

# Semicontinuous Emulsion Polymerization of Vinyl Acetate: Effect of Ethoxylation Degree of Nonionic Emulsifiers

Ayfer Sarac,<sup>1</sup> H. Yildirim Erbil,<sup>2</sup> Hüseyin Yildirim<sup>1</sup>

<sup>1</sup> Yıldız Technical University, Faculty of Sciences and Arts, Chemistry Department, 34210 Davutpaşa, Esenler, Istanbul, Turkey

<sup>2</sup> Kocaeli University, Faculty of Sciences and Arts, Department of Chemistry, 41300 Izmit, Kocaeli, Turkey

Received 31 July 2001; accepted 9 January 2002

**ABSTRACT:** Poly(vinyl acetate) latices were prepared in the presence of an ammonium persulfate initiator, 10–50 mol of an ethoxylated nonylphenol nonionic emulsifier, and a poly(vinyl alcohol) colloid stabilizer by applying semicontinuous emulsion polymerization (delayed monomer and initiator addition process) in a laboratory scale similar to industrial practice. Two approaches were applied: the molar concentration of the nonionic emulsifier was kept constant and the weight ratios in the polymerization recipe varied or the weight ratios were kept constant. The effects of the change in the ethoxylation degree of the emulsifier to the final latex viscosity, average polymer molecular weight,

polymer grafting degree, surface tension of the latex, and the surface free energy of the dried films were investigated. It was determined that the resultant latex viscosity decreases and the viscosity-average polymer molecular weight increases with increase of the nonionic emulsifier ethoxylation degree. The increase of the ethoxylation degree does not seriously affect the surface tension of the resultant latex or the surface free energy of the dried poly(vinyl acetate) films. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 844–851, 2002

**Key words:** poly(vinyl acetate); emulsion polymerization; surfactants; latices; adhesives

## INTRODUCTION

Commercial poly(vinyl acetate) emulsions are milky-white liquids containing 40–55% polymer solids, the balance being water and small amounts of emulsifiers, protective colloids, and other additives. They are water-based, cheap, and durable polymeric coatings, eliminating the expensive, toxic, odorous, and flammable solvents.<sup>1,2</sup> Poly(vinyl acetate) and vinyl acetate (VAc)–acrylic copolymer latices are very important in adhesives, paint, binders for nonwovens, paper and textile additive industries, and many related industries.<sup>1,3</sup> Their production is growing steadily both in actual quantities and different applications. They also possess rather unique properties among emulsion polymers in general, due to the high water-soluble nature of the VAc monomer, its high monomer–polymer swelling ratio, and its high chain-transfer constant.<sup>1,2</sup>

There are three important processes for preparing emulsion polymers: batch, semicontinuous (semibatch or delayed addition), and continuous. In the semicontinuous process, the monomer (which may or may not be emulsified) and the other ingredients are added

gradually to the stirred batch reaction vessel which is fitted with a reflux condenser and heating and cooling jacket. This is the most generally used process in industrial practice of VAc emulsion polymerization.<sup>1</sup> In this approach, most of the water and stabilizers and some of the initiator are added together with 0–10% of the VAc monomer. The initiator decomposes on heating the reactor contents to a suitable temperature and the monomer polymerizes. The exothermic heat output increases in temperature to a degree that is considered as the optimum temperature for the process. The remaining monomer and initiator is added incrementally during the polymerization period at a temperature higher than 75°C (usually between 75 and 85°C) over a period of 3–5 h. The rate at which a monomer can be introduced depends on the rate of polymerization and the cooling available. Emulsions prepared in this manner appear to be more stable than are emulsions prepared by the batch process and also have a smaller particle size.<sup>1,2</sup> Also, there are the continuous stirred tank reactor process (CSTR) and the loop reactor continuous process, which are outside of the scope of this paper.<sup>1</sup>

Chain-transfer reactions in VAc polymerization is important because the chain-transfer process retards the rate of polymerization of VAc much more than in the case for styrene or methyl methacrylate. Since the transfer constant to the polymer of VAc is larger than those for most other common monomers, branching of

Correspondence to: H. Y. Erbil (yerbil@kou.edu.tr).

polyVAc is of great practical and industrial importance.<sup>1</sup> In addition, the polymer film properties are also important. Most applications of polyVAc latices lead to the isolation of the polymer by the removal of water. The polymer acts as a binder between particles of pigment, as an adhesive for wood, paper, or other surfaces, or as a decorative and protective film on the surface. The state of division of the polymer has a strong influence on its properties, even in the dry state. The polymer should have a glass transition temperature below the temperature of drying or be plasticized by a suitable solvent. The surface free-energy properties of the dried films affect the final performance of the polymer as an adhesive or coating.

