

Mechanism of Alkali-Thickening of Acid-Containing Emulsion Polymers. II. Examination of Latexes with the Light Microscope

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Synopsis

The mechanism of alkali thickening of acid-containing emulsion polymers has been confirmed by visual examination of the swelling and disappearance of latex particles with the light microscope. Specially prepared large particle-sized latexes were used in this study. Each latex was examined from 0%-200% neutralization with base. The particle swelling and dissolution behavior correlated with viscosity measurements, high viscosity being present for swollen particle systems and low viscosity for true solutions. The neutralized state of all acid-containing latexes can be pictured in a cube with the important variables being per cent acid, hydrophilicity of the comonomers, and T_g . At the bottom will be latexes only slightly affected by neutralization, above this will be a swollen particle zone, and the largest area will be a true solution zone. The true solution zone will be enlarged by lowering the molecular weight of the latex polymer.

INTRODUCTION

The change undergone by an acid-containing emulsion polymer upon neutralization is accounted for in terms of varying degrees of a single mechanism. This mechanism consists of swelling of the latex particles plus an accompanying solubilization of polymer molecules when the hydrophilicity of the polymer is high enough.¹

If the particles of alkali-soluble latexes were made large enough, it should be possible to visually observe the swelling and disappearance of these particles in the dispersed state with the light microscope. Latexes were prepared of some representative compositions whose average particle size was 500 m μ in diameter.

The latexes were neutralized with base to varying degrees of neutralization and the equilibrated samples were observed and photographed with the light microscope.

EXPERIMENTAL

Materials

Bromotrichloromethane (BTCM) was supplied by Eastman Chemical Products, Inc., and used as received. Sodium hydroxide, 98.5%, was

supplied by Fisher Scientific Company. All other materials were the same as described previously.¹ The monomers used in this study were methyl methacrylate (MMA), ethyl acrylate (EA), methacrylic acid (MAA), and styrene (S).

Polymerization Procedure

The emulsion polymers were prepared in a 1-liter four-necked flask equipped with a stirrer, a reflux condenser, a nitrogen inlet thermometer, and a dropping funnel. The water, 2% of the surfactants (0.02% based on total monomers), and 10% of the monomers listed in Table I were intro-

TABLE I
Polymerization Recipe

Ingredients	Weight, g
Monomers	200.0
Sodium lauryl sulfate	0.67
Triton X-200 (at 28%)	1.20
Ammonium persulfate	1.00
Distilled, deionized water	382.0

duced into the flask. The temperature was raised to 80°C and ammonium persulfate dissolved in a small amount of water retained from above was added to the flask. After polymerization was well underway, about 3 to 5 min, the remaining 90% of the monomers and 98% of the surfactants (0.48% based on total monomers) were added dropwise over a period of 1 hr at a temperature of $80 \pm 2^\circ\text{C}$. At the end of the addition, the temperature was held at 80°C for 5 min and then raised to 90°–95°C where it was maintained for several minutes. The emulsion was then cooled with a water bath to room temperature and filtered through cheesecloth. Coagulum was negligible. Conversions were nearly 100%. All latexes were prepared at 35% total solids content. All monomer ratios are given in wt-%. When BTCN was employed, it was mixed in with the monomers.

Characterization Methods

Viscosity. Standardized NaOH and NH₄OH were added to diluted samples of the latex such that the appropriate degree of neutralization was obtained at exactly 2% total polymer content. The samples were permitted to stand at room temperature for one week prior to the viscosity measurement to assure equilibrium. Most of the viscosity measurements were made with an Ubbelohde viscometer. Where the viscosity was too high, measurements were made with a Brookfield viscometer. Viscosity measurements were made at 25°C.

Microscope Observations. A small portion of the above samples was diluted to 0.25% polymer content for microscopic studies. The emulsion particles were viewed with a Zeiss research microscope using phase contrast optics. Because of Brownian motion, short exposure times were necessary

for photographing the particles, resulting in some loss of contrast. In addition, some particles were in perfect focus whereas others were out of focus. For example, on photographs of unneutralized particles, the black particles are in perfect focus and the white particles are completely out of focus, with the remaining ones in between these two extremes.

RESULTS

Large particle-sized latexes of four different compositions were prepared for this study. These were MMA/EA/MAA latexes at ratios of 80/0/20 (I), 60/20/20 (II), 40/40/20 (III), and 0/80/20 (IV). Latexes I and III were prepared with 0% (a) and 1.0% (c) BTCM as a chain-transfer agent and latexes II and IV were made with 0% (a), 0.5% (b), 1.0% (c), and 2.0% (d) BTCM.

Viscosity studies were run on each latex from II and IV. Each latex was neutralized with NaOH and NH_4OH at degrees of neutralization (used here to denote OH^-/COOH ratio times 100) of 0 to 100 in 10% increments,

