

An Investigation of the Emulsion Terpolymerization of 2-Ethylhexylacrylate–Vinyl Acetate–Acrylic Acid

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Synopsis

An investigation of the emulsion polymerization of 2-ethylhexylacrylate (EHA)–vinyl acetate (VAc)–acrylic acid (AA) has been done. It was found that the polymerization rate depends on the AA level and that particle nucleation occurs throughout the entire conversion range. At the 5% AA level, there is significant coagulation. The number of particles depends on the balance between nucleation and coagulation. Addition of a small amount of water-soluble comonomer has no significant effect on the course of polymerization, but the viscosity of the latex can increase significantly. The dependence of latex viscosity on pH on neutralization has been studied. The maximum viscosity reached on neutralization depends on the acrylic acid level and the semibatch policy used in the latex synthesis. Addition of salt is a simple and effective way to control viscosity buildup during neutralization.

INTRODUCTION

Although carboxylated polyacrylic latexes have found use in a wide variety of applications, very few fundamental studies have been reported on its polymerization features and the dispersed state properties of these interesting latexes. Especially for 2-ethylhexyl acrylate–vinyl acetate–acrylic acid terpolymer latexes, which have been used widely in pressure-sensitive adhesive formulations, a glance through the literature would reveal that few data are reported. The patent literature is an exception.^{1–3} Most of the studies on carboxylated latices were focused on carboxylated polystyrene, polyethylacrylate, and poly(methyl methacrylate) latexes. In this preliminary study, attempts were made to observe the overall polymerization features of EHA–VAc–AA emulsion system, the effect of semibatch policy, and the swelling that the latexes undergo on neutralization.

EXPERIMENTAL

Materials

Deionized water was used in all of the polymerization recipes. All other components of the recipes were used as received from the suppliers without

further purification. All of the monomer types were technical grade. 2-Ethylhexylacrylate and Aerosol A-102 (sulfosuccinate type emulsifier) were obtained from Franklin International, Columbus, OH. Aerosol A-102 was prepared as a 30 wt % aqueous solution. Acrylic acid was supplied by Celanese Canada, Toronto, Ontario. The remaining monomers were obtained from C.I.L. Paints, Inc., Toronto, Ontario. Other recipe ingredients were: dodecylbenzenesulfonic acid sodium salt (SDBS), technical grade supplied by Fluka AG; sodium phosphate monobasic by Fisher; and dodecyl mercaptans by Aldrich Chemical through distributors in Toronto. Other ingredients are reagent grade and were supplied by BDH, Toronto, Ontario. At full monomer conversion, all of the recipes used gave a solids level for the latex of about 45%. A more accurate estimate of the solids levels may be made by using actual recipes quoted in tables and figures.

Polymerization Procedure

Emulsion polymerizations were conducted in a 2-gal pilot plant stainless-steel reactor. Temperature was controlled by a PI controller to within $\pm 2^\circ\text{C}$.

Batch Polymerization. Deionized water, surfactant and buffer were introduced into the reactor and stirred until dissolved. A mixture of monomers and chain transfer agent was added slowly with suitable agitation. The mixture was emulsified for 15–30 min, purged with N_2 for 0.5 h, and then the temperature was raised to the desired level. Finally, potassium persulfate, dissolved in a small amount of deionized water, was rapidly added to the reactor. After completion of polymerization, the emulsion was cooled to room temperature, and neutralization with sodium hydroxide solution was carried out in the reactor.

Semibatch Polymerization. A preemulsion was prepared in the reactor following the procedure as described under batch polymerization. The preemulsion was then transferred to a feeding tank for later post feeding. An initial charge was introduced into the reactor, emulsified sufficiently, and purged with N_2 for 0.5 h. The temperature was then raised to the desired level and an initial part of the potassium persulfate which was dissolved in a small amount of water was added to the reactor. The initial charge was polymerized for about 30 min and then the remainder of the preemulsion and retained potassium persulfate solution were fed to the reactor at a designated rate with calibrated metering pumps. After semibatch feeding in all of the preemulsion and potassium persulfate solution, the polymerization was continued batchwise for another 0.5 h. The final latex was cooled at room temperature and neutralized with sodium hydroxide solution.

