Mechanism of Alkali Thickening of Acid-Containing Emulsion Polymers.   I.   Examination of Latexes by Means of Viscosity

C. J. VERBRUGGE, *Chemical Research Department, S. C. Johnson & Son, Inc., Racine, Wisconsin 53403*

Synopsis

Viscosity-versus-pH relationships for a large number of methacrylic acid-containing emulsion polymers have been measured.   The monomers chosen for this study were so selected because they represent synthesized latexes of high and low T_g and comparative hydrophilicity.   These were styrene, methyl methacrylate, ethyl acrylate, n-butyl acrylate, and 2-ethylhexyl acrylate.   The postulated mechanism involved in the transition from an unneutralized latex particle to the neutralized species is accounted for in terms of varying degrees of particle swelling.   In the limiting case, particle swelling is followed by complete solution of the polymer.   The most important variables are the per cent methacrylic acid and the polymer T_g and hydrophilicity as determined by the comonomers present.   The degree of particle swelling ranges from none for high styrene-containing latexes to high degrees of swelling followed by polymer solubilization for high ethyl acrylate-containing latexes.

INTRODUCTION

Although acid-containing emulsion polymers have found uses in a wide variety of applications, very few fundamental studies have been reported on the dispersed state properties of these interesting latexes.   Of particular interest are the unique changes which these latexes undergo upon addition of a base such as ammonia.

Fordyce et al.[1,2] report the marked viscosity increase which latexes composed of methyl methacrylate, ethyl acrylate, and methacrylic acid undergo upon addition of base.   Muroi[3-5] carried out some extensive studies on polymers of alkyl acrylates and methacrylates with acrylic and methacrylic acid.   Included in the latter works were titration curves and changes in optical density upon addition of alkali.   The influence of surfactant on the alkali thickening of acrylic emulsions was reported[6] for a latex containing 1 wt-% acrylic acid.   Guziak and Maclay[7] investigated the redispersion of acid-containing emulsion polymers.   A light-scattering study on neutralized acid-containing latexes was carried out by Wesslau.[8]   Generally, the acrylic acid content of his polymers was less than 10 wt-%.   A direct relationship between the ability of a latex to thicken and the volume change of the latex particles upon addition of ammonia was found.

For latexes composed of high percentages of methacrylic acid, clear solutions are produced upon neutralization for many systems. This could mean that either a true solution, swollen particles, or a mixture of both are present. Such a phenomenon would present difficulties for study by light scattering. In addition, the time involved would limit the study to a few selected polymers. It was felt that a viscosity-versus-pH study on a large number of latexes would be very informative as to the changes the latex particles undergo as a result of neutralization.

The monomers chosen were so selected because they represent synthesized polymers of high and low T_g and of comparative hydrophilicity. Two "hard" monomers, styrene (S) and methyl methacrylate (MMA), were each paired with 0, 20, 40, and 60 wt-% of three "soft" monomers, ethyl acrylate (EA), n-butyl acrylate (BA), and 2-ethylhexyl acrylate (2-EHA). Each combination was polymerized with 15, 20, 25, and 30 wt-% methacrylic acid (MAA).

EXPERIMENTAL

Materials

The raw materials used in preparing the emulsion polymers were used without purification. Styrene was obtained from Monsanto Chemical Company. All other monomers were obtained from Rohm and Haas Company. Ammonium persulfate was supplied by Mallinckrodt Chemical Works. Maprofix 563, sodium lauryl sulfate, from Onyx Chemical Corporation and Triton X-200, the sodium salt of an alkylaryl polyether sulfonate, were used as emulsifiers. Ammonium hydroxide, 28 wt.-%, from E. I. du Pont de Nemours & Company, was used in the pH adjustments.

