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ORIGINAL PAPER

Synthesis and characterization of water-based poly(vinyl acetate-co-butyl acrylate) latexes containing oligomeric protective colloid

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Abstract Poly(vinyl acetate-co-butyl acrylate) latexes having oligomeric *N*-methylol acrylamide were prepared by semi-continuous emulsion polymerization. The effects of new protective colloid and comonomer ratios on the physicochemical and colloidal properties of latexes were investigated. The changes in homopolymer and copolymer latexes were determined by measuring viscosity, particle size, molecular weight (MW), molecular weight distribution (MWD), and surface tension. $\bar{M}_n$ values of copolymer latexes were found to be lower than the MWs of the poly(vinyl acetate) and poly(butyl acrylate) homopolymers. In general, $\bar{M}_n$ and $\bar{M}_\mathrm{w}$ values of copolymer latexes changed irregularly with increasing BuA ratio in the copolymer composition.

Keywords Emulsion polymerization · Water-based latex · Copolymer · Stabilization · *N*-methylol acrylamide · Molecular weight distribution

Introduction

Protective colloids used in emulsion polymerizations generally affect the colloidal and film properties of latexes. In addition, properties of copolymer latexes depend on the copolymer composition, initiator, polymerization medium, and colloidal characteristics of the copolymer particles.

In emulsion polymerizations of vinyl acetate (VAc), stabilization is classically carried out by using poly(vinyl alcohol) (PVOH), hydroxyethyl cellulose (HEC), and poly(ethylene glycol)s (PEGs), generally called protective colloids [1–7]. Partially hydrolyzed PVOH is mostly preferred in the emulsion polymerization processes of VAc to facilitate small particle diameter, thixotropic flow, high

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viscosity, and stability even at low temperatures. However, it shows weak resistance against water and heat for latex films. Although PVOH is mainly utilized in VAc systems, it is not used for some vinylic monomers such as styrene (St) and acrylic monomers due to the weak grafting capability of these monomers on PVOH.

N-methylol acrylamide (NMA) was used as a comonomer in emulsion copolymerization with various monomers [8–11]. Bonardi et al. synthesized butyl acrylate–styrene (BuA–St) and butyl acrylate–methyl methacrylate (BuA–MMA) copolymers by using NMA (maximal 1.67 wt% in total) as a functional comonomer [8]. They observed that water-soluble polymers containing NMA units were produced at the end of the polymerization process and separated with centrifugation. It was found that NMA units were located around the particles as a hairy shell of grafted or strongly adsorbed polymers.

Wu and Schork carried out VAc copolymerizations with BuA, dioctyl maleate, and NMA by applying mini- and macro-emulsion polymerizations in batch and semibatch processes [9]. NMA was copolymerized as a comonomer (5.0 wt% in total) with VAc in the presence of an anionic emulsifier (sodium lauryl sulfate, SLS) and potassium persulfate as the initiator. It was found that the polymer particles in these latexes were not stable; therefore, the anionic emulsifier was not a good stabilizer for this monomer couple.

St–BuA copolymer dispersions with core/shell particles functionalized by NMA (maximal 3.0 wt% in total) were prepared through two-step emulsion polymerization [10, 11]. NMA was added with St in the first step or with BuA in the second step of polymerization. Volfova et al. studied mechanical properties and organic solvent resistance of films cast from PolySt/PolyBuA latexes. These experiments have shown that crosslinking, in which methylol groups took part, proceeded during the polymerization. The high content of insoluble parts was caused by unreacted methylol groups reacting with butyl ester groups at ambient temperatures. Their intra-particle or inter-particle crosslinking could proceed according to the location of the functional groups in the latex particle.

Oligomeric-NMA was synthesized for polymerization of VAc–BuA latexes with the aim of providing them with better colloidal stability and low viscosity than other protective colloids. This protective colloid also developed physical, chemical, and surface properties of the latexes. The present article reports the use of oligomeric-NMA as a protective colloid in semi-continuous emulsion polymerization of the VAc–BuA system while NMA was used as the comonomer in the other studies. In addition, the influence of the co-monomer ratio (VAc/BuA) in the presence of the oligomeric protective colloid was studied by measuring viscosity, particle size, molecular weight (MW), molecular weight distribution (MWD), and surface tension.

