The Grafting Reactions Of Poly(vinyl Alcohol) During The Emulsion Copolymerization Of Poly(vinyl Acetate-co-butyl Acrylate).

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THE GRAFTING REACTIONS OF POLY(VINYL ALCOHOL) DURING THE EMULSION COPOLYMERIZATION OF POLY(VINYL ACETATE - CO - BUTYL ACRYLATE)

by

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To all my friends that have been and still are in the EPI. I've seen you come, and I've seen most of you go, and now...

... I am out of here !

DEDICATION

To my mother,

who gave her love and support through the years.

To my father,

who was the greatest man I've ever known,

I wish you were here to share this moment.

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ABSTRACT

The emulsion copolymerization of vinyl acetate (VAc) and n-butyl acrylate (BuA) with poly(vinyl alcohol) (PVOH) of similar molecular weight and different degrees of hydrolysis as the sole emulsifier has been studied.

The grafting reactions of the poly(vinyl alcohol) and the vinyl acetate in the aqueous phase affected the rates of individual monomer consumption as predicted by the copolymerization reactivity ratios and the overall polymerization kinetics. The graft copolymer products of this reaction were analyzed by Fourier Transform Infrared (FT-IR) spectroscopy. A limiting value for the amount of vinyl acetate grafted to the poly(vinyl alcohol) to maintain water-solubility has been determined.

The presence of poly(vinyl alcohol) of different concentrations on the water-solubility of vinyl acetate and n-butyl acrylate was studied. Poly(vinyl alcohol) had no apparent effect on the monomer water-solubilities at room temperature.

The fully and partially hydrolyzed poly(vinyl alcohol) used in the emulsion copolymerization of VAc and BuA where modified by reaction with VAc monomer to the minimum degree of hydrolysis necessary to maintain water-solubility. The modified PVOH were then used as the emulsifier in the batch

emulsion copolymerization of VAc and BuA and the semi-continuous polymerization of vinyl acetate at different monomer feed rates. The batch polymerization experiments indicated that when the fully and partially hydrolyzed PVOH were modified to the same degree of hydrolysis they performed similarly in terms of kinetics of polymerization and particle size. The individual rates of monomer consumption were not affected by the presence of the modified PVOH. The semi-continuous polymerization of vinyl acetate under starved and flooded monomer feed conditions resulted in two different sets of data pertaining to polymerization kinetic profiles, particle size and number density data.

The experimental results indicate that the mechanism of particle nucleation involves the grafting of PVOH and VAc in the aqueous phase, resulting in the formation of water-insoluble graft copolymer products. The water-insoluble graft copolymer then precipitate from the aqueous phase and act as the loci for particle nucleation.

1. GENERAL INTRODUCTION

1.1 EMULSION POLYMERIZATION

Emulsion polymerization is a type of radical chain polymerization that involves the polymerization of monomers that are in the form of emulsions. An emulsion, according to Becher [1], is a heterogeneous system, consisting of an immiscible liquid dispersed in another in the form of droplets. The phase present as droplets is called the disperse or internal phase; the phase which forms the media in which these droplets are suspended is called the continuous or external phase.

An emulsion polymerization system is comprised of a monomer, usually water-insoluble,(dispersed phase), the dispersion medium, usually water, (continuous phase), a soap-like micelle generating molecule (surfactant or emulsifier), and a free radical generating initiator (usually water-soluble such as potassium persulfate). The role of the surfactant is to aid in the emulsification of the dispersed phase in the continuous phase due to the molecule having both hydrophobic and hydrophilic segments.

The original description of an emulsion polymerization was based on the work of Harkins [2] and Smith and Ewart [3,4]. Where, at the beginning of an emulsion polymerization, the monomer is combined with water and

surfactant and is emulsified by sufficient agitation to disperse the monomer in numerous small droplets. At this point in the process there are three phases present: (1) The continuous water phase, in which there is a small amount of monomer and soap dissolved. (2) The emulsified monomer droplets which are dispersed in the water phase. (3) Micelles generated by the action of the surfactant which contain solubilized monomer. By decomposition of the initiator in the water phase a free radical is generated. The initiator radical then diffuses into the monomer swollen surfactant micelles where the polymerization takes place. As the polymerization proceeds, the micelles grow by the addition of monomer that diffuses through the water phase from the monomer droplets which act as a reservoir during the polymerization. The polymerization proceeds until the surfactant micelles disappear and the surfactant begins to adsorb on the surface of the monomer-particles, which helps in the stabilization of the particles. The particles are supplied with free radicals from the water phase and with monomer until the monomer droplets disappear. The monomer concentration decreases with increasing conversion until the polymerization reaction is complete at which point all of the monomer has been converted to polymer. The final polymer product of an emulsion polymerization is termed a latex.

The emulsion polymerization process, then, can be

broken down into three different stages or intervals, which is described by a conversion-time curve as shown in Figure 1.1. During Interval I, particle nucleation occurs and the rate of polymerization increases with the particle number. The particle number will become constant as the polymerization enters Interval II, which is the particle growth stage. During Interval II the micelles and monomer droplets disappear and a constant rate of polymerization is established (no new particle nucleation). At interval III the particle number is the same as in Interval II and the

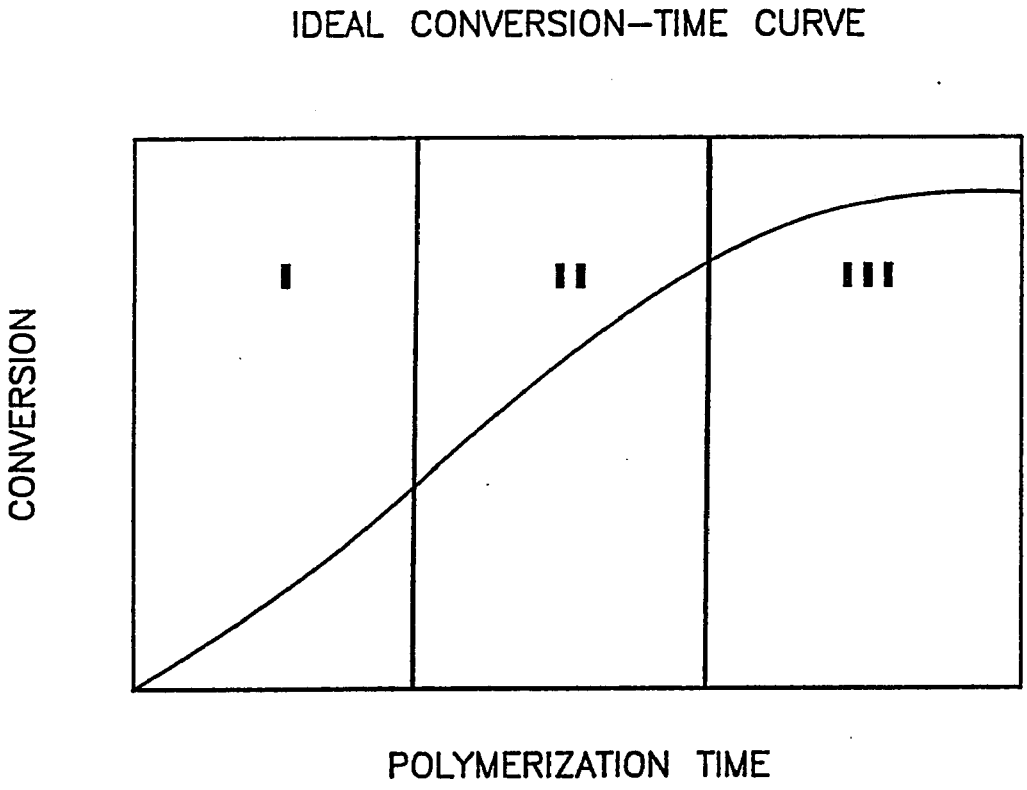


Figure 1.1: Ideal Conversion-Time Curve, Illustrating the Three Stages of Emulsion Polymerization.

monomer phase has disappeared and all of the unreacted monomer is located in the polymer particles until it is consumed and the reaction is completed.

The mechanism for particle nucleation can be described by two different processes. One is the entry of the free radicals, from the aqueous phase, into the monomer swollen micelles known as micellar nucleation or heterogeneous nucleation as described by Smith and Ewart [3-4]. The other nucleation mechanism, is termed homogeneous nucleation [5-9].

Monomer water-solubility and surfactant concentration effect the type of nucleation mechanism present in an emulsion polymerization.

In the case of a very water-insoluble monomer such as styrene, micellar nucleation is the predominate mechanism [3,4,10].

For a water-soluble monomer like vinyl acetate, homogeneous nucleation is the primary mechanism for particle nucleation [11,12].

For partially water-soluble monomers, such as vinyl acetate or methyl methacrylate, the micellar theory of Smith and Ewart does not hold true. In the case of such water-soluble monomers the radical formation takes place in the aqueous phase and the polymerization is initiated resulting in the formation of oligomeric radicals. These oligomeric

radicals will grow to some critical length at which point they will no longer be water-soluble and precipitate from the aqueous phase to form primary particles. Oligomeric radicals formed after this process would either grow to the critical size and precipitate as described above or be captured by already existing polymer particles.

1.2 POLY(VINYL ALCOHOL)

1.2.1 Introduction

Poly(vinyl alcohol) (PVOH) was first discovered by the German scientists W.O. Herrmann and W. Haehnel in 1924 [13,14]. The first industrial production of poly(vinyl alcohol) occurred in 1926 for use in textile sizing [15] and was commercially introduced in the United States by the Dupont Company in 1939.

Poly(vinyl alcohol) is structurally the simplest water-soluble polymer. The polymer repeating unit $-CH_2-CHOH-$ has a formula weight of 44.05 grams/mole and a glass transition temperature, T_g of 85^oC . Poly(vinyl alcohol) is insoluble in most common organic solvents and is soluble in only water, DMF, formamide, and hot glycols, glycerols, and DMSO [16].

Poly(vinyl alcohol) has uses in adhesives, binders, paper sizing, paper coatings, textile sizing and finishing,

cosmetics, and as an nonionic emulsifying and stabilizing agent for use in emulsion and suspension polymerization.

Vinyl alcohol, the theoretical monomer of poly(vinyl alcohol), does not exist as a stable compound. Attempts to synthesize vinyl alcohol have lead to the formation of its isomer acetaldehyde.

Poly(vinyl alcohol) is prepared by a hydrolysis reaction of poly(vinyl acetate). The polymerization method of vinyl acetate monomer has a significant effect on the final properties of the poly(vinyl alcohol) after hydrolysis of the poly(vinyl acetate). The four types of radical chain polymerization, bulk, solution, emulsion and suspension, can be used to prepare poly(vinyl acetate). Solution polymerization of vinyl acetate seems to be the most suitable method for the polymerization of vinyl acetate to be used for making poly(vinyl alcohol) with excellent overall properties [17].

1.2.2 Preparation by Hydrolysis of Poly(vinyl acetate)

Different methods of hydrolysis of poly(vinyl acetate) to poly(vinyl alcohol) are used and can be grouped according to the catalyst used [18]. The different chemical reactions are outlined as followed:

Alcoholysis:

$$\text{PV-OAc} + n\text{ROH} \xrightarrow{\text{acid or alkali}} \text{PV-OH} + n\text{ROAc} \qquad (1.1)$$

Hydrolysis:

$$PV\text{-}OAc + nH_2O \xrightarrow{\text{acid or alkali}} PV\text{-}OH + nHOAc \quad (1.2)$$

Direct Hydrolysis:

$$PV\text{-}OAc + nNaOH \xrightarrow{H2O} PV\text{-}OH + nNaOAc \quad (1.3)$$

Aminolysis:

$$PV\text{-}OAc + nHNR_2 \xrightarrow{H2O} PV\text{-}OH + nAcNR_2 \quad (1.4)$$

Ammonlysis:

$$PV\text{-}OAc + nNH_3 \xrightarrow{NH4Cl \text{ or } NH4OAc} PV\text{-}OH + nAcNH_2 \quad (1.5)$$

Along with the above reactions, side reactions occur to give sodium acetate and acetaldehyde formed from residual vinyl acetate monomer.

The preferred industrial method of hydrolysis of poly(vinyl acetate) to poly(vinyl alcohol) is alcoholysis. The vinyl acetate is solution polymerized in methanol which then can be directly used in the alcoholysis reaction using sodium hydroxide or sodium methoxide as catalysts [19]. The poly(vinyl alcohol) prepared from the reaction is insoluble in the methanol and methyl acetate by-product and thus precipitates out. It is then filtered, washed, dried and packaged.

Poly(vinyl alcohol), in general, is commercially available in three different molecular weight ranges. The three ranges are specified in terms of viscosity of a 4.0% aqueous solution at 20°C of the PVOH and are high-viscosity:

55.0-65.0 cps, medium- viscosity: 26.0-30.0 cps and low-viscosity: 4.0-6.0 cps.

The molecular weight of the PVOH product is a direct function of the molecular weight of the precursor poly(vinyl acetate) used in the hydrolysis reaction.

The percent hydrolysis is controlled by stopping the reaction at a desired level by the neutralization of the catalyst or allowing it to go to completion.

Two basic grades are available in each of the molecular weight ranges. Partially hydrolyzed grade represents products that have been hydrolyzed to 87.0-89.0 percent and the completely hydrolyzed grade is hydrolyzed to 98.0-99.0 percent. The molecular weight and degree of hydrolysis control the properties of the poly(vinyl alcohol). As the molecular weight decreases water-solubility increases. When increasing the molecular weight the tensile strength, elongation, tear resistance and flexibility increase. As the degree hydrolysis increases so does the tensile strength, elongation and tear resistance. As the degree of hydrolysis increases towards 100% there is increased difficulty for the water to solubilize the PVOH due to hydrogen bonding between the hydroxyl groups on the PVOH chains.

PVOH, as a result of its appreciable crystalline content, does not dissolve in water at normal temperatures. Heating to a well defined dissolution temperature (usually

above 85°C) is required. This temperature must be maintained for a period of time to allow for full molecular dispersion to take place [20]. Upon cooling down of the PVOH solution to room temperature, the solution can gelate, aggregate, or even crystallize on standing.

1.2.3 Poly(vinyl alcohol) in Emulsion Polymerization

Poly(vinyl alcohol) with different degrees of hydrolysis is often used as the sole emulsifier and stabilizer in the emulsion polymerization of vinyl acetate. Industrially, poly(vinyl alcohol) with up to 20.0% mole percent acetyl groups are preferred for use as emulsifiers for the production of poly(vinyl acetate) by emulsion polymerization.

The stability of colloidal systems using PVOH as a protective colloid depends on the structure of the PVOH used in terms of: molecular weight, molecular weight distribution, the acetyl group content and distribution. During an emulsion polymerization of vinyl acetate using PVOH as the emulsifier, the particle size and size distribution of the monomer droplets is dependent on the grafting and crosslinking reactions of the PVOH and VAc.

When poly(vinyl alcohol) is used as the sole stabilizing agent in an emulsion polymerization, it performs two functions: emulsifying the monomer and stabilizing the

polymer particles formed [21]. The poly(vinyl alcohol) also serves as a viscosity-builder which helps to retard creaming and settling. The stabilizing ability and viscosity-building effect increases with molecular weight of the PVOH, the emulsifying capability is enhanced by lowering the molecular weight [22].

It has been found that the poly(vinyl alcohol) stabilizes the poly(vinyl acetate) emulsion by grafting with the vinyl acetate in the aqueous phase and by chemically bonding to the surface of the polymerizing poly(vinyl acetate) particle by creating a graft copolymer [23-30]. These grafting reactions between the PVOH and VAc can affect the kinetic characteristics of the polymerization process as well as the surface, colloidal, and bulk properties of the resulting latex.

How the poly(vinyl alcohol) is prepared from the poly(vinyl acetate) effects the performance of the PVOH as an emulsifier and its ability to graft with the VAc. A partially hydrolyzed PVOH has different intermolecular and intramolecular distributions of residual acetate groups according to its method of production [31-33]. Noro [34] found that during the hydrolysis of PVAc, if methyl acetate was added the intermolecular distribution of the residual acetate groups is changed. A more "blocky" distribution was achieved which increased the viscosity and stability against

"salting out" by sodium sulfate for PVAc latexes prepared with PVOH.

Hayashi, et. al., found that by adding benzene to the alkaline hydrolysis solvent, the blockiness of the PVOH can also be increased [35]. The compatibility of these blocks of PVAc in the PVOH polymer chain explains why the partially hydrolyzed grades of PVOH are better suited for the emulsion polymerization of vinyl acetate.

Shirinyan, et. al., reported that there is an optimum sequence length for the hydroxyl groups in the PVOH-PVAc block copolymer for the polymerization rate and the stability of the dispersion [36].

Shakhova and Meyerson [37] showed that the blocky structure of the PVAc of partially hydrolyzed grades of PVOH can result in micellization in an aqueous solution. Their experimental results show that benzene was solubilized in PVOH solutions to an extent which increases with the acetyl content of the PVOH. This "micellization" was not observed by O'Donnell et. al. when using PVOH as an emulsifier for the emulsion polymerization of VAc [24].

