

# Emulsion Copolymerization of Vinyl Acetate and 2-Ethyl Hexyl Acrylate Using Nonionic Emulsifiers in Loop Reactor

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**ABSTRACT:** Batch emulsion copolymerization of vinyl acetate and 2-ethyl hexyl acrylate (VAc/2EHA = 90 : 10) was initiated by the thermal initiators ammonium persulfate and potassium persulfate at 70°C in the presence of nonylphenol ethoxylates with varying chain lengths and poly(vinyl alcohol). VAc-2EHA copolymer latexes were synthesized as two different series in a loop reactor. The first series was initiated by ammonium persulfate, and the second series was initiated by potassium persulfate. The influence of the counterions or initiators and chain lengths of a nonionic emulsifier on the properties of VAc-2EHA copolymer latexes were

determined by measuring the viscosities, weight-average molecular weights, number-average molecular weights, molecular weight distribution, and surface tension of latexes to air. The results for the copolymer latexes indicated that some of their physicochemical properties increased with increasing chain length of the nonionic emulsifier, but some of them followed a different trend for the two initiators. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1380–1384, 2005

**Key words:** vinyl acetate; 2-ethyl hexyl acrylate; emulsion polymerization; degree of ethoxylation

## INTRODUCTION

In general, particle stabilization is achieved by the use of various emulsifiers, which are employed in emulsion polymerization formulations. Anionic and nonionic emulsifiers are the most widely utilized emulsifiers because of enhanced compatibility with negatively charged latex particles (usually as a result of persulfate initiator fragments) compared to other emulsifiers. A further complication is that commercial emulsifiers often comprise a distribution of many different homologue molecules: in nonionic emulsifiers with chains of ethylene oxide (EO) units present, the number of EO units per emulsifier molecule chain may vary, as can the alky chain lengths.<sup>1</sup>

Copolymerization of vinyl acetate (VAc) with acrylic monomers can lead to the production of latexes having a wide range of molecular and mechanical properties, depending on the molecular structure of the emulsifier, copolymer composition, and initiating system. One of the most important industrial latexes, which is widely utilized in architectural (exterior or interior) coatings and the adhesives market, is the VAc/2-ethyl hexyl acrylate (2EHA) emulsion copoly-

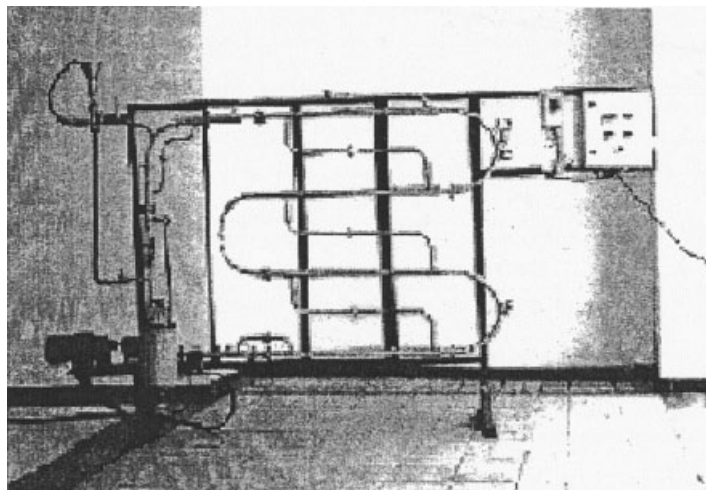
mer,<sup>1–3</sup> which has a 2EHA composition of 5–15%. The emulsion copolymerization of the VAc/2EHA system is characterized by large differences in reactivity ratios ( $r_{\text{VAc}} = 0.04$  and  $r_{\text{2EHA}} = 7.5$ ) and water solubilities (2.3 wt % for VAc and 0.01 wt % for 2EHA)<sup>3</sup> and is produced with various types of emulsifiers and initiators. Because of these significantly different monomer properties and copolymerization ingredients, latexes having a wide range of molecular properties can be obtained by varying the initiator type and chain length of the emulsifier, thus influencing the viscosity and molecular weight of latex paints.