During VAc emulsion polymerization in the absence of a poly(vinyl alcohol) stabilizer,<sup>4-9</sup> the initiation takes place in the water phase with a water-soluble persulfate initiator, and an oligomeric aqueous polymer is formed. It is solubilized in water by its end groups, but it becomes insoluble as polymerization proceeds. The polymer particles formed absorb the monomer, and when conversion becomes about 14%, the rest of the monomer is absorbed substantially into the polymer particles and the separate monomer phase disappears at about 14–20% conversion. Then, the polymerization proceeds in the particles, which can be treated as a compartmentalized system. The molecular weights of polyVAc are independent of all variables and depend mainly on the chain transfer to monomer or chain-transfer agents. The number of particles in the reaction system was observed to decrease rapidly over the first 20% of conversion, but, thereafter, remained constant between 20 and 100% conversion, within experimental error. It was proposed that the loci of polymerization are both in the aqueous phase and in the micelles. The oligomers thus formed attain a certain size and then are precipitated from the aqueous phase. During precipitation, oligomeric particles release the emulsifier that kept them in equilibrium in the aqueous phase. The emulsifier release would form micelles to generate new particles. This theory explains the decrease in the number of particles during the course of the reaction and the fresh nucleation of particles even at high conversion.<sup>4-9</sup>

The number of particles in the same unit weight of latex is an increasing function of the emulsifier concentration. The percentage of the monomer converted to a polymer appeared to be most closely related to the total particle surface area per milliliter of emulsion. The total particle area was found to be the most important parameter to control the rate of VAc emulsion polymerization. When the total surface area of the particles exceeds the covering power of the emulsifier, the remaining polymer macromolecules and micro-particles are destabilized and can be swept up by larger particles.<sup>4-9</sup>

Elgood et al. were the first to investigate the semi-continuous emulsion polymerization of VAc.<sup>10</sup> They compared the results of two different recipes where only a nonionic emulsifier was used in the first one and both nonionic and anionic emulsifiers were used in the second recipe. They concluded that the total particle area was the most important parameter to control the rate of polymerization of the high water-soluble VAc monomer.<sup>10</sup> Bataille et al. found that the conversion–time curves were linear and dependent on the feed rates for all the runs in the semicontinuous emulsion polymerization of VAc.<sup>11</sup> The conversion of monomer to polymer was found to be a first-order reaction. Similar to Elgood et al.,<sup>10</sup> a linear increase in the rate of polymerization with increase in the surface area of particles per cm<sup>3</sup> of latex was also found.<sup>11</sup> Yeliseeva pointed out that the dependency of the polymerization rate to the emulsifier concentration was a function of the area occupied by the emulsifier molecule in the saturated adsorption layer on the polymer particles.<sup>12</sup> Depending on the extent of the dispersion, polar orientation, and hydrogen-bonding interactions, the emulsifier molecules adsorbed on the solid phase–liquid interface may acquire a nonvertical orientation, and the greater that the interaction acts upon the polar part of the emulsifier molecule, they may be arranged with greater planarity. The emulsifier adsorption decreases with increasing polarity of the polymer surface. Therefore, less emulsifier may be consumed for the formation of a given surface such as polyVAc, which facilitates increase of the overall surface area and decrease in the particle size.<sup>12</sup>

Warson pointed out that, for semicontinuous polymerization processes, only a limited quantity of a monomer, that is, 2–5%, is present in the system throughout the reaction. This is a *de facto* “seed” process, the seed quantity depending on the extent of the original addition of the initial monomer and other ingredients.<sup>13</sup> As long as the monomer weight percentage relative to the monomer plus the polymer is below 14%, there will be no monomer decreases as separate entities. Particle formation is complete at an early stage, stabilized by the adsorption of poly(vinyl alcohol), with possible extra stabilization due to initiator residues. Particle sizes increase by monomer absorption and by adsorption of initiated radicals from the water phase. Sometimes, bimodal molecular distribution occurs, indicating two different modes of polymerization: One is in the monomer-swollen particles and the other is the result of aqueous or surface initiation.<sup>13</sup> El-Aasser et al. examined the difference between batch and semicontinuous VAc emulsion homo- and copolymerization.<sup>14</sup> They determined that batch homopolymerization produced a narrower molecular weight distribution than did the semicontinuous process. The semicontinuous process produced a bimodal molecular weight distribution having a high

molecular weight fraction, which was attributed to chain transfer to a polymer due to monomer-starved conditions, and with a substantial amount of a low molecular weight fraction.<sup>14</sup>

In industrial practice, it has been customary to use a "protective colloid," notably hydroxyethyl cellulose or poly(vinyl alcohol), as the principal surface-active material in the VAc homopolymerization system rather than micelle generator emulsifiers. Some emulsifiers may also be added to the system, but their role seems to be secondary to that of the protective colloid. Protective colloids increase the viscosity of the water phase and impart water-sensitivity, haziness, and low scrub resistance to the film obtained by drying the latex. Experimental results showed that the viscosity, particle size, colloidal stability, and freeze-thaw stability of the final latex were determined largely by the fine chemical structure of the poly(vinyl alcohol) used in the polymerization. The final viscosity of polyVAc latices is very sensitive to the properties of the poly(vinyl alcohol)s used in their preparations. Increased adsorption of poly(vinyl alcohol) will result in a reduction of the average particle size and thus increase the latex viscosity. The addition of the poly(vinyl alcohol) reduced the maximum rate of VAc polymerization and the particle size. In 1958, O'Donnell et al. reported on a kinetics investigation of VAc emulsion polymerization at 70°C using potassium persulfate as the initiator and poly(vinyl alcohol) as the protective colloid.<sup>15</sup> It was observed that an increase in the poly(vinyl alcohol) concentration increased the rate of polymerization and there was a near constant ratio of the rate of polymerization to the 3/5th power of the poly(vinyl alcohol) concentration. Light-scattering measurements failed to provide evidence of micelle formation and the authors concluded that each molecule of poly(vinyl alcohol) might be a locus for the emulsion polymerization reaction.<sup>15</sup> Dunn and Taylor proposed that chain-transfer reactions between VAc and poly(vinyl alcohol) could occur, giving a graft copolymer, and retard the rate of polymerization because of the introduction of an alternative termination. Since the approach of a charged radical to a charged particle is not involved, then the termination between poly(VAc) and poly(vinyl alcohol) may be favored.<sup>7</sup>