The adsorption of PVOH by PVAc latexes showed that the blockier samples adsorbed more strongly on the PVAc latex particles than fully hydrolyzed PVOH which only weakly adsorbed or not at all. The strongly adsorbed grades seem to be those which have the greatest affect on the rates of

polymerization of VAc [38].

The high water solubility of vinyl acetate [39], (2.50 g/100g H_2O at 23°C) and the use of a water-soluble initiator, such as potassium persulfate, leads to polymerization being initiated in the aqueous phase and particle nucleation occurring by the homogeneous nucleation theory, as described in section 1.1.

The relative ease of grafting on polymer chain backbone is expressed by a quantity known as the polymeric transfer constant, C_p, and is calculated by the ratio of $K_{tr,m}/K_p$. This value is dimensionless. $K_{tr,m}$ is the rate constant for chain transfer of a propagating radical to monomer and K_p is the propagation rate constant of the radical.

Okamura, et. al., determined the transfer rate constants of monomer to polymer, C_p, at 60°C of vinyl acetate to poly(vinyl acetate) and poly(vinyl alcohol) and found the transfer constants to be:

VAc to PVAc $\quad C_{p(AC)} = 1.5 \times 10^{-4}$

VAc to PVOH $\quad C_{p(OH)} = 35 \times 10^{-4}$

The alpha hydrogen on the PVOH chain is easily abstractable by the radical than the OH of the PVOH and consequently produces a graft copolymer with PVOH as the backbone and the PVAc as the branches according to the following reaction scheme:

$$K_2S_2O_8 \longrightarrow 2K^+ + 2SO_4^{\bullet -} \qquad (1.6)$$

$$SO_4^{\bullet -} + PVOH \longrightarrow SO_4H^{=} + PVO^{\bullet} \qquad (1.7)$$

$$PVO^{\bullet} + nCH_2{=}\underset{\underset{OAc}{|}}{CH} \longrightarrow PVO\text{-}(\text{-}CH_2\text{-}\underset{\underset{OAc}{|}}{CH}\text{-})_n^{\bullet} \qquad (1.8)$$

$$PVO\text{-}(\text{-}CH_2\text{-}\underset{\underset{OAc}{|}}{CH}\text{-})_n^{\bullet} + PVOH \longrightarrow PVO\text{-}(\text{-}CH_2\text{-}\underset{\underset{OAc}{|}}{CH}\text{-})_nH + PVO^{\bullet} \qquad (1.9)$$

$$PVO^{\bullet} + VAc \longrightarrow \text{Goto (1.8)}$$

The initiator radicals formed in the aqueous phase interact with the PVOH forming macroradicals. The macroradicals then polymerize with the VAc in the aqueous phase whereby the formation of graft products takes place. As the grafted macroradicals become water-soluble they precipitate from solution and then cause polymerization in the dispersed phase. Through transfer reactions to the monomer, homopolymer PVAc is formed.

O'Donnell et.al. [24] reports that the grafting reaction between the PVOH and VAc in the aqueous phase is the locus of polymerization, where as the graft copolymer becomes water-insoluble it will precipitate from the aqueous phase as particle nucleation can occur according to the homogeneous particle nucleation theory, as described in section 1.1. O'Donnell also suggests that the latex particles produced by this homogeneous nucleation scheme follow Case III in the Smith-Ewart theory. Where the average

number of radicals per particle is less than 0.5 at the beginning of the polymerization. At that time radical desorption predominates the reaction rate like in an ionic system. However, during the course of the polymerization the average number of radicals per particle increases to a value greater than 0.5.

This grafting reaction between the PVOH and the VAc produces two different types of graft copolymers: water-soluble (low degree of grafting and unreacted PVOH), water-insoluble acetone-soluble (high degree of grafting and PVAc homopolymer). A third product of the reaction is also formed consisting of a water and acetone-insoluble fraction (high degree of grafting and crosslinking). The fraction of each of these components depends critically on the amount of PVOH used in the reaction [25,27].

Dimonie, et. al., further described the grafting process in the aqueous phase by monitoring the variation of the water-soluble fraction. They found that the water-soluble fraction increases at the beginning of the graft reaction due to formation of PVOH-PVAc graft copolymers which still have a sufficient amount of hydroxyl groups to maintain its water-solubility. As the grafting reaction continues the water-soluble fraction decreases and the water-insoluble fraction increases as the graft copolymer becomes water-insoluble and precipitates from the aqueous

phase [27,29].

Heublien [28] also examined the grafting reaction of VAc and PVOH in the aqueous phase by using infrared spectroscopy. During the course of the reaction, they monitored the increase in the carbonyl band of the water-soluble fraction at 1740 cm^{-1} due to the grafted VAc.

During the emulsion polymerization of VAc using PVOH as an emulsifier, the extent of the grafting reaction of the PVOH and VAc can be affected by the reaction conditions; concentration of initiator, PVOH, and monomer. The degree of hydrolysis of the PVOH and the presence or absence of a chain transfer agent.

Okamura [23] showed that grafting reaction of VAc to fully hydrolyzed PVOH in an homogeneous solution was more extensive than with the partially hydrolyzed PVOH. The hydrophobic acetyl groups were preferentially adsorbed by the monomer droplets, thus, are closer to the polymerization site. This fact is one reason why the partially hydrolyzed PVOH serves as a better emulsifier than the fully hydrolyzed PVOH. The fully hydrolyzed PVOH has to participate in the grafting reaction with the VAc in the aqueous phase to establish the hydrophobic acetyl groups [40,41].

The overall rate of emulsion polymerization of vinyl acetate when using poly(vinyl alcohol) as the emulsifier is

affected by the characteristics of the PVOH used. It has been found [12,29] that the rate of emulsion polymerization of vinyl acetate increases with the PVOH concentration. The degree of hydrolysis also affects the rates of polymerization. It was found [12] as the acetyl content of the PVOH increases the rate of polymerization decreased, but varies between samples. An optimum acetyl content was suggested by Shirinyan et. al. at which the rate of polymerization would be the fastest. No correlation was found between the molecular weight of the poly(vinyl alcohol) and the rate of emulsion polymerization of vinyl acetate [27,29,42].

The properties of poly(vinyl alcohol) and the latexes prepared with PVOH vary drastically between similar grades prepared from different manufacturers. The properties can vary even between different batches prepared by the same manufacturer. Commercial grades of PVOH are characterized in terms of residual acetyl content and viscosity of a 4% wt./vol. aqueous solution, but these data alone cannot fully describe the differences in the PVOH samples. The hydrolysis reaction used, reaction conditions, purity of the solvents all affect the PVOH final properties. Some of the factors that affect the properties of the PVOH for samples with the same degree of hydrolysis and viscosity are: (1) 1:2 glycol groups (2) stereoregularity (3) conjugated

unsaturated ketonic structures (4) residual poly(vinyl acetate) and (5) long and short chain branching [42-45]. Dunn et. al.[43] determined by instrumental methods that the difference in properties of similar grades of PVOH can be attributed to non-hydrolyzable short chain branching.

1.3 EMULSION COPOLYMERIZATION OF VINYL ACETATE AND n-BUTYL ACRYLATE

Poly(vinyl acetate) and Poly(butyl acrylate) as homopolymers vave very different properties [16,39]. The glass transition temperature of PVAc is 32^{o}C and polymer density is 1.19 g/ml at 20^{o}C. Poly(butyl acrylate) has a glass transition temperature of -54^{o}C and a polymer density of 1.05 g/ml at 20^{o}C.

Vinyl Acetate and n-butyl acrylate copolymer latex systems have been extensively studied in terms of their copolymerization kinetics, mode of monomer addition (as reflected by the copolymer composition, molecular weight, and particle morphology) and the particle nucleation mechanism [46-51].

In emulsion copolymerization the homogeneity of the copolymer composition can be affected by the: (1) the polymerization process (batch, semi-continuous, or continuous) (2) differences in the reactivity ratios of the monomers and (3) the water-solubility of the monomers [46].

Vinyl acetate and n-butyl acrylate monomers differ greatly in both water-solubility (VAc 2.50g/100g water, BuA 0.14g/100g water [39]) and copolymerization reactivity ratios (VAc r_1 = 0.05, BuA r_2 = 5.0 [16,52]). The homogeneity within the PVAc-PBuA copolymer particle will be very dependent on the mode of monomer addition. Chujo et. al. [47] and other researchers [46-51] have shown that an homogeneous copolymer composition can be obtained by a semi-continuous polymerization process, where the monomer was added at rate which was less than the rate of polymerization (starved semi-continuous conditions) for the system. The semi-continuous polymerization should have a copolymer composition similar to the comonomer composition. When a batch polymerization, all the monomer is added initially, was used an heterogeneous copolymer composition was obtained. The batch polymerization latex particles should have a core-shell morphology with a butyl acrylate-rich core and a vinyl acetate-rich shell, due to the differences in the properties of the monomers.

The mode of monomer addition will also affect the glass transition temperature of the copolymer latex [46]. The batch monomer addition gave two distinct glass transition temperatures for the copolymer latex ,temperatures depending on the comonomer ratio. The semi-continuous monomer addition gave a single glass transition peak, again the T_g is

dependent on the comonomer ratio.

1.4 OBJECTIVES

The objectives of this study were: (1) the determination of the effect of poly(vinyl alcohol) on the mechanism and kinetics of the emulsion copolymerization of vinyl acetate and n-butyl acrylate. (2) to examine the grafting reaction of poly(vinyl alcohol) and poly(vinyl acetate) and to determine their role in particle nucleation.

1.5 EXPERIMENTAL OVERVIEW

The effect of poly(vinyl alcohol) on the emulsion copolymerization of vinyl acetate and n-butyl acrylate will be described in the following chapters. Chapter 2 describes the development of the latex recipes and the experimental procedures involved in preparation and characterization of the copolymer latexes. Chapter 3 discusses the polymerization kinetics of the VAc/BuA copolymer latexes using PVOH as an emulsifier in varied concentrations and with varied potassium persulfate initiator concentrations. Chapter 4 describes the characterization of the VAc/BuA copolymer latexes using Fourier Transform Infrared (FT-IR) spectroscopy. Emphasis will be placed on determining the acetyl content of the water-soluble serum separated from the

copolymer latex. Chapter 5 will describe the preparation and subsequent use in polymerizations, batch and semi-continuous, of poly(vinyl alcohol) that have been modified to an overall degree of hydrolysis of 82.0%. Chapter 6 will discuss the conclusions drawn from the experimental data presented in the previous chapters and offer recommemdations for future work.

2. EXPERIMENTAL

2.1 MATERIALS

The poly(vinyl alcohol) (PVOH) was supplied by Air Products and Chemicals, Inc. Two low-viscosity grades were used: Vinol 205, 87.0-89.0 percent hydrolyzed, (lot number 01100433) and Vinol 107, 98.0-98.8 percent hydrolyzed, (lot number 07020344). The molecular weight of the two PVOH samples was determined by aqueous-phase Gel Permeation Chromatography and was found to be:

Vinol 107	M_w = 26,250	M_n = 15,570
Vinol 205	M_w = 34,940	M_n = 18,470

Vinyl acetate (VAc) (Polysciences, Ins.)has a molecular weight of 86.09 g/mole and a density at 20°C of 0.9317 g/ml. The VAc was distilled, in order to remove inhibitor used for shipping and storage, at 760mm Hg at 72°C using a packed Raschig ring column. N-butyl acrylate (BuA) (Badische Corp.) has a molecular weight of 128.17 g/mole and a density at 20°C of 0.8986 g/ml. To remove inhibitor, the BuA was washed with a 5.0% sodium hydroxide (NaOH) solution and then with distilled-deionized (DDI) water. The n-butyl acrylate was dried over anhydrous sodium sulfate (Na_2SO_4) and distilled under 50mm Hg vacuum at 60°C. Both of the purified monomers were stored at -5°C until use.

The reagents used in the polymerization process, sodium bicarbonate ($NaHCO_3$) (Certified ACS Grade, Fischer), potassium persulfate ($K_2S_2O_8$) (FMC Corp.), tertiary dodecyl mercaptan (PennWalt), sodium lauryl sulfate (SLS) (Certified ACS Grade, Fischer) and hydroquinone (Certified ACS Grade, Fischer), were used as received without further purification.

The reagents used in the polymer characterization, namely, 1,4-dioxane (Purified HPLC Grade, Aldrich), methyl sulfoxide (DMSO, $(CH_3)_2SO$) (Spectrophotometric Grade, Aldrich), potassium thiocyanate (KSCN) (Aldrich), chloroform ($CHCl_3$) and toluene ($C_6H_5CH_3$) (both were Spectrophotometric Grade, Mallinckrodt), were also used as received.

Poly(vinyl acetate) (M_w= 194,800, M_n= 63,600) and poly(butyl acrylate) (26.0% solids in toluene, M_w= 61,800, M_n= 20,700) (Scientific Polymer Products, Inc.) were used as polymer reference standards in the Fourier Transform Infrared (FT-IR) Spectroscopy experiments.

The water used throughout the experiments was distilled and deionized to a final resistivity of 17.8 megohm-cm.

The nitrogen gas (N_2) (Blue Valley) used for all experiments was zero-grade.

2.2 EXPERIMENTAL APPARATUS

2.2.1 Polymerization Reactor

The polymerization reactor used throughout the experiments was a 300 ml four-neck round bottom Pyrex flask. A stainless steel stirring shaft with a half-moon shaped impeller blade and teflon adapter gland was inserted through the center neck of the flask. The agitation speed was held constant at 110 rpm. One side neck of the flask was equipped with the sampling port, which consisted of a 1/4 inch i.d. teflon tube equipped with a two-way stopcock (one direction for nitrogen purge and the other for withdrawing a sample). The other side neck was fitted with a reflux condenser and bubbler to monitor the N_2 flow. A thermometer was inserted into the last neck of the flask to monitor the temperature in the reactor. The reactor was placed into a 60 $\pm$ 0.5^{o}C thermostated water bath.

2.2.2 Analytical Instrumentation

A Hewlett Packard model 5890A gas chromatograph with a flame ionization detector (FID) and Integrator model 3393A was used to determine the monomer conversions during the course of the polymerizations.

Infrared spectroscopy analysis was carried out using a Mattson Sirius model 100 Fourier Transform Infrared (FT-IR) spectrophotometer. The mirrors and sample holder in the FT-IR sample chamber were in the transmission analysis configuration.

The particle size of the latexes was determined by photon correlation spectroscopy using the Coulter Electronics model N4M Multiangle Submicron Particle Size Analyzer. The angle of incident laser light to the sample chamber was held constant at 90^{o}.

The latex samples were centrifuged using a Dupont Sorvall RCB-5 Refrigerated Centrifuge with an SS-34 fixed angle rotor. A Fisher Microcentrifuge model 235B was also used.

2.3 EXPERIMENTAL RECIPES

2.3.1 Standard Recipe

The standard recipe used for the emulsion copolymerization of vinyl acetate and n-butyl acrylate using poly(vinyl alcohol) is given in Table 2.3.1. Each component in the recipe was added on a weight basis.

Any changes to the standard recipe will be discussed in their relevant sections.

TABLE 2.3.1

STANDARD EMULSION COPOLYMERIZATION RECIPE

Component	Weight (grams)
Vinyl Acetate (VAc)	25.00
n-Butyl Acrylate (BuA)	25.00
Distilled Deionized Water	150.00
Poly(vinyl alcohol) (PVOH)	2.50 - 5.00
Sodium Bicarbonate ($NaHCO_3$)	0.05
Tertiary Dodecyl Mercaptan	0.05
Potassium Persulfate ($K_2S_2O_8$)	0.0125 - 0.10

The standard recipe yields a latex product with approximately 26 percent solids, depending on the exact weight of each component.

2.3.2 Preparation of Poly(vinyl alcohol) Solutions

The poly(vinyl alcohol) solutions were prepared by dispersing granulated PVOH into room temperature distilled-deionized water. The solution was stirred for about 20 minutes to allow the water to thoroughly wet the PVOH surface. The PVOH dispersion was then heated, to 85°C for the partially hydrolyzed Vinol 205 and to 95°C for the fully hydrolyzed Vinol 107, for 30 minutes to allow the PVOH to completely dissolve.

When the heating was complete, the solutions were filtered through glass-wool and cooled to room temperature. Zero-grade N_2 was bubbled through the solution to remove dissolved oxygen. The solutions were stored at room temperature under N_2 until use. The poly(vinyl alcohol) solutions were prepared fresh 24 hours in advance of the experiments and were discarded afterwards.

The actual PVOH concentration of the solutions was determined by gravimetric analysis.

2.4 EXPERIMENTAL PROCEDURES

2.4.1 Preparation of Poly(vinyl acetate-co-butyl acrylate) Latexes

(1) The temperature of the water bath was adjusted to 60°C.

(2) The polymerization reactor assembly was placed into the water bath and clamped into position. The stirrer speed was set to 110 rpm.