Characterization Methods

Conversion. Conversion was measured gravimetrically.

Particle Size and Concentration. Particle size was measured by hydrodynamic chromatography (HDC) with two 9.5×1500 mm stainless-steel columns packed with Controlled Pore Glass (CPG) (Electronucleonics, Fairfield, NJ, mesh size 80/120, pore size 3000 \AA). A Beckman 160 UV/VIS spectrophotometer was used as a detector at 254 nm wavelength. The aqueous mobile phase contained 0.65 g/L Aerosol OT, 0.65 g/L NaNO_3 , and 0.32 g/L sodium

azide. The mobile phase flowrate was 2 mL/min. A series of monodisperse polystyrene particle standards was used for calibration. The polymer particle concentration was estimated using measurements of monomer conversion and the volume-average particle diameter (D_V) measured by HDC. D_V was calculated using the frequency distribution (after correction for axial dispersion) and the following equation:

$$D_V = \left(\int_0^\infty D^3 f(D) dD \right)^{1/3} \quad (1)$$

The number of polymer particles per liter (N) was then calculated using

$$N = C_p / \left(\frac{\pi}{6} \rho_p D_V^3 \right) \quad (2)$$

where C_p is g polymer/L in the latex and ρ_p is the polymer density. ρ_p was not measured but arbitrarily set equal to 1000 g/L.

Viscosity. A sodium hydroxide solution, 0.15 g/mL, was added to approximately 400 mL of latex to adjust the pH to about 5–8, depending on the apparent change in viscosity of the latex. Preliminary measurements showed that the viscosity of freshly neutralized latex increased with time slowly. The samples with higher viscosity were permitted to stand at room temperature for about 1 h prior to the viscosity measurement. Viscosity was measured with a Brookfield viscometer using spindle no. 3 at 30 rpm. For most measurements, this lowest speed was used so as to minimize the effect of shear rate on viscosity. However, for some measurements, viscosity vs. shear rate was done. A sodium chloride solution, 0.1 g/mL, was used for adjusting the electrolyte level.

RESULTS AND DISCUSSION

Effects of AA Level for Batch and Semibatch Operation

Conversion history, particle size growth rate, and particle-number curves of EHA–VAc–AA emulsion polymerization for two levels of acrylic acid (5% and 1%), batch and semibatch operation, are shown in Figures 1–4. One can see from these curves that the polymerization rate with the higher level (5%) of AA is slower than that with the lower level (1%) of AA. However, particle size growth rate with 5% AA is faster than that with 1% AA because the number of particles formed with 5% AA is much less than that with 1% AA.

No experimental rate data have been reported in the literature for this latex system. However, several investigations on the mechanism of particle nucleation and growth have been reported for carboxylated emulsion polystyrene.^{4–7} For carboxylated polystyrene it was found that polymerization rate increases as the acrylic acid level increases, but polymerization rate per polymer particle is almost the same at all acrylic acid levels used. The difference in polymerization rate is a result of difference in particle concentration. The results obtained in this study differ from those for carboxylated polystyrene. The difference is considered to be a result of higher coagulation tendency with

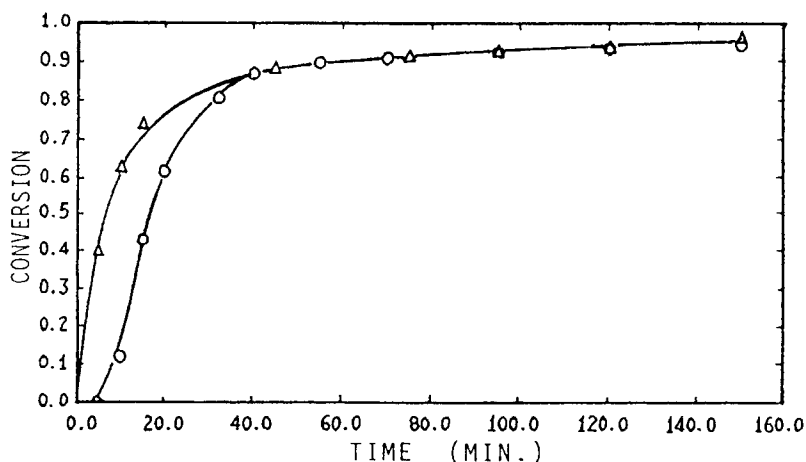


Fig. 1. Conversion history (batch polymerization): (○) 5% AA; (△) 1% AA. Recipe: EHA/VAc/AA/SDBS/ $K_2S_2O_8$ / H_2O = 80/15/variable/1.2/0.3/120. Temperature: 70°C.

