the synthesized polystyrene latex were measured. The physicochemical properties of DMLL aqueous solution, such as surface tension, CMC, mean aggregation number of the micelles, micelle concentration, and the solubilized amount of monomer were also measured. The effects of the physicochemical properties of aqueous DMLL solution on the polymerization process and on the characteristics of the latex particles formed are discussed.

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 a 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 absence of a minimum in its surface tension vs the concentration curve [19].

Styrene monomer (Wako Pure Industries) was distilled under dried nitrogen and stored in a refrigerator under nitrogen before use. Potassium peroxodisulfate ($K_2S_2O_8$), used as initiator (Wako Pure Industries) and potassium chloride (KCl), used to keep the ionic strength constant (Kokusan Chemical Works), were of analytical grade. Water used in all experiments was purified by passing through a Milli-Q water purification system.

Determination of Isoelectric Region of DMLL

To estimate the isoelectric region of DMLL, Michaelis' method was adopted [11]. At first, pairs of buffer solutions with different known pH values were prepared. Into one of each pair of buffer solutions, 10 cm^3 of DMLL (10 mmol/L) dissolved in an ethanol-water mixture (50:50) was poured, while 10 cm^3 of ethanol-water solution (50:50) was added to the other solution. The pH of each solution was measured with a pH meter (Model COM-8, Denki Kagaku Keiki Co.) at 25.0°C under nitrogen. The pH of the former solution was disignated as pH_s, and the pH of the latter was as pH_i. The absolute value of the difference between pH_s and pH_i was expressed as

$$\Delta pH = | pH_s - pH_i |. \tag{1}$$

This ΔpH is plotted as a function of pH_i in Fig. 1. The pH_i region where the pH was between 0.01 and 0 was regarded as the isoelectric one. In the measurement of pH, acetic acid-sodium acetate buffer solutions with pH 2.0-5.2, phosphate buffer solutions with pH 5.2-8.6, and glycine-sodium hydroxide solutions with pH 8.6-12.0 were used.

Emulsion Polymerization

Each emulsion polymerization was performed by using a batch process in a 1-L glass reactor, fitted with a metal screw, a thermometer, and facilities for charging and sampling. The polymerization recipe is shown in Table 1. First, water, potassium chloride, and emulsifier were added to the reactor at room temperature. Then the pH of the mixture was adjusted and further styrene monomer was added. The reactor was immersed in a constant temperature bath adjusted to 60 ± 1°C, and the mixture was stirred at 250 rpm

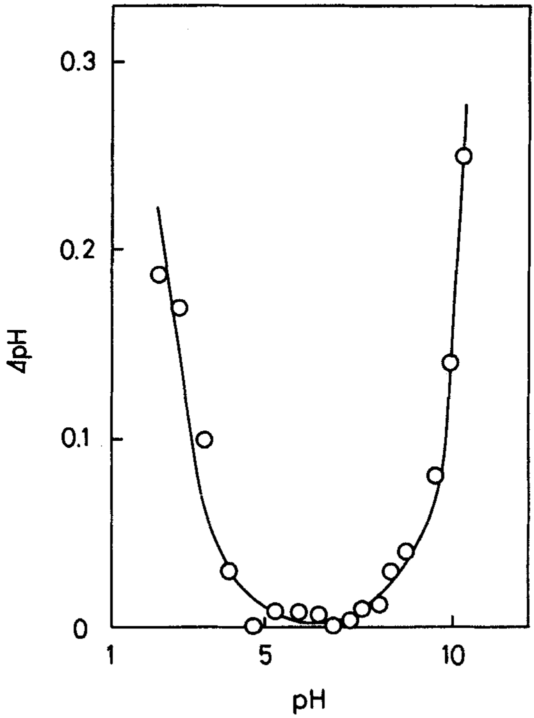


FIG. 1. Isoelectric region of aqueous DMLL solution at 25°C.

TABLE 1. Emulsion Polymerization Recipe

Ingredients	g
Styrene	50
Water	250
Potassium chloride	0.0186
Potassium peroxodisulfate	0.25
N^{ϵ}-Lauroyl-N^{α},N^{α}-dimethyllysine (DMLL)	3.5

under nitrogen. After the temperature had reached 60°C, aqueous potassium peroxodisulfate (0.25 g/50 cm^3) was added to the polymerization.

