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Original Paper

Effect of monomer partitioning on vinyl acetate-butyl acrylate emulsion copolymers

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ABSTRACT

Semi-continuous free radical emulsion polymerizations of vinyl acetate and butyl acrylate initiated by a water-soluble (potassium peroxydisulfate, KPS) initiator in the presence of a N-methylol acrylamide (NMA) at 70°C were investigated. 12 different monomer compositions (BuA ratio, from 0/100 to 100/0) were prepared and the effect of Vinyl acetate /Butyl acrylate (Vac/BuA) monomer ratio on viscosity, molecular weights (Mn, Mw, Mv), conversion, and molecular weight distribution were also investigated. It was found that as a protective colloid, N-methylol acrylamide worked perfectly for maintaining emulsion stability. Viscosity and molecular weights were increased with BuA ratio in the synthesized copolymers. High conversion values (above 90%) were reached. It was seen that the molecular weight distributions (PDI) of the synthesized copolymers showed a narrow distribution between 3-5.

I. INTRODUCTION

Emulsion polymerization is a significant and well-established process that is frequently used for the manufacture of polymers in industrial settings (e. g., for paints and coatings) due to several explicit advantages [1]. Among various stabilizers used in industry, amphiphilic block or graft copolymers are the most effective in stabilizing emulsion polymerization [2]. Conjugated dienes such as butadiene and isoprene, vinyl acetate, vinyl chloride, various acrylates, polymerization of methacrylate and different copolymers of these monomers can be produced by emulsion polymerization [3-6].

The first industrial-scale manufacturing of polymer emulsions used as binders took place between 1925 and 1930 thanks to the emulsion polymerization technique, the foundations of which were laid in 1910. Conventional emulsion polymerization comprises emulsification of a water-immiscible monomer in a continuous water medium using an oil-in water emulsifier and polymerization using a water-soluble or oil-soluble initiator to give a colloidal dispersion of polymer particles in water [7-9]. The finished product, known as "Latex," is a stable and colloidal dispersion of polymers in aqueous medium [10]. By applying shear to the mixture, the monomer is dispersed into droplets of typically about 10 µm diameter. The droplets are stabilized by adsorption of surfactant at the monomer–water interface. The most commonly used process in industry is the free-radical polymerization of a surfactant-stabilised oil-in-water emulsion [11]. As a method, emulsion polymerization has many advantages over other polymerization methods in addition to being affordable and reliable in the water environment, as it enables the production of excellent high molecular weight products that can be used directly in many applications with

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quick and simple polymerization reactions. Even though the emulsion polymerization process has been used for many years to create synthetic polymers and copolymers, all the details of the reaction mechanism are still not completely understood [12]. The quantity of chemicals presents in the emulsion system and the numerous physical and chemical processes occurring therein are the cause of this. Latexes prepared by Semibatch emulsion polymerization are widely used in a variety of applications such as adhesives, paper coatings, paints, varnishes, and synthetic rubbers [13, 14].

Some water-soluble polymers such as polyvinyl alcohol (PVOH) and hydroxyethyl cellulose (HEC) are commonly used stabilizers. However, N-methylol acrylamide (NMA) is rarely used as the protective colloid in stabilizing the vinyl acetate-based emulsion polymerizations [2].

Different copolymers of vinyl monomers can be produced by emulsion polymerization. Example of such compounds with which vinyl acetate is commercially copolymerized are vinyl chloride, vinyl propionate, higher vinyl esters such as vinyl versatate, acrylates, methacrylates, maleates, fumarates, ethylene, and acrylonitrile. The selection of the comonomer to be used to produce latices for any given application depends principally upon the functional suitability of the comonomer and its cost [4]. Terpolymers of vinyl acetate are also widely used to further enhance the exceptional qualities of vinyl acetate polymers in a variety of applications, copolymers (particularly vinyl acetate-ethylene (EVA), vinyl acetate-butyl acrylate, vinyl acetate-methyl methacrylate, etc.) and even terpolymers have been made recently (paint, coating, bonding, etc.) [15-17].

In this study, emulsion copolymerization of vinyl acetate and butyl acrylate was carried out with a semi-batch feed. Potassium persulfate was used as a thermal initiator, together with a non-ionic emulsifier and protective colloid, N-methylol acrylamide (NMA). NMA is a bifunctional monomer with reactive vinyl and hydroxymethyl groups. Thermoplastic polymers can be formed by copolymerization of NMA with a variety of vinyl monomers by emulsion, solution, and suspension techniques [18]. Emulsion co-polymerizations were carried out by changing the monomer ratios in the same copolymerization recipe, so that copolymer latexes with different monomer ratios and different physical properties were synthesized [19-22].