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 and surfactants, listed in Table I, were introduced 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 1 min, monomer addition was begun. The monomers were added dropwise over a period of 1 hr at a temperature

TABLE I
Polymerization Recipe

Ingredients	Weight, g
Monomers	200.0
Sodium lauryl sulfate	4.0
Triton X-200 (at 28%)	7.2
Ammonium persulfate	1.00
Distilled deionized water	378.0

of 80 ± 2°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. Conversion was nearly 100% in every case.

All latexes except the S and MMA copolymers were prepared at 35% total solids content. The latter polymers were made at 20% solids, except for 10% solids for the two highest acid content polymers to prevent coagulation. All monomer ratios are given in wt-%.

Characterization Methods

Viscosity. Aqueous ammonia, 28%, was added to approximatey 300-ml portions of the latex diluted to 2% polymer solids. About ten pH adjustments were made for most latexes, most of them in the region of the viscosity change. For latexes with little or no apparent change in viscosity with pH, as few as five pH adjustments were made. The samples were permitted to stand at room temperature for a minimum of two days prior to the viscosity measurement to insure that they reached equilibrium. Viscosity was measured in a 300-ml beaker with a Brookfield viscometer. Spindles No. 1 to 3, depending on the viscosity, at 60 rpm were used. Only this speed was selected to minimize the rate of shear effect. The viscosity measurements were carried out in a constant temperature room, 22.5 ± 0.3°C. The viscosity readings are reported to the nearest centipoise.

Titration. The titrations were carried out with a pH meter. Aqueous 0.25N NaOH was added in increments to 100 g of the latex at 2% polymer solids. After the pH had come to equilibrium, the next increment of titrant was added.

RESULTS

Preliminary Results

In selecting a measurement to characterize the change which an acid-containing emulsion polymer undergoes upon neutralization, the governing factors were the ease of the measurement and as great a lack of ambiguity of the results as possible.

Differences are found in the titration behavior of these latexes. Examples of five copolymers with 20% MAA are shown in Figure 1. However, this gives only limited information about the state of the latex with pH. This is particularly evident when one compares the difference between the latexes EA/MAA and MMA/MAA, 80/20. The large differences in swelling behavior concluded from viscosity are not apparent from the titration curves.

Changes also occur in the optical density upon neutralization. However, the optical density is greatly affected by small amounts of impurities
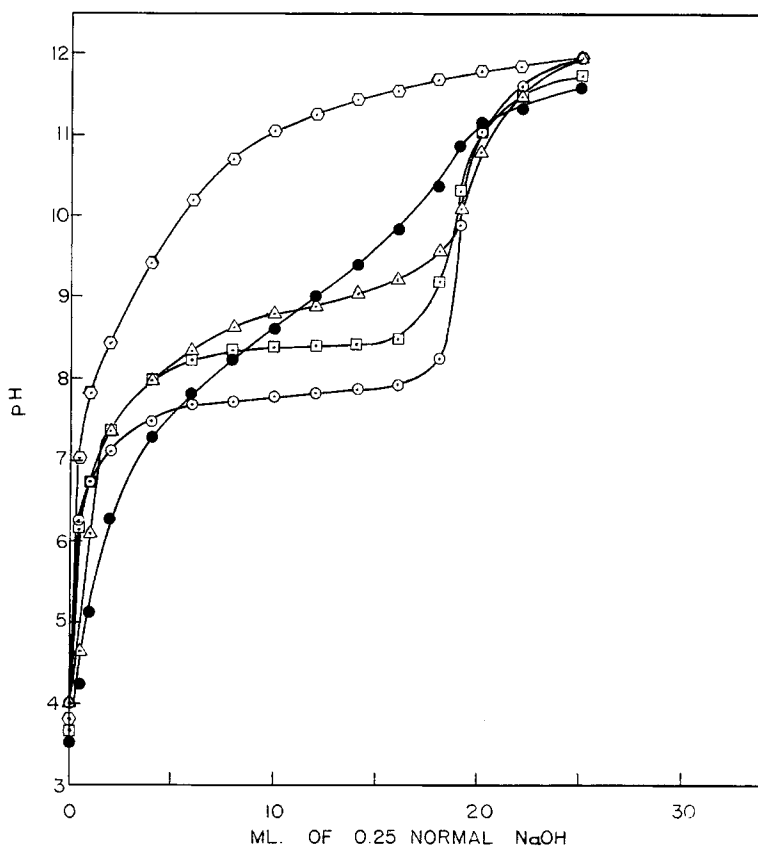
Fig. 1. Titration curves of copolymer latexes, 100 g at 2% solids. Ratio of comono-mer/MAA, 80/20: (○) S/MAA; (●) 2-EHA/MAA; (△) BA/MAA; (□) MMA/MAA; (◉) EA/MAA.