(3) The poly(vinyl alcohol) solution, sodium bicarbonate (pH buffer), vinyl acetate, butyl acrylate, and the t-dodecyl mercaptan (chain transfer agent) were added in batch to the reactor and placed under a positive pressure N_2 gas blanket.

(4) The potassium persulfate initiator was dissolved in 10ml of DDI water, which was deoxygenated with N_2 gas, and injected into the reactor through the two-way stopcock. At this point the polymerization was started. The polymerization was allowed to proceed until the 360 minute mark at which time the polymerization was completed, final polymer conversion values differed throughout the experiments.

2.4.2 Determination of Monomer Conversion

(1) The percent solids for a 100% converted latex was calculated from the weights of the ingredients in the recipe. This value was termed the theoretical percent solids.

(2) 5 ml Samples were withdrawn via the sampling port by syringe periodically throughout the course of the polymerization. The samples were injected into sealed vials that contained 0.30 grams of a 0.50% hydroquinone in water solution to quench the reaction.

(3) The overall conversion at each sampling time was determined gravimetrically based on the percent solids of the sample when compared to the theoretical percent solids at 100% conversion.

(5) Fractional monomer conversion is determined by gas chromatography using the HP 5890A GC. A calibration curve, constructed by plotting the GC ratio of the peak area of VAc to BuA as a function of the weight ratio of VAc to BuA, is shown in Figure 2.1. The linear regression coefficient was calculated for the calibration curve and was found to be R^2= 0.9897. The fractional conversion of each monomer is calculated by the combination of the GC data and the gravimetric conversion data.

(6) The polymerization conversion data was plotted three-ways: overall conversion versus time, fractional monomer conversion versus time, and fractional monomer conversion versus overall conversion.

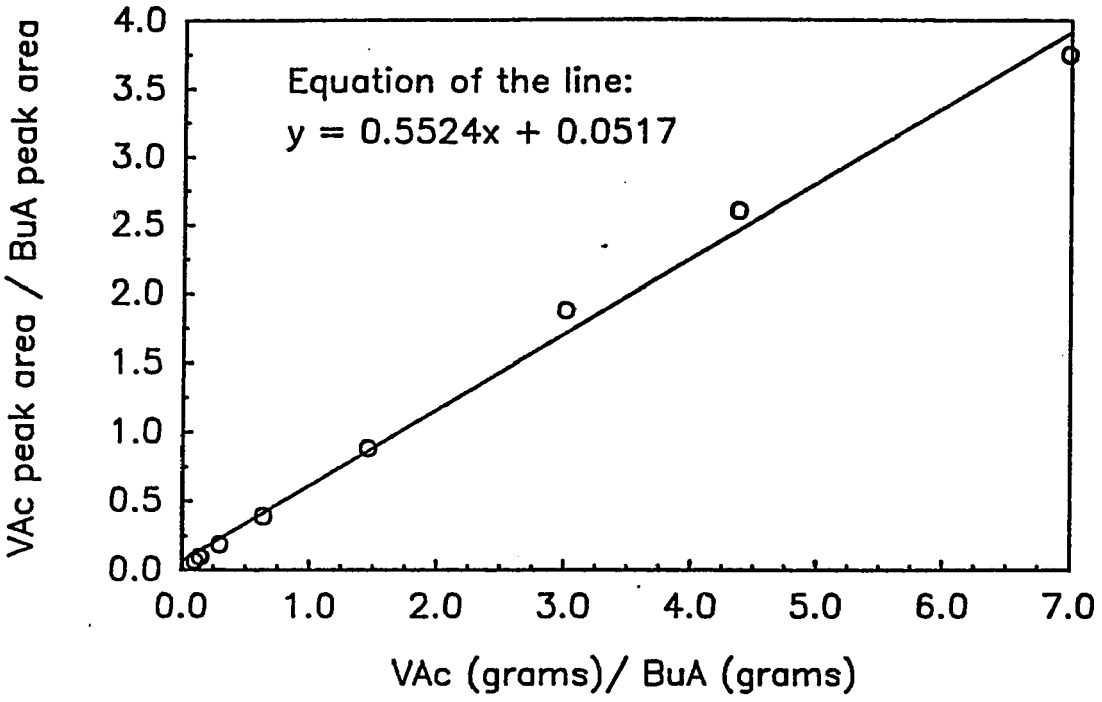


Figure 2.1: Gas chromatograph calibration curve for VAc and BuA standards.

2.4.3 Determination of Particle Size

(1) The particle diameters for each sample, as a function of conversion, and for the fully converted latexes was determined using the Coulter N4M. Each sample was placed in a poly(styrene) cuvette and was diluted with DDI water until the particle concentration was within the required range of the instrument. Samples at low conversion, less than 20.0% were placed in a quartz cuvette due to the presence of residual monomer. Every sample was analyzed five times by the Coulter N4M and the average of the runs was calculated along with the standard deviation. The particle number density (number of particles, N_p/ ml of H_2O) was

calculated by the following equation:

$$\bar{V}_{1,m}N_{1,0} + N_{1,0}X_1(\bar{V}_{1,m}-\bar{V}_{1,p}) + \bar{V}_{2,m}N_{2,0} + N_{2,0}X_2(\bar{V}_{2,m}-\bar{V}_{2,p}) = 4/3\,\pi r_p^3 N_p \qquad (2.4.1)$$

where: $\bar{V}_{n,m}$ is the molar volume of monomer n
$\bar{V}_{n,p}$ is the density of polymer n/ MW of monomer n
$N_{n,0}$ is the initial number of moles of monomer n
X_n is the fractional conversion of monomer n
n is 1 for VAc and 2 for BuA
r_p is the radius of the particle
N_p is the number of particles

(2) The particle size data was plotted as particle diameter (nanometers, nm) and number of particles/ml versus overall conversion and time.

2.4.4 Separation of the Polymer Phase and Serum of the Latexes by Centrifugation

(1) 30 ml of the latex samples were placed into a 50ml Oak Ridge type polyallomer centrifuge tube. The tube was then placed into the SS-34 rotor inside the chamber of the Dupont Sorvall RCB-5 centrifuge. The samples were centrifuged at 18,000 rpm at 4^{o}C for 2 hours.

Small volume samples, less than 1.5 ml, used a Fisher Microcentrifuge model 235B with a fixed angle rotor. 1.5 ml Eppendorf type centrifuge tubes were used. The microcentrifuge conditions were the same as the RCB-5.

(2) After centrifugation was complete, the serum was

collected by pipetting from the centrifuge tube and stored at room temperature until use. The solid polymer fraction was removed, washed with DDI water, and dried in a vacuum oven at 30°C for 24 hours.

2.4.5 Fourier Transform Infrared (FT-IR) Spectroscopy Analysis

2.4.5.1 Introduction

Fourier Transform Infrared (FT-IR) Spectroscopy was used to determine the increase in the number of acetate groups of the PVOH polymer chains in the aqueous phase serum resulting from the grafting reaction between the poly(vinyl alcohol) and the vinyl acetate. The original PVOH solutions before polymerization were compared to the latex serum. Potassium thiocyanate (KSCN) was used as the internal reference standard for the FT-IR spectra.

2.4.5.2 FT-IR Analysis of the Latex Serum

The percent solids of the serum obtained by centrifugation was determined gravimetrically.

A 1.00% KSCN in water standard solution was prepared. The actual concentration was determined gravimetrically.

The weighed amount of the KSCN standard solution was added to the serum and to the pure PVOH solutions of known

concentrations. Films of the samples were then cast onto zinc-selenide (Zn-Se) IR disks (25 x 4mm). The disks were dried for 24 hours at 30°C in an oven and then stored in a dessicator. The FT-IR absorbance spectra for each sample was obtained. The absorbances were measured for the KSCN nitrile group stretch at 2052 cm^{-1} and for the carbonyl group stretch at 1728 cm^{-1}. The increase in the carbonyl absorbance was recorded and the percent increase in the number of acetate groups of the PVOH due to VAc grafting was calculated.

Figure 2.2 shows a sample FT-IR spectra of Vinol 205 with the KSCN standard and the relative peak wavelengths.

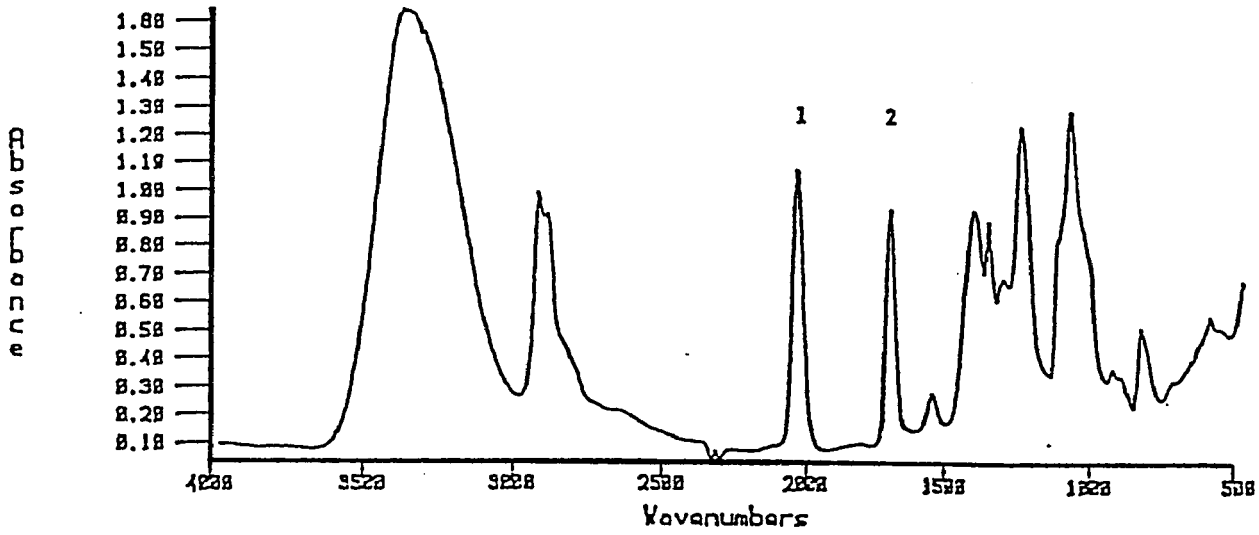


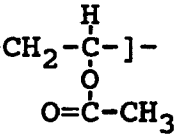
Figure 2.2: Fourier Transform Infrared (FT-IR) spectra of the serum of a poly(VAc-co-BuA) latex using partially hydrolyzed Vinol 205 PVOH. Peak 1: KSCN (-C≡N) stretch at 2052 cm^{-1}. Peak 2: Carbonyl (-C=O) stretch at 1728cm^{-1}.

2.4.5.3 FT-IR Analysis of the Copolymer Composition

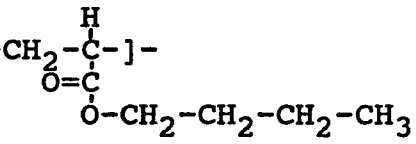
To determine the poly(vinyl acetate - co - butyl acrylate) composition by FT-IR:

(1) Solutions of different weight ratios of the poly(vinyl acetate) and poly(butyl acrylate) polymer standards in toluene were prepared and dried as films onto Zn-Se disks. The peak absorbances were recorded for the -C-O- stretch of VAc at 1248 cm^{-1} and BuA at 1167 cm^{-1} for the different functional groups of each monomer:

Poly(vinyl acetate)



Poly(butyl acrylate)



A calibration curve, Figure 2.3, plotting the absorbance ratio of PVAc/PBuA versus the weight ratio of PVAc/PBuA was generated. The linear regression coefficient of the line defined by the data points was found to be R^2= 0.9936.

(2) The dried copolymer sample was dissolved in a 10/90 weight ratio mixture of methyl sulfoxide (DMSO) and

chloroform ($CHCl_3$). The concentration of the solution was adjusted to approximately 2.0% by the addition of more solvent. A film was cast onto the Zn-Se disks and dried in a oven for 24 hours at 30°C and then placed into a dessicator. The FT-IR absorbance spectra was obtained and the peak absorbances were measured. The copolymer composition of the sample was then calculated by using the calibration curve.

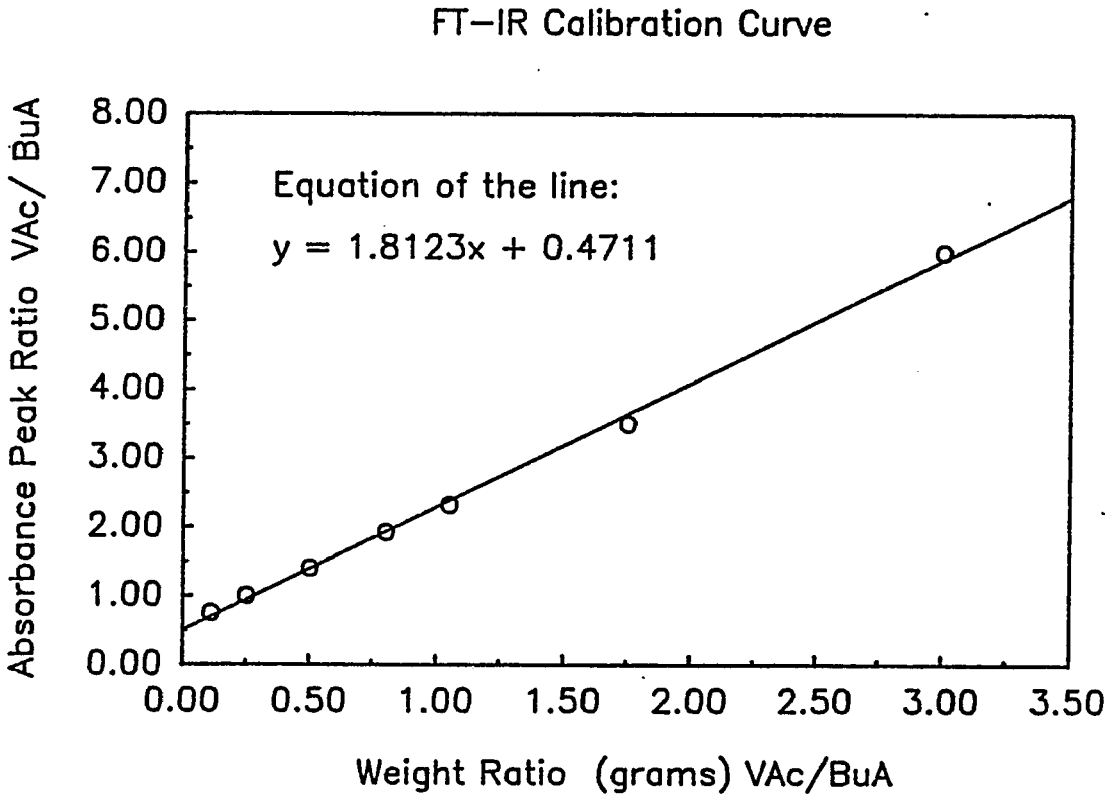


Figure 2.3: Fourier Transform Infrared (FT-IR) calibration curve to determine copolymer composition.

3. SYNTHESIS OF POLY(VINYL ACETATE - CO - BUTYL ACRYLATE) COPOLYMER LATEXES

3.1 Poly(vinyl alcohol) as the Emulsifier

3.1.1 Introduction

The objectives for this research program was to examine the polymerization kinetics of identically prepared latex systems using different types of poly(vinyl alcohol) that have a similar molecular weight (M_n and M_w), but a different degree of hydrolysis (% OH) as given in Table 3.1.1.

TABLE 3.1.1.

CHARACTERISTICS OF THE POLY(VINYL ALCOHOL)

Sample	% OH	M_n	M_w
Vinol 205	87.0-89.0	18,470	34,940
Vinol 107	98.0-98.8	15,570	26,250

3.1.2 Latex Recipe

The standard recipe given in Table 2.3.1 and experimental procedures described in sections 2.3 and 2.4 were used throughout this section to prepare poly(vinyl acetate -co- butyl acrylate) latexes using PVOH as the emulsifier-surfactant.

3.1.3. Overall Polymerization Kinetics

Initially, the concentration of poly(vinyl alcohol) in the recipe was held constant while the initiator

concentration (potassium persulfate, $K_2S_2O_8$) was varied.

The overall conversion-time curves for latexes prepared with 10.0% (based on total monomer weight) Vinol 205 or Vinol 107 for varying initiator concentrations are given in Figure 3.1. The use of higher initiator concentrations in the recipe resulted in faster initial rates of polymerization (calculated from the slope of the initial region of the conversion-time curves, up to 60.0% overall conversion) for both types of poly(vinyl alcohol) as shown in Table 3.1.2.

