

Effect of Initiators and Ethoxylation Degree of Non-Ionic Emulsifiers on Vinyl Acetate and Butyl Acrylate Emulsion Copolymerization in the Loop Reactor

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Received 22 May 2002; accepted 13 January 2002

Abstract: Vinyl acetate and butyl acrylate copolymers were synthesized in the presence of ammonium persulfate and potassium persulfate initiators, mixture of non-ionic and anionic emulsifiers, and polyvinyl alcohol as protective colloid in a loop reactor. The monomer ratio was chosen 85:15. The series of non-ionic emulsifiers, which have 10–40 moles ethoxylated nonyl phenol, were combined with Nansa 66 (sodium dodecyl benzene sulfonate). The effects of the initiators on the physicochemical properties of copolymers were investigated by measuring conversion, viscosity, molecular weight, molecular weight distribution, and surface tension, respectively by using gravimetric method, Brookfield viscometer, gel permeation chromatography (GPC), and ring method. The effects of ethoxylation degrees of the non-ionic emulsifiers to the same properties of copolymers were also investigated. It was determined that the copolymer viscosities showed different tendency for two

initiators. They were increased by the increasing ethoxylation degree of the non-ionic emulsifier for ammonium persulfate. In contrast, latex viscosity was decreased by increasing the ethoxylation degree in presence of potassium persulfate. Similar changes were also found in number average molecular weights of copolymers. On the other hand, weight average molecular weights of copolymers increased by increasing the ethoxylation degree of the non-ionic emulsifier for both initiators. In the case of potassium persulfate, the surface tension values of copolymers increased by increasing the ethoxylation degree, but generally increasing the ethoxylation degree did not affect the surface tension of copolymer very seriously for two initiators. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 537–543, 2003

Key words: vinyl acetate; butyl acrylate; emulsion polymerization; degree of ethoxylation

INTRODUCTION

Vinyl acetate (VAc) copolymers are generally water based, milky-white liquids containing 48–55% solids, the balance being water and small amounts of emulsifiers, protective colloids, and other additives. VAc can be copolymerized with many monomers, especially butyl acrylate^{1–19} (BuA), 2-ethyl hexyl acrylate, Veova 10, methyl metacrylate, and so on, by applying different monomer compositions and using bulk, suspension, and emulsion polymerization methods. Among them, the most preferred is VAc-BuA monomer couple (due to their superior product properties) and the commonly used method for copolymerization is emulsion polymerization.²⁰ This is true because emulsion polymerization produces polymerization products (latex) having the most convenient properties. Polyvinyl acetate (PVAc) and VAc-acrylic copolymer latexes are generally used as binders in water-based interior and exterior architectural paints, since they have higher mechanical and water resistance properties than the homopolymers of both monomers.

Emulsion homo- and copolymers can be synthesized by applying different production process and using different reactors, such as continuous stirred tank reactor (CSTR), the multireactor train, and the tubular or loop reactor (LR).²¹ Especially in the last three decades, many kinds of reactors have been developed by researchers.^{22,23} LR is one of the most important and attractive alternative production method for the emulsion homo- and copolymers. LR was used for the first time in emulsion polymerization by Lanthier²⁴ at the beginning of 1970s, and then it was improved as a continuous loop reactor (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. That means 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 minutes, owing to the large heat transfer area/small reactor volume.²⁵ This was achieved by the decrease of the reactor's volume. With small volume and short retention time, CLR can be used in the production of various emulsion polymers with minimum losses and high flexibility. LR has been very advantageous in producing emulsion homo- or copolymers in research and industry.

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Lazaridis, Alexopoulos, and Kiparissides investigated the effect of the surfactant molecular structure and concentration on the polymerization kinetics, latex stability, and particle size distribution for semi-batch emulsion copolymerization of VAc and BuA.¹⁹ It was found that the latex particle stability and the rate of polymerization increased with an increase in the surfactant concentration, and the latex particle stabilization significantly depended on the surfactant structure. They also found that optimum particle stabilization could be achieved at a specific hydrophilic/hydrophobic chain length ratio of the surfactant.