a higher level of AA in this study. In Figure 4 one can see that, in the 5% AA case, the number of particles reaches a maximum and then falls. This suggests that there is significant coagulation occurring. In the 1% AA case, number of particles continues to increase slightly. It suggests that coagulation may be insignificant. At least particle nucleation is predominant in the balance.

Sakota and Okaya⁶ noticed that carboxylated polystyrene prepared with unneutralized acrylic acid (low pH) is unstable. Particles undergo rapid coagulation in the low pH region. Loncar et al.⁸ found also that for a carboxylated polyacrylate latex series prepared with acrylic acid seems to be less stable. Sherman⁹ reported that at a degree of neutralization less than 0.8, soap-free carboxylated polystyrene coagulated through phase inversion from O/W emulsion to O/W/O emulsion. We also found that unneutralized carboxylated EHA-VAc copolymer, especially that with high level AA, is

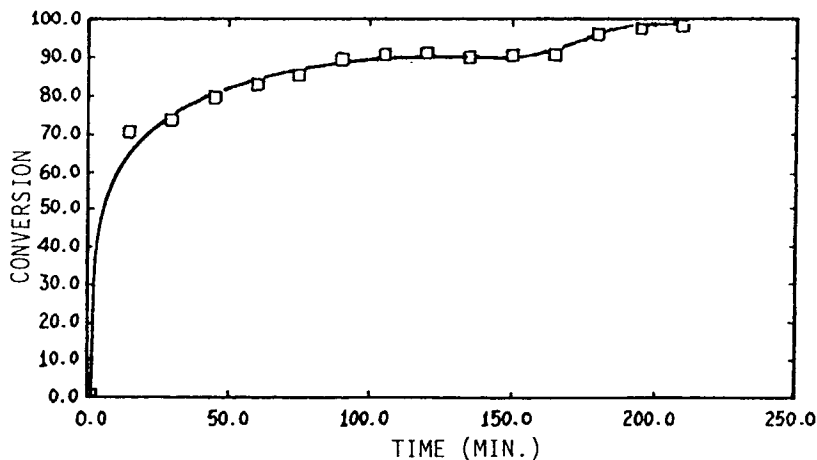


Fig. 2. Conversion history (semibatch polymerization) (recipe and conditions as in Fig. 1 with 5% AA).

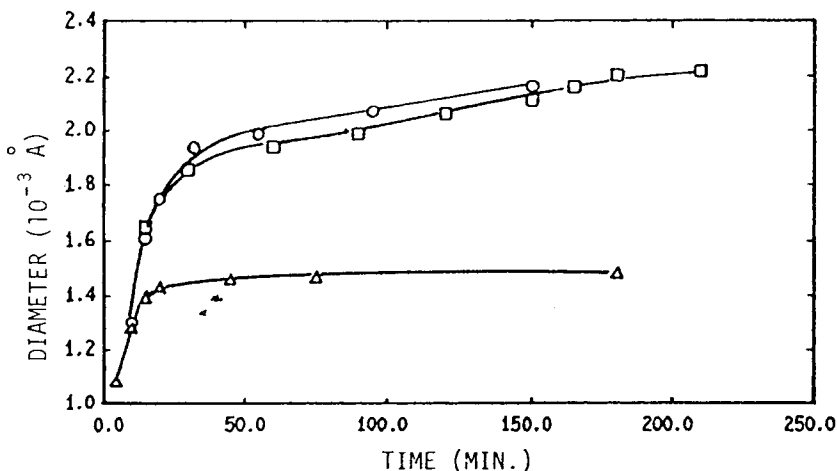


Fig. 3. Polymer particle growth rate (HDC peak diameter in \AA): (\circ) 5% AA (batch polymerization); (Δ) 1% AA (batch polymerization); (\square) 5% AA (semi-batch polymerization). Recipe and conditions: same as in Figures 1 and 2.

unstable during storage. After a few days, the latex becomes a gel. It can, however, be reemulsified under vigorous agitation. After a couple of weeks latex particles coagulate and the polymer phase separates from the water phase. Thereafter, it cannot be reemulsified even under vigorous agitation. If the latex is stored after neutralization, it is stable.