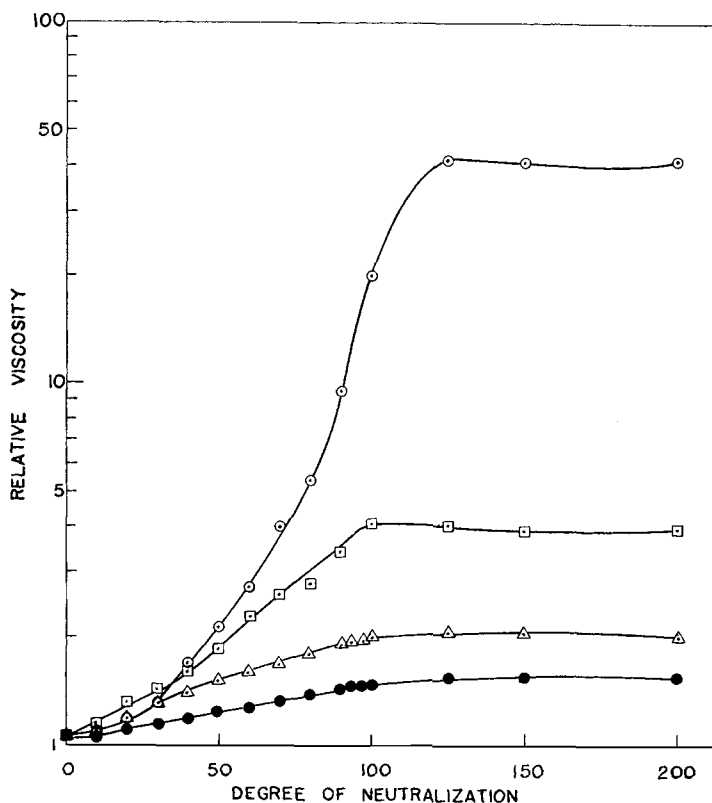


Fig. 1. Relative viscosity vs. degree of neutralization for latexes at 2% polymer solids content. Composition MMA/EA/MAA, 60/20/20: (○) 0% BTCM; (◻) 0.5% BTCM; (△) 1.0% BTCM; (●) 2.0% BTCM.

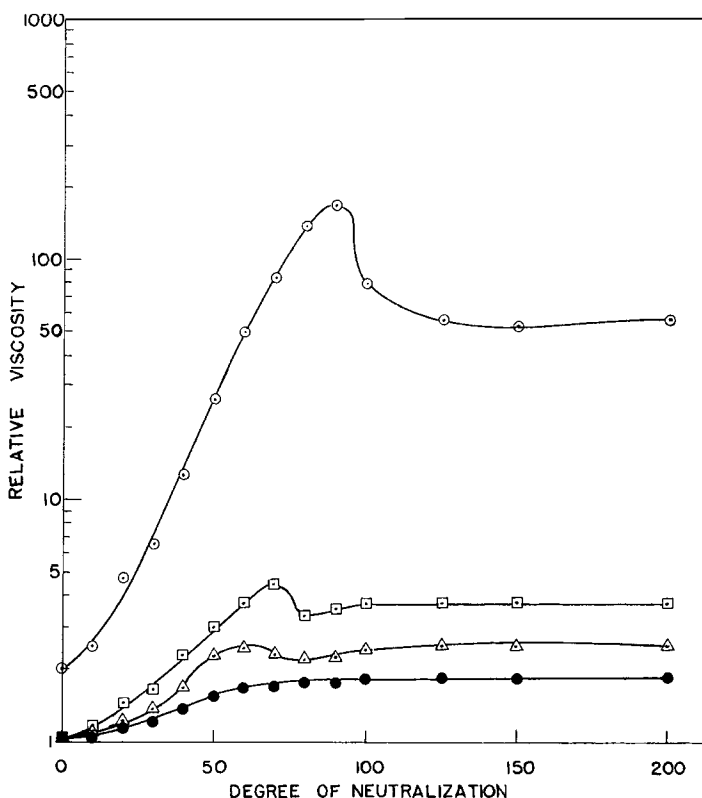


Fig. 2. Relative viscosity vs. degree of neutralization for latexes at 2% polymer solids content. Composition EA/MAA, 80/20. Curve (○) actually run as the Brookfield viscosity in cps: (○) 0% BTCM; (□) 0.5% BTCM; (△) 1.0% BTCM; (●) 2.0% BTCM.

125%, 150%, and 200%. The results for the neutralization with NH_4OH are plotted in Figures 1 and 2.

The samples were also observed and photographed with the light microscope. Selected photographs of these systems are presented in Figures 3 to 5. The type of base used for neutralization did not affect the appearance of the particles.

Viscosity and Microscopic Studies of Latex MMA/EA/MAA, 60/20/20

In Figure 1, latex IIa shows a large increase in viscosity to $\eta_{\text{rel}} = 41$ by 125% neutralization. After this, additional ammonia has no effect on the viscosity. Figure 3 shows that there is a large increase in particle diameter in going from the unneutralized latex to the completely neutralized species. The intermediate samples show a progressive increase in particle diameter. After 125% neutralization, the swollen particles remain unchanged.

Latexes IIb, IIc, and II d show relatively small increases in viscosity to η_{rel} 4.0, 2.0, and 1.55, respectively. Unlike IIa above, all three latexes

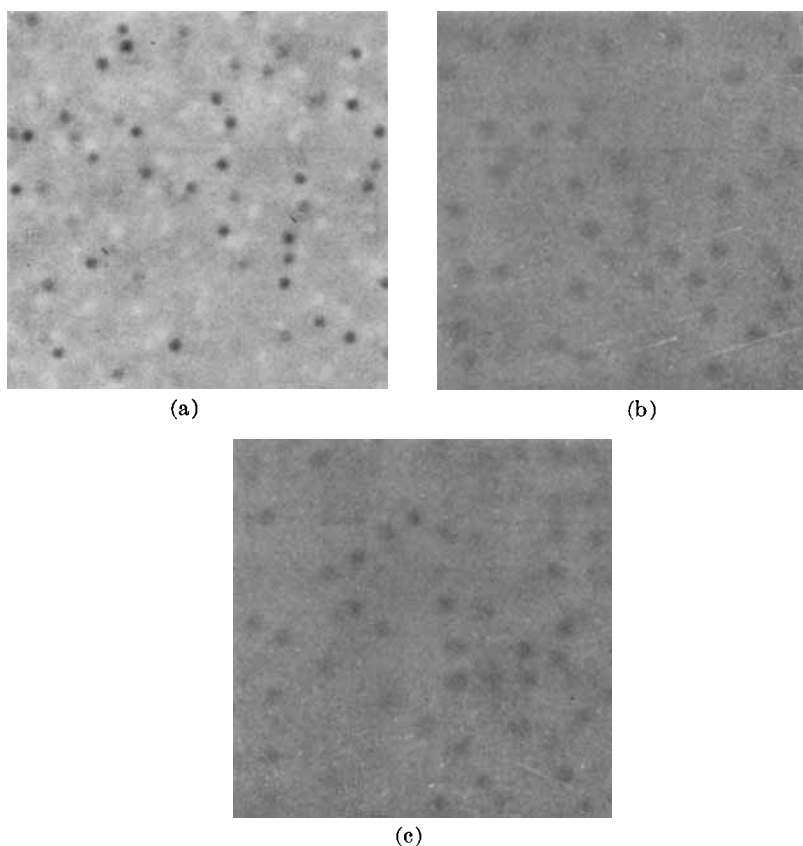


Fig. 3. Light micrographs of latex MMA/EA/MAA, 60/20/20, no chain transfer agent, at different degrees of neutralization: (a) 0%; (b) 100%; (c) 200%. 3200 \times .