Noro showed that the viscosity, particle size, stability, and freeze-thaw stability of the final latex were determined largely by the fine chemical structure of the poly(vinyl alcohol) used in the polymerization.<sup>16</sup> Gulbekian and Reynolds examined the optimum properties of the poly(vinyl alcohol) types, that is, their degree of hydrolysis and the average molecular weight on the polyVAc emulsion polymerization mechanism and the stability of the final latices.<sup>17</sup> They stated that the maximum conversion and minimum precipitate were obtained when 82.6–91.5% hydrolyzed poly(vinyl alcohol) with the maximum molecu-

lar weight of 4% (of the weight of the monomer) was used in conjunction with 2% of the monomer weight, 10 mol of an ethoxylated nonylphenol nonionic emulsifier. Gulbekian and Reynolds also pointed out the interactions of the poly(vinyl alcohol) with the persulfate initiators, which degrades the poly(vinyl alcohol) macromolecule by an oxidation reaction, resulting in a loss in emulsion viscosity.<sup>17</sup> Warson pointed out that, usually, 88% hydrolyzed poly(vinyl alcohol) is used as a stabilizer in the VAc polymerization, but the variations in the structure, branching, tacticity, and production methods of poly(vinyl alcohol) resulted in latices having different properties.<sup>18</sup> He suggested that the VAc polymer has a grafting tendency onto poly(vinyl alcohol) in the semicontinuous process and sometimes excessive grafting would cause instability when nonionic emulsifiers are also added, since the overall molecules of poly(vinyl alcohol) are not sufficiently hydrophilic after grafting unless some ionic groups have been introduced.<sup>18</sup> Dunn showed that the final viscosity of polyVAc latices is very sensitive to the properties of the poly(vinyl alcohol)s used in their preparations. Increased adsorption of poly(vinyl alcohol) will result in a reduction of the average particle size and, thus, an increase in latex viscosity.<sup>19</sup> Donescu et al. determined that the glass transition temperature of polyVAc decreases due to formation of a hydration shell when polyVAc latices are obtained in the semicontinuous process in the presence of poly(vinyl alcohol).<sup>20</sup> They reported the existence of bound water on the polymer particles using DTG and TGA measurements during the evaporation of polyVAc latices. Water was considered as a true plastifier.<sup>20</sup>

Lepizzera and Hamielec investigated the particle nucleation mechanism in seeded emulsion polymerization of VAc in the presence and absence of poly(vinyl alcohol).<sup>21</sup> In the absence of poly(vinyl alcohol), no new nucleation was observed by electron microscopy, while in its presence, new particles were formed, giving a bimodal particle-size distribution. The number of new particles was greater with a higher molecular weight poly(vinyl alcohol). The authors proposed that nucleation of new particles occurs via precipitation of "copolymer" poly(vinyl alcohol)–polyVAc radicals in the water phase.<sup>21</sup> Warson suggested that, in the semicontinuous process, under monomer-starved and high temperature conditions, high grafting to poly(vinyl alcohol) or possibly onto polyVAc molecules occurs. Excessive grafting to poly(vinyl alcohol) causes an increase in latex viscosity and instability.<sup>13</sup> Okaya et al. used 88% hydrolyzed poly(vinyl alcohol) and 40 mol of an ethoxylated nonylphenol nonionic surfactant as an emulsifier in the semicontinuous polymerization of VAc.<sup>22</sup> Short branches and a low degree of polymerization resulted due to the higher chain-transfer reactions. Polymer films obtained from the latices prepared in the presence of poly(vinyl alcohol) re-

sulted in higher tensile strengths than of those prepared with only nonylphenol ethoxylates, presumably due to the formation of a reinforcing poly(vinyl alcohol) structure.<sup>22</sup> Gilmore et al. modeled poly(vinyl alcohol)-stabilized semicontinuous VAc emulsion polymerization<sup>23</sup> and compared their model with experimental findings. Their model suggests that, when the molar ratio of VAc to poly(vinyl alcohol) is high, physical adsorption of poly(vinyl alcohol) onto the latex particle is a more important process than is grafting.<sup>23</sup>

In our work, the effect of the ethoxylation degree of ethoxylated nonylphenol nonionic emulsifiers in the semicontinuous emulsion polymerization of the VAc monomer in the presence of 88% of a hydrolyzed poly(vinyl alcohol) colloid stabilizer was examined to determine the effect to the final latex viscosity, average polymer molecular weight, polymer grafting degree, latex surface tension, and surface free energy of the dried films.