TABLE 3.1.2

EFFECT OF INITIATOR CONCENTRATION ON THE INITIAL RATES OF POLYMERIZATION

PVOH Sample	$K_2S_2O_8$ (%)	R_p,initial (g/l-min)
Vinol 205	0.025	2.00×10^{-3}
	0.10	5.76×10^{-3}
	0.20	5.98×10^{-3}
Vinol 107	0.025	1.14×10^{-3}
	0.10	2.30×10^{-3}
	0.20	2.61×10^{-3}

In the case of the latexes prepared with the Vinol 107, the initial rates of polymerization are much lower than those of the latexes prepared with the Vinol 205 for similar amounts of initiator.The final overall conversion at the 360 minute mark is also lower for latexes prepared with a lower

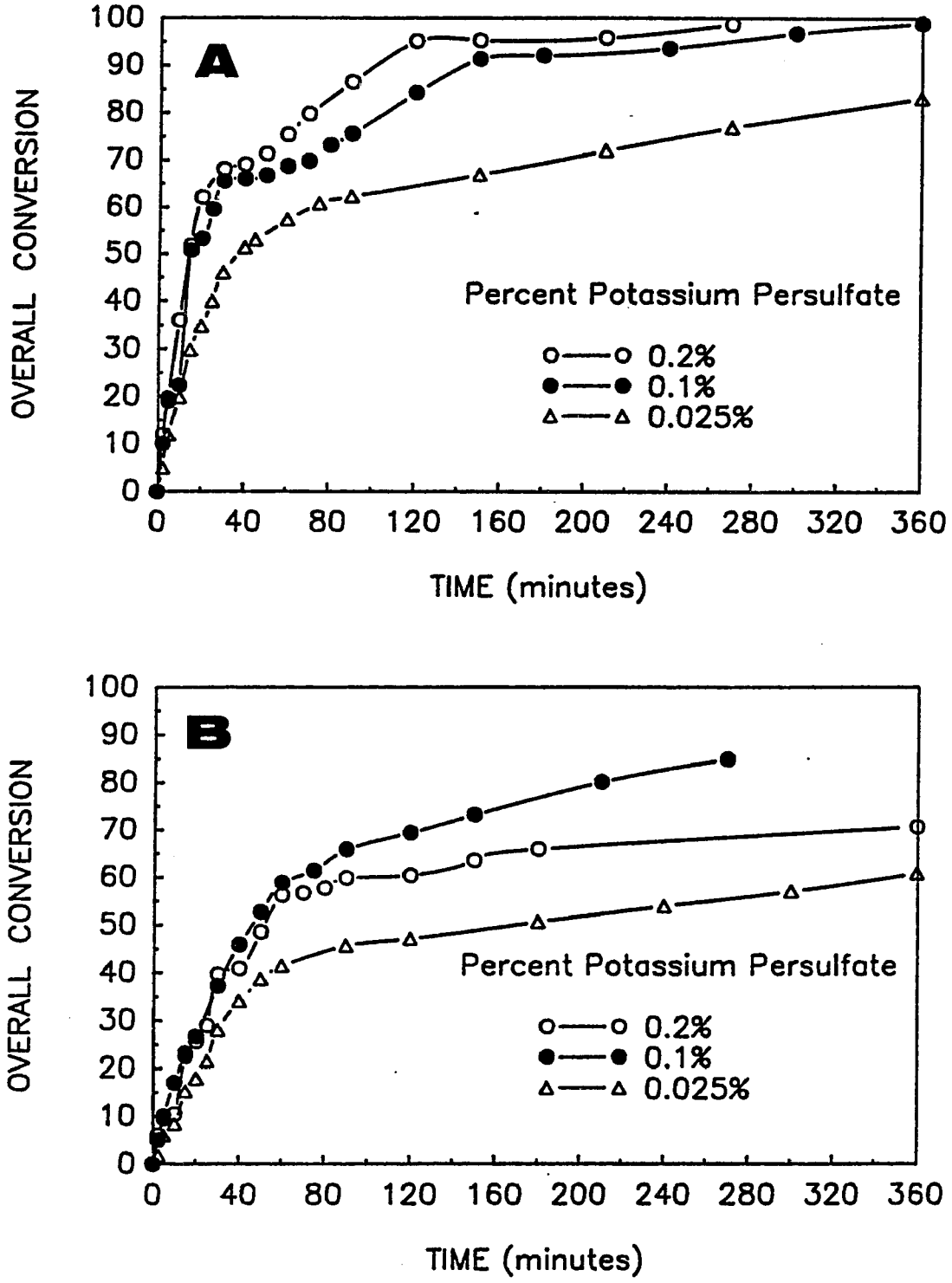


Figure 3.1: Overall conversion versus time data for 50:50 (wt.ratio) VAc-BuA copolymer latexes prepared with (A) 10.0% Vinol 205 and (B) 10.0% Vinol 107 at different $K_2S_2O_8$ initiator concentrations.

concentration of initiator. The final conversion for the latexes prepared with the fully hydrolyzed Vinol 107 is less than the final conversion achieved by the latexes made with the partially hydrolyzed Vinol 205.

When the concentration of initiator is held constant, at 0.10%, and the poly(vinyl alcohol) concentration is reduced from 10.0% to 5.0% the rate of polymerization is decreased for latexes made with both the Vinol 205 and Vinol 107 as shown in Figure 3.2 and Table 3.1.3

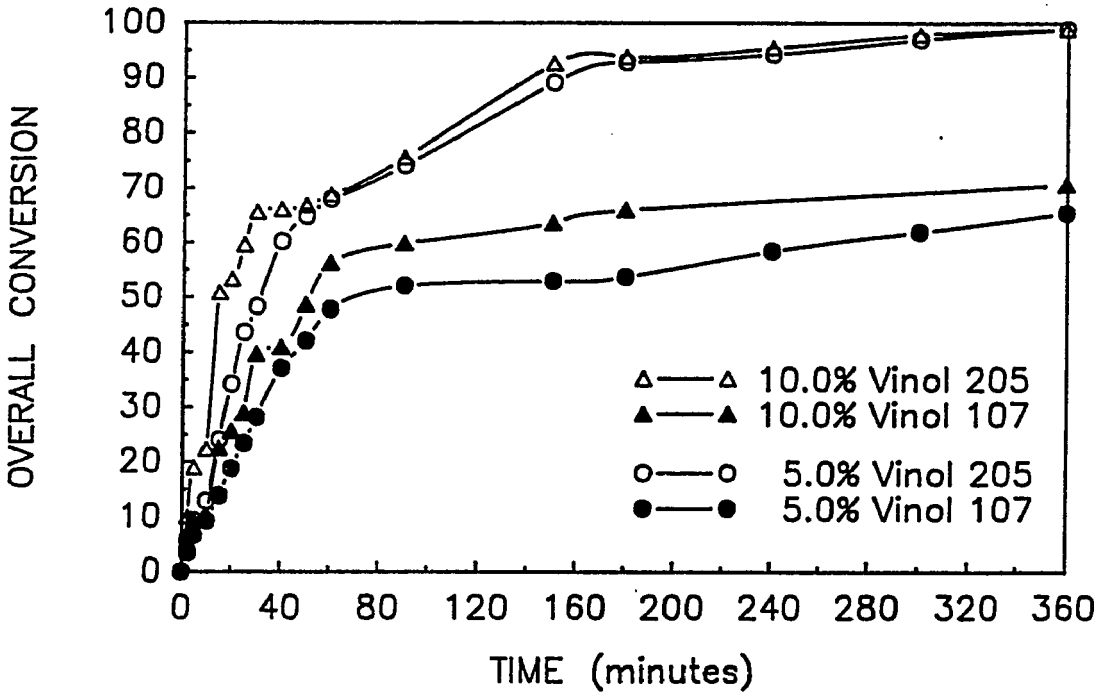


Figure 3.2: Overall conversion versus time data for 50:50 (wt. ratio) VAc-BuA copolymer latexes prepared with 10.0% and 5.0% PVOH concentrations at a 0.10% $K_2S_2O_8$ concentration.

TABLE 3.1.3

EFFECT OF PVOH CONCENTRATION ON THE INITIAL RATES OF POLYMERIZATION AT THE SAME INITIATOR CONCENTRATION

Sample	% PVOH	$R_{p,initial}$ (g/l-min)
Vinol 205	10.0	5.76×10^{-3}
	5.0	4.22×10^{-3}
Vinol 107	10.0	2.30×10^{-3}
	5.0	1.92×10^{-3}

The differences in the kinetic data can be attributed to the effectiveness of each type of poly(vinyl alcohol) as an emulsifier; the partially hydrolyzed Vinol 205 is a much better emulsifier than the fully hydrolyzed Vinol 107. This difference can also be illustrated by the particle size data for latexes made with each of the PVOH samples. Figure 3.3 and Table 3.1.4 show the particle diameter (nm) and particle number density (N_p/cc H_2O) as determined by the Coulter N4M as a function of overall conversion for the latexes containing 5.0 and 10.0 percent PVOH. The polymerization recipes using the fully hydrolyzed Vinol 107 result in larger sized latex particles as compared to those formed using the Vinol 205. This shows that the Vinol 107 is a less efficient emulsifier than the Vinol 205 with a lower degree of hydrolysis. A larger latex particle size is also noted when comparing the latexes prepared with 5.0% PVOH to those prepared with 10.0% PVOH.

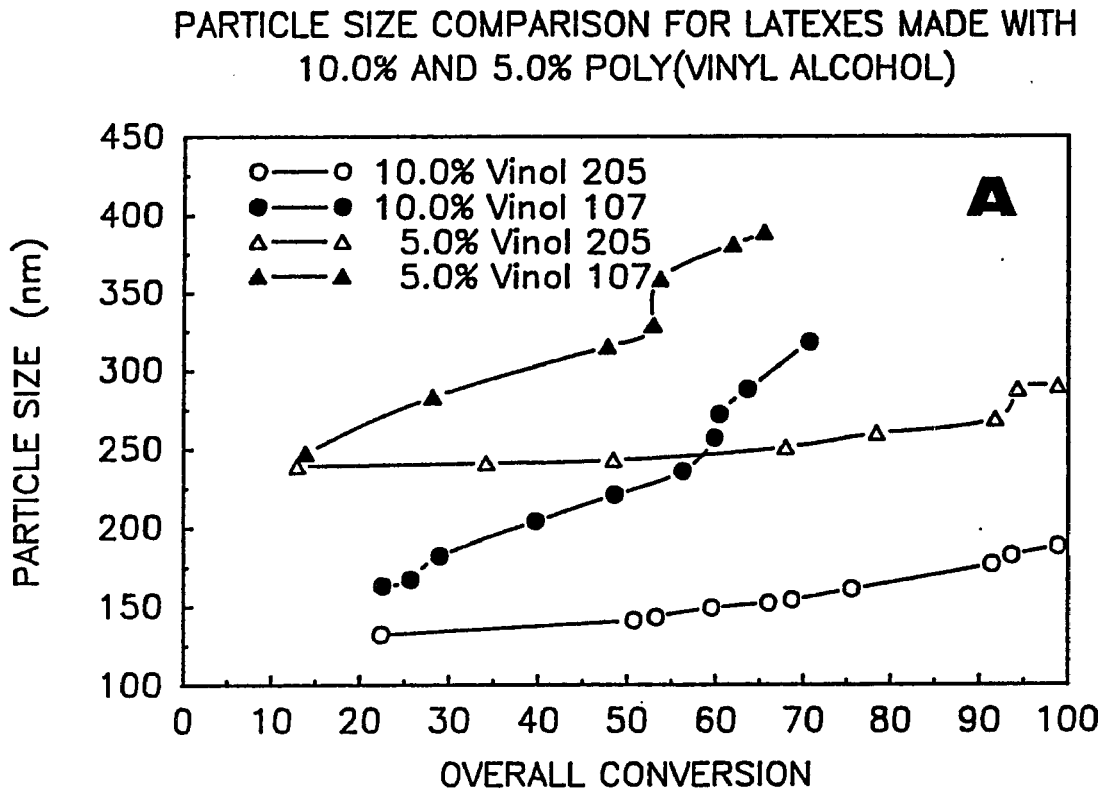
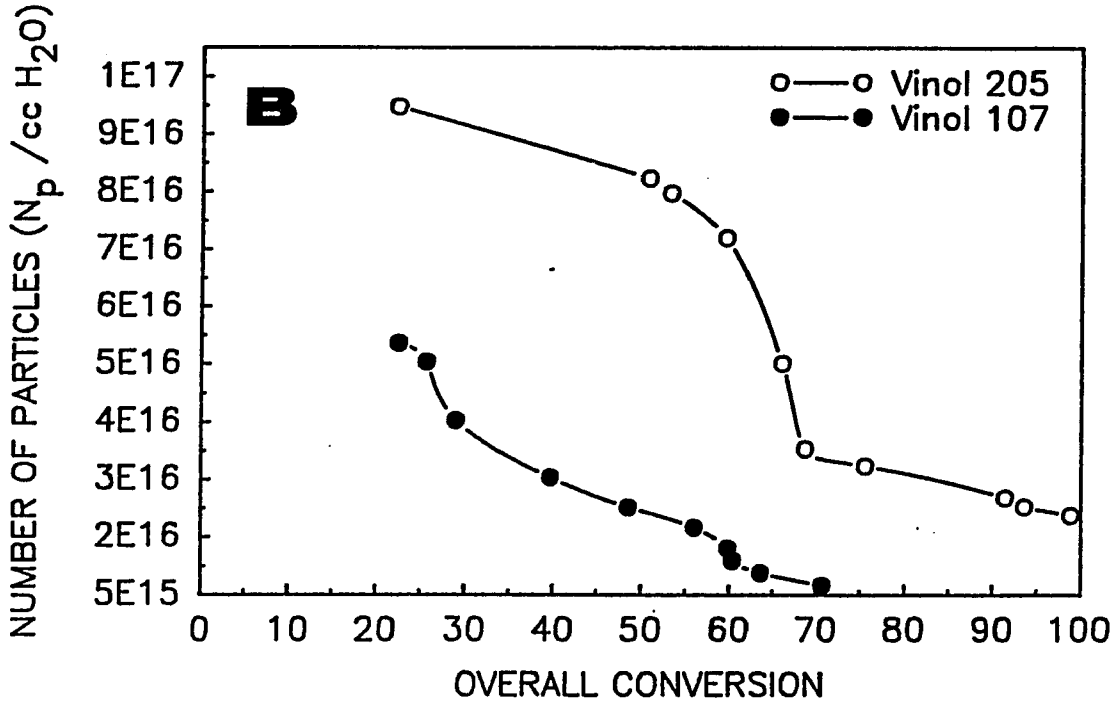


Figure 3.3: (A) Particle size comparison for 50:50 (wt.ratio) VAc-BuA copolymer latexes prepared with 10.0% and 5.0% PVOH concentrations.



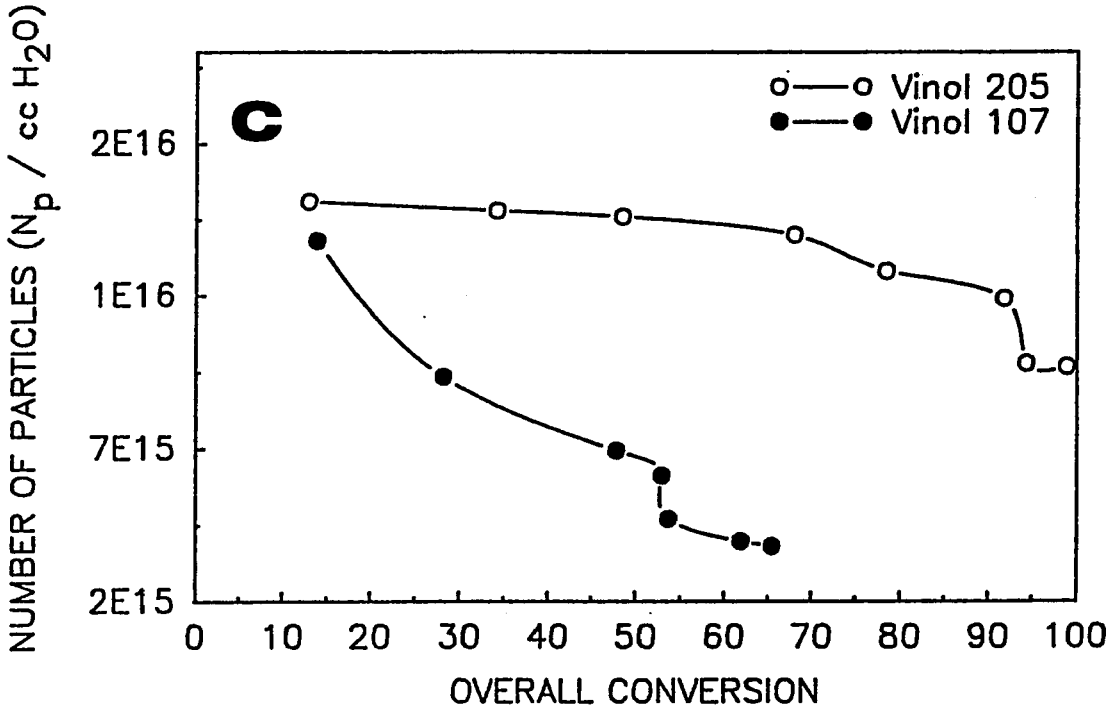


Figure 3.3 cont.: Number of particles / cc of H_2O for 50:50 (wt. ratio) VAc-BuA copolymer latexes prepared with:
(B) 10.0% PVOH (C) 5.0% PVOH

This is attributed to a decreased amount of emulsifier available to generate particles or particle coalescence at lower PVOH concentrations. In all cases, however, the particle size increases during the course of the polymerization. This can be explained by a particle coalescence mechanism which occurs during the course of the polymerization. This is supported by the data shown in Table 3.1.4, which shows that the particle number decreases during the course of the polymerization.