The samples for determination of the conversion, the particle size, and the molecular weight were withdrawn with pipettes at fixed intervals. The procedure for the determination was as follows: 5 cm^3 of the samples were poured into 5 cm^3 of a methanol solution of *p*-benzoquinone (0.015 g/L) to terminate the polymerization. Then the unreacted styrene monomer, methanol, and water were evaporated at 70°C. The conversions of styrene to polystyrene were estimated from the weight of dried samples on the assumption that the ratio (monomer + polymer)/water was constant throughout the reaction.

Measurements

In order to determine the particle sizes and the molecular weight distribution of the latex particles after 90 min of reaction time, the samples were cooled rapidly in 0°C water. The particle sizes (number-average diameter, D_n) and their distributions were determined by transmission electron microscopy (TEM). The molecular weights and MW distributions of the polystyrene samples dissolved in tetrahydrofuran were measured with a gel permeation chromatograph (GPC) connected to a packed column (Showa Denko K.K. A-80M). The weight-average molecular weights ($\bar{M}_w$) were calculated by means of a Shimadzu Chromatopac C-R2AX.

The surface tension and CMC of aqueous DMLL solutions at various pH values were measured by Wilhelmy's vertical-plate method with a Shimadzu tensometer ST-1 at 25.0°C under nitrogen. The surface tension vs the concentration curve was plotted, and the CMC value was determined from the break point. To obtain the mean aggregation number (N_{ag}) of aqueous DMLL micellar solutions, the luminescence quenching method proposed by Turro and Yekta was adopted [12]. In this experimental system, pyrene was used as luminescent donor and dodecyl pyridinium chloride as luminescence quencher (Q). The aggregation numbers were evaluated by measuring (I°/I) as a function of quencher concentration [Q] at a fixed DMLL concentration [DMLL] as in the following expression:

$$\ln\left(\frac{I^\circ}{I}\right) = \frac{N_{ag}[\mathrm{Q}]}{[\mathrm{DMLL}] - \mathrm{CMC}}, \tag{2}$$

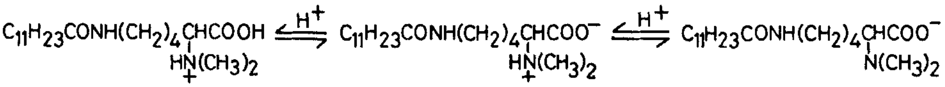
where (I°/I) is the measured ratio of luminescence intensity in the presence of Q to that in the absence of Q. The fluorescence spectra were recorded on a Hitachi 650-10S fluorescence spectrophotometer, exciting at 335 nm, and the fluorescence intensities were measured at a band maximum of 385 nm.

The solubilized amounts of ethylbenzene as a substitute for styrene in the aqueous DMLL solution were determined by measuring the absorbance of ethylbenzene with a Hitachi 220A spectrophotometer at a wavelength of 262.6 nm at 25.0°C. All the aqueous solutions for measurement were prepared by adding enough aqueous potassium chloride (10^{-3} mol/L) to keep the ionic strength as constant as possible. The pH of the solutions was adjusted by the addition of potassium hydroxide or hydrochloric acid.

RESULTS AND DISCUSSION

Characterization of DMLL

DMLL as an amphoteric emulsifier of the amino-acid type has both acidic and basic groups in the same molecule, and its ionic form in aqueous solution depends on the pH. These forms are indicated in Eq. (3):



$$C_{11}H_{23}CONH(CH_2)_4\underset{H\underset{+}{N}(CH_3)_2}{C}HCOOH \xrightleftharpoons{H^+} C_{11}H_{23}CONH(CH_2)_4\underset{H\underset{+}{N}(CH_3)_2}{C}HCOO^- \xrightleftharpoons{H^+} C_{11}H_{23}CONH(CH_2)_4\underset{N(CH_3)_2}{C}HCOO^-$$

a) Cationic form b) Zwitterionic form c) Anionic form

(3)

Figure 1 indicates that aqueous DMLL solution has a wide isoelectric, ranging from pH 4 to 9. The cationic structure, a) in Eq. (3), is predominant in acidic solutions below pH 4, the zwitterionic one, b) in Eq. (3), exists from pH 4 to 9, whereas the anionic one, c) in Eq. (3), exists mainly in basic solutions with pH > 9.