Characterizations of the obtained vinyl acetate-co-butyl acrylate latexes; The content of solids and conversion percentages were determined by gravimetric method, and molecular weights were determined by gel permeation chromatography and viscosity method.

II. EXPERIMENTAL METHOD / TEORETICAL METHOD

In case of research driven by experimental study, test procedure / method should be explained in a clear way. If a theoretical study has been carried out, the theoretical method should be given in detail. If the method has been previously mentioned in published studies, the difference of the current study should be stated by referring to the previous studies.

2.1 Materials and Preparation Techniques

Vinyl Acetate (VAc) and butyl acrylate monomers are product of Sigma Aldrich. The monomer was used directly without any purification. Potassium Peroxydisulfate (KPS) is purchased Merck product $K_2S_20_8$ was used as initiator in the experiments without any purification process. NMA is a specially prepared protective colloid used to narrow the molecular weight distribution and ensure emulsion stability. The preparation of NMA is given below.

N-methylol acrylamide Preparation: Water, methyl ethyl hydroxy quinone is added and heated to 60 ˚C. Then acrylamide is added and dissolved. After the dissolution is completed, the solution is cooled down to 20-30 °C (Room temp.). After adding formaldehyde, the pH is checked. It is desirable that the pH be 2.5-3.5. At 20-30 °C 95% of the NaOH solution is added and the temperature rises to 35-40 °C spontaneously. The pH is checked again if pH < 10.5 the remaining NaOH solution is added. The resulting solution is mixed for 1 hour, adjusted to pH: 5,5-6 with H2SO4, mixed for 15 minutes and mixed for another 10 minutes by adding methyl ethyl hydroxyquinone (2), the pH is controlled.

Sodium Hydrogen carbonate ($NaHCO_3$) was purchased from Merck and was used without any purification to adjust the pH of the polymerization solution.

Nonyl phenol ethoxylate (NP 30), a non-ionic emulsifier, purchased from Türk Henkel Kimyevi Maddeler Sanayi ve Ticaret A.Ş. NP with an ethoxylation number of 30 was used without any purification. Deionized water was used in all polymerization reactions.

Water Bath with thermostat and circulator: Hot-cold water inlet-outlet and circulation was provided to the reactor jacket with the MLW U2 C brand thermostat with a sensitivity of 1 °C.

2.1.1. Brookfield viscosimeter

To determine the original viscosities of the obtained latex, measurements were made with a programmable DV-II model Brookfield viscometer using number 4 spindle.

2.1.2. Ubbelohde viscosimeter

Ubbelohde viscometer with a flow time of 18.19 s for pure acetone at 25±0.1 °C was used to calculate the average molecular weights and viscosities of the obtained latexes.

2.1.3. Gel permeation chromatography (GPC)

Agilent model 1100 type GPC consisting of 3 Waters silica gel columns (HR 4, HR 3, and HR 2) calibrated with 3 polystyrene standards with refractive index detectors was used to determine the number average (Mn) and weight average (Mw) of molecular weights, molecular weight distributions (PDI) of the copolymers respectively. THF was used as diluent at flow rate 0.3 ml/min at 30 °C.

The reactions were carried out at atmospheric pressure without the use of inert atmosphere (nitrogen gas, etc.), as in the industry since VAc was used commercially without distillation.

2.2 Synthesis of Latexes

In the study, it was aimed to examine the effects of different Vac/BuA ratios on the physicochemical properties of latexes. In the synthesis of latexes, VAc, BuA, NMA, $NaHCO_3$, deionized water, KPS as initiator and NP30 as emulsifier were used. The physicochemical properties of the synthesized VAc and BuA copolymers were investigated by measuring viscosities (Ubbelohde and Brookfield), molecular weights (Mv, Mn, Mw), and molecular weight distributions (HI). Emulsion copolymerization reactions were carried out under atmospheric conditions. An example of the emulsion recipe used in the copolymerization reactions is given in the Table1.