TABLE 3.1.4

PARTICLE SIZE AND NUMBER VERSUS CONVERSION FOR LATEXES PREPARED WITH DIFFERENT CONCENTRATIONS OF PVOH

PVOH SAMPLE	PERCENT PVOH	PERCENT CONVERSION	PARTICLE SIZE (nm)	PARTICLE DENSITY (N_p/cc H_2Ox10^{16})
Vinol 205	10.0	22.29	132	8.97
		68.65	154	3.03
		91.38	177	2.18
		98.92	188	1.87
Vinol 205	5.0	24.00	239	1.51
		67.93	251	1.40
		91.76	269	1.19
		98.93	290	0.97
Vinol 107	10.0	22.48	163	4.86
		39.65	204	2.53
		59.62	257	1.29
		63.54	288	0.88
Vinol 107	5.0	23.36	283	0.94
		47.75	315	0.69
		53.66	359	0.47
		65.41	386	0.38

Transmission Electron Microscopy (TEM), using a Phillips Model 400 EM, was used to determine the final particle size distribution of the latexes prepared with 10.0% (based on monomer) of the Vinol 205 and Vinol 107, latexes L205/10 and L107/10 respectively. The TEM data provided good agreement with the particle diameters obtained by the Coulter N4M as show in Table 3.1.5.

TABLE 3.1.5

PARTICLE SIZE COMPARISON BETWEEN THE COULTER N4M ANS TRANSMISSION ELECTRON MICROSCOPY

	Particle Diameter (nm)			
Latex	Coulter N4M	TEM		
		D_N	D_W	D_V
L205/10 (10.0% Vinol 205)	188.0	132.5	150.2	138.0
L107/10	288.4	283.4	314.3	293.6

Figure 3.4 shows the electron micrographs and the particle distribution analysis curves for latexes prepared with 10.0% Vinol 205, latex L205/10, and 10.0% Vinol 107, latex L107/10. Both latex samples showed a wide particle size distribution.

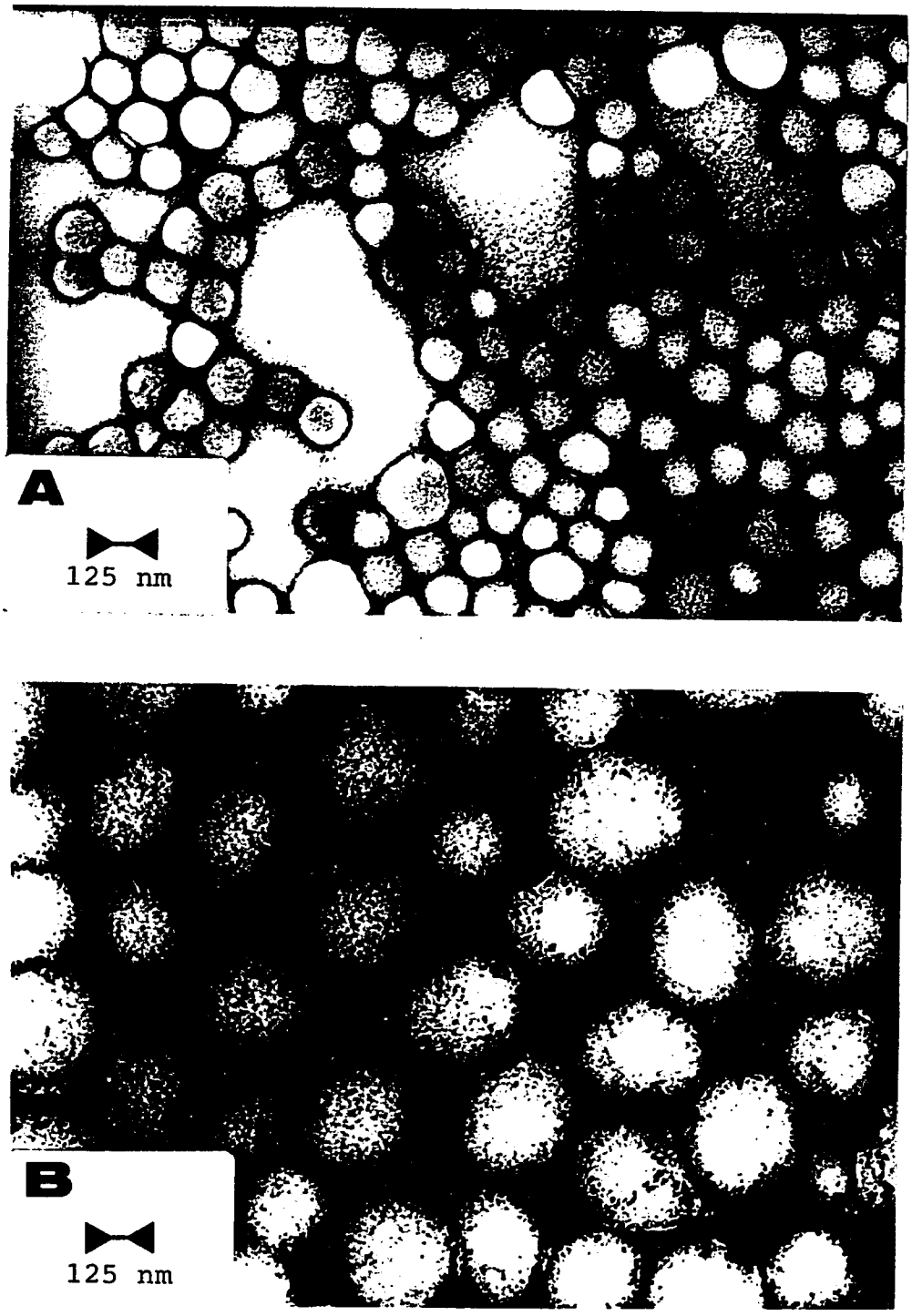


Figure 3.4: Electron micrographs of 50:50 (by wt.) VAc-BuA copolymer latexes prepared with 10.0% (based on monomer) of:
(A) Vinol 205
(B) Vinol 107

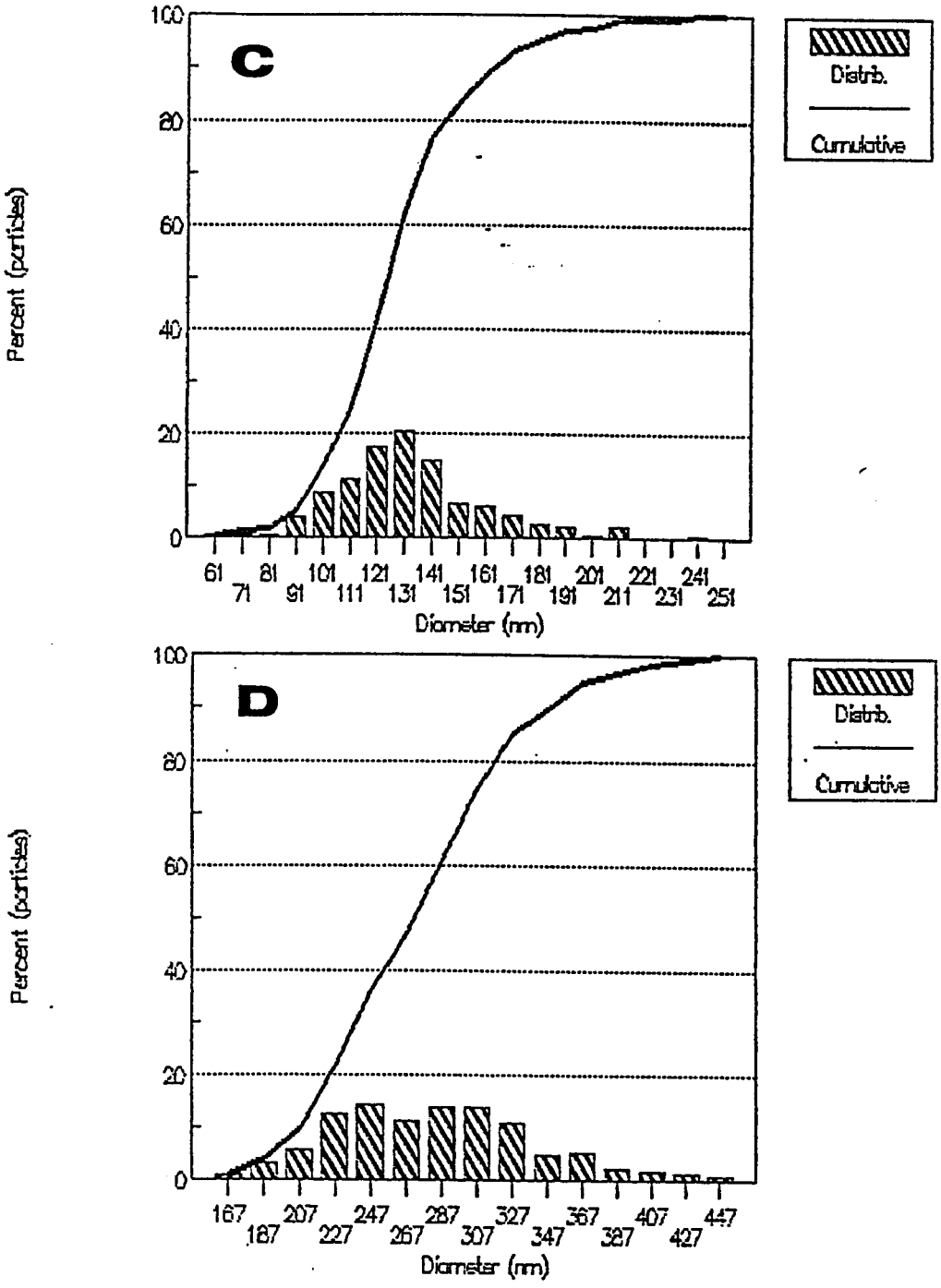


Figure 3.4 cont.: Particle size distibution analysis for 50:50 (by wt.) VAc-BuA copolymer latexes prepared using 10.0% (based on monomer):
(C) Vinol 205
(D) Vinol 107

3.1.4 Fractional Monomer Conversion

The large difference in the copolymerization reactivity ratio values for VAc and BuA ($r_{1,VAc}$ = 0.04, $r_{2,BuA}$ = 5.5) [16,52] will predict that both VAc and BuA radicals will add BuA monomer preferentially during the course of the polymerization. This means that the butyl acrylate monomer should be consumed at a much faster rate than the vinyl acetate monomer until it has been exhausted. The reaction will then shift to the vinyl acetate which will then be consumed at a faster rate. This behavior was observed when sodium lauryl sulfate (SLS) was used as the emulsifier.

Sodium lauryl sulfate (SLS) was used in place of the poly(vinyl alcohol) as the emulsifier in the standard recipe, as given in Table 2.3.1. The SLS was added to the recipe at a 20mM aqueous concentration (0.8640 grams). The potassium persulfate initiator concentration was 0.10% by weight based on total monomer weight. The polymerization was carried out according to the experimental procedure given in section 2.4.

The fractional monomer conversion for vinyl acetate and butyl acrylate was determined throughout the course of each polymerization.

The data in Figure 3.5 show that in the case of the

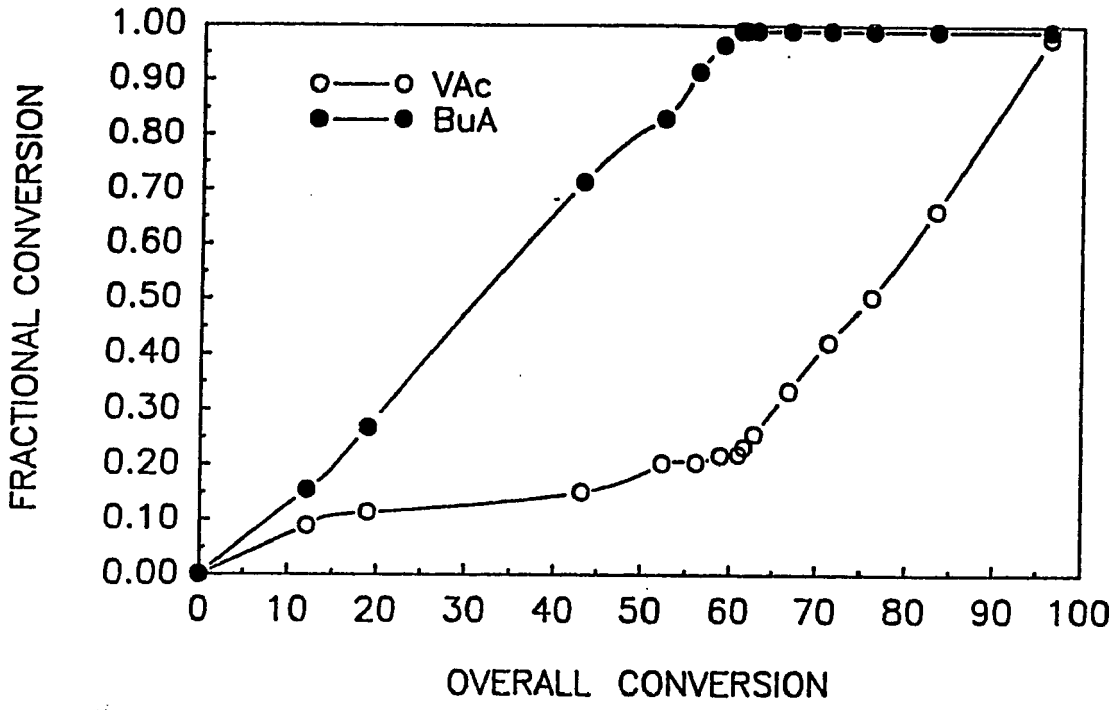


Figure 3.5: Fractional conversion versus overall conversion for the 50:50 (wt. ratio) VAc-BuA copolymer latex prepared with a 20mM SLS and 0.10% $K_2S_2O_8$ concentration.

latex prepared with sodium lauryl sulfate emulsifier (no PVOH present) the fractional conversion of the vinyl acetate and butyl acrylate reflect the predicted difference in the reactivity ratios as expected.

When poly(vinyl alcohol), either the fully hydrolyzed Vinol 107 or the partially hydrolyzed Vinol 205, was used as the emulsifier, a reversal in the prediction of the copolymerization reactivity ratios was observed. In all cases, in the initial stages of the polymerizations (less

than 30.0% conversion), the vinyl acetate monomer was consumed at a faster rate than the butyl acrylate. This trend was observed at 10.0% and 5.0% poly(vinyl alcohol) concentrations, Figure 3.6, and for the different potassium persulfate initiator concentrations, Figure 3.7.

It has been proposed that the faster initial consumption of the vinyl acetate monomer observed when poly(vinyl alcohol) is used as an emulsifier is due to an aqueous phase grafting reaction between the vinyl acetate monomer dissolved in the aqueous phase and the poly(vinyl alcohol) chains. This hypothesis will be analyzed further in the following sections of this dissertation.

The vinyl acetate monomer is soluble in water to an extent of 2.50 g/100 g water [39]. The initiator used is water-soluble potassium persulfate. In the aqueous phase, the vinyl acetate and the poly(vinyl alcohol) are initiated by the persulfate radicals. The grafting reaction can occur and continue until t he poly(vinyl alcohol -graft- vinyl acetate) copolymer becomes water-insoluble, at which point the PVOH-VAc chains precipitate from the aqueous phase and generate loci for particle nucleation as per the homogeneous particle nucleation mechanism described in section 1.1 and 1.2.3.