Experimental section

Materials

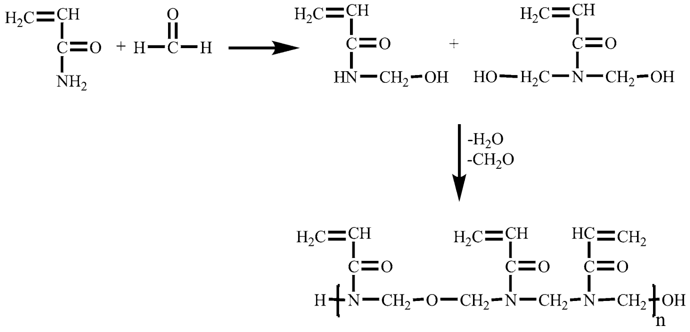
Elsan Fibre Co. (Turkey) VAc and BuA monomers were used without purification in six different monomer ratios (100:0, 75:25, 60:40, 40:60, 25:75, and 0:100). The stability of the latexes was achieved by 30 mol ethoxylated nonyl phenol (NP 30) (Turkish-Henkel Chemicals Industry Co.) as an emulsifier. The NP 30 was used above the critical micelle concentration (CMC) in polymerization. Ammonium persulfate (APS) (Merck), Nopco-1497, and sodium bicarbonate (Merck) were used, respectively, as a thermal initiator, an antifoam agent and a buffer to keep the pH degree of the reaction medium between 4.5 and 5.5. All substances were used without further purification. Synthesis and characterization of protective colloid, oligomeric-NMA (48 wt% in water) are explained in detail in further sections. Deionized water was used in the polymerizations. To supply this water, an SG water model euro 10 AFU type instrument was used and then the water was passed through the active carbon column.

Preparation of oligomeric *N*-methylol acrylamide

NMA was prepared from the reactions between acrylamide and formaldehyde by following the reaction steps in Scheme 1. 4-Methoxyphenol was added to the solution to prevent polymerization of acrylamide pendant vinyl groups. NMA and *N*, *N*-dimethylol acrylamide were formed from the reaction between acrylamide and formaldehyde. Condensation reactions occurred over the functional groups of those molecules.

Synthesis of copolymer latexes

Polymerization was performed in a conventional 1 L glass emulsion polymerization reactor equipped with a mechanical stirrer at a constant speed of 200 rpm, dropping funnel and a reflux condenser. Only 10% of the total monomer or monomer mixture was placed at the beginning of the reaction at 60 °C and the remaining monomer mixture was added dropwise at 71 ± 2 °C from dropping funnels over 3 h. Polymerizations were carried out at constant temperature, 71 ± 2 °C by using Julabo Mc model digitally controlled thermostatic circulation bath. Cold water circulation was obtained via the reactor wall as soon as the reaction temperature rose above 71 ± 2 °C due to the exothermicity of the reaction. APS initiator was



Scheme 1 Synthesis of oligomeric *N*-methylol acrylamide

Table 1 Recipe used in polymerization experiments

Substance	Weight (%)
Monomer/mixture	43.71
Protective colloid	1.88
NP 30	3.60
APS	0.24
$NaHCO_3$	0.12
Nopco-1497	0.08
Water	50.37
Total	100.00

dissolved in a small amount of water and these freshly prepared initiator solutions were added at 30-min interval throughout the reaction. Either homopolymerization or copolymerization of both monomers was carried out by semi-continuous emulsion polymerization process, in the presence of oligomeric-NMA as a protective colloid, under atmospheric conditions according to the recipe shown in Table 1. Stable latexes could not form without oligomeric-NMA.