or inhomogeneity in the polymer sample. This would seriously hamper analysis of the results.

Consequently, viscosity was chosen as a measurement for characterization. A comprehensive viscosity study on the changes which accompany neutralization was undertaken. Preliminary experiments showed that the viscosity of a freshly neutralized latex decreases with time at all pH's. The decrease was significant only for those latexes which gave the higher equilibrium viscosities. The decrease was almost complete after one day and was complete after two days. The viscosity was then stable. Consequently, no viscosity readings were made for this study until the samples had stood for at least two days.

Viscosity Study

Equilibrium viscosity-versus-pH measurements were made with each latex. All the data obtained fit one of three general categories, as shown
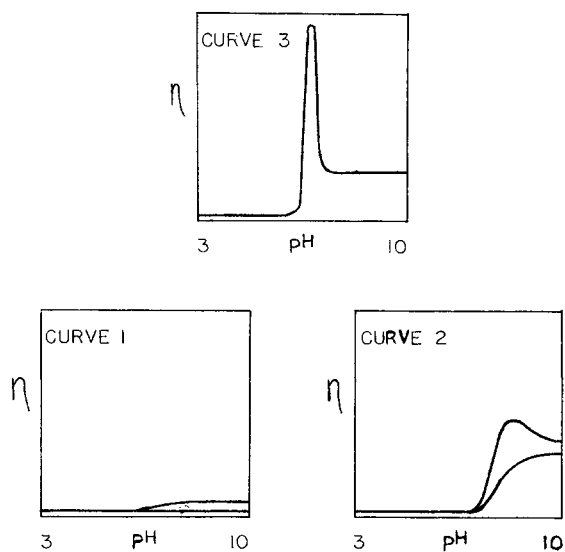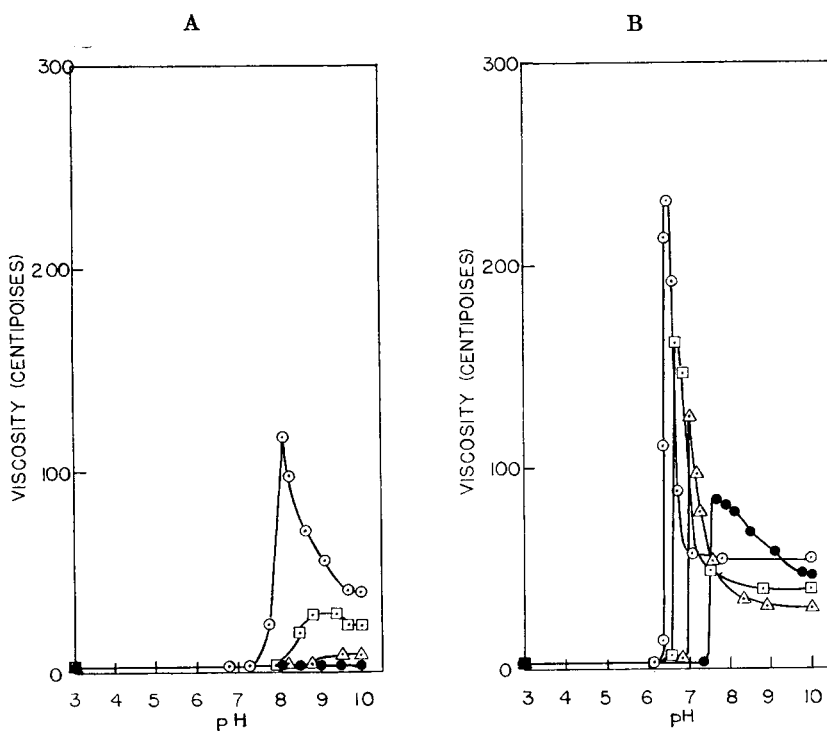
Fig. 2. Types of viscosity-vs.-pH curves.