exhibit a similar behavior with the particles regularly disappearing as shown for IIc in Figure 4. Interestingly, there is no particle swelling and the particles are individually entering true solution. There is a steady decrease in the total number of particles until, at 95% neutralization, all the particles have disappeared. The decreased viscosities at complete neutralization correlate with the increased amount of chain transfer agent used due to the lowered molecular weights.

Viscosity and Microscopic Studies of Latex EA/MAA, 80/20

In Figure 2, latex IVa, 0% BTCM, shows a very high increase in viscosity, reaching a peak at 90% neutralization. Thereafter, the viscosity drops and levels off to 54 centipoises at 125% neutralization. The photographs in Figure 5 show that the viscosity increase is due to the uniform increase in swelling of the latex particles. At 60% neutralization, a high degree of swelling is very evident. At 80% neutralization, the particles are so highly swollen that the slight phase contrast makes them barely percep-

tible. At 90% and 100% neutralization, the particles are gone and a true solution is being formed. The maximum swelling observed here is about a fourfold increase in particle diameter or a 64-fold increase in volume.

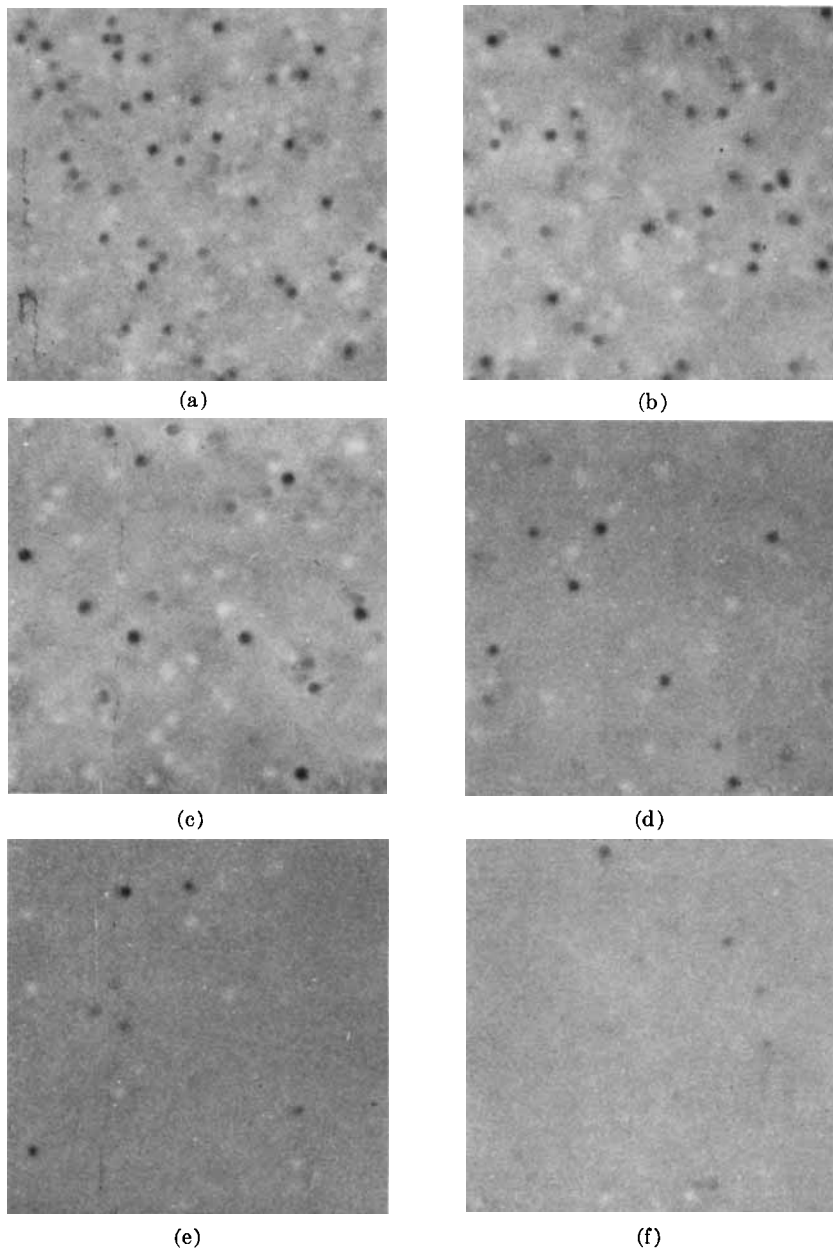


Fig. 4. Light micrographs of latexes MMA/EA/MAA, 60/20/20, 0.5, 1.0, or 2.0% BTCM, at different degrees of neutralization: (a) 0%; (b) 40%; (c) 60%; (d) 80%; (e) 90%; (f) 93%. Photograph at 95% neutralization, blank like Figure 5(f). 3200 \times .

Based on the viscosity results, it is likely that swollen particles are still present at 90% neutralization but cannot be seen because of the very low phase contrast.