Vijayendran, Bone, and Gajria classified the adsorption behavior of anionic emulsifiers as penetrating and nonpenetrating types, especially interaction of anionic emulsifiers with PVAc latex.²⁶ It was found that latex thickening was dependent on polymer composition using penetrating type anionic emulsifiers such as sodium dodecyl benzene sulfonate.

El-Asser, Makgawinata, and Vanderhoff synthesized VAc-BuA copolymers with various composition by applying batch and semi-continuous emulsion polymerization processes.⁴ In their study, the monomer composition had been changed from 0 to 100 (wt), thus they obtained VAc and BuA homopolymers in addition to copolymers. As a result of these studies, the average particle size was independent from copolymer composition, and molecular weight distribution was narrow and less dependent on monomer composition in batch process. But in semi-continuous process, the average particle size decreased with increasing BuA content and molecular weight distribution was slightly dependent on composition. If PVAc content was increased above 50 mol % for semi-continuous process, the polymerization reaction might have resulted in a proportional increase and ultimately dominant role of steric stabilization. They emphasized firstly that VAc and BuA have different reactivity ratios and water solubility, and secondly the effects of these parameters on the locus of initiation and growth differ in the two polymerization processes.

Cavaille et al. compared micromechanical behavior of VAc-BuA copolymer films by applying four different emulsion processes as conventional batch, two-step polymerization, corrected batch, and mixture of the two homopolymers.⁷ The real dynamic shear modulus G' , the imaginary part of the dynamic shear modulus (G''), and the internal friction ($\tan \delta = G''/G'$) of these films were measured as a function of temperatures. Large differences were found between batch copolymer and homopolymer blends.

Lee et al. tried the emulsion polymerization of styrene with low solids content in CLR.²⁷ They studied the effects of temperature, emulsifier, initiator and monomer concentrations on conversion, and average particle diameter, number, and weight average molecular weight of the polymer molecules. Bataille and

Dalpe²¹ and Iabbadene and Bataille²⁸ worked on the homopolymerization of styrene and vinyl acetate in the batch loop reactor. They compared results with the results of the LR and tank reactor. It was found out that under all conditions the conversions achieved in the batch loop reactor were somewhat lower than the conversions in the batch tank reactor. The value of this conversion is maximum or optimum for the laminar-turbulent flow transition region for both monomers.

Abad, De La Cal, and Asua carried out the copolymerization of Veova-10 monomers with VAc under the same conditions in CLR and CSTR and compared the results.²⁹ As a result of these studies, it was found that both reactors gave almost the same performance, but CSTR was found to have a tendency towards thermal leakage under aggressive conditions, whereas CLR, can be regarded as safer. Another result of these studies is the reaction time in LR is much shorter than in CSTR.

Abad, De La Cal, and Asua³⁰ and Araujo et al.³¹ studied with a redox initiated emulsion copolymerization of VAc and Veova 10 including emulsifier mixture and hydroxyethyl cellulose (HEC) in CLR. Abad and coworkers³⁰ searched for the effect of the flow rate on the shear-induced coagulation using different amounts of surfactants and they have developed a mathematical model for their process. According to that study, if the reactivity ratios of monomers in emulsion copolymerization are close to each other, homogeneous copolymers can be obtained very easily for VAc and Veova 10. They have also reported that the close packing of the protective colloid and emulsifiers on the surface of the polymer particles has hindered the radical entry. Araujo et al.³¹ investigated the effect of the temperature, residence time, emulsifier concentration, and initiator concentration on monomer conversion, particle size distribution, and molecular weight distribution. It is possible that high conversions at low temperatures can be achieved. If the reaction is started for a long residence time and then reduced until reaching steady state condition, high conversion in short residence times can be obtained.

Studies were very limited about VAc-BuA copolymerization in the presence of protective colloids, such as polyvinyl alcohol (PVOH), and HEC. The first study on it was in 1969 by Chujo et al.¹ They applied different monomer addition methods in VAc and BuA emulsion copolymerization with same composition of VAc/BuA (70/30) using PVOH (Gohsenol GH-20) and potassium persulfate initiator. They reported on how fractionation of emulsion copolymers can be done, and explained all separated fractions and grafting reactions. Having different properties of copolymers of VAc and BuA was dependent on changing the monomer addition methods.