Fig. 3. Viscosity-vs.-pH curves for two representative series. A: S/EA/MAA (⊙) 30/40/30; (⊡) 35/40/25; (△) 40/40/20; (●) 45/40/15. B: MMA/BA/MAA (⊙) 10/60/30; (⊡) 15/60/25; (△) 20/60/20; (●) 25/60/15.

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TABLE II
Peak and Plateau Viscosity Values from Viscosity-versus-pH Curves

Composition		Viscosity, centipoise		Composition		Viscosity, centipoise	
		Peak	Plateau			Peak	Plateau
S/EA/MAA	65/20/15	2	2	S/BA/MAA	25/60/15	4	4
	60/20/20	2	2		20/60/20	8	6
	55/20/25	2	2		15/60/25	14	12
	50/20/30	33	33		10/60/30	28	21
	45/40/15	2	2	S/2-EHA/MAA	65/20/15	2	2
	40/40/20	8	8		60/20/20	2	2
	35/40/25	29	24		55/20/25	2	2
	30/40/30	110	38		50/20/30	7	7
	25/60/15	9	9		45/40/15	2	2
	20/60/20	36	25		40/40/20	2	2
	15/60/25	100	21		35/40/25	7	7
	10/60/30	280	36		30/40/30	17	17
S/BA/MAA	65/20/15	2	2		25/60/15	2	2
	60/20/20	2	2		20/60/20	3	3
	55/20/25	2	2		15/60/25	8	8
	50/20/30	7	7		10/60/30	19	19
	45/40/15	2	2	S/MAA	85/15	2	2
	40/40/20	4	4		80/20	2	2
	35/40/25	10	10		75/25	2	2
	30/40/30	20	19		70/30	2	2

MMA/EA/MAA		
65/20/15	16	12
60/20/20	100	84
55/20/25	152	52
50/20/30	220	28
45/40/15	39	36
40/40/20	120	38
35/40/25	180	38
30/40/30	154	43
25/60/15	84	47
20/60/20	120	30
15/60/25	160	39
10/60/30	230	55

MMA/BA/MAA		
65/20/15	6	6
60/20/20	30	30
55/20/25	120	120
50/20/30	125	50
45/40/15	8	8
40/40/20	40	39
35/40/25	54	46
30/40/30	94	42
25/60/15	7	7
20/60/20	26	26
15/60/25	41	40
10/60/30	76	64

MMA/2-EHA/MAA		
65/20/15	4	4
60/20/20	10	10
55/20/25	37	37
50/20/30	290	290
45/40/15	6	6
40/40/20	12	12
35/40/25	11	11
30/40/30	120	120
25/60/15	5	5
20/60/20	12	12
15/60/25	31	31
10/60/30	43	43

MMA/MAA		
85/15	5	5
80/20	103	90
75/25	53	48
70/30	58	46

EA/MAA		
85/15	24	24
80/20	130	40
75/25	230	52
70/30	230	66

BA/MAA		
85/15	5	5
80/20	10	10
75/25	27	24
70/30	55	52

2-EHA/MAA		
85/15	2	2
80/20	4	4
75/25	6	6
70/30	15	15

by three typical curves in Figure 2. Curve 1 shows either little or no increase in viscosity with increasing pH. Curve 2 shows a significant increase in viscosity with pH with either no decrease in viscosity at high pH or a plateau only slightly below the peak. Curve 3 shows a very large increase in viscosity with pH. A peak is obtained which is very narrow and the plateau falls well below the peak. An example of two representative series is plotted in Figure 3.