Effect of Semibatch Operating Policy

As mentioned above, polymerization rate of EHA-VAc-AA is very fast. Polymerization heat generation is concentrated in a very short time with batch operation, and thus it is difficult to control temperature and easy to obtain a runaway reaction. It is known that for pressure-sensitive adhesive applications, high branching frequencies are preferred.¹⁰ Semibatch operation with monomer-starved feed is expected therefore to be advantageous, in that it gives higher branching frequencies as well as better temperature control.¹¹ Results obtained with different semi-batch and batch operating policies are shown in Figures 1-4 and listed in Tables I and II.

In Figure 2 it can be seen that the conversion level remains high (80-90%) during the semibatch feed period. Particles form throughout the feeding period and particle number depends on the balance between nucleation and coagulation.

As will be seen later, the swelling of the latex prepared by batch operation seems to be much greater than that for latex produced by semibatch operation. It may be the result of differences in carboxyl group distribution with different operating modes. With batch operation more acrylic acid seems to be located on the particle surface which results in greater particle swelling and a larger electroviscous effect.

With an initial charge of a portion of the recipe and prepolymerization (somewhat like a seed emulsion polymerization), one gets fewer but much

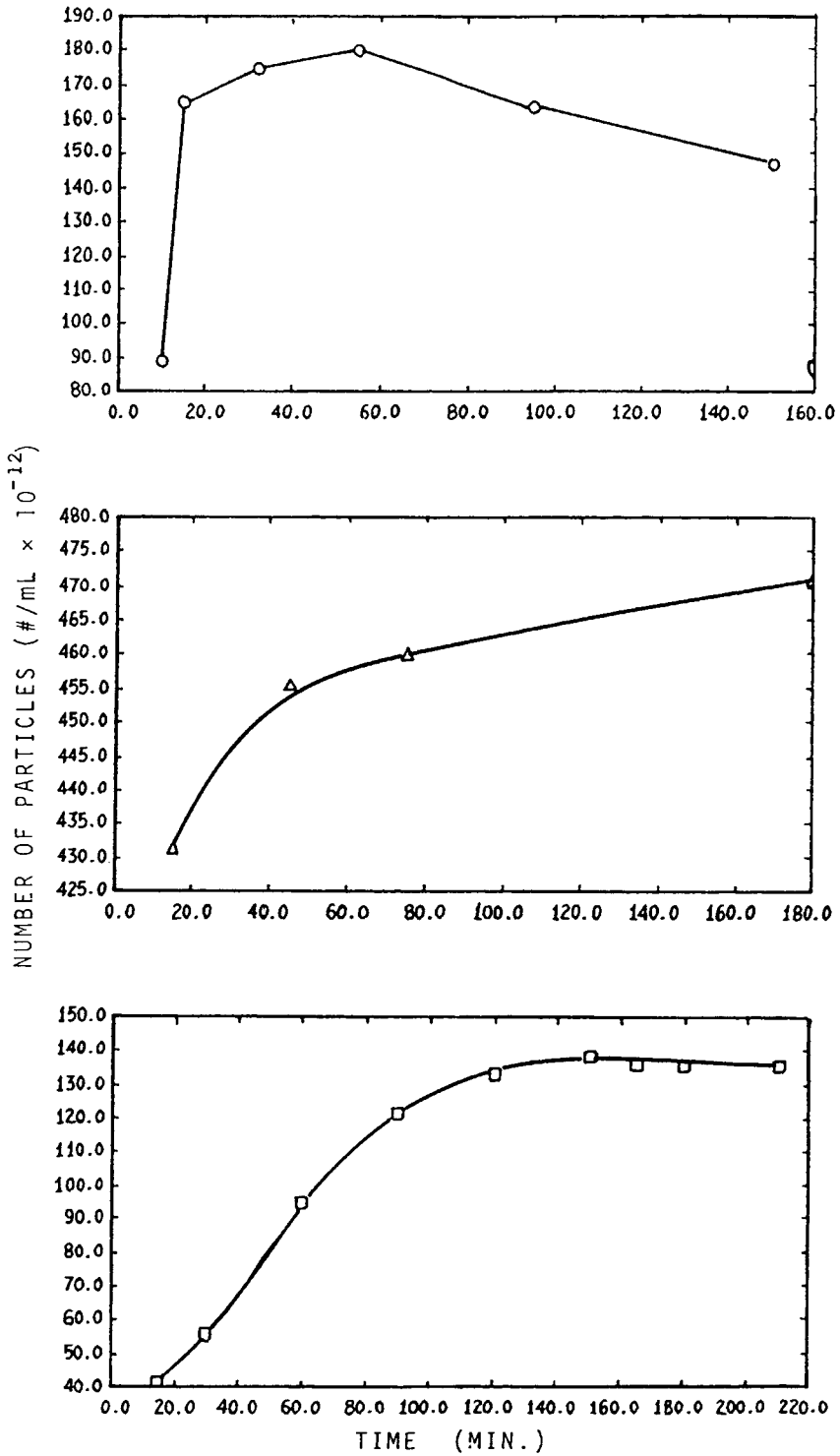


Fig. 4. Polymer particle concentration history: (○) 5% AA (batch polymerization); (△) 1% AA (batch polymerization); (□) 5% AA (semi-batch polymerization). Recipe and condition as in Figure 1.

TABLE I
Comparison of Latex Properties for Batch and Semibatch Polymerizations^a

Operating mode	Initial reactor charge	Characteristics of latex			
		HDC peak Diameter (Å)	Viscosity (cP)		Performance as pressure-sensitive adhesives ^b