The types of copolymerization processes are batch, semicontinuous, or continuous. The feeding type is an important factor affecting the final latex properties.<sup>4,5</sup> On the laboratory scale, the batch and semicontinuous methods are preferred because the reaction temperature can be controlled and homogeneous latexes are obtained in both cases.

Polymerization can be performed in classical reactors (such as glass or stainless steel) and a loop reactor (LR). The LR is one of the most important and attractive alternative production methods for emulsion homopolymers and copolymers. It was used for the first time in emulsion polymerization by Lanthier<sup>6</sup> at the beginning of the 1970s, and then it was improved as a continuous LR (CLR). Thanks to the effect of reactor geometries, the polymerization heat can be easily removed from the reactor and therefore high rates of polymerization can be reached during the process.

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**Figure 1** The configuration of the loop reactor.

This means that high conversions can be achieved during the short retention time in the reactor. A high conversion (98%) was obtained with a retention time in the reactor as short as 8 min, because of the large heat transfer area/small reactor volume.<sup>7</sup> It was achieved by decreasing the reactor volume. With a small volume and short retention time, a CLR can be used in the production of various emulsion polymers with minimum losses and high flexibility. Thus, the LR has been very advantageous to produce emulsion homopolymers or copolymers not only in industry but also in research or projects.

A number of studies have been published regarding the influence of the initiator type<sup>8,9</sup> and the chain length of the emulsifier<sup>10,11</sup> on the emulsion copolymerization of VAc-acrylic monomers [butyl acrylate (BuA), 2EHA, methyl methacrylate, etc.] and the latex properties.<sup>2-4</sup> Although 2EHA is one of the most preferable comonomers in emulsion copolymerization of VAc, there are also limited numbers of publications dealing with the use of nonionic emulsifiers for VAc-2EHA copolymer latex stabilization. Donescu et al. studied the microemulsion system that consisted of VAc, 2EHA, and nonyl phenol (NP) ethoxylate with 25 mol EO (NPEO25) or maleic monoester of NPEO25.<sup>12</sup> They used benzoyl peroxide as the initiator for that copolymerization.

In the present work, the emulsion copolymerization system containing VAc, 2EHA, ammonium persulfate (APS) or potassium persulfate (PPS), hydrolyzed poly(vinyl alcohol) (PVOH), NP ethoxylate (NP-*n*, where *n* designates the average chain length of the ethoxylate chain), NaHCO<sub>3</sub>, and water was studied in an LR. The effects of counterions and the chain lengths of the EO in the emulsifier on the physicochemical properties of the obtained VAc-co-2EHA latex properties were investigated.

## EXPERIMENTAL

### Materials

Argon Chemistry Inc. VAc and 2EHA monomers were used as commercial products. The stability of the latexes was achieved by a series of NPs (NP10, NP30, and NP40, Turkish-Henkel Chemicals Industry Co.) and alkyl aryl polyglycol ether with 25 mol EO (OP25, Turkish-Henkel Chemicals Industry Co.). Eighty-eight percent PVOH product (17-88, Argon Chemistry Inc.) was used as the protective colloid, APS (Merck) and PPS (Merck) were used as thermal initiators, Nopco 1497-V (nonsilicone antifoam agent based on octyl alcohol and tributyl phosphate) was used as an anti-foaming agent, and sodium bicarbonate (Merck) was used for adjusting the pH value of the polymerization media. The mixture of monomers was 90:10 (w/w) VAc/2EHA. All substances were used as received. Deionized water was used in all studies.