Characterizations

FTIR–ATR spectra of monomeric- and oligomeric-NMA were recorded using a Perkin Elmer, Spectrum One FTIR Spectrometer from 4000 to 650 cm^{-1} after the drying process at 60 °C under vacuum. A sampling accessory Universal ATR equipped with diamond/ZnSe crystals with a 45° incidence angle was used. The background spectra were recorded in air at room temperature by using the same instrumental conditions as the samples. Scan number and resolution were optimized to four scans and 4 cm^{-1}. The MS spectrum of oligomeric-NMA was acquired in linear modes with an average of 50 shots on a Bruker Daltonics Microflex mass spectrometer (Germany) equipped with a nitrogen UV-Laser operating at 337 nm without using a matrix.

Copolymer latexes were characterized by measuring Brookfield viscosity, MWs ($\bar{M}_n$ and $\bar{M}_w$), particle size and surface tension of copolymer latexes to air. The viscosities of the copolymer latexes were determined by Brookfield Programmable DV-II model viscometer with spindle number 4 at 20 °C after the all samples were diluted to 40% (wt/wt) solids with de-ionized water. Because of the grafting between the VAc and the protective colloid, the fractionation of dried polymer films was carried out according to Chujo et al. [5] and Sarac et al. [9] for determination of the MWs. Crosslinked portions of the polymers (between 5 and 10%) were separated after the samples were extracted with THF. The number average ($\bar{M}_n$) and the weight average ($\bar{M}_w$) MWs of the copolymers were determined with an Agilent model 1100 type instrument gel permeation chromatography (GPC) with a refractive index detector and calibrated with polystyrene standards having narrow MW distribution. The four Waters styragel columns (HR5E, HR4E, HR3, and HR2) were used in series. The effective MW ranges were 2,000–4,000,000, 50–100,000, 500–30,000, and 500–20,000, respectively. THF was used as the diluent solvent with a flow rate of 0.3 mL/min at 30 °C. The particle size of the latexes was determined by Malvern Zetasizer Nano ZS model instrument. The surface tensions of produced latexes were measured after total solid contents of the samples were adjusted to 25 wt% by dilution. The surface tension measurements were done by the ring-detachment method with a torsion tensiometer and a platinum ring at 20 °C.

Results and discussion

Characterization of oligomeric *N*-methylol acrylamide

NMA is a water-soluble functional monomer retaining its methylol group upon polymerization. This group can later undergo crosslinking reactions and self-condensation, and even reactions with groups of other polymers [12]. Because of these important properties, NMA and its polymers are used in many industrial applications include coatings, tanning agents, sealants, adhesives, and elastomers [13]. Furthermore, NMA comprised polymers prepared by emulsion polymerization are widely used in applications such as binders for nonwoven fabrics, protective coatings, latex paints, and adhesives [14]. In this study, oligomeric-NMA was synthesized as a protective colloid by self-condensation polymerization which took place between the functional groups of NMA and *N*, *N*-dimethylol acrylamide to improve the properties of VAc–BuA latexes.

Characterization of oligomeric-NMA was achieved mainly by FTIR spectroscopy and MALDI-TOF mass spectrophotometry (MALDI-TOF MS). In the FTIR–ATR spectra of monomeric- and oligomeric-NMA, a narrow peak appeared at 3264 cm^{-1} which related to the associated N–H stretching band belonging to the oligomeric form of NMA. Moreover, the broad O–H peak relating to the methylol group disappeared in this area, although there is a broad band belonging to the overlapping O–H and N–H stretching vibrations centered about 3304 cm^{-1} in the NMA monomer. The new bands were observed at 1384, 1449, 2890, and 2942 cm^{-1}. These bands show, respectively, C–H symmetric bending, C–H asymmetric bending, C–H asymmetric, and C–H symmetric stretching of CH_2O–. Furthermore, when comparison of monomeric-NMA with oligomeric-NMA is made, the differences are clear in the 1000–1300 cm^{-1} region, where the strong bands of reacted and unreacted functional methylol groups from NMA can be seen due to C–O and C–N vibrations. These results indicate that condensation polymerization was taken into account over the methylol groups between the end groups of NMA and *N*, *N*-dimethylol acrylamide molecules. The MW of the oligomeric-NMA was found to be 855 g mol^{-1} by MALDI-TOF MS. Its MS spectrum confirmed the oligomeric structure of NMA shown in Scheme 1.