			Before neut.	After neut.	
Batch	Entire recipe	2160	50	2600	Poor
Semibatch	50% of recipe	2220	120	1360	Good

^a Recipe: EHA/VAc/AA/SDBS/K₂S₂O₈/H₂O = 80/15/1.2/0.3/120. Polymerization temperature: 70°C.

^b Tested by Franklin International, Columbus, OH.

TABLE II
Comparison of Latex Properties for Various Semibatch Polymerizations^a

Operating mode	Initial reactor charge	Characteristics of latex			
		HDC peak diameter (Å)	Viscosity (cP)		Performance as pressure-sensitive adhesives ^b
			Before neut.	After neut.	
Semibatch ^c	40 % of recipe	4169	—	2320	Good
Semibatch ^d	20% of recipe	4268	—	2860	Good
Semibatch	50% of recipe	2168	—	2870	Good

^a Recipe: EHA/VAc/AA/AM/SDBS/K₂S₂O₈/H₂O = 80/15/4.25/0.75/0.8/0.3/120.

^b Tested by Franklin International, Columbus, OH.

^c Initial charge polymerized at 70°C for 0.5 h and then semibatch feeding was started.

^d 1/4 of the total emulsifier in the recipe was added in the initial reactor charge.

larger polymer particles. It is expected that such a latex is easier to dry with saving in energy.

Results of application tests show that the performance of the latex produced by semibatch operation are better than those by batch operation when used as pressure-sensitive adhesives.

Effect of Water-Soluble Comonomer

Results with and without small amounts of acrylamide as the water-soluble comonomer are summarized in Figure 5 and Table III.

It seems that a small amount of water-soluble comonomer, such as acrylamide, has no significant effect on the polymerization. However, the viscosity of the latex does increase significantly with the use of acrylamide. It is expected that acrylamide would increase the swelling of particle surface where it would normally concentrate; hence the "effective hydrodynamic volume" of polymer particles is greater. Acrylamide bound in the copolymer on the particle surface will undergo hydrolysis under alkaline conditions; this would also increase swelling and the electroviscous effect.