The pertinent data of each latex can be obtained from the viscosity value of the peak and plateau from each curve. This has been tabulated in Table II. "Peak" is defined in this study as the maximum viscosity value observed. "Plateau" is defined as the minimum occurring after the peak.
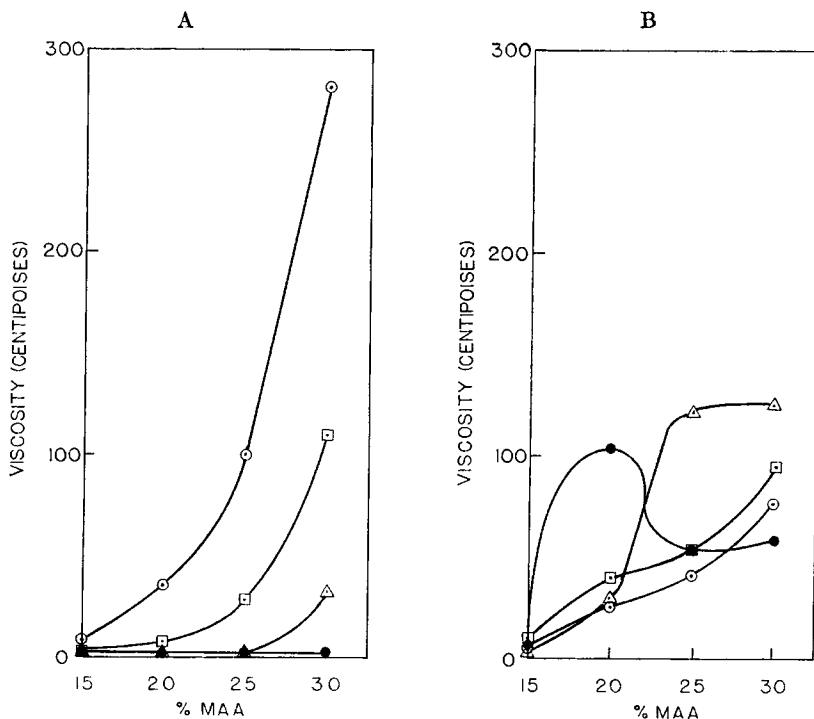
Fig. 4. Representative plots of peak viscosities vs. % MAA.   A: S/EA/MAA (⊙) 60% EA; (□) 40% EA; (△) 20% EA; (●) 0% EA.   B: MMA/BA/MAA (⊙) 60% BA; (□) 40% BA; (△) 20% BA; (●) 0% BA.

In some cases these two are identical, as when there is no increase in viscosity with pH or when there is an increase which levels off between pH 9 to 10.