Polymerization Rate and Particle Number Concentration

The polymerization rate (in %/min) at various pH values of aqueous DMLL solution was determined from the initial slope of the time-conversion curve of the emulsion polymerization. Figure 2 shows how the polymerization rate increased with the pH and that the slope changed at about both pH 4 and 9.

Figure 3 shows that the particle number concentration calculated from the conversion and (D_n) also increases with the pH and that this curve is flat in the region from about pH 4 to 7. The change in the particle number concentration is very similar to that in the polymerization rate.

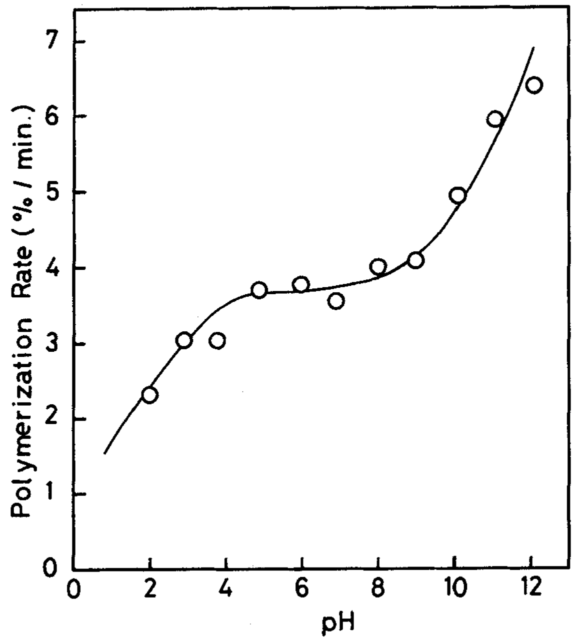


FIG. 2. Change of polymerization rate with pH of aqueous DMLL solution.

The mechanisms of particle formation in emulsion polymerization have been investigated by many workers [13-16]. According to the Smith-Ewart micellar nucleation theory [13], the polymerization rate (R_p) as a function of the number of latex particles (N) formed can be expressed as

$$R_p \propto (N/2)[M], \tag{4}$$

where [M] is the monomer concentration in the growing particles, i.e., the polymerization rate increases in proportion to the number of latex particles. In this work it was confirmed that the polymerization rate is mainly determined by the number concentration of latex particles in our emulsion polymerization system. Furthermore, the curves shown in Figs. 2 and 3 have two break points, at about pH 4 and at about pH 8. This is attributed to the change of the ionic forms of DMLL with pH. Both R_p and N increase gradually for the cationic structure of DMLL and much faster for the anionic one, whereas they hardly change for the zwitterionic region.

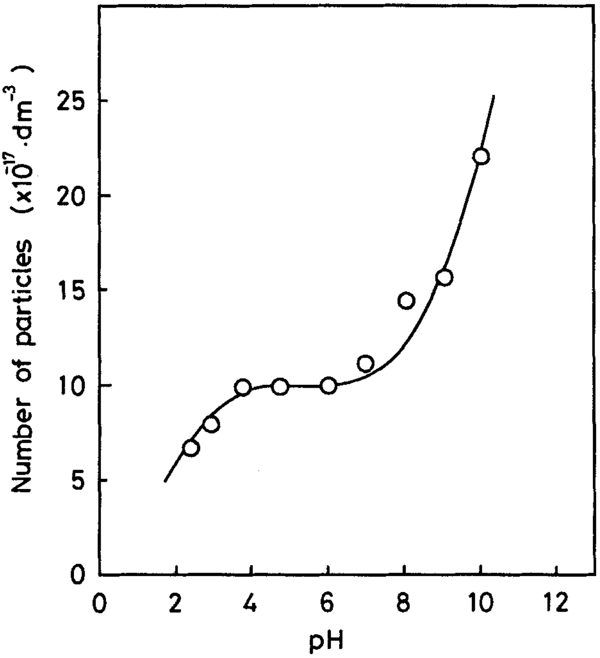


FIG. 3. Change of number of synthesized latex particles with pH of aqueous DMLL solution.

Properties of Aqueous DMLL Solutions

Figure 4 shows that the CMC of DMLL solutions increases with increasing pH, and this curve also exhibits two break points at pH 4 and pH 9.