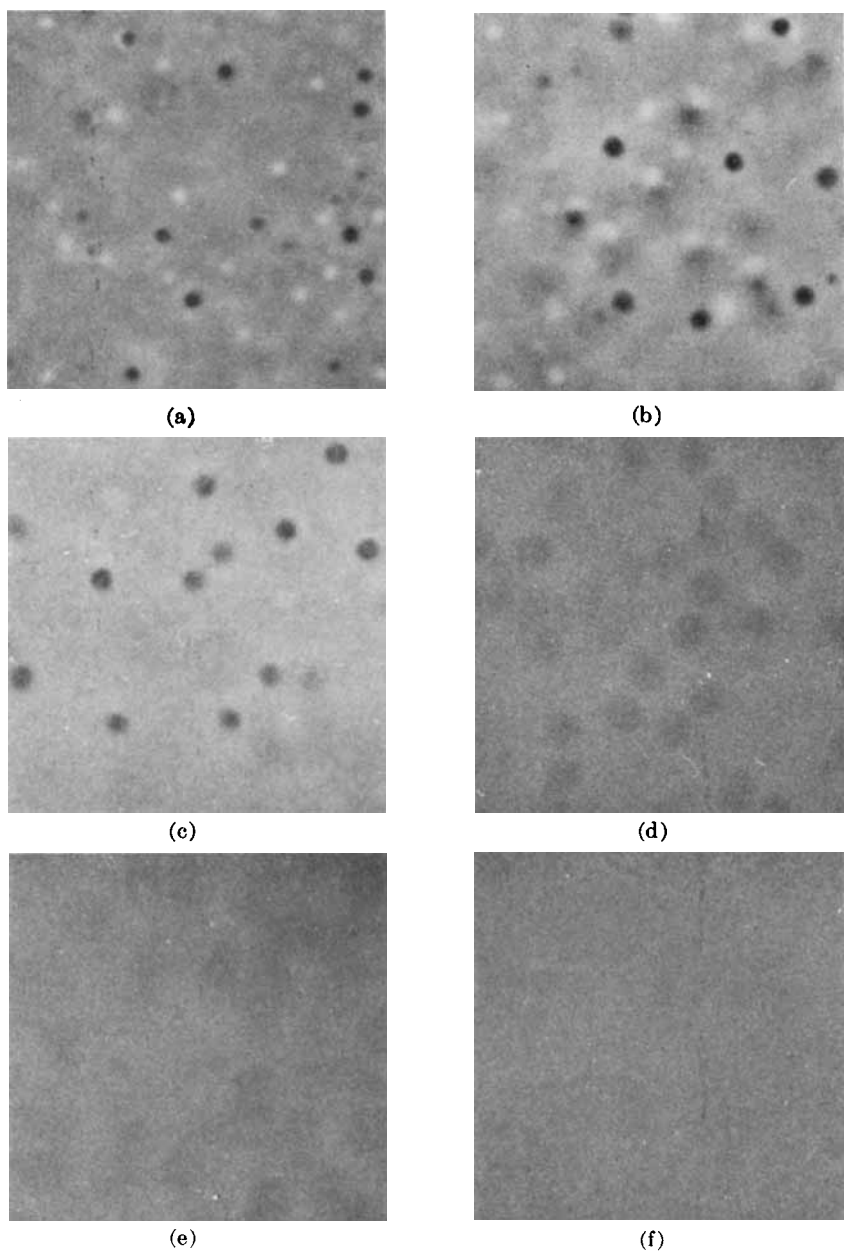


Fig. 5. Light micrographs of latex EA/MAA, 80/20, no chain transfer agent, at different degrees of neutralization: (a) 0%; (b) 20%; (c) 40%; (d) 60%; (e) 80%; (f) 100%. 3200 \times .

Latex IVb, 0.5% BTCM, shows the same type of uniform swelling as IVa. It is exactly like IVa except that the maximum swelling observable is now at 70% neutralization and the increase in particle diameter at this point is about a threefold increase or a 27-fold increase in volume. Thereafter no particles are visible.

Latex IVc, 1.0% BTCM, reaches a maximum swelling, about a twofold increase in diameter, at 60% neutralization. Thereafter no particles are visible.

Latex IVd, 2.0% BTCM, shows very little particle swelling. Instead, the particles go into solution individually as do the particles of latexes I Ib-d. At 70% neutralization, nearly all the particles are gone.

Optical Density Changes

The optical density changes which these systems undergo are shown in Figures 6 to 11. Only one of the three MMA/EA/MAA, 60/20/20 latexes

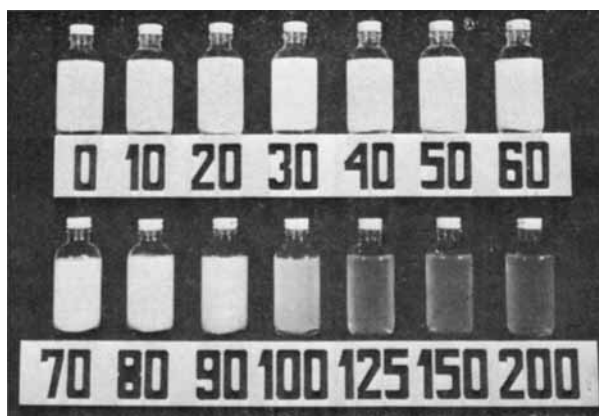


Fig. 6. Optical density changes undergone by latex MMA/EA/MAA, 60/20/20, no chain transfer agent, at stated degrees of neutralization (2.0% polymer solids).

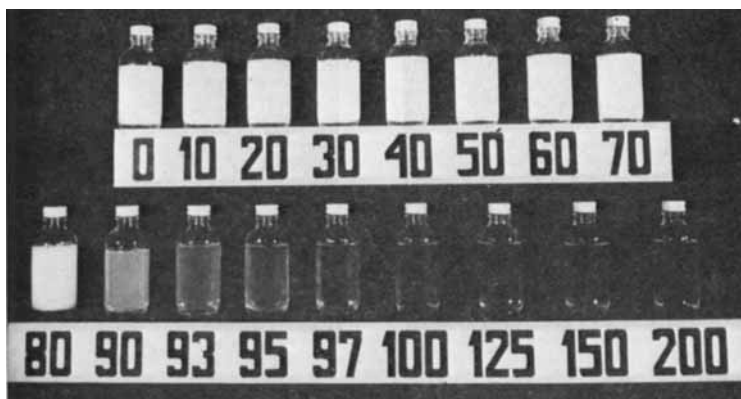


Fig. 7. Optical density changes undergone by latexes MMA/EA/MAA, 60/20/20, 0.5, 1.0, or 2.0% BTCM, at stated degrees of neutralization (2.0% polymer solids).