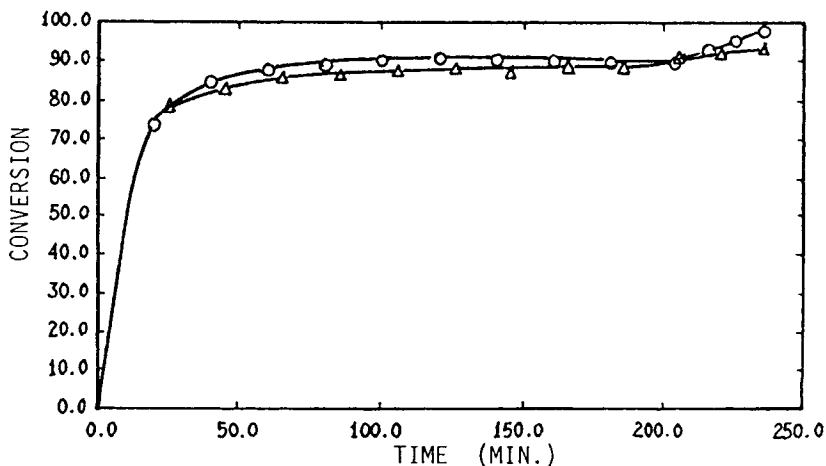


Fig. 5. Conversion history (semibatch polymerization)—effect of water-soluble comonomer acrylamide: (○) 0% acrylamide; (△) 0.5% acrylamide. Recipe: EHA/VAc/AA/AM/Aerosol A-102/ $K_2S_2O_8$ / H_2O = 68.6/29.4/1.5/variable/10.5/0.5/110. Temperature: batch periods 90°C; semibatch period 86°C.

TABLE III
Comparison of Latex Properties for Semibatch Polymerization at Different Acrylamide Levels^a

Level of acrylamide (%)	HDC peak diameter (Å)	Viscosity of latex (cP)	
		Before neut.	After neut.
0	1055	~ 200	260
0.5	1094	520	1240

^a Recipe: EHA/VAc/AA/AM/Aerosol A-102/ $K_2S_2O_8$ / H_2O = 68.6/29.4/1.5/variable/10.5/0.5/110. Polymerization temperature: 86°C. Operating policy: initial reactor charge 50% of recipe except for emulsifier, for which 1/21 parts is in the initial reactor charge.

Viscosity of Latex

The rheological properties of a latex are of practical importance because most uses of latexes in processing and in various coating applications require some control of viscosity. Therefore, knowledge of the factors that can be used to alter the rheological behavior of the latex system is of considerable value.

Carboxylated EHA-VAc latex is usually stored and applied under neutralized form in order to increase the stability of the latex and prevent potential corrosion problems. It is useful to measure the change of viscosity of the latex vs. pH under different degrees of neutralization.

As for most viscous latex systems, non-Newtonian flow is an interesting property of the carboxylated EHA-VAc system. Its behavior is shear thinning (pseudoplastic) in that the viscosity decreases with increasing shear rate (Fig. 6). The higher the viscosity, the more sensitive is the viscosity to shear rate.

A number of studies have been reported on the colloidal properties of carboxylated latexes showing the effect of neutralization on the viscosity and particle swelling characteristics of the latex. Fordyce et al.¹² reported a marked viscosity increase for latexes composed of MMA, EA, and MAA upon