Characterization of copolymer latexes

Particle size

Figure 1 shows the relationship between the particle size of the latexes and butyl acrylate content in the copolymer composition. The average particle size of the copolymer latexes was found to vary with the changing BuA content in the copolymer composition. This difference in particle size depending on the copolymer composition of the latexes could be explained in terms of the nature of the semi-continuous process and the differences in the properties of the two monomers. In semi-continuous emulsion polymerization, the formed particles are homogeneous with respect to the copolymer composition due to the starved monomer condition during the course of the polymerization. When the comonomer mixture contains a high content of the relatively more hydrophobic BuA monomer, favorable adsorption of emulsifier onto the particle surface occurs. Thus, the stability of these small size particles against coalescence with larger size particles increases, which results in a latex system with small average size, as shown in Fig. 1 [3]. As the BuA content decreases in the comonomer composition, the copolymer particles consist of the hydrophilic VAc monomer. In this situation, the emulsifier packing on these more hydrophilic particle surfaces becomes less, so the colloidal stability of the latex particles decreases. The coalescence of the small size particles among themselves or coalescence with existing large size particles leads to an increase in particle size of these copolymer particles. In the semi-continuous process, these results are also in agreement with the data of El-Aasser et al. [2–4] and Sarac et al. [5].

In addition, it was found that the PVAc latex particles have the largest size particles. This result could be explained in terms of the propensity of VAc radicals to undergo chain transfer reactions. The chain transfer reactions took place between the oligomeric-NMA and the VAc chains on the particle surface during polymerization at high conversion, which caused branching. Most of the data in the available literature indicate the formation of these branching reactions when VAc is polymerized in the presence of a nonionic emulsifier and polymeric stabilizer. In the semi-continuous process, the particle generation time is long (where the monomer feeding rate is smaller than the polymerization rate), and polymerization is carried

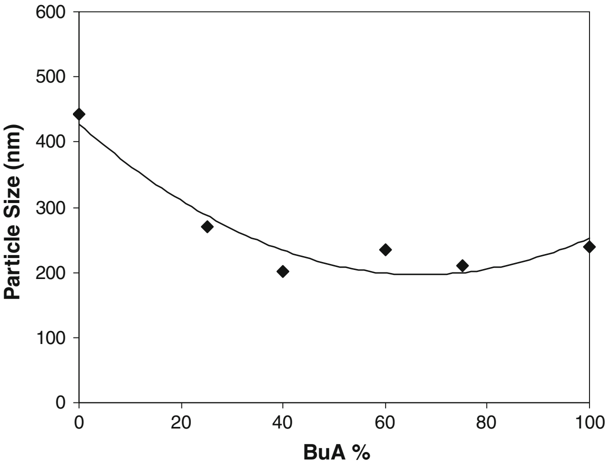


Fig. 1 Change of particle size of copolymers versus BuA% in the copolymer composition

out under starved monomer conditions and conversion is close to 100% all the time. Consequently, it is expected that the degree of branching will be quite extensive on the particle surface and this also causes the highest stability besides increasing the particle size, as shown in Fig. 1.

Viscosity

Surface layers of the polymer particles may occur due to the adsorbed surfactants, adsorbed or reacted polymeric stabilizers such as PVOH, HEC, or poly(ethylene oxide) (PEO) and surface charges on the polymer particles. Such layers can significantly increase the effective volume of the latex particles [4]. The effective volume is another measure for the particle size and as the effective volume of the particles increases, the particle size of the latex becomes small. Furthermore, for latex with a content of constant solids, its viscosity increases with decreasing particle size [15, 16]. Figure 2 shows the relation between the viscosities of the copolymer latexes and BuA% content. It can be seen that the viscosity results support the particle size results of the latexes. The viscosities of the copolymer latexes increased with adding even 40% BuA (w/w) into the comonomer composition, but this increase in viscosity was not sharp.