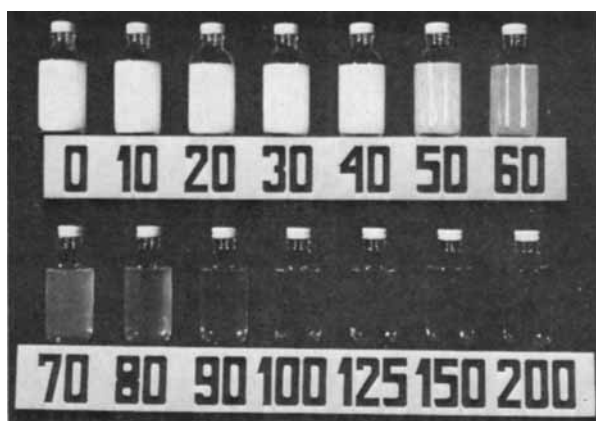


Fig. 8. Optical density changes undergone by latex EA/MAA, 80/20, no chain transfer agent, at stated degrees of neutralization (2.0% polymer solids).



Fig. 9. Optical density changes undergone by latex EA/MAA, 80/20, 0.5% BTCM, at stated degrees of neutralization (2.0% polymer solids).

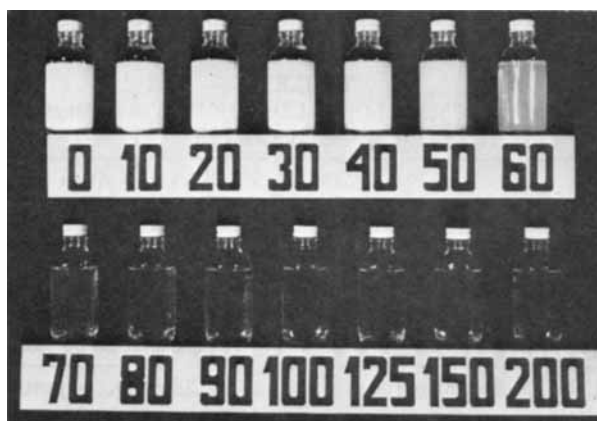


Fig. 10. Optical density changes undergone by latex EA/MAA, 80/20, 1.0% BTCM, at stated degrees of neutralization (2.0% polymer solids).

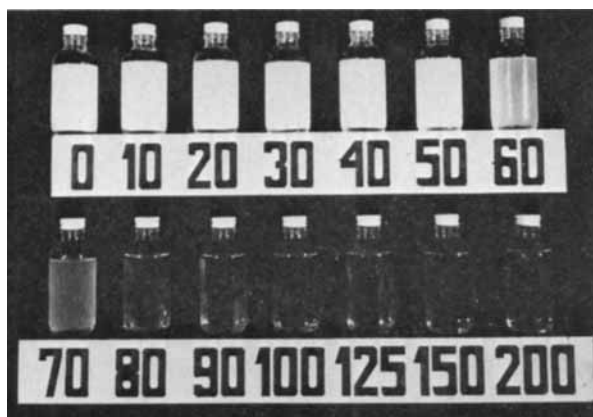


Fig. 11. Optical density changes undergone by latex EA/MAA, 80/20, 2.0% BTCM, at stated degrees of neutralization (2.0% polymer solids).

made with BTCM is shown since all three were very similar in particle disappearance and optical density behavior.

These results correlate with the disappearance of particles shown in Figures 3 to 5, complete clarity being achieved when the particles have all disappeared.

Results From Latexes MMA/MAA, 80/20 and MMA/EA/MAA, 40/40/20

Latex Ia showed swelling of particles without going into solution, identical to IIa. Latex Ic showed no swelling with a noticeable decrease in the number of particles by 90% neutralization. At 125% neutralization, about one third of the original number of particles is still present. Beyond this, however, there is no observable decrease in the number of particles visible. Hence clarity is not achieved with either latex.

Latex IIIa showed substantial uniform swelling of all particles, reaching a maximum swelling of a threefold increase in particle diameter at 100% neutralization. The particles do not disappear after this and appear un-

TABLE II
Particle Swelling and Optical Density Data as a Function
of Latex Composition

	%	MMA/EA/MAA composition			
		BTCM 80/0/20	60/20/20	40/40/20	0/80/20
D_n/D_u^a	0	1.5	2	3	4
	1	1	1	1	2
Point of clarity ^b	0	not c.	nearl. c. at 100%	nearl. c. at 90%	compl. c. at 80%
	1	not c.	compl. c. at 95%	compl. c. at 80%	compl. c. at 70%

^a D_n = particle diameter at maximum point of swelling; D_u = particle diameter of unneutralized latex.

^b Not c. = not clear; nearl. c. = nearly clear; compl. c. = completely clear, at stated degree of neutralization.

changed at 200% neutralization. Latex IIIc shows the same phenomenon as the other MMA-containing latexes made with BTCM—little or no swelling is observed. There is a decrease in the total number of particles present. At 80% neutralization, the particles are gone and clarity has been achieved.

A summary of particle swelling and optical density data is presented in Table II.