Copolymerization was carried out in the LR shown in Figure 1. The LR was designed with a jacket of stainless steel with a length of 6 m, an inner diameter of 1.34 cm, and an inner volume of 2.7 L. The loops connect the discharge and the suction of a gear pump that is made from stainless steel. This pump promotes emulsion movement by the eccentric rotation of a stainless steel rotor in a poly(tetrafluoroethylene) stator in order to prevent corrosion. The fluid velocity in the reactor can be changed by varying the pump speed between 0 and 400 rpm. A heat exchanger with a 3-kW resistance was used. The resistance has a thermostat operating between 50 and 150°C with a precision of  $\pm 1^\circ\text{C}$ . A pump was used to circulate the water in the reactor. Two solenoids were used to remove the excess heat in the environment during the polymerization reaction. The reaction temperature was measured digitally using two thermocouples. The pressure within

**TABLE I**  
**Recipes Used in Copolymerization Experiments**

Substance	Weight (%)
VAc	45.00
2EHA	5.00
PVOH 17-88	1.85
Emulsifier	2.00
APS or PPS	0.20
NaHCO <sub>3</sub>	0.12
Nopco	0.08
Water	45.75
Total	100.00

the loops was read from a manometer placed in the system.

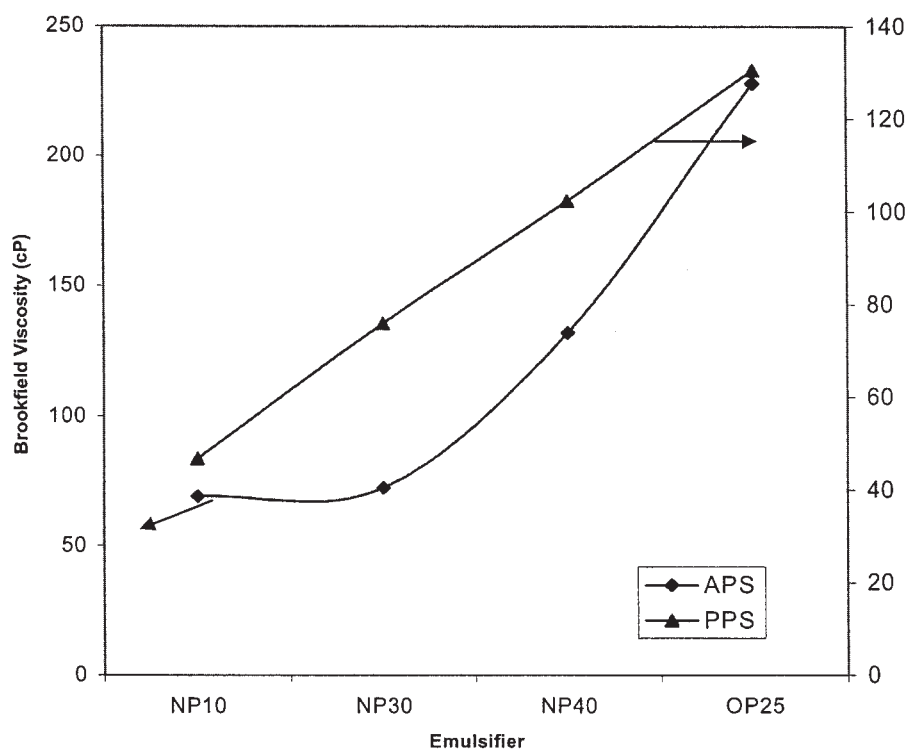
### Procedures

The 500 mL of water specified in the recipe was put into a beaker and a 10% stock PVOH solution and an emulsifier dissolved in water were added. All substances except the initiator were mixed thoroughly by a mechanical stirrer. NaHCO<sub>3</sub> (to maintain the emulsion pH at a fixed value between 4.5 and 5.5), Nopco, and monomers were added to this mixture and then stirred until a preemulsion was obtained. Before this preemulsion was fed into the reactor, the total amount of the initiator was dissolved in water and it was