## EXPERIMENTAL

### Materials

A Hoechst-Celanese (Germany) VAc monomer inhibited with 15 ppm *p*-hydroquinone was used directly without any purification. Eighty-eight percent hydrolyzed Goshenol (Japan) PVOH products were used in two different molecular weights and viscosities. Gohsenol-GL-05 (5-88) and Gohsenol,-GM (23-88). 10, 20, 30, 40, and 50 mol ethoxylated nonylphenol products of the Turkish-Henkel Chemicals Industry Co. (Turkey) were used as nonionic emulsifiers without any purification. Merck ammonium persulfate was used as received as an initiator. Nopco-1497 was used as an antifoam agent. Merck sodium bicarbonate was used as a buffer to keep the pH of the reaction medium between 4.5 and 5.5. Deionized water was used in all the polymerizations. A typical recipe of the emulsion polymerization used in the experiments is given in Table I.<sup>24</sup>

TABLE I  
Typical Emulsion Polymerization Recipe

	Percent weight
VAc	50.00
PVOH (5-88)	1.00
PVOH (23-88)	1.50
Nonionic emulsifier	0.80
Ammonium persulfate	0.25
Sodium bicarbonate	0.12
Antifoam agent	0.04
Deionized water	46.29
Total	100.00

### Methods

Polymerizations were done in a 1-L glass emulsion polymerization reactor equipped with a mechanical stirrer having a constant speed of 175 rpm and a reflux condenser in a total batch period of 6 h. Only 10% of the total VAc monomer was introduced at the beginning of the reaction at 60°C and the remaining monomer was added dropwise at  $71 \pm 2^\circ\text{C}$  from dropping funnels during the remaining time. An ammonium persulfate initiator was dissolved in a small amount of water and these freshly prepared initiator portions were added at 30-min intervals throughout the reaction.

Polymer conversion was monitored gravimetrically. The viscosities of the latices were determined by using a Brookfield LVT viscometer with spindle number 4 at 24°C. The fractionation of the dried latex film was carried out as follows: Dried film was first extracted by distilled water at the boiling point to separate "water-soluble" (WS) poly(vinyl alcohol) and poly(vinyl alcohol)-poly(VAc) graft copolymer portions. Then, the linear and branched poly(VAc) polymer was extracted by benzene from the remaining dried polymer as "water-insoluble-benzene soluble" (WI-BS) portions. The last undissolved portion was the cross-linked polymer.

Molecular weights of the benzene-extracted fraction of the polymer were determined by GPC in the THF solvent and by capillary intrinsic viscometry. Viscosity-average molecular weight ( $M_v$ ) values of the polymers were determined using a Ubbelohde-type viscometer in a benzene solvent at 30°C. Mark-Houwink constant values of  $a = 0.62$  and  $k = 56.3 \times 10^{-5} \text{ (dL/g)}^{24}$  were used in the calculations. Number-average ( $M_n$ ) and weight-average ( $M_w$ ) polymer molecular weights were determined using a GPC Waters Model M 6000-A type instrument with a refractive index detector and calibrated with polystyrene standards.

The surface tensions of the produced latices were measured after the total solids concentration of the latex was adjusted to 25% by weight by diluting the latex with deionized water. A ring-detachment method was used with a torsion tensiometer and a platinum ring at 25°C. The surface free energies of the dried poly(VAc) films were calculated by determining the contact angles of water, glycerol, ethylene glycol, formamide, and paraffin oil drops on the dried polymer substrate and by applying van Oss-Good surface tension component methodology. A Kernco model contact angle tester was used.

## RESULTS AND DISCUSSION

The polymer conversions were found to vary between 97.8 and 99.8% and, thus, the emulsion homopolymerization was assumed to be complete in all the runs.

TABLE II  
Physical Properties of Nonylphenol Ethoxylate Nonionic Emulsifiers<sup>25</sup>

Ethoxylate no: (Moles)	Molecular weight (g/mol)	Ethylene oxide (wt %)	Solidification point ( $\pm 1^\circ\text{C}$ )	CMC aq (25°C) ( $10^{-6}$ mol/L)	$\gamma^a$ 0.01% Water Sl.	$A^b$ in water at CMC
10	660	66.7	7	75	32	58
20	1100	80.0	30	140	39	82
30	1540	85.7	40	153	41	101
40	1980	88.9	41	200	45	115
50	2420	90.9	42	280	48	126

<sup>a</sup> Surface tension of aqueous solution at 25°C (mN/m).

<sup>b</sup> Molecular area ( $\text{\AA}^2$ ).