Neutralization With Sodium Hydroxide

The viscosity data for the NaOH-neutralized latexes are complicated by several factors. Latex IIa showed a peak at 100% neutralization of η_{rel} 48.0, which then dropped to 10.0 at 200% neutralization. The particles appeared unchanged, however. In fact, there was no discernible difference from the comparable NH_4OH -neutralized samples. Latex IIb showed a peak at 100% neutralization of η_{rel} 4.40 which then dropped to 2.96 at 200% neutralization. Latex IIc and IId neutralized with NaOH were quite comparable in viscosity to the ammonia-neutralized samples.

The soft latexes, EA/MAA, 80/20, apparently are hydrolyzed by NaOH after complete neutralization. All four viscosity curves are very comparable to the ammonia-neutralized samples until 100% neutralization. Thereafter the viscosity rises. The following η_{rel} values are those at 200% neutralization, with the comparable ammonia-neutralized values from Figure 2 in parentheses: latex IVa, 75 (53) (these values in centipoises); IVb, 6.60 (3.71); IVc, 3.89 (2.45); IVd, 2.62 (1.86). It is thus not possible to get data on thoroughly equilibrated NaOH-neutralized samples of this composition. Viscosity values for these NaOH-neutralized latexes which were measured shortly after their preparation were: IVa, 21.0 centipoises; IVb, 2.95; IVc, 2.39; IVd, 1.74.

Viscosity Versus Concentration Study

An additional viscosity study which is very important from the standpoint of interpretation of these data is the viscosity-versus-concentration of these systems. Data obtained at constant degree of neutralization, 100%, is summarized in Table III. These data confirm that very high viscosity results when swollen particles of neutralized acid-containing emulsion polymers are present. Further confirmation of this fact was obtained by neutralizing both of the 0% BTCM latexes (IIa and IVa) at 10% solids from 0% to 100% neutralization with NH_4OH . Viscosity readings were not obtainable with IVa at 40% through 80% neutralization ($>2 \times 10^6$ centipoises). This is the same region where very high particle swelling is observed, as seen in Figure 5. Latex IIa showed gradually increasing viscosity values with increasing neutralization, but none were gels as with IVa.

TABLE III
Viscosity Data for Several Concentrations at 100% Neutralization

Latex composition	BTCM %	NH ₄ OH-Neutralized ^a			NaOH-Neutralized ^a		
		2% NV	5% NV	10% NV	2% NV	5% NV	10% NV
MMA/EA/MAA, 60/20/20	0	19.6 ^b	320	7.4 × 10 ⁸	61.7	284	7.3 × 10 ⁴
	0.5	4.10 ^b	10.0	115	4.45 ^b	11.3	114
	1.0	2.00 ^b	6.1	16.1	2.13 ^b	6.3	18.2
EA/MAA, 80/20	2.0	1.47 ^b	4.7	7.3	1.53 ^b	4.8	7.7
	0	76.6	390	6.6 × 10 ⁸	55.1	260	5.2 × 10 ⁸
	0.5	3.72 ^b	11.5	202	3.96 ^b	12.7	144
	1.0	2.38 ^b	7.1	33	2.56 ^b	7.3	36
	2.0	1.82 ^b	5.8	13.7	1.92 ^b	5.9	14.0

^a NV = Nonvolatile-polymer solids content; values in columns, η in centipoises.

^b η_{rel} .

DISCUSSION

The light microscope observations of the changes undergone by acid-containing latexes upon neutralization with alkali is in complete agreement with the mechanism developed on the basis of viscosity measurements.¹ At weight equivalents of MAA, a hard latex will have less tendency to go into solution than a soft latex. The degree of particle swelling will also be much less for the former latex than for the latter.

Although the type of alkali used to neutralize the latex did not have any observable effect on the equilibrium swelling and dissolution behavior of the latex particles, viscosity differences were apparent as already noted. The most likely explanation for this is that an ionic effect is lowering the viscosity after 100% neutralization when NaOH is used.

The viscosity results of latexes II show the effect of swollen particles versus solution at full neutralization as determined by the absence or presence of a chain transfer agent, respectively. When no BTCM is present, as in IIa, the molecular weight is high and there is insufficient mobility and energy in the polymer chain to free itself from the particle and go into solution. We thus end up with a microgel and a very high viscosity.

If these swollen particles were rigid spheres, the viscosity increase should be slight. If they had tentacles sticking out from a central core, very high viscosity could result if the tentacles from different particles were to stick together.

Higher resolution, obtainable with the electron microscope, was employed to confirm this possibility. Accordingly, the NaOH-neutralized latex (100% neutralization) was dried, replicated, and observed with the electron microscope. This photograph is shown in Figure 12. Very clearly numerous tentacles project from the central core of the neutralized particle. These polymer chains, anchored in the core, result in the association, or sticking together, of particles which in turn result in high viscosity. For

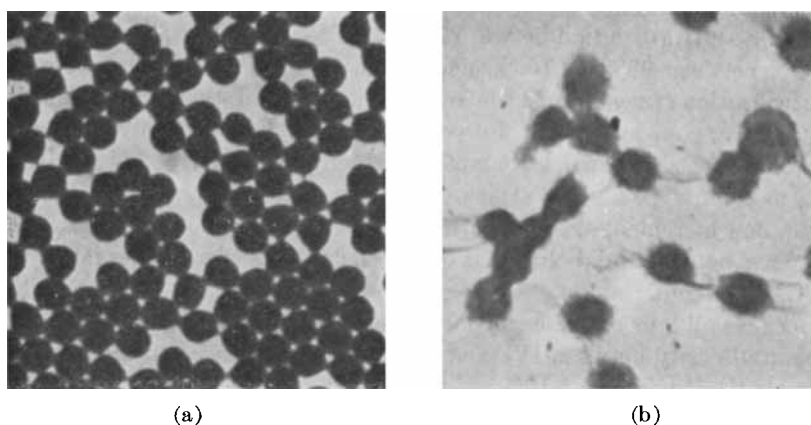


Fig. 12. Electron micrographs of latex particles of MMA/EA/MAA, 60/20/20, no chain transfer agent, at different degrees of neutralization: (a) 0%; (b) 100%. 12,500 \times .

comparison, the electron micrographs of the unneutralized particles are also shown in Figure 12. The relative sizes should not be compared with those in Figure 3, since the electron micrographs are of dried particles whereas the light micrographs are from the latex. The particles from the latex appear much smaller with the light microscope after drying.