TABLE I
Recipes Used in Copolymerization Experiments

Substance	Weight (%)
VAc	42.50
BuA	7.50
PVOH 17-88	2.00
NP-n (n = 10 - 40)	0.80
Nansa 66	0.20
APS or PPS	0.20
NaHCO ₃	0.12
Nopco	0.10
Water	46.29
Total	100.00

In this study, the effects of the ethoxylation degree of ethoxylated nonyl phenol and initiator on physico-chemical properties in the batch emulsion copolymerization of VAc and BuA in the loop reactor were studied under similar conditions in industry such as high solid content latexes (51 wt %) and high conversions (> 98%). Because any literature can be found on the emulsion copolymerization started with the same kinds of initiator, the interest of this article is "to fill this gap" and try to find out how the same type of initiator affects the product properties.

EXPERIMENTAL

Materials

VAc and BuA monomers (Argon Chemistry Inc.) were used at commercial purification and monomer ratio was 85:15. The stability of the latexes was achieved by mixtures consisting of a series of nonyl phenol ethoxylate (NP 10, 10+30, 30, 40) (Turkish-Henkel Chemicals Industry Co.) and anionic emulsifier (Nansa 66) (Turkish-Henkel Chemicals Industry Co.). Nansa 66 and one of the ethoxylated nonyl phenol were used in each copolymerization. For protective colloid, 88% hydrolyzed PVOH product (17-88) (Argon Chemistry Inc.) was used; ammonium persulfate (APS) (Merck) and potassium persulfate (PPS) (Merck) were used as thermal initiators. Nopco-1497 was used as an antifoam agent, and sodium bicarbonate (Merck) was used for adjusting the pH value of the polymerization media. All substances were used without further purification. De-ionized water was used in all studies (Argon Chemistry, Inc., Turkey). The general copolymerization recipe is given in Table I.

The copolymerization was carried out in the LR shown in Figure 1. The LR was designed with a jacket and stainless steel, length 6 m, inner diameter 1.34 cm, and inner volume 2.7 L. The loops connect the discharge and the suction of a gear pump that is made from stainless steel. This pump promotes the emulsion movement by the eccentric rotation of a stainless steel rotor in a PTFE 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 had 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 selenoids 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 the loops were read from the manometer placed in the system.

Procedure

Water (500 mL) was put into a beaker and a 10% stock PVA solution was added to the emulsifier. All substances except the initiator were mixed thoroughly with the mechanical stirrer. NaHCO₃ (to maintain the pH of the emulsion at a fixed value between 4.5 and 5.5), Nopco (to prevent foaming), and monomers were added to this mixture, then stirred until pre-emulsion was obtained. Before this pre-emulsion was fed into the reactor, all of the initiator to be used in the polymerization was dissolved in water and was added into the emulsion. Having fed the emulsion to the system, the reactor was preheated until 40°C. During feeding, the pump rate was kept in the lowest level as possible (12.9 rpm), and circulation was started. The route followed by the emulsion in the reactor is shown in Figure 2.

The pre-emulsion followed route **a** and was fed into the reactor through **B**, which was the feeding point of reactor. At that time valves **D** and **A** were kept open, and valve **C** was kept closed so that pre-emulsion was filled in all of the loops. To discharge the air remaining in the system, valves **A** and **D** were closed and valve **C** was opened. This way, whether the system had air or not could be seen on manometer. After filling reactor completely with the pre-emulsion, the speed of the pump was raised to 35 rpm and it was set at that speed. The reactor temperature was raised to 70°C and

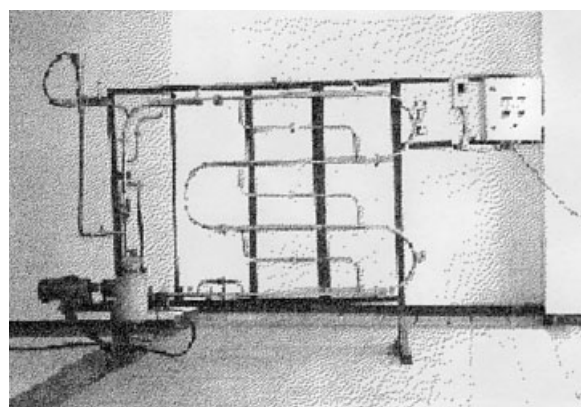


Figure 1 Loop reactor.