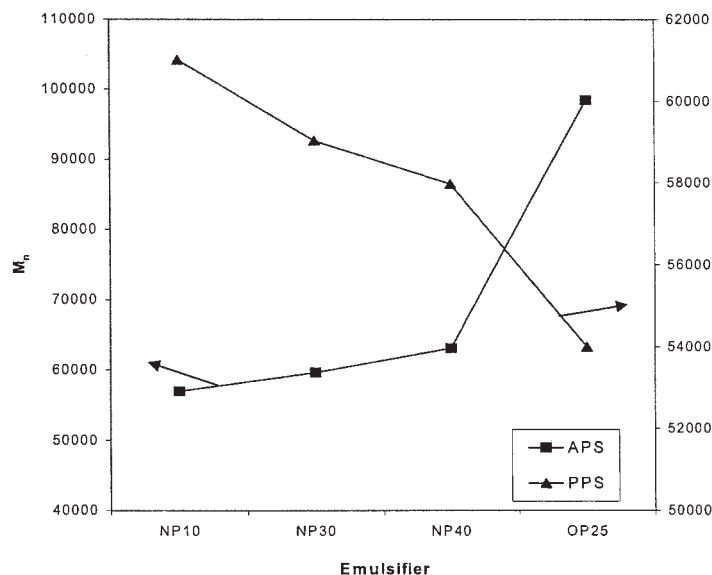
added into the emulsion. The general copolymerization recipe is given in Table I. The copolymerization procedure and the working process of the reactor were described in our previous study.<sup>13</sup>

Conversion was monitored gravimetrically. The viscosities of the copolymer latexes were determined by a Brookfield programmable DV-II model viscometer (using spindle number 4) at 26°C after diluting the 50 wt % solids content of all samples. The fractionation of the dried copolymer films was carried out according to Chujo et al.<sup>14</sup> and Sarac et al.,<sup>15</sup> because of the grafting structure of VAc and PVOH with other monomers. After separation of crosslinked portions of the copolymers, the benzene soluble fractions of the samples were extracted with THF for the determination of the molecular weight. THF was the diluent solvent with a flow rate of 0.3 mL/min at 30°C. The number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights of the copolymers were determined with a gel permeation chromatography (GPC) Agilent model 1100 type instrument with a refractive index detector and calibrated with polystyrene standards. The apparatus consisted of three Waters styragel columns (HR 4, HR 3, and HR 2).

The surface tensions of the produced latexes were measured after the total solids contents of the samples was adjusted to 25 wt % by diluting. The surface tension measurements were done by the ring-detach-



**Figure 2** The changes in the viscosity of the copolymer latexes with the chain length of the emulsifier when using ammonium persulfate or potassium persulfate as the initiator.



**Figure 3** The changes in the number-average molecular weight of the copolymer with the chain length of the emulsifier when using ammonium persulfate or potassium persulfate as the initiator.

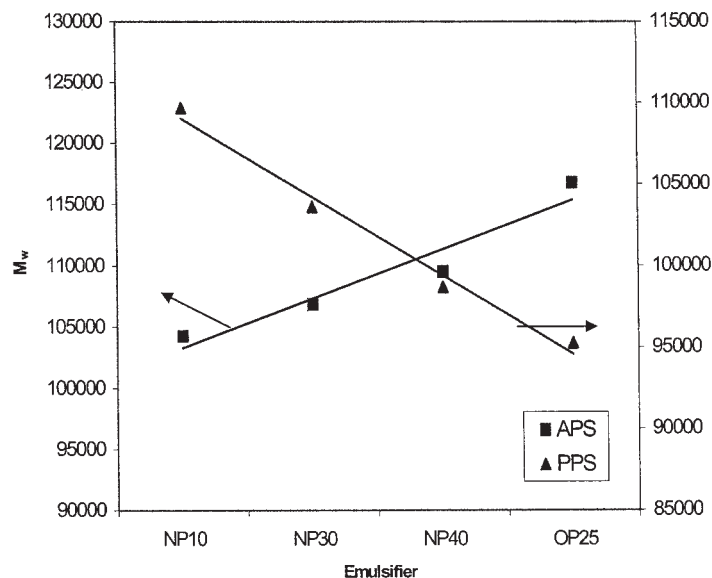
ment method with a torsion tensiometer and a platinum ring at 25°C.