Latexes IIb–II d go into true solution. Since we are now comparing swollen particles versus extended polymer chains, the viscosity reduction from IIa to IIb is enormous (for example, from 7.4×10^5 to 115 centipoises at 10% solids). The difference between IIb and IIc is small because here we are comparing extended chains only of different molecular weights (115 versus 6.1 centipoises).

It is of great interest to observe the mechanism of dissolution for this system. Latex IIa shows uniform particle swelling. But IIb–II d show almost no equilibrium particle swelling. Instead, each particle dissolves individually. As soon as a particle is attacked by base, this apparently permits the entire particle to disintegrate and go into solution. The remaining particles are untouched. The next increment of base attacks other particles and brings them completely into solution whereas the remaining particles are unaffected. This continues until all the particles have disappeared. This also explains why clarity occurs here over a rather narrow range of neutralization. Unswollen particles of high light scattering potential are present until final clarity is achieved.

The results of the softest system studied, latexes IV, show particle swelling and dissolution from the same latex. Since these polymers have a low T_g , a high degree of particle swelling is possible—a fourfold increase in diameter experimentally found for IVa. Being softer and much more flexible than IIa, the individual polymer chains are able to go into solution even though the molecular weight is high. The particles of latex IVb, of lower molecular weight polymer, will not swell up as much because they are able to enter solution more easily. Experimentally, about a threefold increase in diameter is found for IVb and the swollen particles have broken down into a true solution between 70% to 80% neutralization, whereas this occurs between 90% to 100% neutralization for IVa. Seventy per cent neutralization appears to be the lower limit for dissolution for this composition, as IVc goes into true solution at this point but has only achieved a twofold increase in particle diameter. Finally, IVd is so readily solubilized that as soon as particle is attacked by base, the entire particle is dissolved and a new increment of base neutralizes and dissolves other particles. The same mechanism of dissolution is observed as the harder latexes made with BTCM undergo.

Because all four of these soft latexes end up as true solutions, the difference in viscosity between IVa and IVb is small compared to the difference between IIa and IIb at 10% solids. After this, the differences between 0.5% and 1.0% BTCM and between 1.0% and 2.0% BTCM are about the same in the two series.

The mechanism of nonuniform attack of base in IIb–II d and IVd is very

interesting. This would indicate that there is some critical energy of activation which must be overcome and, as soon as it is, the entire neutralization process is completed for that particle. This mechanism is operative only when certain conditions are met. The molecular weight of the polymer must be below some minimum value and ease of swelling must be somewhat restricted. Hence, the tendency for this unique mechanism occurs most readily for high T_g latexes. It will occur for low T_g latexes only if the molecular weight is very low. A consequence of this dissolution mechanism is the great difference in the viscosity of the neutralized latex that a small amount of a chain transfer agent makes for a latex with a high T_g . The chief function of the first increment of the chain transfer agent is to enable the polymer chains to enter solution. This eliminates particle swelling and the viscosity is low throughout the entire range of neutralization. With additional chain transfer agent, the normal lowering of viscosity due to lower polymer molecular weight is observed.

Comparison With Published Results

The data presented here is in general agreement with the findings of Muroi.²⁻⁴ Alkali solubility increases as the per cent MAA is increased, as the hydrophilicity of the comonomers is increased, and as the T_g is lowered. However, the explanation for increased solubility with decreasing molecular weight of the acid-containing latex is because of decreased chain entanglement and not because of increased particle swelling, as proposed by Muroi.² Both viscosity and photographic observations show decreased particle swelling as the molecular weight is decreased for both hard and soft systems.

The detailed mode of disintegration of the particles was not studied. There could be disintegration or dissolution in stages, as suggested by Muroi.³ This is unlikely though in view of the theory that chain entanglement is chiefly responsible for the effect of increased solubility with decreased polymer molecular weight. Furthermore, this is not evident in the photographs of the EA/MAA copolymers where a very high degree of swelling occurred. There is no dark core surrounded by a lighter area. Type II latexes with a chain transfer agent are a mixture of true solution plus unreacted particles. This mechanism of dissolution should be facilitated even further for small particle-sized latexes.

Based on the postulated mechanism of alkali thickening of these latexes, the rate of swelling should be fast for soft latexes and slow for hard latexes. This would also explain the observations of Muroi of the optical density behavior being dependent upon the rate of addition of aqueous NaOH. This effect would be most pronounced for hard latexes with just enough methacrylic acid (or acrylic acid) to give a complete solution at equilibrium.

Schematic Representation

Based on the data presented here and in reference 1, the fully neutralized state of all acid-containing latexes can be schematically represented in a