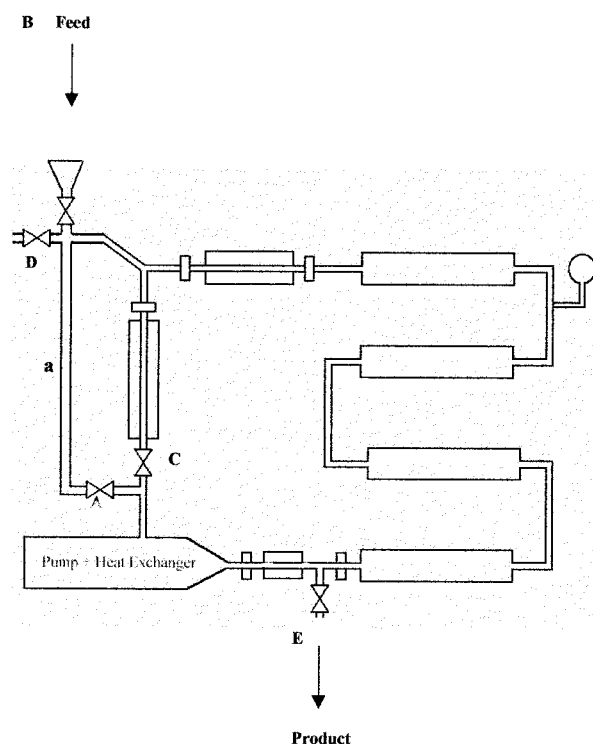


Figure 2 The flow diagram in the loop reactor.

was kept constant for 1.5 h. To decompose and form initiator radicals, the thermal initiators need heat, and the required heat was already provided from the system. When the system temperature changed $\pm 1^\circ\text{C}$ from 70°C , the heat exchanger or cooling system was switch off automatically. The valve D was opened and the system pressure was equalized to the air pressure. A short cooling was made in order to minimize evaporation in the hot product, and the product was taken at $\sim 40^\circ\text{C}$ through E.

Conversion was monitored gravimetrically. The viscosities of the latexes were determined by Brookfield Programmable DV-II model viscometer, with spindle number 4 at 26°C after diluting 50% (wt) solids content of all samples. The fractionation of the dried copolymer films was carried out by combining literature¹ and our previous work,³² because of grafting structure of VAc and PVOH with other monomers. After separating network parts of copolymers, benzene soluble fractions of samples were extracted with THF in order to determine molecular weights of copolymers. Number average molecular weights (\bar{M}_n) and weight average molecular weights (\bar{M}_w) of copolymers were determined by the GPC Agilent model 1100 type instrument with a refractive index detector and calibrated with polystyrene standarts consisting of three Waters styragel columns (HR 4, HR 3, and HR 2). THF was diluent solvent at a flow rate of 0.3 mL/min at 30°C .

The surface tensions of the produced latexes were measured after the total solids contents of the samples

were adjusted to 25% by weight by diluting. The surface tension measurements were done with ring-detachment method by torsion tensiometer and a platinum ring at 25°C .

RESULTS AND DISCUSSION

The effects of the ethoxylation degree on the properties of all synthesized copolymers were determined. For this purpose, the following analyses were done, and the figures were drawn, in which obtained data on copolymer viscosity and molecular weight of copolymers versus increasing ethoxylation degree of non-ionic emulsifiers (in the emulsifier mixture), in order to better explain results.

Conversion

The copolymer conversions were found to vary between 97.71 and 99.89. According to these results, almost all monomers of VAc and BuA were polymerized.

Viscosity

In the presence of PPS, the obtained copolymers viscosities were found higher than obtained viscosities with APS except for 40 ethoxylated nonyl phenol. When APS initiator was used in the synthesis of latexes, the increase in the viscosity with the ethoxylation number can be explained by the decreasing in the volumes of the micelles formed by the increasing in the ethoxylation number, thus increasing the number of particles in unit volume, which leads to the increase in the viscosity of the latexes. In contrast to the measured viscosity with APS, when PPS is used in the copolymerization viscosity of the latexes was decreased by increasing ethoxylation number of emulsifier (Fig. 3). In this case, the volumes of the micelles grow with the increase in the ethoxylation number and the decrease in the number of particles in unit volume leads to a decrease in the viscosity of the latexes.