Ethoxylated nonylphenol emulsifiers [ $\text{C}_9\text{H}_{19}-\text{C}_4\text{H}_4-(\text{OCH}_2\text{CH}_2)_n\text{OH}$ ] are not pure products; they are a mixture of many ethoxylated molecules which are synthesized during the ethoxylation process and usually the Poisson distribution can be applied.<sup>25</sup> The highest ethoxylation proportion is used to name the product, such as  $n = 10$  mol ethoxylated. In practice, the stoichiometric molecular weights are used to calculate molar concentrations. Some of their physical properties were taken from ref. 25 and are given in Table II. As seen in this table, large differences take place in average molecular weights and the molecular area of emulsifiers in water solutions at critical micelle concentrations (CMCs) by changing the ethoxylation degree from 10 to 50.

When the ethoxylation degree (the number of ethylene oxide units per unit of nonylphenol) in the nonionic emulsifier was increased from 10 to 50, it was found that the viscosities of the resulting latices decreased. This factor was examined in two different ways: In the first case, the emulsifier was used in a constant weight ratio (0.8%) in the polymerization recipe and the type of the emulsifier was varied. Thus, by increasing the ethoxylation number, the molar con-

centration of the emulsifier was decreased. This case is given in Figure 1. A sharp latex viscosity decrease is seen with an increase of the ethoxylation degree for the latices having a constant emulsifier weight percent in this figure. When the emulsifier molar concentration decreases, it is expected that the number of initial polymer particles should decrease, thus increasing the size of the particles at the end of the polymerization. The particle size is inversely proportional to the latex viscosity and an increase of the particle size results in a decrease of the latex viscosity. As an indication of this fact, Figure 2 shows an increase of the latex viscosity with an increase of the emulsifier concentration for the constant weight concentration. In this figure, emulsifier concentrations were calculated using the average molecular weights of each emulsifier type for a constant (0.8% wt) recipe ratio.

For the second case, where the emulsifier molar concentration was kept constant ( $0.52 \times 10^{-3}$  mol/L) and, thus, the weight ratios in the polymerization recipe were varied, a nearly linear decrease of latex viscosity with increase of the ethoxylation degree is seen in Figure 3. This constant emulsifier molar con-

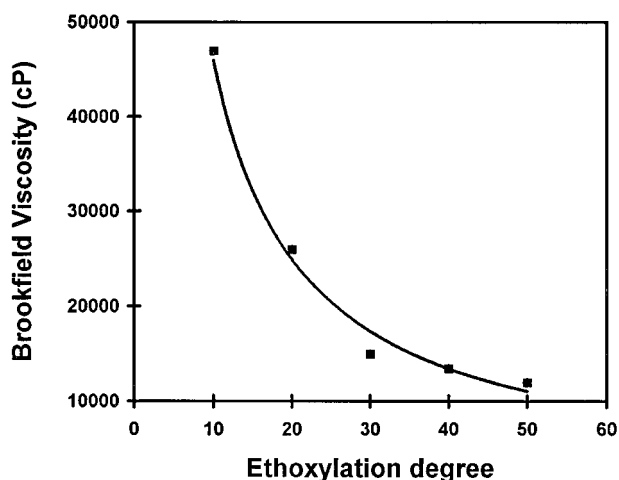


Figure 1 Change of latex viscosity with change in the ethoxylation degree of the emulsifier, when a constant emulsifier weight ratio is applied in the polymerization recipe.

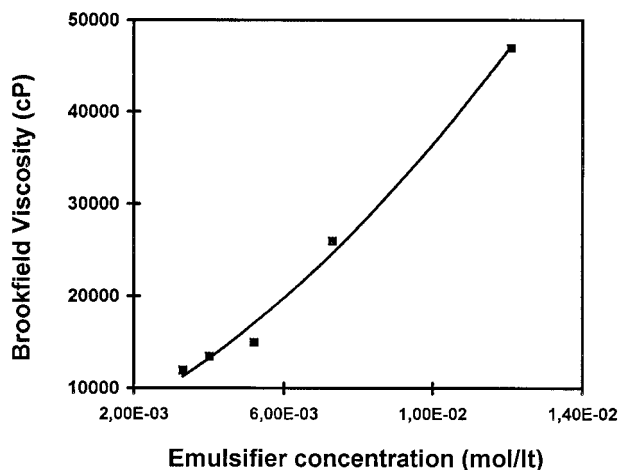
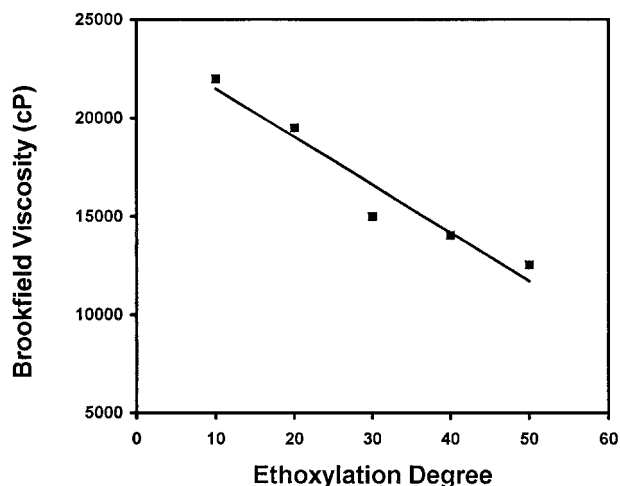
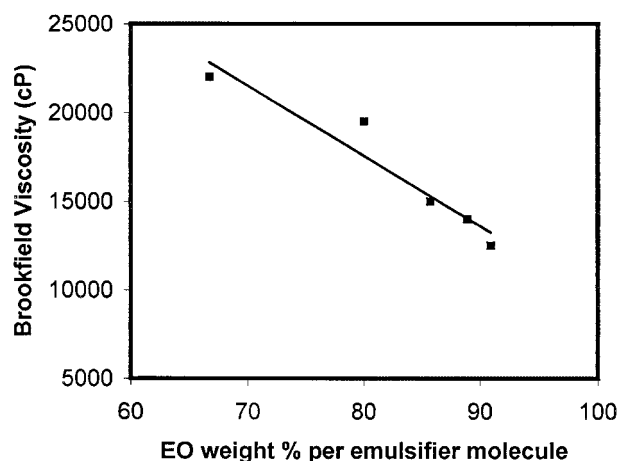