## RESULTS AND DISCUSSION

### Viscosity

The copolymer viscosities were generally higher with the APS initiator than with PPS, except for ethoxylated NP40. Increasing the poly(EO) (PEO) block length caused an increase in the viscosities of copolymer latexes for two initiators (Fig. 2).

Latexes usually show Newtonian fluid behavior at very low concentrations, and surface layers can significantly increase the effective volume of latex particles. Such layers may be due to the adsorbed surfactants; adsorbed or reacted polymeric stabilizers such as PVOH, HEC, or PEO; and surface charges on the polymer particle. The smaller the particle size is, the greater will be the contribution of a surface layer of given thickness to the effective volume of the particle. The greater viscosity is, the greater will be the contribution of a surface layer of given thickness to the



**Figure 4** The changes in the weight-average molecular weight of the copolymer with the chain length of the emulsifier when using ammonium persulfate or potassium persulfate as the initiator.

effective volume of the particle. That effect can be explained by the fact that the viscosity depends on an effective particle volume that increases with increasing PEO block length. These results are in good agreement with the data of the viscosity of VAc-co-BuA latexes.<sup>1</sup> No data were found in the literature about the viscosities of VAc-co-2EHA latexes that were obtained by using nonionic emulsifiers with different chain lengths. We think that VAc-co-2EHA latexes can show core-shell structures like other VAc-co-acrylic latexes, especially VAc-co-BuA latexes. Acrylates (butyl and 2-ethylhexyl) are similar in their chemical properties, so a core-shell type structure can cause increases in the viscosities of VAc-co-2EHA latexes.

### Molecular weights of copolymers

The  $M_w$  and  $M_n$  of the poly(VAc-co-2EHA) copolymers were determined by GPC. Figure 3 shows that, despite using the same type of initiators, the  $M_n$  values increased when APS was used as the initiator in the synthesis of copolymers, but when PPS was used the  $M_n$  decreased with increasing PEO block lengths. The results are valid not only for the  $M_n$  but also for the  $M_w$  of the copolymers (Fig. 4).

As a result, the molecular weights of VAc-2EHA copolymers in the presence of PPS were higher than APS. According to the GPC results given in Table II, monodisperse copolymers (heterogeneity/polydispersity (HI) = 1.70–1.83) were obtained by using different initiators and nonionic emulsifiers with different chain lengths.

### Surface properties of latexes

Surface tension studies were carried out for surface characterization of latex films. The results obtained are shown in the Table III.

It was determined that the surface tensions of the copolymers increased with increasing chain length of the nonionic emulsifier when APS was used as the initiator. While the chain length was changing from 10 to 30, the surface tension increased very sharply for APS, in contrast to PPS. Generally, the surface tensions of copolymers obtained by using the same chain length of emulsifier did not reveal a large difference between them for the two initiators. Because of the

**TABLE II**  
Heterogeneity or Polydispersity Results of Copolymers

Initiator	Emulsifier			
	NP 10	NP 30	NP 40	OP 25
APS	1.83	1.79	1.73	1.70
PPS	1.80	1.76	1.71	1.70

**TABLE III**  
Surface Tensions of Copolymers

Initiator	$\gamma$ (mN/m)			
	Emulsifier			
	NP 10	NP 30	NP 40	OP 25
APS	30.6	43.9	44.5	41.8
PPS	37.5	42.6	43.2	41.8

adsorption nonionic emulsifier at the latex surface, the surface tensions of the samples were found to be 30–45 mN/m.

### CONCLUSION

Poly(VAc-co-2EHA) copolymer latexes were synthesized by using APS or PPS initiators, PVOH, and nonionic emulsifiers that have different chain lengths. A comparison of the physicochemical characteristics of VAc-2EHA copolymer latexes stabilized by NP ethoxylate molecules with varying chain lengths and PVOH was presented. The viscosities of copolymer latexes increased with increasing chain length of the emulsifier for the two initiators, and the molecular weights (number average and weight average) followed different trends. The surface tension of copolymer latexes to air increased with increasing chain length of emulsifier for two initiators.

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