The mean aggregation number of the micelles (N_{ag}) was determined by the luminescence quenching method. Figure 5 shows that N_{ag} decreases with increasing pH. The change of N_{ag} in acidic solutions below pH 4 is rather small, whereas in basic solutions it is larger. There are many reports concerning with the micelle aggregation numbers and the micelle molecular weights of various amphoteric surfactants determined by light-scattering methods [5, 6] or fluorescence intensity measurements [7, 8]. Micelle aggregation numbers are dependent on the molecular structures, such as hydrophilic groups and alkyl chain lengths, and especially the charge density at the surface of the micelles. Since the ionic forms of DMLL molecules change with pH, the aggregation

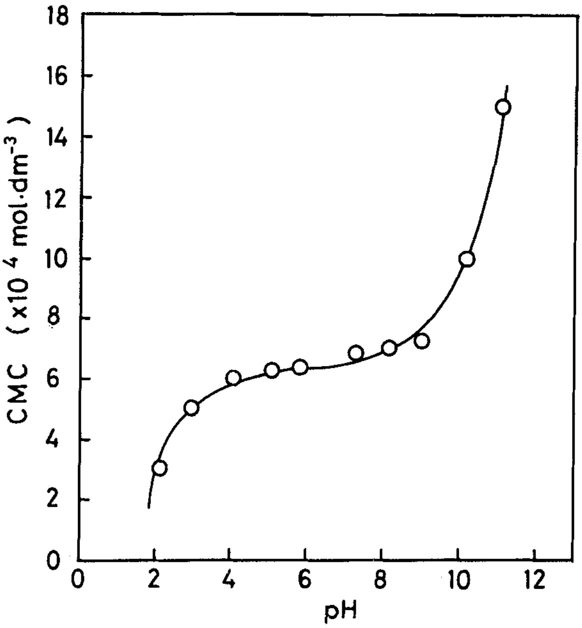


FIG. 4. Change of CMC of aqueous DMLL solution with pH.

number of its micelles changes similarly. This cannot be interpreted fully, but it is considered that the aggregation number would be affected by electric repulsion of DMLL molecules and by the effect of destruction of "icebergs" for DMLL with its carboxylic or amino group [2].

The number of DMLL micelles per unit volume ($N_{micelle}$) was calculated from

$$N_{micelle} = N_0 \frac{[\text{DMLL}] - \text{CMC}}{N_{ag}}. \tag{5}$$

As Fig. 6 shows, the micelle concentration is almost constant in the pH region from 4 to 7, which is in good agreement with the isoelectric region of DMLL where the DMLL molecules are present as zwitterion. $N_{micelle}$ increases gradually in acidic solutions below pH 4, where DMLL has a cationic structure, and it increases remarkably in basic solutions above pH 9 where DMLL is anionic.

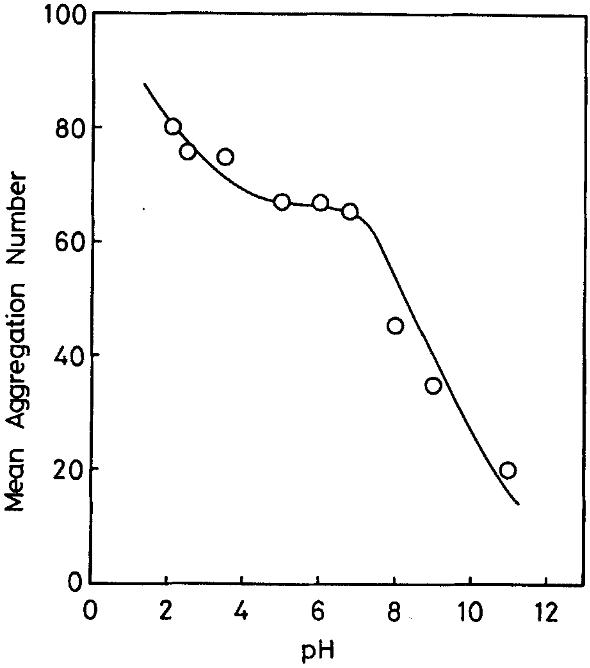


FIG. 5. Mean aggregation number of micelles in aqueous DMLL solution as a function of pH.