These data can be treated in several ways. One way is to plot the peak or plateau viscosity versus % MAA for a given terpolymer series. An example of such a plot of peak viscosities is given in Figure 4 for the S/EA/ MAA and the MMA/BA/MAA polymers. The corresponding plateau viscosities are plotted in Figure 5.
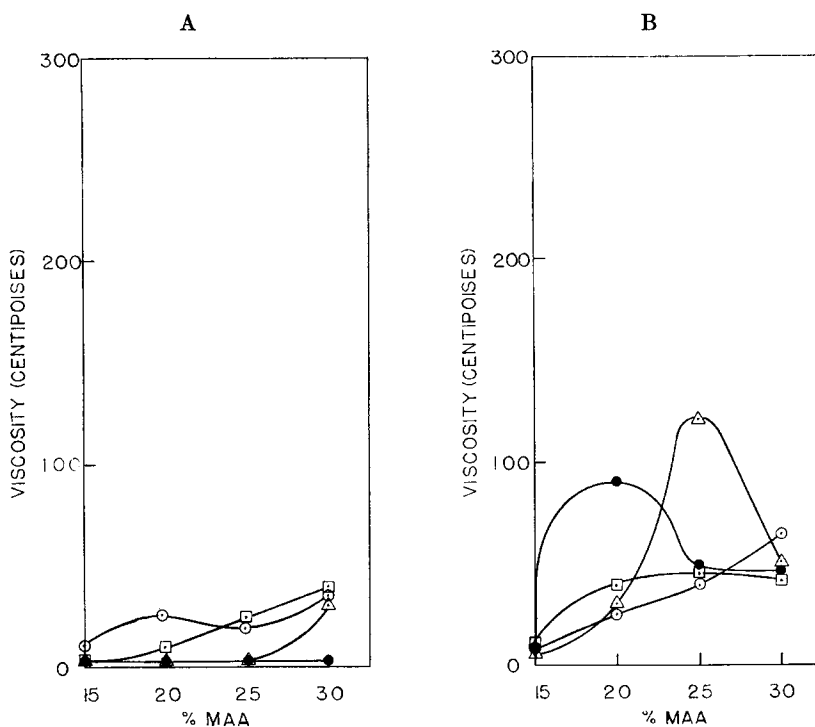
Fig. 5. Representative plots of plateau viscosities vs. % MAA. A: S/EA/MAA (⊙) 60% EA; (□) 40% EA; (△) 20% EA; (●) 0% EA. B: MMA/BA/MAA (⊙) 60% BA; (□) 40% BA; (△) 20% BA; (●) 0% BA.

DISCUSSION

The viscosity data presented in Table II show that three factors are predominant in the viscosity increase which occurs to acid-containing latexes upon neutralization with base. Foremost is the % MAA present in the polymer; second, the relative hydrophilicity of the comonomers; and third, the T_g of the polymer.

Peak Viscosity

It is evident that the peaks are higher in any given series (e.g., constant acrylate monomer) as the % MAA increases. The importance of hydrophilicity is seen in a comparison of MMA- versus S-containing polymers. The former have a much steeper rise in peak viscosity as a function of % MAA than the latter. In addition, the peaks increase in height with the hydrophilicity of the "soft" comonomers in the order 2-EHA < BuA < EA.

These data are explained as follows: The addition of alkali is causing the latex particles to swell as neutralization of the carboxyl groups occurs. This swelling is slight for low acid-containing latexes and for high acid-

containing latexes with hydrophobic comonomers. As the % MAA in a series at constant percent "soft" monomer (acrylate) content increases, the particle swelling also increases. The effect of polymer T_g is best seen in a comparison of the EA/MAA and MMA/MAA copolymer latexes. The relative hydrophilicities are quite comparable here, but the EA/MAA latexes show a much greater degree of particle swelling.

Plateau Viscosity

After the particle has reached its maximum swelling, at a certain pH, it will either remain unchanged or disintegrate into a true solution upon addition of more base. The actual state of the neutralized latex which is obtained can be determined from the plateau viscosities.

The overall features of the plateau viscosity-versus-% MAA data (see Fig. 5) are similar to the peak viscosity data—there is a general upward trend in viscosity with increasing % MAA. Since the latex at the plateau can consist of essentially unchanged emulsion, swollen particles, or a true solution, the best way to analyze the data is to observe the difference between the peak and the plateau viscosities.

In the styrene series, there is no difference between the peak and the plateau for the latexes high in styrene content. In fact, an appreciable difference is found only with several of the S/EA/MAA latexes. For all the others then, the state of the latex at high pH ranges from unchanged emulsion where no increase in viscosity was observed to moderately swollen particles where there was an increase in viscosity but no subsequent decrease at high pH.