Figure 2 Change of latex viscosity with change in the emulsifier concentration of different types, when a constant emulsifier weight ratio is applied in the polymerization recipe.

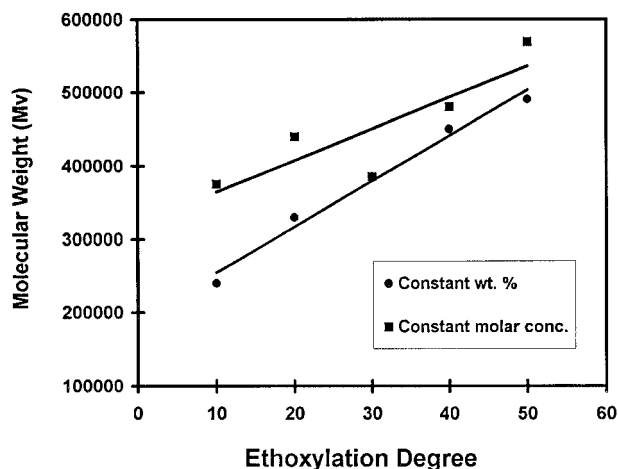


**Figure 3** Change of latex viscosity with change in the ethoxylation degree of the emulsifier, when a constant emulsifier molar concentration is applied in the polymerization recipe.

centration corresponds to the increase of the emulsifier weight concentration from 0.34 to 1.26 g/L with the increase of the ethoxylation degree from 10 to 50, but the molar concentration of nonylphenol groups are constant in all runs. The only variation is an increase in the ethylene oxide units. Since all the emulsifier molar concentrations are the same, theoretically, no effect on the particle size is expected from the emulsifier concentration per particle for this case. However, the higher the ethylene oxide content per emulsifier molecule, the lower is the latex viscosity, as seen in Figure 4, indicating that the higher the ethylene oxide content, the higher is the particle size, which corresponds to that the higher the ethylene oxide content, the lower is the initial number of polymer particles. This is the indirect result of an adsorption of



**Figure 4** Change of latex viscosity with change in the ethoxylation weight percent per emulsifier molecule, when a constant emulsifier molar concentration is applied in the polymerization recipe.

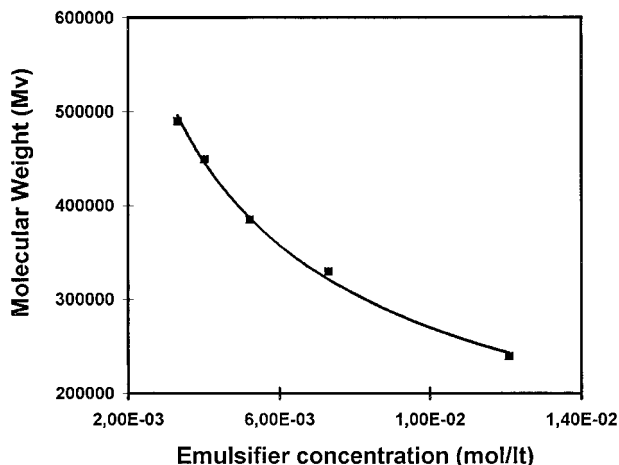


**Figure 5** Change of viscosity-average molecular weight with change in the ethoxylation degree of the emulsifier, both when a constant emulsifier weight ratio and a constant emulsifier molar concentration are applied in the polymerization recipe.

emulsifier on the polymer particle by the hydrophobic nonylphenol group. When the nonylphenol group concentration is kept constant, the higher the ethoxylation degree, the larger is the final polymer particle due to the resulting higher molecular surface area and of the higher covering power of the emulsifier molecules on the polymer particle surface. This means that the use of high nonylphenol content (low ethylene oxide content) emulsifiers, such as 10-mol ethoxylated types, resulted in small particle sizes and high latex viscosities for the constant emulsifier molar concentration experiments due to their low particle covering power.