The Relationship between the Emulsion Polymerization Process and the Properties of Aqueous DMLL Solutions

The tendencies in the change of the properties of aqueous DMLL solutions are in good agreement with those in the change of the polymerization rate and the particle number concentration. All the curves have two break points at about pH 4 and 9, with constant values between these points. Since the ionic form of the DMLL molecule changes from cationic to zwitterionic at about pH 4 and from zwitterionic to anionic at about pH 9, the changes in the emulsion polymerization process and the various properties of aqueous DMLL solution are considered to be influenced by the change of the ionic form of DMLL with pH because the emulsion polymerization of a water-insoluble monomer, such as a styrene, proceeds in the micelles.

Further, the changes of the micelle concentration ($N_{micelle}$), the particle

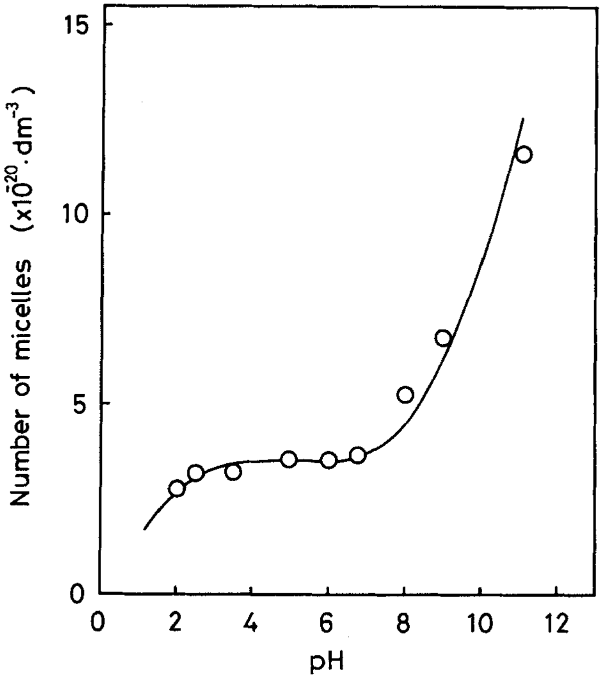


FIG. 6. Micelle concentration in aqueous DMLL solution as a function of pH.

number concentration (N), and the polymerization rate (R_p) considerably semble each other. It is confirmed from Figs. 3 and 6 that the number concentration of the latex particles (N) can be directly affected by the micelle concentration ($N_{micelle}$).

The amount of ethylbenzene solubilized in the DMLL micellar solution as a function of pH (Fig. 7) is different from the other ones described above. Thus, the amount of monomer solubilized would not have much influence on the emulsion polymerization processes. Accordingly, it is suggested that the polymerization rate and the number of latex particles formed are largely dominated by the number of emulsifier micelles, not by the amount of monomer solubilized.

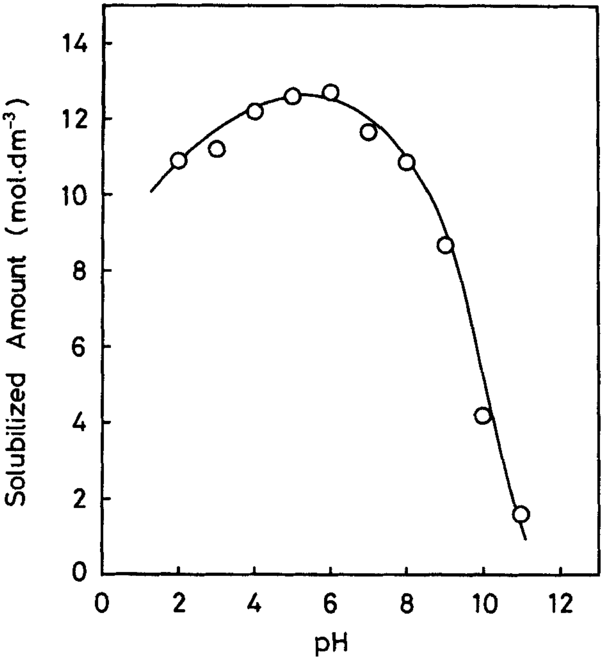


FIG. 7. Change of amount of ethylbenzene solubilized in aqueous DMLL solution with pH.