Because of the differences between the properties of VAc and BuA monomers, the particle interactions with emulsifier affected the viscosities of the latexes with changes to the co-monomer ratio in the copolymer composition. The increment of BuA% in the copolymer composition caused an increase in viscosities of the copolymer latexes in general (Fig. 2). The emulsifier adsorption on the polymer particles having high BuA content was higher than the other particles due to the hydrophobic structure of the particles which consisted of more BuA. This effect increased the particle stability, decreased the particle size and increased the viscosity of the latexes consisting of particles having high BuA content. In addition,

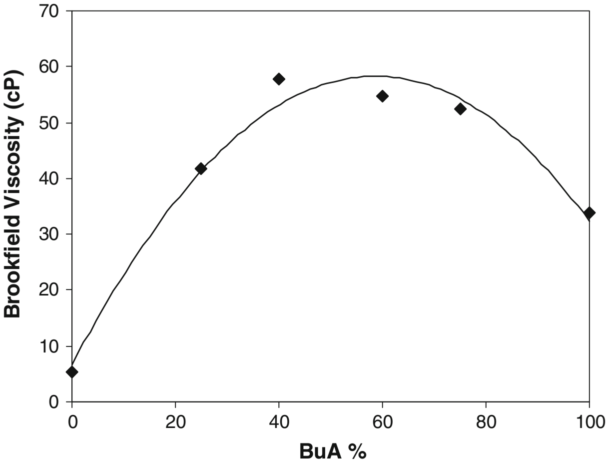


Fig. 2 Change of Brookfield viscosity of copolymers versus BuA% in the copolymer composition

the efficient emulsifier adsorption on the particle surface inhibited the chain transfer reactions between the oligomeric-NMA and VAc chains. However, this adsorption was poor on the particles' surface, where the content of VAc was high and the chain transfer reactions took place between the VAc radicals and oligomeric-NMA which has hydrophilic and functional structures. These reactions caused the branched structures on the particle surface, hence the particle size increased and viscosity decreased.

Molecular weight and molecular weight distribution of copolymers

The emulsion copolymerization of VAc/BuA system is characterized by differences in the reactivity ratios ($r_{\mathrm{VAc}} = 0.05$ and $r_{\mathrm{BuA}} = 5.5$) and water solubilities (2.3 wt% for VAc and 0.04 wt% for BuA). Due to these significantly different monomer properties and copolymerization ingredients, latexes having a wide range of molecular properties can be obtained by varying the monomer ratios. This change influences the viscosity and MW of latex paints [16].

$\bar{M}_{\mathrm{w}}$, $\bar{M}_n$, and MWDs of the poly(VAc-co-BuA) copolymers were determined by GPC. Figures 3 and 4 show the $\bar{M}_n$ and $\bar{M}_{\mathrm{w}}$ of the poly(VAc-co-BuA) copolymers having oligomeric-NMA as protective colloid. According to the results of determining the $\bar{M}_n$ of VAc–BuA copolymers, it was seen that $\bar{M}_n$ of the copolymers changed irregularly with increasing BuA% in the copolymer composition. $\bar{M}_{\mathrm{w}}$ of the copolymers did not show profound effects when increasing BuA% in the copolymer mixture. Due to the high amounts of emulsifier in the polymerization, $\bar{M}_n$ values of the copolymers were found to be low unlike $\bar{M}_{\mathrm{w}}$ values. Because of the reasons explained above, these results were expected for the new oligomeric protective colloids [17].