Molecular weights of the copolymers

The weight average (\bar{M}_w) and number average (\bar{M}_n) of molecular weights of the poly(VAc-co-BuA) were determined by GPC. Figure 4 shows that the number average (\bar{M}_n) and weight average (\bar{M}_w) molecular weights increased by increasing the ethoxylation number of the participating emulsifiers when ammonium persulfate was used as initiator. When potassium persulfate was used as initiator it was seen that the weight average molecular weight (\bar{M}_w) increased whereas the number average molecular weight (\bar{M}_n) decreased as the ethoxylation number of the emulsi-

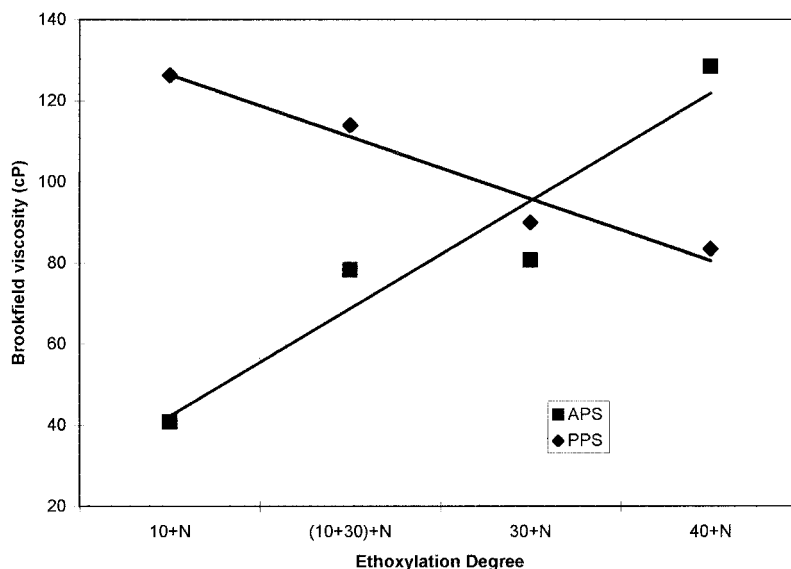


Figure 3 The change of latex viscosity with the change in ethoxylation degree of emulsifier, when ammonium persulfate and potassium persulfate are used as initiators.

fier mixture increased (Fig. 5). As a result of determination of molecular weight of VAc-BuA copolymers, APS gave having higher molecular weight copolymers than PPS. Moreover the molecular weight increased with increasing ethoxylation degree of emulsifier mixture for APS. Although obtained higher molecular weights with PPS than APS for same ethoxylation degree, the molecular weight slightly decreased (almost constant) with increasing ethoxylation degree of emulsifier mixture when PPS used in polymerization.

It was also determined from molecular weight results that monodisperse copolymers ($HI = 1.23-1.87$) were obtained with both initiators, using a mixture of anionic and nonionic emulsifiers. This result is in con-

formity with the literature.³³ El-Aasser and Vanderhoff³⁴ found the similar results for molecular weights of copolymers having 85/15 monomer ratio for batch process, but obtained copolymers in this work have highly smaller polydispersity value than in the work of El-Aasser and Vanderhoff.

Surface properties of the latexes

In the surface tension studies carried out for surface characterization of latex films, a correlation was found between the ethoxylation number and the surface tension, and the obtained results are shown in the Table II.