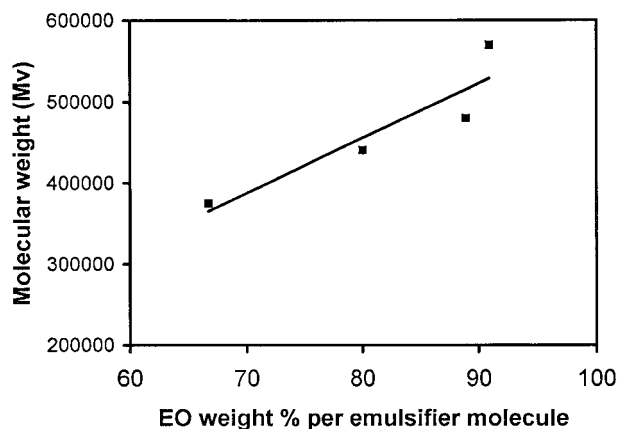
Fractionation results of the dried latex films gave only a small scattering: In the water-soluble fraction, only  $4.2 \pm 2.5$  wt % of the total solids, consisting of free poly(vinyl alcohol), a free nonionic emulsifier, and poly(vinyl alcohol)-poly(VAc) graft copolymers with very small amounts of PVAc, was found. In the benzene-soluble fraction,  $86.9 \pm 4.1$  wt % of the total solids, consisting of ungrafted PVAc and a graft copolymer with a high content of PVAc, was found. In the insoluble fraction,  $8.2 \pm 4.8$  wt % of the total solids, networks consisting of PVAc crosslinked with poly(vinyl alcohol) and also a semi-interpenetrating PVAc polymer structure, was found. Only one proportionality was realized: When the molar concentration of the emulsifier was kept constant, the higher the ethoxylation number, the higher was the benzene soluble fraction and the lower the insoluble fraction obtained. This shows that the adsorption of nonionic emulsifiers having long ethoxyl chains on PVAc particles has the effect of preventing crosslinking and interpenetrating network formation.

Molecular weights (viscosity average) of the benzene-extracted linear and branched poly(VAc) in-



**Figure 6** Change of viscosity-average molecular weight with change in the emulsifier concentration of different types, when a constant emulsifier weight ratio is applied in the polymerization recipe.

creased with increase in the ethoxylation number, as seen in Figure 5 for both cases of when a constant emulsifier weight ratio and a constant emulsifier molar concentration are applied in the polymerization recipe. For the latices having a constant emulsifier weight percent, a decrease of polymer molecular weights is seen with increase in the emulsifier concentration, as given in Figure 6. The higher emulsifier concentration resulted in smaller polymer particles and the higher number of particles per milliliter of latex increases the rate of polymerization and thus decreases the resultant polymer molecular weight. The increase of the ethylene oxide phenol content for the constant emulsifier concentration resulted in a decrease in the polymer molecular weight, as seen in Figure 7.



**Figure 7** Change of viscosity-average molecular weight with change in the ethoxylation weight percent per emulsifier molecule, when a constant emulsifier molar concentration is applied in the polymerization recipe.

**TABLE III**  
Relation Between Ethoxylation Degree and Surface Tension of the Latices

Measurement	Latex surface tension (mN/m)				
Ethoxylation degree	10	20	30	40	50
Constant weight ratio	41.7	41.7	43.0	43.2	42.4
Constant molar concentration	36.5	41.9	43.0	43.2	43.2

It was determined that increase of the ethoxylation degree of the nonionic emulsifier in an emulsion homopolymerization of VAc initiated by a persulfate does not affect the surface tension of the resultant latex seriously, as seen in Table III. Table IV shows that the measurement of the surface free energy of dried latex films gave reasonably scattered results. After measuring the contact angles of water, glycerol, ethylene glycol, formamide, and paraffin oil drops on dried polymer films, van Oss–Good methodology<sup>26</sup> was applied, and the average Lifshits–van der Waals surface free-energy component,  $\gamma^{LW}$ , which is related mainly to long-range dispersion and polar and induction forces, was found to be  $27.2 \pm 0.6$  mJ/m<sup>2</sup> and the acid–base surface free-energy component,  $\gamma^{AB}$ , which is related mainly to short-range hydrogen-bonding forces, was found to be  $15.5 \pm 3.0$  mJ/m<sup>2</sup>, giving a total surface free-energy component of  $\gamma^{TOT} = 42.7 \pm 2.8$  mJ/m<sup>2</sup>. As seen in Table IV, the main variation was seen in the Lewis-base (electron-donor) component ( $\gamma^-$ ), which is given by the relation

$$\gamma^{AB} = 2 \sqrt{\gamma^- \gamma^+} \quad (1)$$

and can be calculated directly from the simultaneous solution of the general contact angle equation:

$$\begin{aligned} \gamma L (1 + \cos \theta) \\ = 2 (\sqrt{\gamma_s^{LW} \gamma_L^{LW}} + \sqrt{\gamma_s^+ \gamma_L^-} + \sqrt{\gamma_s^- \gamma_L^+}) \quad (2) \end{aligned}$$

When the molar concentration of the emulsifier was kept constant, the higher the ethoxylation number, the higher was the  $\gamma^-$  found, showing the effect of additional oxygen atoms in the ethoxyl group on the surface energetic properties.