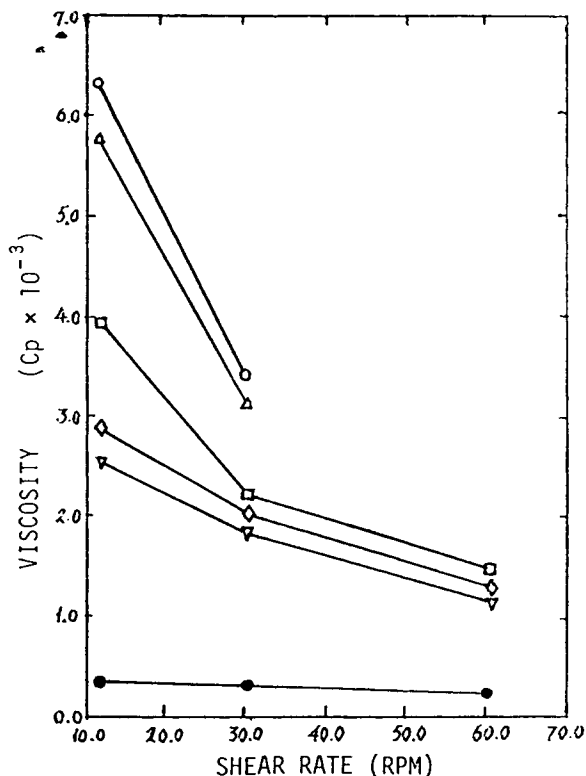


Fig. 6. Effect of pH and shear rate on latex viscosity: (○) pH 8.2; (△) pH 8.0; (□) pH 7.3; (◇) pH 6.08; (▽) pH 5.0; (●) pH 3.0.

addition of base. Wesslau¹³ developed a direct relationship between the ability of a latex to thicken and the volume change of the latex particle upon addition of ammonia. Muroi^{14,15} carried out some extensive swelling studies on polymers of alkyl acrylates and methacrylates with acrylic and methacrylic acid. Verbrugge^{16,17} has investigated the mechanism of alkali thickening of a number of acid-containing polymers by means of viscosity and light microscopy. He concluded that the peak viscosity of carboxylated latex on neutralization depends on (1) level of the carboxylic acid, (2) T_g of the copolymer, (3) hydrophobicity of the comonomer, and (4) to a certain extent, the configuration of an individual polymer chain. Peak viscosity increases with an increase in the level of carboxylic acid, with a decrease in T_g of a copolymer, and with increase in hydrophobicity of the comonomer.

As shown in Figure 7, the sensitivity of viscosity to pH depends on the level of AA and preparation method for the latex. The higher the level of AA, the higher the maximum viscosity. The viscosity of the latex produced by the semibatch operation is much less sensitive to pH than that by the batch mode. This suggests that for the semibatch operation more of the acid groups are trapped in the interior of the particle. Branching and crosslinking may be partially responsible for this lack of mobility of acid groups.

For most of the roll-coating equipment used commercially, it is preferred that the viscosity of the latex be in the range of 15–30 P. The viscosity

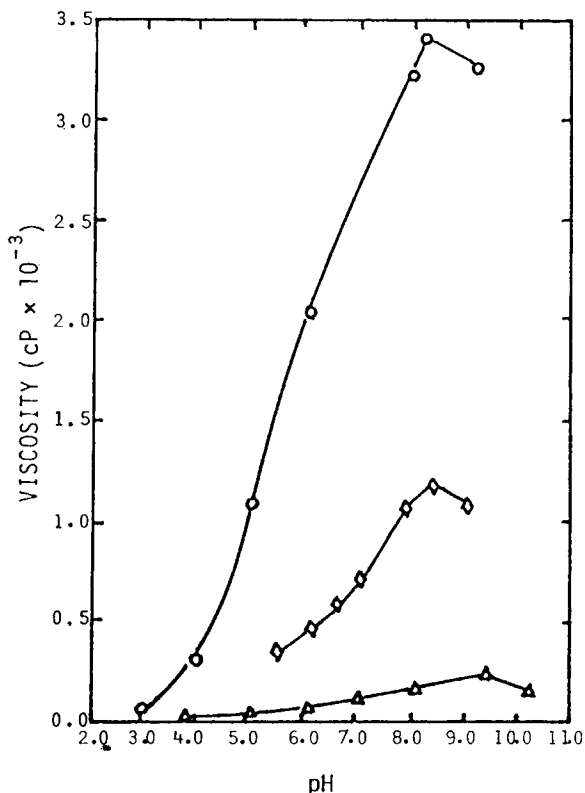


Fig. 7. Effect of acrylic acid level in terpolymer, synthesis process, and pH on latex viscosity: (○) 5% AA (batch polymerization); (◇) 5% AA (semi-batch polymerization); (△) 1% AA (batch polymerization).