Table1. Sample Recipe for Emulsion Copolymerization of VAc and BuA

	Weight (%)
VAc	37.15
BuA	6.56
NMA	1.88
NP30	3.69
KPS	0.24
NaHCO3	0.12
Deionized Water	50.36
Total	**100.0**

The polymerization processes applied for the synthesis of latexes are given below. (In the experiments, 5 times the prescription amounts were used.) Before starting the reaction, VAc, BuA, NMA, emulsifier (2/3) and water (117 ml) were mixed in a beaker for 30-40 min at 800 rpm using a mechanical stirrer to form a pre-emulsion. This mixture was transferred to the dropping funnel and the dropping funnel was placed on top of the reactor. The polymerization setup was heated to 70-75 °C for at least 30 minutes and continuous circulation was provided. The remainder of the emulsifier (1/3), the remainder of the water (117 ml) and $NaHCO_3$ were added to the reactor and mixed. The solution in the reactor was kept at 70 °C for at least 10 minutes. 0.12 g of KPS was dissolved in small amount of water and then added. After the addition of the first initiator, 10% of the total monomer mass was introduced within 30 minutes at 70-72 °C and rest of the initiator and monomer were added at 30 min intervals throughout the reaction. The amounts of Initiator added are respectively 0.12g, 0.2g (4 times) and 0.28g. The resulting latex was stirred for another 10 minutes and allowed the latex to cool down slowly to 30 °C to prevent the formation of cream.

2.3 Determination of Viscosities of Latexes

The viscosities of the original latexes were measured at 19 °C with a programmable DV-II model Brookfield viscometer using number 4 spindle. During measurements, viscosity of each latex was read as cP from the instrument's digital display after at least 2 minutes of mixing.

2.3 Determination of Solid Percentages of Latexes

The viscosities of the original latexes were measured at 19 °C with a programmable DV-II model Brookfield viscometer using number 4 spindle. During measurements, viscosity of each latex was read as cP from the instrument's digital display after at least 2 minutes of mixing. For the determination of experimental (practical) solids of latexes obtained by emulsion polymerization; approximately 1.5 g of latex was weighed on a precision balance (m_1) in small containers made of aluminum foil, of which the tare was determined. The containers with latex were kept in an oven at (70 ± 2) °C for 1 day and all the water in the latex was evaporated. Completely dried latexes in aluminum containers were taken to a desiccator and cooled to room temperature, then reweighed (m_2). According to the weighing results, the % solids of each latex was calculated experimentally using equation 1.

$$\%\ Solid = [(m_1) - (m_2) / (m_1)]100 \tag{1}$$

For calculating the theoretical solid contents (TSC) of the obtained latexes; The % by weight in the emulsion polymerization recipe and Equation 2 was used.

$$TSC\ (\%) = (Vac+BuA)\ \% + 0.95\ x\ NMA\ \% + 0.76\ x\ Emulsifier\ \% + APS\ \% + NaHCO_3\ \% \tag{2}$$

2.4 Determination of the Conversions

The % conversions of polymers were also found from experimental and practical solid percentages calculated for latexes. Equation 3 was used to calculate the % conversions.

$$\%\ conversion = (\%\ Solids / TSC) *100 \tag{3}$$

2.5 Determination of Molecular Weights of Latexes

2.5.1. With Intrinsic Viscosity (Mv)

The polymer solutions at different concentrations were prepared by dissolving the polymer directly in acetone without separating the linear, graft and intertwined network fractions by extraction method.

$$[\eta]=KM_v^a \tag{4}$$

To calculate the average molecular weight of polymers; The Mark–Houwink–Sakurada Equation (Equation 4) and K= 6.85x10-5 (dl/g) and a=0.75 values were used for copolymers in the acetone at 25 °C [19].

The flow times of the copolymer solutions diluted at different concentrations were found with the Ubbelohde viscometer in a constant temperature bath at 25±0.1 °C. Flow times for each solution were repeated at least 5 times and repetitive results were obtained. Specific viscosity-concentration graphs were drawn by calculating the specific viscosities of the solutions with the help of the flow times found, and the intrinsic viscosity of each latex was calculated from the graphs drawn.

2.5.2. With GPC (Gel permeation Chromatography)

1.0 % solutions of latex films, which were previously filmed on glass plates, in THF (ultra-pure) solution were prepared and the results were evaluated.

III. RESULTS AND DISCUSSIONS

3.1 Effect of Monomer Ratio on Viscosity

The effects of the thermal initiator on the copolymer viscosities were determined depending on the VAc/BuA monomer ratios used in the copolymerization. The results found are given in Table 2 and Figure 1.