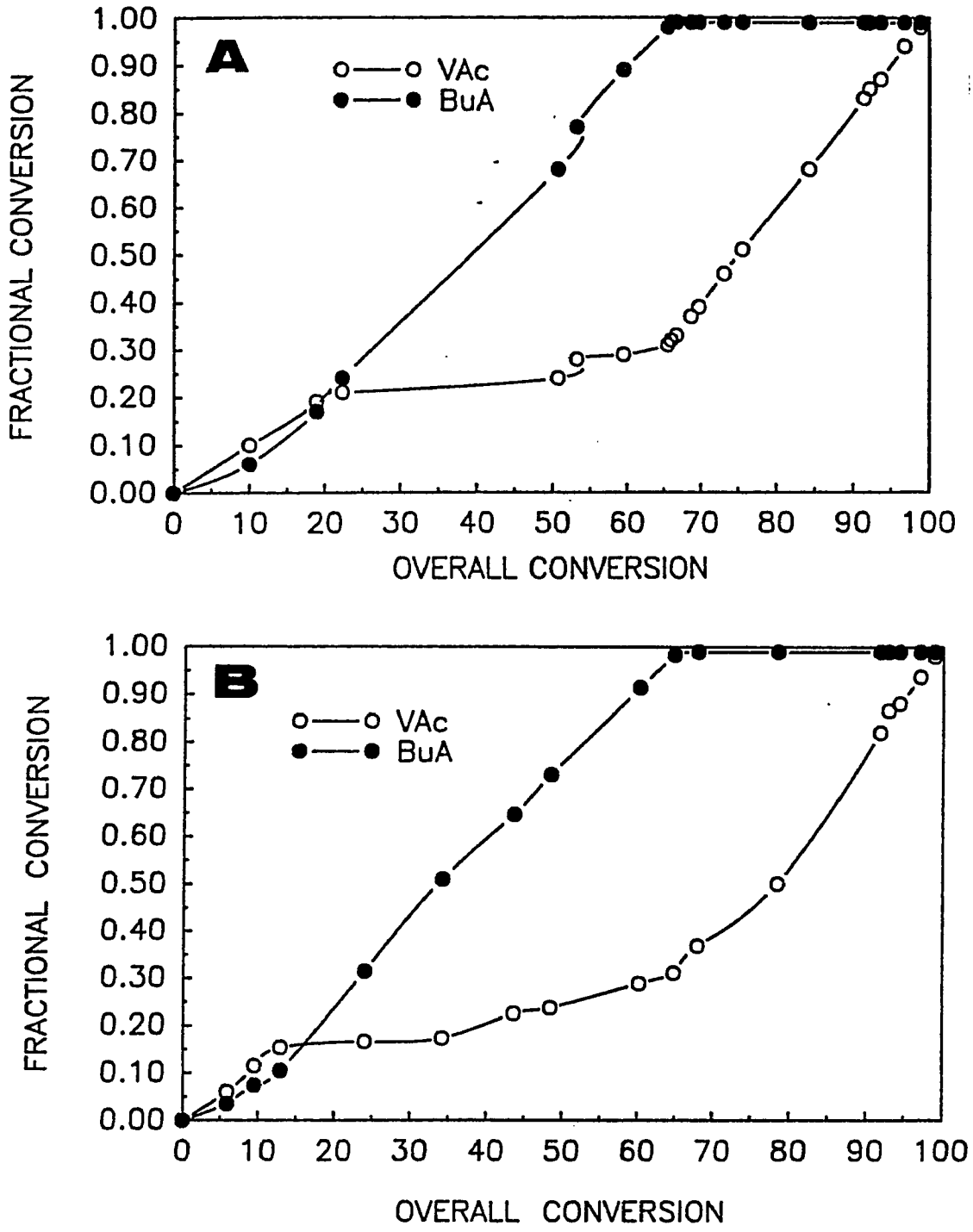


Figure 3.6: Fractional conversion versus overall conversion for 50:50 (wt. ratio) VAc-BuA copolymer latexes prepared with 0.10% $K_2S_2O_8$ concentration at different PVOH concentrations:
(A) 10.0% Vinol 205 (B) 5.0% Vinol 205

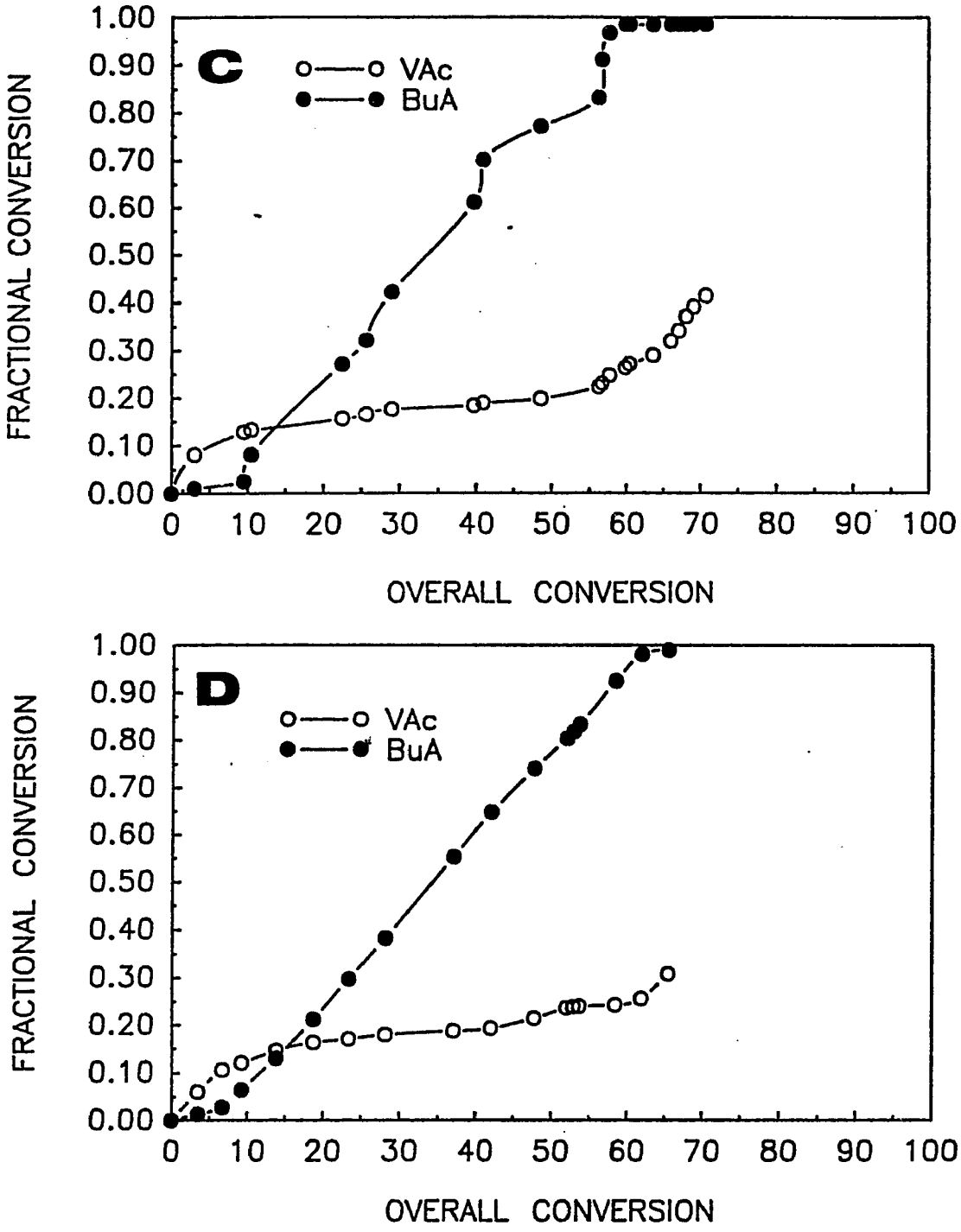


Figure 3.6 cont.: Fractional conversion versus overall conversion for 50:50 (by wt.) VAc-BuA copolymer latexes prepared with a 0.10% $K_2S_2O_8$ concentration at different PVOH concentrations:
(C) 10.0% Vinol 107 (D) 5.0% Vinol 107

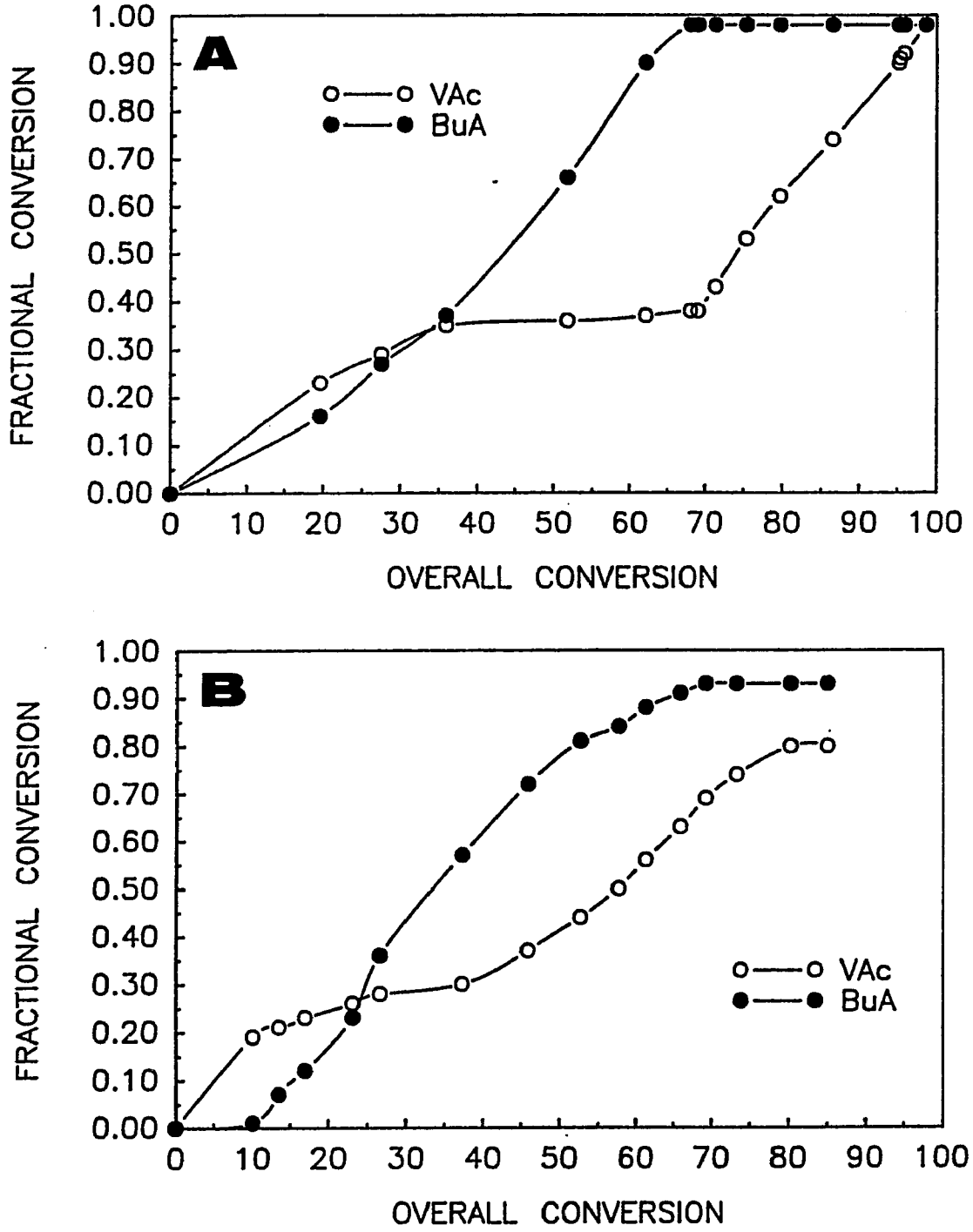
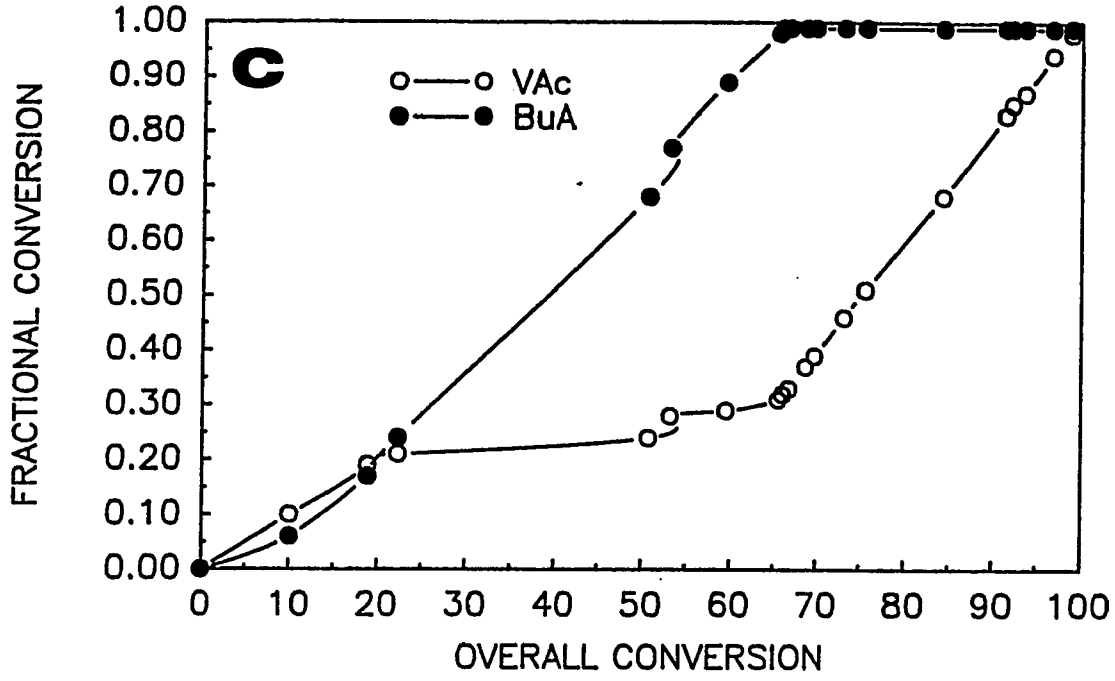


Figure 3.7: Fractional conversion versus overall conversion for 50:50 (wt. ratio) VAc-BuA copolymer latexes prepared with 10.0% Vinol 205 (A) and 10.0% Vinol 107 (B) at a 0.20% (based monomer wt.) $K_2S_2O_8$ initiator concentration.



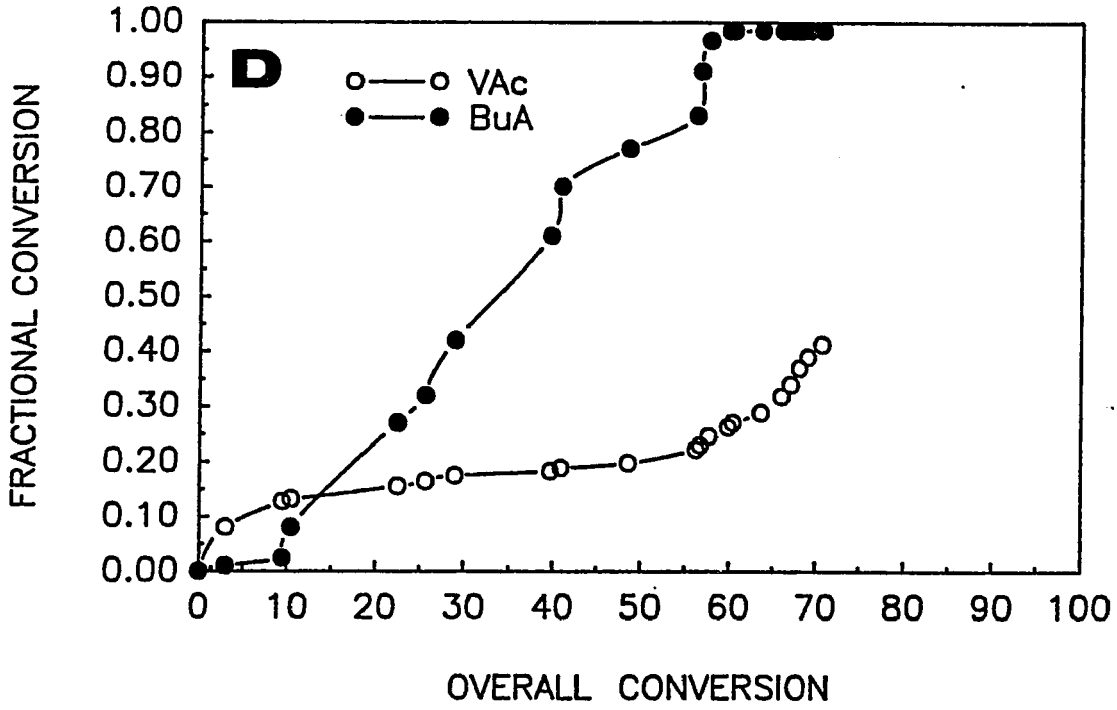


Figure 3.7 cont.: Fractional conversion versus overall conversion for 50:50 (wt. ratio) VAc-BuA copolymer latexes prepared with 10.0% Vinol 205 (C) and 10.0% Vinol 107 (D) at a 0.10% (based on monomer wt.) $K_2S_2O_8$ initiator concentrations.