In the MMA series, many of the MMA/EA/MAA and MMA/BA/MAA latexes end up as a true solution of a polyelectrolyte. As the % MAA increases in a series at constant % "soft" monomer, there is a greater tendency for the swollen particles to break down into a true solution. In a series such as MMA/20%EA/MAA, a maximum plateau viscosity is observed at 20% MAA. In this series, we have little swelling with 15% MAA and we end up with a slightly swollen particle. With 20% MAA, there is considerable swelling of the particle and only a slight breakdown of the swollen particle. With 25% MAA, there is even more swelling of the particle followed by extensive breakdown to a true solution. With 30% MAA, there is a high degree of swelling followed by a nearly complete breakdown to a true solution. For this reason we have a low viscosity even though the 30% MAA latex has the greatest number of charged groups present. This trend is also present in the MMA/MAA and MMA/20%BA/MAA series. In the latter polymer, the change to breakdown of the swollen particle does not occur until 30% MAA. This is consistent with the effect of decreased hydrophilicity of the comonomers requiring more MAA in the polymer to achieve solubility.

It is clear in examining all the data in Table II that predicting the viscosity of the plateau for a given composition is fairly difficult. The factor of hydrophobic bonding greatly affects the configuration of an individual

polymer chain as well as the degree of aggregation. This in turn directly affects the viscosity obtained.

Confirming Experiments

We have seen how the process occurring during neutralization for all acid-containing latexes are part of a single mechanism—varying degrees of particle swelling followed by solubilization for the more hydrophilic latexes.

If this mechanism is correct, it should be possible to take a hydrophilic combination of monomers plus a hydrophilic crosslinking agent, prepare the latex, and obtain a system which will undergo a marked viscosity increase but not have a dramatic lowering of viscosity after this point. Accordingly, an EA/MAA combination of monomers, 80/20 and 70/30, was selected and 15% and 30% ethylene dimethacrylate (EDMA) was incorporated in place of the EA. The viscosity-versus-pH results are plotted in Figure 6.
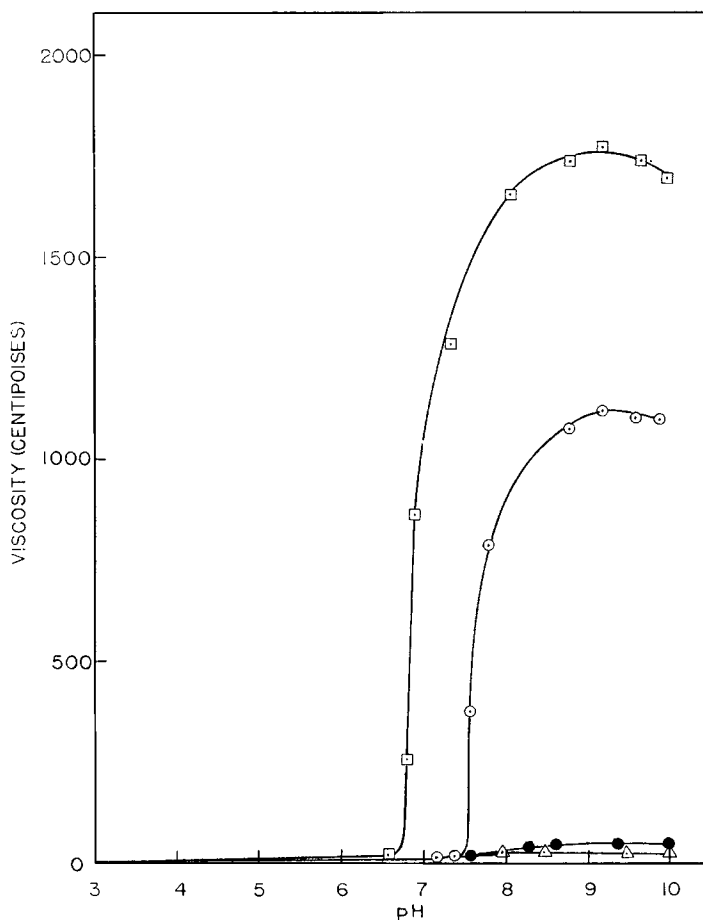

Fig. 6. Viscosity-vs.-pH curves for crosslinked latexes: EA/EDMA/MAA (⊙) 65/15/20: (▫) 55/15/30; (●) 50/30/20; (△) 40/30/30.