Properties of the Synthesized Latex Particles

Figure 8 shows that the latex particle size becomes smaller with increasing pH and is almost constant in the range of pH 4-8, possibly owing to the increase of the particle number concentration with increasing pH. Since the polymerization of the water-insoluble monomer occurs in the growing particles containing the monomer supplied from emulsion droplets, the slower the polymerization is, the longer the period during which polymer particles and emulsion droplets coexist. As a result, the latex particle sizes continuously increase up to the depletion of droplets of monomer. The weight-average molecular weights increase with increasing pH, and the change in the pH 4-8 region is small (Fig. 9). This behavior can be explained by an increase of the polymerization rate. In the ideal case, the degree of polymerization is proportional to the polymerization rate [17, 18]. In practice, however, since

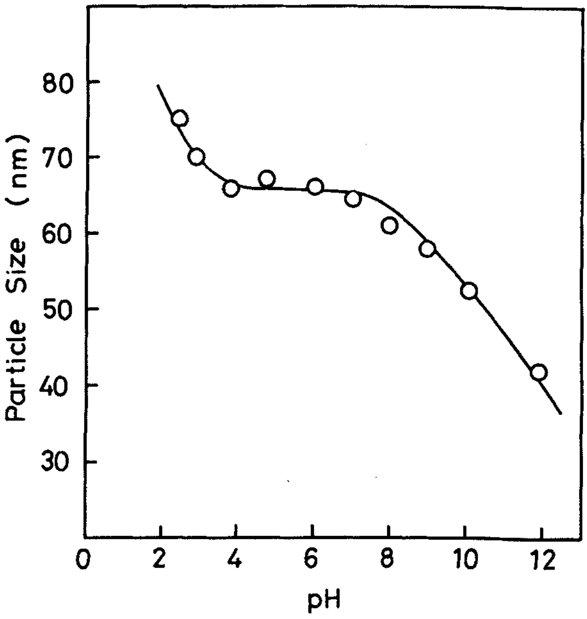


FIG. 8. Effect of pH of aqueous DMLL solution on particle sizes of synthesized latices.

several factors (e.g., the volume of latex particles, the average number of free radicals in the growing particles, and chain transfer) change throughout the reaction, the relationship between the molecular weight of the synthesized latex polymer and the polymerization rate deviates from the ideal proportionality [19].

Thus, the changes of the particle size and molecular weight of the latex particles were affected by the change of physicochemical properties of aqueous DMLL solution with pH.

CONCLUSIONS

(1) DMLL as an amino-acid amphoteric emulsifier can exist in three ionic forms, depending on the pH of their aqueous solutions.

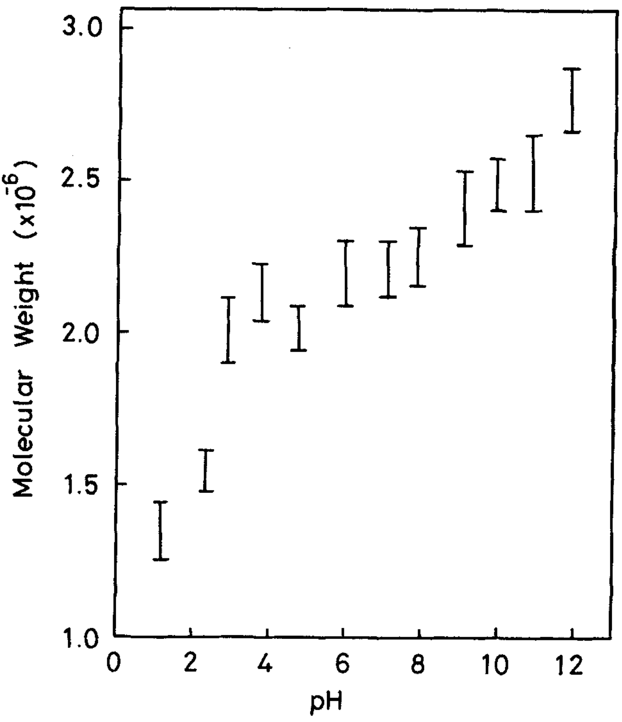


FIG. 9. Weight-average molecular weight ($\bar{M}_w$) of polystyrene latex synthesized in aqueous DMLL solution as a function of pH

(2) The properties of DMLL solution change with the pH, along with changes of the ionic form of DMLL.

(3) The emulsion polymerization processes change with the changes in the properties of aqueous DMLL solutions with pH.

(4) The number of latex particles can be directly affected by the number of the micelles of the emulsifier.

(5) The properties of the latex particles are also dependent on the properties of aqueous DMLL solutions.

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Received February 10, 1987
Revision received April 6, 1987