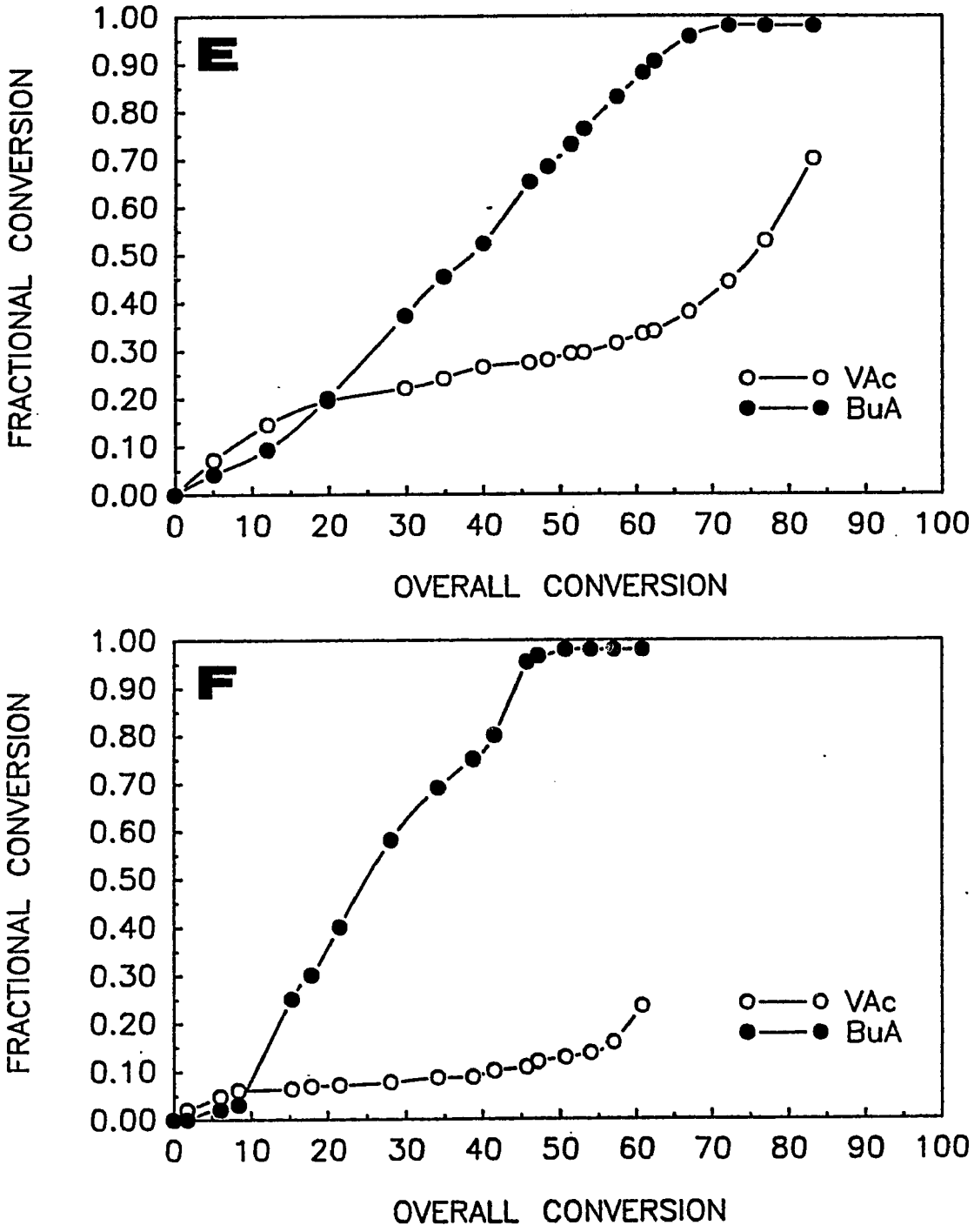


Figure 3.7 cont.: Fractional conversion versus overall conversion for 50:50 (wt. ratio) VAc-BuA copolymer latexes prepared with 10.0% Vinol 205 (E) and 10.0% Vinol 107 (F) at a 0.025% (based on monomer wt.) $K_2S_2O_8$ initiator concentration.

3.2 Effect of Poly(vinyl alcohol) on the Water-Solubility of Vinyl Acetate and n-Butyl Acrylate

3.2.1 Introduction

The objective of this section is to determine the effect, if any, of the presence of both partially and fully hydrolyzed poly(vinyl alcohol) on the solubility of vinyl acetate and n-butyl acrylate in water.

The literature value for the water solubility of vinyl acetate is 2.50 g/100 g H_2O and that of n-butyl acrylate is 0.14 g/100 g H_2O at 20^{o}C [39].

The water-solubility of the vinyl acetate and butyl acrylate monomers was determined in the presence of both fully hydrolyzed Vinol 107 and partially hydrolyzed Vinol 205 to further illustrate the aqueous phase grafting reaction between the vinyl acetate and poly(vinyl alcohol).

3.2.2 Experimental

Solutions were prepared, as described earlier, of partially hydrolyzed Vinol 205 and fully hydrolyzed Vinol 107 poly(vinyl alcohol) in distilled-deionized water at three different concentrations by weight: 10.0%, 5.0% and 2.5%. Vinyl acetate and n-butyl acrylate monomers were mixed in a 50/50 weight ratio. The monomer mixture was added to

the PVOH solutions in four different weight ratios: 0.175, 0.425, 0.665 and 1.00. A monomer mixture/pure water blank was also prepared using identical ratios. The solutions were shaken and then let stand for 48 hours at room temperature. The solutions were then centrifuged at 18,000 rpm for 2 hours. After centrifugation was complete, 1.00 gram samples of the serum were removed and quantitatively added to a 1.00 gram quantity of a 1.00% by weight dioxane-in-water gas chromatography standard. A gas chromatography calibration curve was prepared for vinyl acetate and butyl acrylate with dioxane. Each sample was injected into the GC and the amount of each monomer present in the water phase was calculated. For each of the different monomer mixture/ PVOH solution ratios an average value was calculated.

3.2.3 Results and Discussion

The water solubility of vinyl acetate and n-butyl acrylate was determined in pure water and in fully and partially hydrolyzed PVOH solutions. Table 3.2.1 compares the literature value to the average values of monomer water-solubility obtained from the experimental data.

TABLE 3.2.1

THE WATER SOLUBILITY OF VINYL ACETATE AND n-BUTYL ACRYLATE AT ROOM TEMPERATURE

	Monomer Water-Solubility (g/100 g H_2O)	
	VAc	BuA
Literature Value [39]	2.50	0.14
Average Value For:		
DDI Water	2.47	0.14
10.0% Vinol 205	2.57	0.14
10.0% Vinol 107	2.48	0.14
5.0% Vinol 205	2.56	0.12
5.0% Vinol 107	2.46	0.13
2.5% Vinol 205	2.59	0.14
2.5% Vinol 107	2.52	0.15

From the data given in Table 3.2.1, it can be seen that the poly(vinyl alcohol), whether fully or partially hydrolyzed, has no apparent affect on the water-solubility of either vinyl acetate or n-butyl acrylate. It can be assumed that during the course of the polymerization, the vinyl acetate is in equilibrium between the aqueous and the monomer phases and is present in the aqueous phase to an extent of 2.50 g/100 g water.

3.3 Emulsifier-Free Polymerization of Vinyl Acetate and Butyl Acrylate

3.3.1 Introduction

The objective of this section is to further examine the aqueous phase grafting reaction between the poly(vinyl alcohol) and the vinyl acetate in the absence of emulsifier. Vinyl acetate can be polymerized in water to approximately 10.0% solids and give a stable emulsion in the absence of an emulsifier. If the grafting reaction is the sole explanation for the increased initial vinyl acetate consumption, then the fractional monomer conversions for vinyl acetate and butyl acrylate should follow the prediction of the copolymerization reactivity ratios. If the increased vinyl acetate consumption, on the other hand, is due to the higher water-solubility of the VAc monomer, then the fractional monomer conversion data should be similar to the trends observed when poly(vinyl alcohol) is present in the system.

3.3.2 Experimental

The recipe used for the emulsifier-free polymerization of PVAc-BuA is similar to the standard recipe as given in Table 2.3.1. The PVOH emulsifier is omitted from the recipe and the monomer content is adjusted to give a total solids of the system of 8.0%. A 0.5% by weight (based on total monomer weight) initiator concentration was used to prepare emulsifier-free latex due to an induction period observed

with a 0.1% initiator concentration. The higher initiator concentration provided a better reaction rate so as to improve the sampling of the latex for analysis. The experimental procedure used is given in section 2.4.

3.3.3 Results and Discussion

The data presented in Figure 3.8 show that in the system where there is no emulsifier present, the rates at which the vinyl acetate and butyl acrylate are consumed follow the prediction of the difference in the copolymerization reactivity ratios.

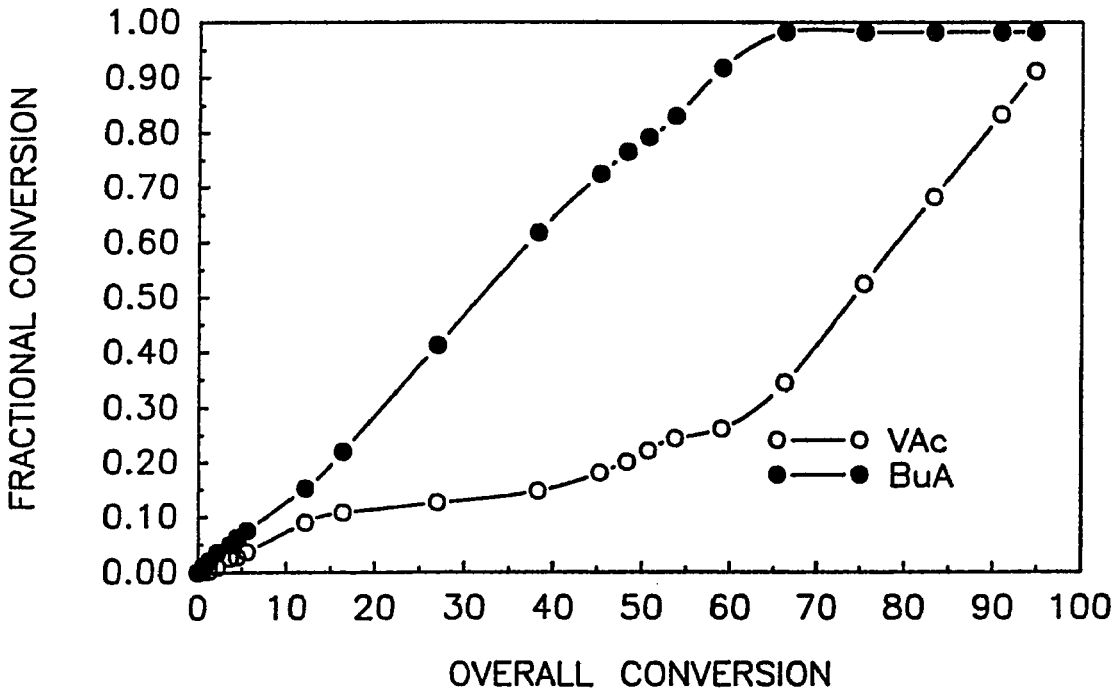


Figure 3.8: Fractional conversion versus overall conversion for the 50:50 (wt. ratio) VAc-BuA copolymer latex prepared without a PVOH emulsifier.

This experimental data supports the findings that the aqueous phase grafting reaction between the poly(vinyl alcohol) and the vinyl acetate monomer is the main mechanism to explain the faster consumption of vinyl acetate compared to the more reactive butyl acrylate monomer in the initial stages of polymerization.

3.4 Polymerization of VAc - BuA Copolymer Latexes using SLS in the Presence of 2-Propanol

3.4.1 Introduction

In earlier sections of this chapter, data was presented showing that when sodium lauryl sulfate was used as the emulsifier in the emulsion copolymerization of vinyl acetate and butyl acrylate, the fractional conversion of each monomer followed what was predicted by the copolymerization reactivity ratios. When poly(vinyl alcohol) was used, however, the fractional monomer conversion was much higher for the VAc monomer in the initial stages of the polymerization. This was contradictory to the prediction of the copolymerization reactivity ratios for the VAc and BuA.

The objective of this section is to prepare a latex recipe that contains SLS and 2-Propanol. The 2-propanol was added to the recipe simulating the presence of the hydroxyl groups of the PVOH.

3.4.2 Experimental

The latex recipe and experimental procedures used to prepare the PVAc-co-PBuA latex with SLS and 2-propanol are given in Table 2.3.1 and section 2.4. The standard recipe was modified to yield a total recipe weight of 50.00 grams. The potassium persulfate initiator concentration was 0.10% (based on total monomer weight). The SLS was added in place of the PVOH as the emulsifier in a 20mM aqueous concentration. The 2-propanol was added to the recipe in the same number of moles of hydroxyl groups that would be present if the fully hydrolyzed Vinol 107 PVOH was used in a 10.0% (based on monomer content) concentration.

3.4.3 Results and Discussion

When 2-propanol was present in the latex recipe, it must be considered whether or not the 2-propanol will be consumed in the reaction to yield solid material or will the 2-propanol be evaporated off in an oven when the percent solids of each sample is determined. To eliminate this problem, gas chromatography was used to determine the amount of each monomer and 2-propanol consumed during the polymerization. For each time interval sample, 0.50 grams of the sample was added to 0.50 grams of a dioxane-water standard, as described in section 3.2.2. The samples were

injected into the GC and the amount of each monomer and 2-propanol present was determined.

In Figure 3.9, which plots grams of VAc, BuA and 2-propanol consumed versus time, the data shows that the butyl acrylate is being consumed faster than the vinyl acetate monomer, which is the same behavior observed when SLS was used alone in the latex recipe. If the 2-propanol, however, was inert during the reaction its concentration should be constant throughout the course of the polymerization. But, what is observed is the 2-propanol seems to be consumed in the early stages of the polymerization (less than approximately 45 minutes) and then levels off to a constant value. This consumption of the 2-propanol could be a transfer reaction from monomer to solvent occurring in the aqueous phase. In section 1.2.3, values for the transfer constant from monomer to polymer, C_p, were given for VAc to PVAc and PVOH at 60°C. The values were for: VAc to PVAc C_p = 1.5×10^{-4} and VAc to PVOH C_p = 35×10^{-4}. When comparing the literature value for transfer from monomer to solvent, C_s [16], for VAc to 2-propanol, with the C_p values the C_s value is larger, 44.6×10^{-4}. From these data then the transfer rate of VAc to 2-propanol is very high, but that reaction does not affect the rate of VAc monomer consumption compared to BuA in the copolymerization as does the grafting reaction of VAc with PVOH.

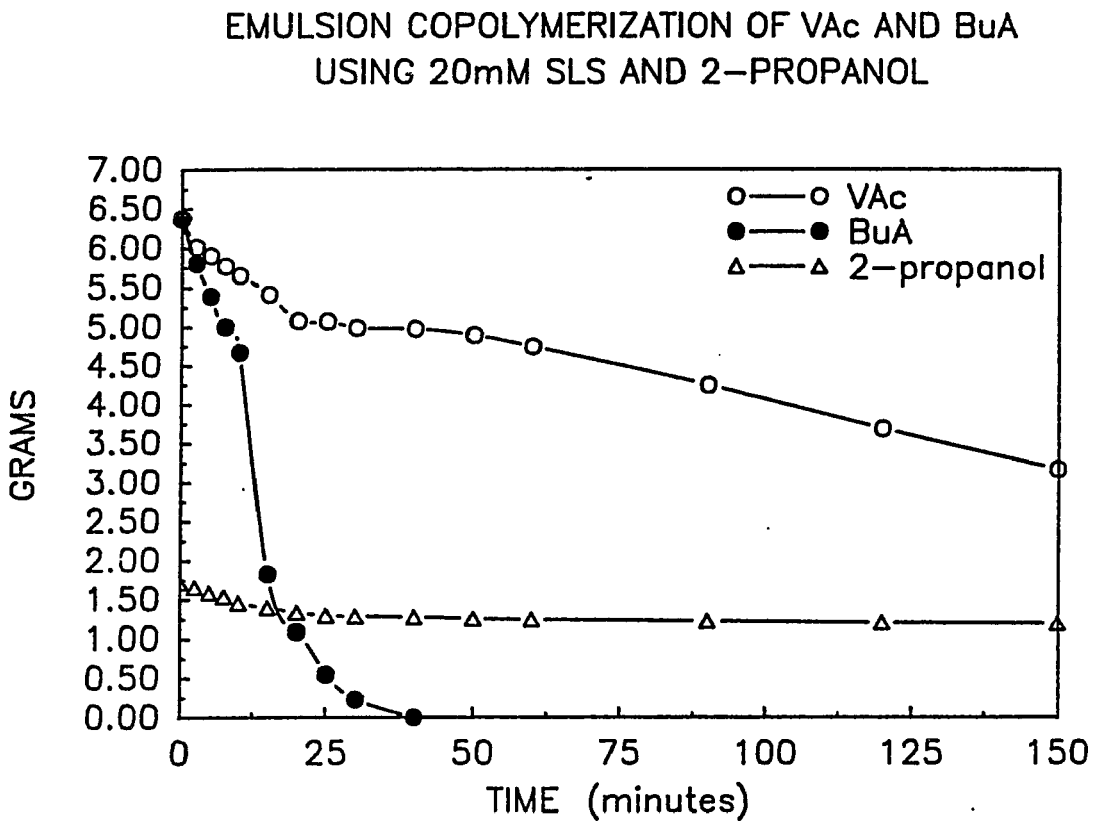


Figure 3.9: Grams consumed of VAc, BuA and 2-propanol versus time for the emulsion copolymerization of 50:50 (wt. ratio) of VAc-BuA latex using 20mM SLS.