Latex MWD's results are shown in Fig. 5. Homopolymers and copolymers of VAc and BuA indicated bimodal distribution in the GPC chromatogram when

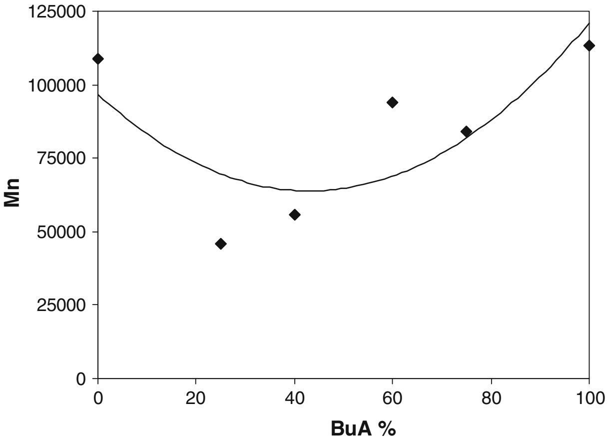


Fig. 3 Change of number average molecular weight of copolymers versus BuA% in the copolymer composition

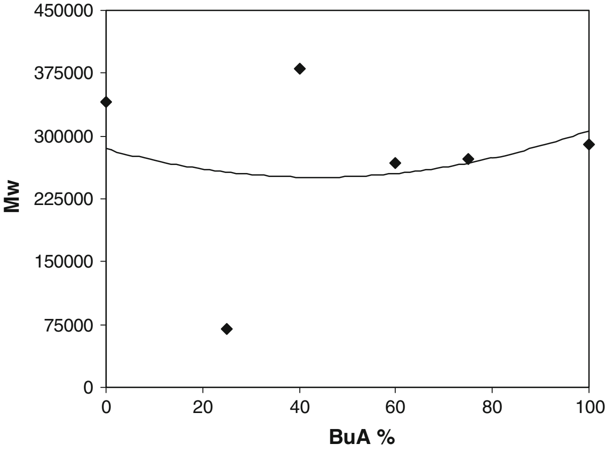


Fig. 4 Change of weight average molecular weight of copolymers versus BuA% in the copolymer composition

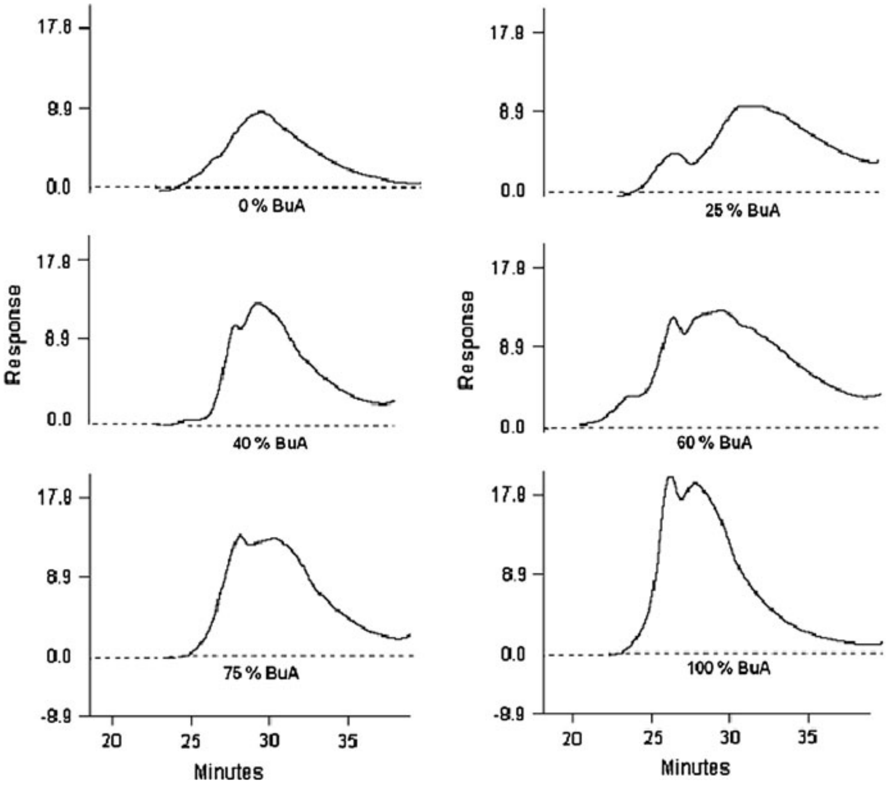


Fig. 5 Change of molecular weight distribution of copolymers versus BuA% in the copolymer composition