increase of the latex containing a higher level of AA on neutralization must be controlled, therefore, to lower viscosity levels. It is well accepted that the increase in viscosity of carboxylated latices on neutralization is attributed to an increase of the effective hydrodynamic volume which results from an expansion of the electrical double layer and an increase of surface swelling. As the level of AA increases, so does the density of acid group on the surface and the surface charge density. As the electrical double layer thickens, the coulombic repulsion among particles increases, causing an increase in the latex viscosity. This is usually called the electroviscous effect. Surface swelling also increases as the density of acid groups on the surface increases. The viscosity of the latex increases because of the increase in the particle volume fraction due to surface swelling. Any method which can reduce the double layer expansion and surface swelling can reduce the viscosity increase on neutralization. The thickness of the electrical double layer and the surface swelling are very sensitive to the surface charge density and the electrolyte content. The addition of a salt such as sodium chloride is a simple and effective method to control the viscosity of latex. An increase of ionic strength by addition of salt can decrease the thickness of double layer and surface swelling and thus reduce the viscosity. However, if the ionic strength is too high, it would reduce

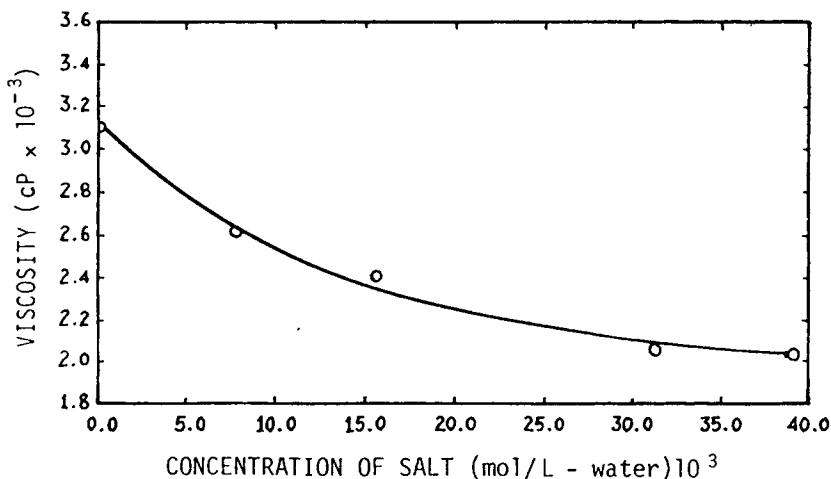


Fig. 8. Effect of salt (NaCl) on latex viscosity.

TABLE IV
Effect of Sodium Chloride Level on Latex Properties

NaCl [(mol/L) $\times 10^3$]	Latex viscosity (cP)	HDC peak diameter (\AA)
0	3108	1094
23.5	1960	1115
31.3	2060	1108

the stability of the latex. Since the concentration of salt has a significant effect on colloidal properties of emulsion systems, in order to prevent its effect on polymerization, salt should be added during the neutralization period.

The effect of salt addition on reduction in viscosity of latex is shown in Figure 8. It can be seen that viscosity of the latex decreases as the concentration of salt increases. In Table IV one can see that in the range of salt levels used the latex is stable with insignificant coagulation.

CONCLUSIONS

1. Polymerization rate of EHA-VAc-AA emulsion system depends on AA level for batch polymerization. With 5% AA there is significant coagulation so that the number of particles and the polymerization rate are less than that with 1% AA.

2. With semibatch operation with initial charge of portions of the recipe and a prepolymerization prior to semibatch feed, one gets a latex with larger particle and less surface swelling. This is preferred for high-speed, pressure-sensitive adhesives applications.

3. Addition of small amounts of acrylamide in the recipe has no significant effect on polymerization rate for semibatch polymerization. However, the viscosity of latex does increase.

4. The change of viscosity of EHA-VAc-AA latex depends on the level of AA and the operation policy with which the latex was prepared. With 5% AA the viscosity of the latex greatly depends on pH. Viscosity builds up significantly on neutralization. Addition of suitable amounts of sodium chloride can reduce this viscosity buildup without causing significant coagulation.

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