The results are in accord with expectation. For the two latexes containing 15% EDMA, the viscosity rises much higher than any of the other non-crosslinked latexes. This implies that while the noncrosslinked latexes swell to a certain point and then enter true solution, the crosslinked latexes continue to swell. Little lowering of viscosity occurs at high pH, further evidence that the particle swelling which occurs is stopped at the highly swollen state and no true solution occurs. For the two latexes containing 30% EDMA, the latex particles are so highly crosslinked that very little particle swelling can occur and consequently little viscosity increase occurs. Its curve is like curve 1, Figure 2.

Another confirming experiment is based on an observation of the viscosity behavior a latex undergoes immediately after complete neutralization. If the pH of a latex as S/BA/MAA, 30/40/30, is raised at once to pH 9, the viscosity increases to only a few centipoises above its equilibrium value of 19 cps. However, if a latex such as MMA/EA/MAA, 10/60/30, which has a pH-viscosity curve with a very high peak followed by a low plateau, is adjusted at once to the pH region of the plateau, a momentary gel is formed. In a few minutes it is fluid, being only 50 cps above its equilibrium value of 55 cps, which is finally reached between one to two days. Particle swelling followed by solubilization of the polymer chains is occurring during this initial rapid rise and drop in viscosity.

Large particle-sized latexes were also prepared and the mechanism of particle swelling proposed in this paper was visually confirmed with the light microscope. This study is the subject of the next paper.[9]

Other Factors Influencing Viscosity Change

Two other factors which have thus far been neglected in our discussion of the mechanism of the alkali thickening of acid-containing emulsion polymers but which are important in the solution properties of polyelectrolytes will now be discussed.

Each set of monomers will have different reactivity ratios. The resultant differences in distribution of groups along the chain will have an effect on the viscosity of the neutralized latex. However, such an effect would be random and not coincident with the correlations noted above. In addition, the use of acrylic acid in place of MAA gives comparable results since our viscosity results are in accord with the findings of Wesslau.[8] The reactivity ratios for these two acid monomers with the other monomers are greatly different. If reactivity ratios and the resultant variation in polymer structure were a dominant factor, the results of this work and those of Wesslau would have been greatly different.

The polymer molecular weight will affect the viscosity-versus-pH results. It is felt that the molecular weights of these polymers are quite similar, based on the following results. A homopolymer of MMA and S, both prepared with 2% sodium lauryl sulfate and 1% Triton X-200 and 0.5% ammonium persulfate, had comparable viscosity-average molecular weights (3.4×10^5 and 4.15×10^5, respectively). Poly(MMA/EA/MAA), 60/20/20,

55/20/25, and 50/20/30, had $M_w = 4.1 \times 10^5$, 4.8×10^5, and 4.5×10^5, respectively. This was obtained by methylation of the polymers with diazomethane and light-scattering measurements on the resulting MMA/EA copolymers in methyl ethyl ketone. The estimated M_v values are 3.2×10^5, 3.7×10^5, and 3.5×10^5, respectively. With such a wide spectrum of polymer types and the resulting small range of molecular weights, the effect of polymer molecular weight can be assumed to be small in comparison to the effect of latex composition, hydrophilicity, and T_g.

CONCLUSION

This study shows that the changes which occur to an acid-containing latex upon neutralization are accounted for in terms of varying degrees of a single mechanism, regardless of the latex composition. The mechanism consists of swelling of the latex particles plus an accompanying solubilization of polymer molecules when the hydrophilicity of the polymer is high enough. It is this intrinsic property of the latex, the relative hydrophilicity and to a lesser extent the T_g, both governed by the % MAA and the type of comonomers present, which determines the changes occurring in the transition from an unneutralized latex to the neutralized species.

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