Table 2. Brookfield Viscosity of Latexes

Monomer Ratio ***(% BuA)***	**Brookfield** ***(cP)***
0	1.20
10	5,70
15	8.40
25	12.00
30	9.36
40	15.00
50	20.43
60	17.60
70	20.52
85	28.98
90	24.80
100	32.14

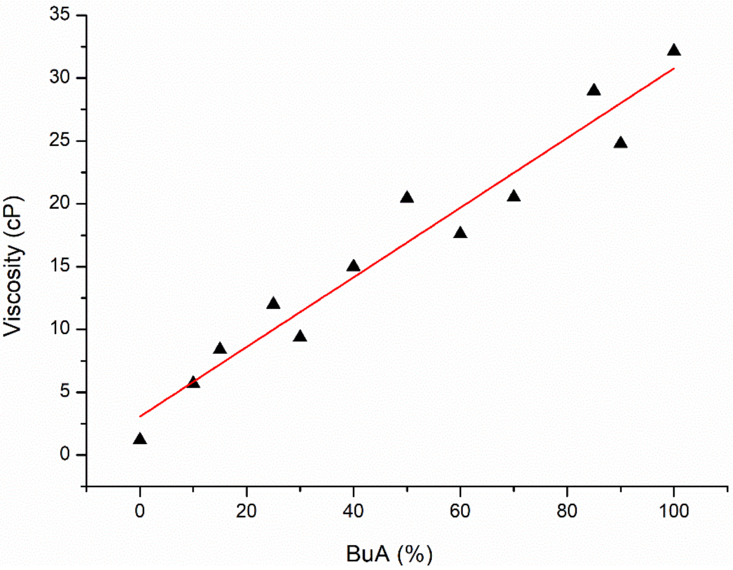

Figure 1. Viscosity against monomer ratio

According to the values found; Although the viscosity increased smoothly until the monomer ratio was 50:50, deviations were observed in both homopolymers (homo VAc and homo BuA), and the highest viscosity value was reached for 0:100 (homo (BuA)). However, in general, it was determined that the viscosity increased in parallel with the increasing BuA percentage. It is known that this increase is due to the core-shell structure of VAc-co-BuA latex [20]. The initial copolymer composition is much richer in BuA than the monomer composition in the particles because of the preference of BuA to react with its monomer (reactivity ratio for BuA $6.2.10^{-1}$) and the preference of VAc to react with BuA (reactivity ratio for VAc $0.028.10^{-3}$) [21].

3.2 Effect of Monomer Ratio on Solid Content

The experimental solid contents of latexes were calculated from Equation 1 are given in Table 3 depending on the monomer ratio. Since the conversions calculated according to the experimental and theoretical solid content found were over 90%, it was determined that the polymerizations were completed, and the conversions increased with increasing BuA percentage.

Table 3. Percent Conversions of Copolymers Initiated with KPS Initiator

Monomer Ratio ***(BuA %)***	**TSC** ***(%)***	**Solid content** ***(%)***	**Conversion** ***(%)***
0	48,66	44.17	90,77
10		46.39	95,34
15		-	-
25		46.40	95,36
30		45.82	94,16
40		46.41	95,37
50		45.93	94,39
60		46.28	95,11
70		44.80	92,08
85		46.22	94,98
90		44.84	92,16
100		47.85	98,33

3.3 Effect of Monomer Ratio on Viscosity Average Molecular Weight (Mv)

The intrinsic viscosities of the synthesized VAc-BuA copolymers were calculated using the a and K constants [13] with the help of the Mark–Houwink–Sakurada equation (Equation 4), and the results were plotted against the increasing BuA percentage (Figure 2). According to this, it was observed that Mv increased with increasing BuA percentage in the copolymer composition.

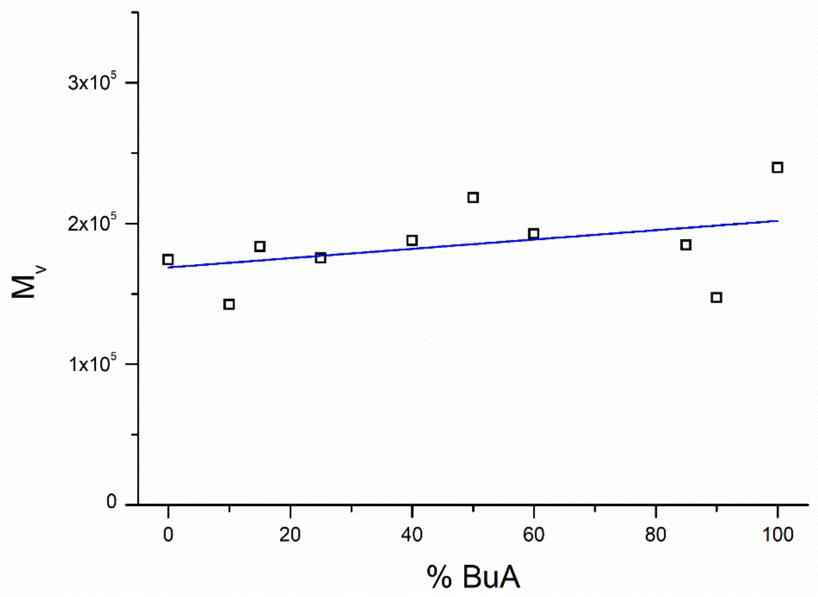

Figure 2. Variation of viscosity average molecular weight with percentage of BuA

3.4 Effect of Monomer Ratio on Molecular Weight Number and Weight Averages and PDI

Copolymer films were filmed on glass plates and dried, then 1% solutions were prepared with THF solvent, and number (Mn) and weight average (Mw) molecular weight measurements were made with GPC. The obtained values are given in Table 4 and Figure 3.