oligomeric-NMA was used. In these chromatograms, the broad peak in the low MW region shows the polymer having short chains and the narrow sharp peak in the high MW region shows the polymer having long branched chains. Low MW oligomers arise from low monomer concentrations in the polymerization medium and initiation took place predominantly in the aqueous phase. Long branched chains form in the inner parts of the particles having high polymer concentration when normal propagation occurs near the particle surface where the monomer concentration is low and constant [3, 4]. Because these reactions are predominant in the homopolymerization of BuA at high conversion, the narrow peak, with a higher relative proportion, is clearly observed in the GPC chromatogram of poly(butyl acrylate) (PBuA). It was evident that the intensity of this narrow peak depends on the composition of the copolymers which have different ratios of BuA and VAc-co-BuA latexes, which showed bimodal distribution with even lower than 25 BuA wt% [18].

The polydispersities of the copolymers showed narrow MWD when oligomeric-NMA was used as a protective colloid. The polydispersity of the copolymers was changed by the copolymer composition, and their values were between 2.21 and 3.24.

Surface tension

The surface tension studies were carried out for surface characterization of the latexes. The surface tensions of the latexes were found to be 45–52 mN/m which are shown in Fig. 6. Surface tension results indicated that surface tensions of the latexes increased regularly for almost all monomer ratios in the copolymer composition. While the BuA ratio was increasing in the copolymer composition, the surface tension increased slowly. When the same chain length of emulsifier was used, the surface tensions of the copolymer latexes did not reveal large differences even by

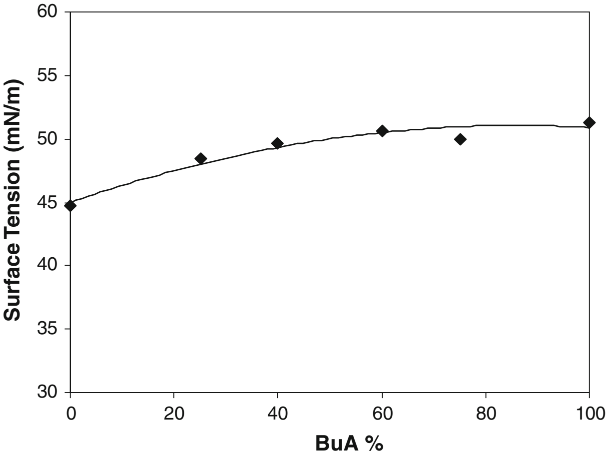


Fig. 6 Change of surface tension of copolymers versus BuA% in the copolymer composition

varying the BuA ratio in the copolymer composition. However, copolymer latexes gained a more hydrophobic character by increasing the BuA ratio in the copolymer composition, and the adsorption of nonionic emulsifier increased on the latex surface, so the surface tensions of the latexes increased.

Conclusion

Vinyl acetate-co-butyl acrylate latexes were synthesized in the presence of oligomeric-NMA by using a semi-continuous emulsion polymerization process. Oligomeric-NMA was used as a protective colloid in these polymerizations. However, particle size and viscosity behaviors of the copolymer latexes showed diversity by changing the BuA ratio in the copolymer composition; copolymer latexes having small particle size and low viscosity were obtained. These properties have improved the colloidal stability of latexes. Furthermore, it was determined that copolymer latexes had narrow MWD. Surface tensions were found to be low especially for the latexes having high VAc content. It is indicated that emulsifier adsorption on the particle surface decreases for these latexes and the amount of free emulsifier in aqueous phase increases. These results show that the interaction between oligomeric-NMA and these particles is higher than latexes having high BuA content. Consequently, oligomeric-NMA contributed to stabilization of the particles having high VAc content by chain transfer reactions, while the hydrophobic effect was dominant in stabilization of the particles having high BuA content.

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