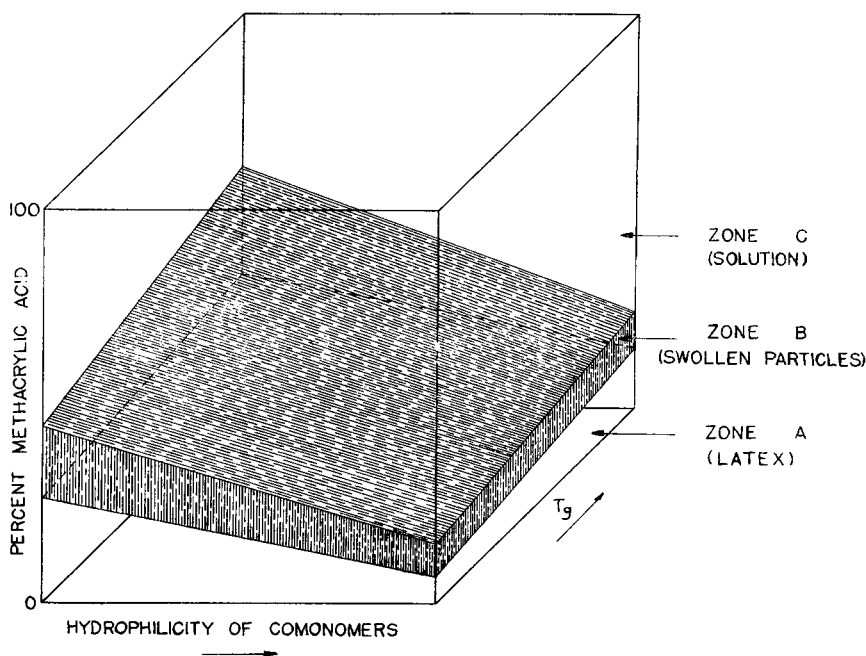


Fig. 13. Schematic representation of the different states of all neutralized acid-containing emulsion polymers—those prepared without a chain transfer agent.

cube, as shown in Figure 13. The precise position of the different areas cannot yet be asserted, but a qualitative picture can be drawn. In zone A, little or no swelling of the latex particle occurs. In zone B, there is considerable swelling of the particle without solubilization. In zone C, a true polymer solution of a polyelectrolyte is present. Actually, the area from no particle swelling to complete solution behavior is a continuous spectrum and polymer chains in true solution can also be present in zone B.

The schematic representation in Figure 13 is for latexes without any chain transfer agent. Using zone B as a reference, this zone rises to slightly higher percentages of MAA at the back face of the cube where the polymer T_g is highest. These would be latexes high in S content on the left and high in MMA content on the right. A much steeper rise is encountered in going from the right side to the left side of the cube, from high polymer hydrophilicity to low hydrophilicity. A low T_g , hydrophilic latex will form a solution upon neutralization with the lowest amount of MAA, whereas a high T_g hydrophobic latex will require the highest amount of MAA to form a solution upon neutralization.

Based on the results in this paper, a different schematic representation is needed for latexes modified with a chain transfer agent. This cube is shown in Figure 14. Zone B is only slightly lower in the front right-hand corner. In all other corners, however, it would be much lower, being lowered most for the high T_g , hydrophobic latexes. This was confirmed

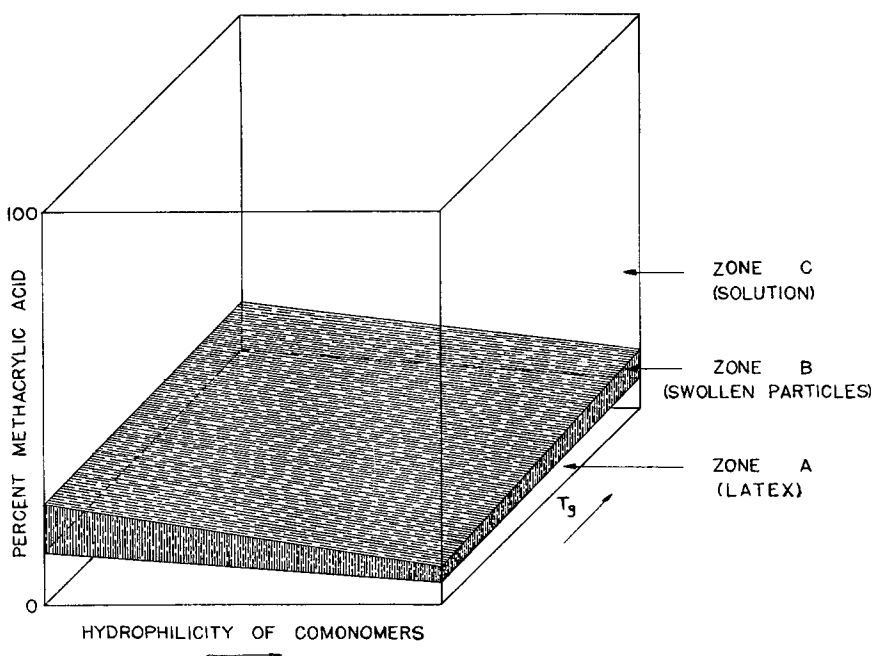


Fig. 14. Schematic representation of the different states of all neutralized acid-containing emulsion polymers—those prepared with a chain transfer agent.

when S/EA/MAA, 50/20/30 was synthesized with 0% and 1% BTCM as large particle-sized latexes. The former latex showed only a slight particle swelling with no dissolution and hence was very opaque at complete neutralization. The latter latex formed a clear, true solution. The net effect of a chain transfer agent is thus to enlarge the true solution zone by lowering the intermediate zone to lower MAA levels.

In both of these cubes there are, of course, an infinite number of comonomer combinations from copolymers to pentapolymers and higher. Presumably all the combinations would have solubility coefficients which could be obtained from additivity of values obtained from the simple systems. In any case, the qualitative shape of the solubility cube would be the same for all comonomer combinations. It is also important to bear in mind that temperature is a constant in this representation since temperature can have a very important effect on solubility.⁴ It is clear from Muroi's work that raising the temperature at which the solubility experiments are carried out would enlarge the true solution zone.

CONCLUSIONS

The photographic observations presented here have confirmed the swelling and dissolution behavior of acid-containing emulsion polymers developed on the basis of viscosity measurements. The great importance of

polymer molecular weight as it affects particle swelling and dissolution behavior was also visually observed. This was also consistent with the viscosity results. Sodium and ammonium hydroxide give identical particle swelling results. The lowering of viscosity with the former base after complete neutralization is likely due to an ionic effect.

The neutralized state of all acid-containing latexes can be pictured in a cube with the important variables being per cent acid, hydrophilicity of the comonomers, and T_g . The large zone of solution polymers will be increased for lowered polymer molecular weight and increased temperature of the system. At this time only a qualitative picture can be drawn. A quantitative picture will require a considerable amount of additional experimental work.

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