Table 4. Effects of monomer ratio on Mn, Mw, and polydispersity (PDI)

VAc/BuA *(%)*	**M_n**	**M_w**	**PDI**
100/0	86.595	344.592	3.979
90/10	107.488	531.187	4.942
85/15	116.998	508.359	4.350
75/25	118.522	580.739	4.900
60/40	124.379	601.217	4.834
50/50	146.979	670.796	4.564
40/60	147.579	644.190	4.365
15/85	202.644	765.155	3.786
10/90	118.446	-	3.085
0/100	142.578	790.164	3.627

The molecular weight number average and molecular weight average of the copolymer latexes increased smoothly with increasing BuA percentage. The increase of Mn with BuA gives information about the reaction kinetics and shows that the copolymerization proceeds at a controllable rate.

According to the obtained dispersity (PDI) values, the copolymer latexes showed relatively a narrow distribution and were found in the range of 3.09-4.90. This proves that the synthesized VAc-co-BuA latexes are monodisperse. In other words, NMA protective colloid gave a lower polydispersity value than those obtained with polyvinyl alcohol, and it was concluded that NMA could be used for molecular weight control. Since there is limited document about NMA in the literature, the results obtained are interesting and important.

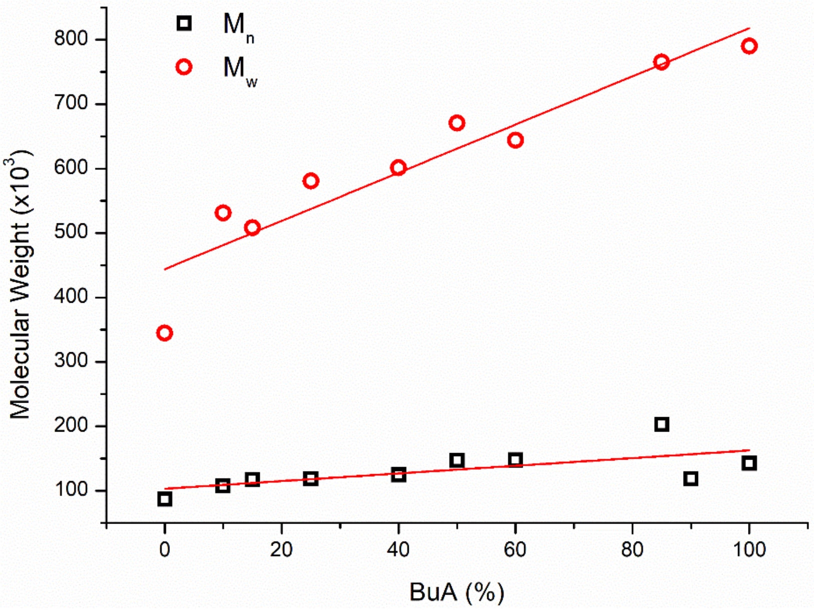

Figure 3. Variation of Mn and Mw with percentage of BuA

IV. CONCLUSIONS

The effects of varying monomer ratios (increasing BuA percentage) on the physicochemical properties of VAc-co-BuA copolymer latex obtained by semi-batch process were investigated. In addition, copolymers were synthesized with a protective colloid, NMA. The results found are summarized below.

As a protective colloid, NMA worked perfectly and maintained emulsion stability in all monomer ratios during co-polymerization reactions. As the percentage of BuA in the VAC/BuA monomer ratio increases, there is a smooth increase in the viscosity of the latex. However, no clear correlation was found between the percentage of BuA in the copolymers and % conversion, but overall, all copolymers achieved the expected conversion. Parallel to the increase in the percentage of BuA in the total monomer, molecular weight viscosity average, number average and weight average increased smoothly. It was also found that the molecular weight distributions (PDI) of the latexes showed a narrow distribution close to monodispersed. Although NMA provides enough emulsion stability, which amount (%) of NMA will be more effective in the emulsion formula may be a research subject in future studies.

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