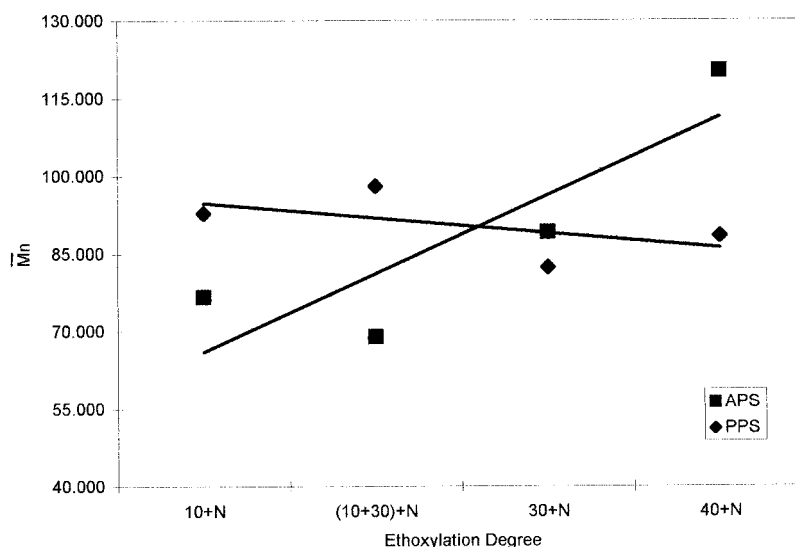


Figure 4 The change of number average molecular weight with the change in ethoxylation degree of emulsifier, when ammonium persulfate and potassium persulfate are used as initiators.

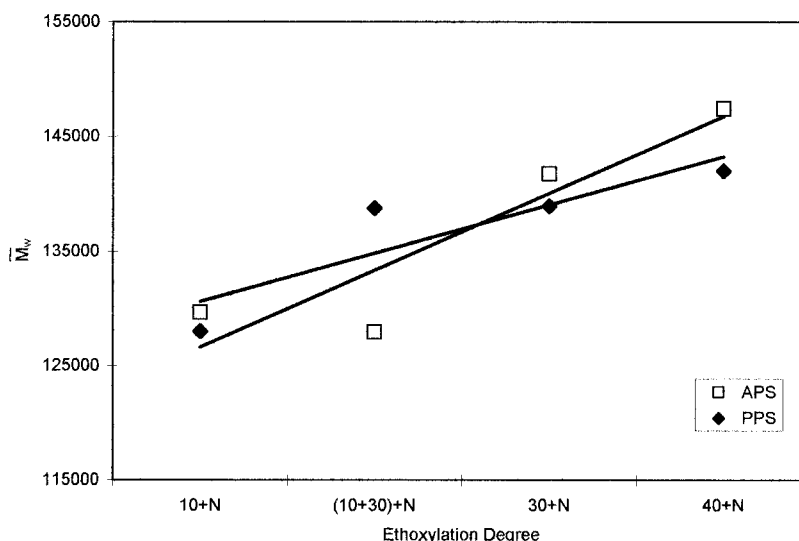


Figure 5 The change of number average molecular weight with the change in ethoxylation degree of emulsifier, when potassium persulfate and potassium persulfate are used as initiators.

When APS was used, it was found that the surface tensions of the copolymers increased with the increase in the ethoxylation number. When PPS was used, it was observed that the surface tension increased with the increase in the ethoxylation number, and no major change was observed in the surface tension values of the copolymers after 30 ethoxylated nonyl phenols. Because of the adsorption non-ionic emulsifier at the latex surface, surface tensions of samples were found as 40–45 mN/m. The result for surface tension of copolymer that was obtained with (10 + 30)+N emulsifier mixture is in agreement with the result of Erbil³⁵ obtained for the semi-continuous emulsion copolymerization of VAc/BuA using APS at 60°C.

CONCLUSION

In this work, vinyl acetate and butyl acrylate copolymer latexes were prepared in the presence of ammonium persulfate and potassium persulfate initiators, 10–40 moles ethoxylated nonyl phenol non-ionic emulsifier and polyvinyl alcohol protective colloid by using batch emulsion polymerizations in the loop reactor. It was determined that when ammonium persulfate initiator was used in the copolymerization recipe, the final latex viscosity decreases and the number average copolymer molecular weight increases by the increase of ethoxylation number. However, when potassium persulfate initiator was used in the copoly-

merization recipe, the final latex viscosity increases and the number average copolymer molecular weight also increases more regularly by the increasing of ethoxylation degree. The increase of ethoxylation degree does not affect the surface tension of the final latex significantly.

The authors gratefully thank State Planning Organization of Turkey (DPT) for financial support to this study.

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TABLE II
Surface Tensions of Copolymers

Initiator	Emulsifier	10+N	(10+30)+N	30+N	40+N
APS	γ (mN/m)	38.5	40.3	40.0	43.8
PPS	γ (mN/m)	37.0	39.8	43.7	43.6

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