## CONCLUSIONS

In this work, poly(VAc) homopolymer latices were prepared in the presence of an ammonium persulfate initiator, a 10–50 mol ethoxylated nonylphenol nonionic emulsifier, and a poly(vinyl alcohol) colloid stabilizer by applying semicontinuous emulsion polymerizations. It was determined that when the weight ratio of the emulsifiers in the recipe was kept constant the resultant latex viscosity decreases and the viscos-

**TABLE IV**  
**Surface Free-energy Change of Dried Latex Films by**  
**Varying the Ethoxylation Degree of Nonionic Emulsifier**  
**for the Constant Emulsifier Molar Concentration**  
**( $0.52 \times 10^{-3}$  mol/L)**

Ethoxylation no.	$\gamma^+$	$\gamma^-$	$\gamma^{AB}$	$\gamma^{LW}$	$\gamma^{TOT}$
10	0.63	49.66	11.19	27.92	39.08
20	1.25	57.98	17.03	26.83	43.83
30	2.85	26.11	17.25	27.50	44.76
40	1.35	45.60	15.69	26.83	42.52
50	1.81	36.96	16.36	26.92	43.26

ity-average polymer molecular weight increases by increase of the ethoxylation degree due to increase of the emulsifier molar concentration for this case. However, when the molar concentration of the emulsifier was kept constant, the weight ratios in the polymerization recipe of each type thus varied; the resultant latex viscosity also decreased and the viscosity-average polymer molecular weight also increased more regularly with increase of the ethoxylation degree, but, this time, the reason is the increase of the ethylene oxide content. Increase of the ethoxylation degree does not seriously affect the surface tension of the resultant latex or the surface free-energy values of the dried PVAc films.

## References

1. Erbil, H. Y. *Vinyl Acetate Emulsion Polymerization and Copolymerization with Acrylic Monomers*; CRC: Boca Raton, FL, 2000.
2. *Emulsion Polymerization of Vinyl Acetate*; El-Aasser, M. S.; Vanderhoff, J. W., Eds.; Applied Science: London, 1981.
3. Erbil, H. Y. *Polymer* 1996, 37, 5483.
4. Priest, W. J. *J Phys Chem* 1952, 56, 1077.
5. French, D. M. *J Polym Sci* 1958, 32, 395.
6. Napper, D. H.; Alexander, A. E. *J Polym Sci* 1962, 61, 127.
7. Dunn, A. S.; Taylor, P. A. *Makromol Chem* 1965, 83, 207.
8. Patsiga, R.; Litt, M.; Stannett, V. *J Phys Chem* 1960, 64, 801.
9. Chang, K. H. S.; Litt, M. H.; Nomura, M. In *Emulsion Polymerization of Vinyl Acetate*; El-Aasser, M. S.; Vanderhoff, J. W., Eds.; Applied Science: London, 1981; Chapter 6, p 89.
10. Elgood, B. G.; Gulbekian, E. V.; Kinsler, D. *Polym Lett* 1964, 2, 257.
11. Bataille, P.; Van, B. T.; Pham, Q. B. *J Appl Polym Sci* 1978, 22, 3145.
12. Yeliseeva, V. I. In *Emulsion Polymerization*; Piirma, I., Ed.; Academic: New York, 1982; Chapter 7.
13. Warson, H. *Chem Ind* 1983, 220.
14. El-Aasser, M. S.; Makgawinata, T.; Vanderhoff, J. W. *J Polym Sci Part A Polym Chem* 1983, 21, 2363.
15. O'Donnell, J. T.; Mersobian, R. B.; Woodward, A. E. *J Polym Sci* 1958, 28, 171.
16. Noro, K. *Br Polym J* 1970, 2, 128.
17. Gulbekian, E. V.; Reynolds, G. E. In *Polyvinyl Alcohol: Properties and Applications*; Finch, C. A., Ed.; Wiley: London, 1973; Chapter 17.
18. Warson, H. In *Emulsion Polymerization of Vinyl Acetate*; El-Aasser, M. S.; Vanderhoff, J. W., Eds.; Applied Science: London, 1981; Chapter 1, p 1.
19. Dunn, A. S. In *Emulsion Polymerization of Vinyl Acetate*; El-Aasser, M. S.; Vanderhoff, J. W., Eds.; Applied Science: London, 1981; Chapter 2, p 11.
20. Donescu, D.; Ciupitoiu, A.; Gosa, K.; Languri, I. *Rev Roum Chim* 1993, 38, 1441.
21. Lepizzera, S. M.; Hamielec, A. E. *Macromol Chem Phys* 1994, 195, 3103.
22. Okaya, T.; Tanaka, T.; Yuki, K. *J Appl Polym Sci* 1993, 50, 745.
23. Gilmore, C. M.; Poehlein, G. W.; Schork, F. J. *J Appl Polym Sci* 1993, 48, 1449, 1461.
24. Sarac, A. Ph.D. Thesis, Yildiz Technical University, Department of Chemistry, 1998.
25. *Nonionic Surfactants*; Schick, M. J., Ed.; Marcel Dekker: New York, 1966.
26. Erbil, H. Y. In *Handbook of Surface and Colloid Chemistry*; Birdi, K. S., Ed.; CRC: Boca Raton, FL, 1997; Chapter 9.