The characterization to further examine the reaction of VAc with the 2-propanol will be presented in Chapter 4.

3.5 SUMMARY AND CONCLUSIONS

The experimental copolymerization kinetic and particle size data has shown that for copolymer latexes prepared with 50:50 (by wt.) VAc/BuA using poly(vinyl alcohol) as the emulsifier the overall rate of polymerization was

increased with increasing PVOH concentration, initiator concentration, and increasing acetyl content of the PVOH. These data confirm results presented in the literature [12,23,27,29]. The fractional conversion of each monomer was determined and the consumption of vinyl acetate in the initial stages of polymerization (less than 30% overall conversion) was faster than the more reactive butyl acrylate for recipes using PVOH, which is contrary to the prediction of the copolymerization reactivity ratios for VAc and BuA. These data show that the vinyl acetate is involved in grafting reaction with the poly(vinyl alcohol) in the aqueous phase.

The water-solubility of VAc and BuA in the presence of the partially hydrolyzed Vinol 205 and the fully hydrolyzed Vinol 107 at room temperature was determined. Results showed that the presence of either of the hydrolyzed grades of PVOH did not affect the water-solubilities of the monomers.

To further demonstrate the dominance of the aqueous phase grafting reaction between the VAc and the PVOH, polymerizations where carried out using an emulsifier-free recipe and a recipe using 20mM SLS and 2-propanol (in an equimolar amount to the fully hydrolyzed Vinol 107 PVOH). In both cases the rates of fractional monomer conversion were as predicted by the copolymerization reactivity ratios with the butyl acrylate reacting faster than the vinyl acetate.

4. CHARACTERIZATION OF THE POLY(VINYL ACETATE - CO - BUTYL ACRYLATE) LATEXES USING POLY(VINYL ALCOHOL) AS THE EMULSIFIER

4.1 Introduction

In Chapter 3, it was shown that during the emulsion copolymerization of vinyl acetate and butyl acrylate using poly(vinyl alcohol) as the emulsifier, there is a grafting reaction in the aqueous phase between the vinyl acetate and the poly(vinyl alcohol). This grafting reaction results in a faster consumption of the vinyl acetate monomer during the initial stages of the polymerization compared to the more reactive butyl acrylate monomer.

The objective of this chapter is to quantify the grafting reaction between the vinyl acetate and poly(vinyl alcohol) by instrumental analysis.

4.2 Latex Separation by Centrifugation

4.2.1 Introduction and Experimental

The latex samples were centrifuged using the procedures given in section 2.4.4.

The solids content of the serum, which contains the water-soluble products of the polymerization, was determined by gravimetric analysis. The water-soluble material should consist of poly(vinyl alcohol) and water-soluble poly(vinyl alcohol) that has grafted with vinyl acetate during the

the polymerization.

4.2.2 Results and Discussion

In Table 4.2.1, the solids content of the serums of the final latex are compared to the initial solids content of the PVOH solutions before polymerization. In the case of the latexes prepared with 0.10% potassium persulfate initiator and the partially hydrolyzed Vinol 205, namely, latex L205/10 (10.0% PVOH) and latex L205/5 (5.0% PVOH), the final serum after polymerization is less than that of the initial. However, in the case of the latexes prepared with the fully hydrolyzed Vinol 107, namely, latex L107/10 (10.0% PVOH) and L107/5 (5.0% PVOH), the solids content of the final serum is greater than that of the initial solids content.

TABLE 4.2.1

COMPARISON OF PERCENT SOLIDS OF THE AQUEOUS PHASE BEFORE AND AFTER POLYMERIZATION

LATEX	% SOLIDS, initial	% SOLIDS, final	% Difference
L205/10	3.58	2.89	19.23 decrease
L205/5	1.52	1.19	21.32 decrease
L107/10	3.24	3.39	4.42 increase
L107/5	1.53	1.61	4.96 increase

This suggests that while grafting is taking place in the aqueous phase, the fully hydrolyzed Vinol 107 PVOH

chains are capable of a greater degree of grafting by the vinyl acetate while still maintaining water-solubility as reflected by, an increase in weight. The partially hydrolyzed Vinol 205, in contrast, attains a certain degree of grafting with the vinyl acetate and becomes water-insoluble, and thus, are not present in the aqueous phase. These results imply that there should be limiting value to which the VAc can graft with the PVOH to maintain water-solubility of the grafted chains.

When analyzing solids content of the serum from the latexes prepared by the emulsifier-free method and prepared with 20mM SLS and 2-propanol, the solids of the aqueous phase before the addition of the initiator was determined and then compared to the serum solids of the final latex after centrifugation. In the case of the emulsifier-free latex, the initial percent solids of the aqueous phase was determined to be 0.0182 %, which is due to the solids contribution of the sodium bicarbonate buffer and the potassium persulfate initiator. The final serum solids after centrifugation showed an increase of the solids content to 0.6745 %. This increase in the serum solids content is possibly due to the presence of aqueous phase oligomeric PVAc which exhibits a degree of water-solubility.

When the serum solids content of the latex prepared with 20mM SLS and 2-propanol was examined the value also

increased from the initial aqueous phase solids of 0.4637 %, due to contributions from the SLS, buffer, and initiator, to the final latex serum solids value of 0.8773 %. This increase is due in part to water-soluble oligomeric PVAc and possibly to PVAc-2-propanol polymer products resulting from a transfer reaction between the VAc or PVAc and the 2-propanol.

4.3 Characterization of the Latex Serum by Fourier Transform Infrared (FT-IR) Spectroscopy

4.3.1 Introduction and Experimental

The procedure for the preparation of the serum samples for FT-IR was given in section 2.4.5.

For each sample the infrared spectra was recorded in absorbance values and the increase in the carbonyl peak absorbance due to the grafting of the VAc with the PVOH was recorded. The peak absorbance spectra for the serum before and after polymerization is shown in Figure 4.1.

4.3.2 Results and Discussion

Infrared spectroscopy absorbance data of the serum for composition has shown that for the fully hydrolyzed Vinol 107 samples (latexes L107/10 and L107/5) and the partially

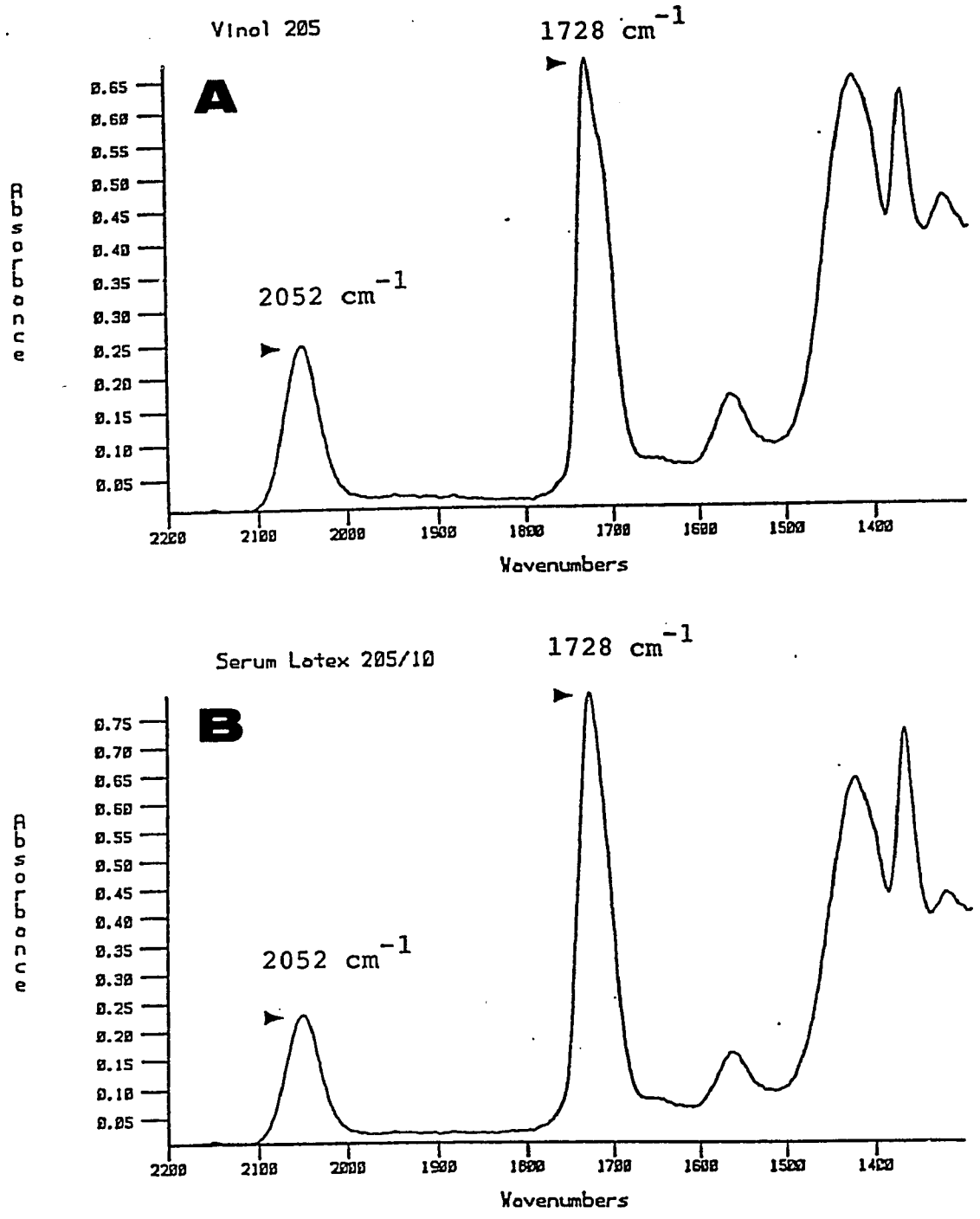


Figure 4.1: FT-IR spectra of the KSCN reference peak at 2052 cm^{-1} and the carbonyl peak at 1728 cm^{-1} for the 50:50 (wt. ratio) VAc-BuA copolymer latex prepared with 10.0 % Vinol 205.
(A) Aqueous PVOH solution before polymerization.
(B) Final latex serum after centrifugation.

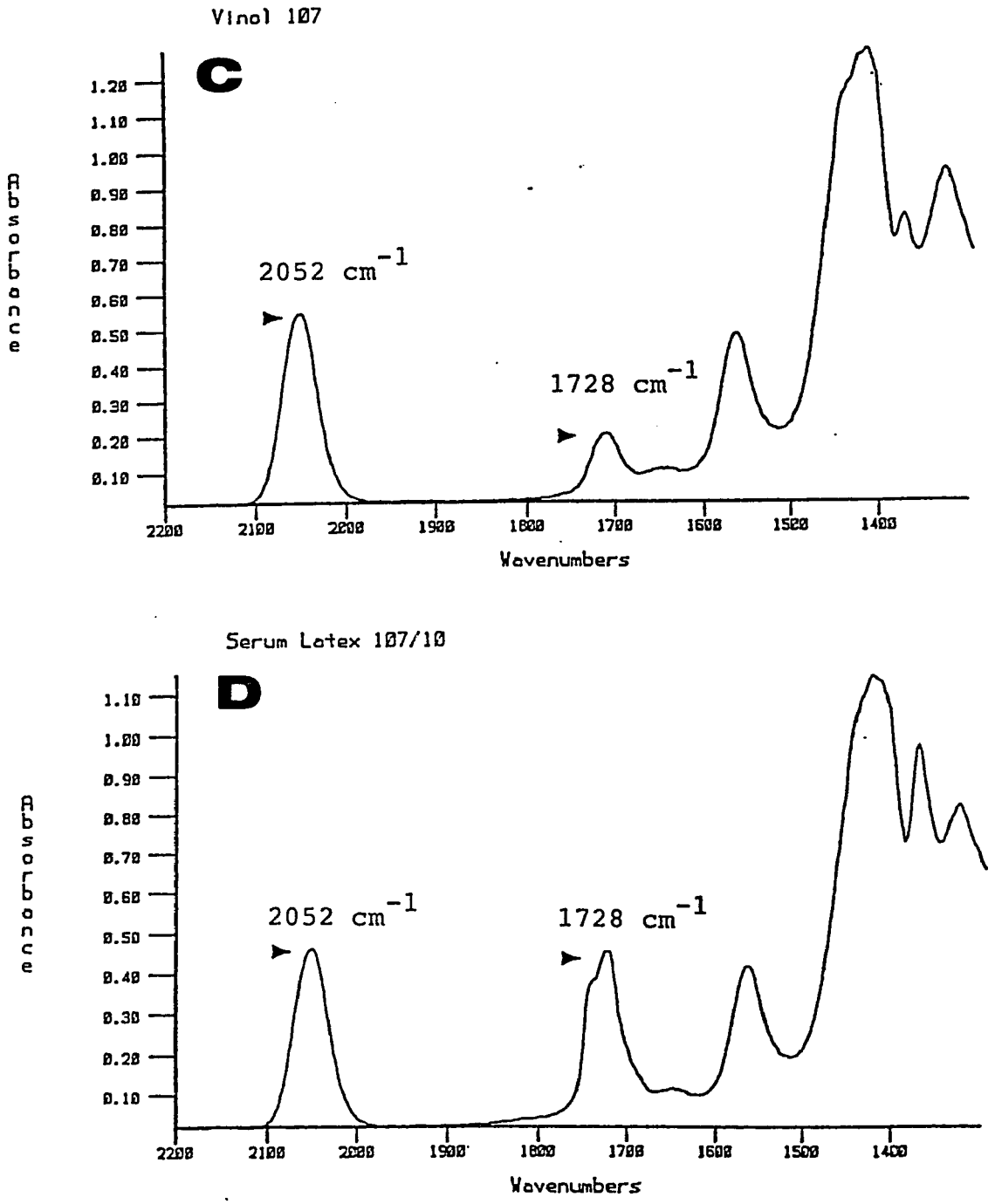


Figure 4.1 cont.: FT-IR spectra for the 50:50 (wt. ratio) VAc-BuA copolymer latex prepared with 10.0% Vinol 107.
(C) Aqueous PVOH solution
(D) Final latex serum

hydrolyzed Vinol 205 samples (latexes L205/10 and L205/5) there is an increase in the number of acetate groups present in the aqueous phase poly(vinyl alcohol) as a result of the vinyl acetate grafting with the PVOH chains during the polymerization.

In both cases, the amount of vinyl acetate grafted to the poly(vinyl alcohol) becomes constant during the polymerization. The latexes prepared with Vinol 205, namely, L205/10 and L205/5 increased in acetate content by 5.65 % and 5.41 % respectively. Latexes L107/10 and L107/5, prepared with Vinol 107, increased in acetate content by 15.60 % and 15.37 % respectively, as shown in Table 4.3.1.

This constant value is a limiting value for the graft PVOH-PVAc copolymer to remain water-soluble. From the initial number of acetate groups present on the PVOH chains and from the data regarding the serum composition by FT-IR, the limiting value for acetate content on the PVOH chains to maintain its water-solubility can be calculated, by adding the increase in acetate content by grafting from the original acetate value for the PVOH, and was found to be approximately 18.0%.

This suggests that both types of poly(vinyl alcohol) can be grafted with vinyl acetate until 18.0% of the PVOH polymer chains are acetate groups with an overall 82.0% degree of hydrolysis.

This limiting value for the percent hydrolysis to maintain water-solubility determines whether or not the

TABLE 4.3.1

LATEX SERUM CHARACTERIZATION BY FT-IR

Latex Sample	Peak Wavelength (cm^{-1})	Absorbance Increase
L205/10	1728	5.65 %
L205/5 (Vinol 205)	1728	5.41 %
L107/10	1728	15.60 %
L107/5 (Vinol 107)	1728	15.37 %

graft copolymer will remain in the aqueous phase (above or equal to the 82.0 % degree of hydrolysis) or become water-insoluble and precipitate out (below the 82.0 % degree of hydrolysis).

The solids content of the serum, as given in Table 4.2, also reflect the the difference in the amount of grafting each type of PVOH can undergo. For the latexes prepared with the fully hydrolyzed Vinol 107 the percent solids of the serum increased an average of 4.69 % , whereas the solids of the latexes prepared with the partially hydrolyzed Vinol 205 exhibited a decrease in percent solids of an average of 28.24 %. These data also show that the fully hydrolyzed PVOH can graft with the PVAc to a greater extent more than the partially hydrolyzed PVOH and still maintain water-

solubility, due to the increase in the solids of the aqueous phase resulting from a greater amount of water-soluble PVOH-PVAc copolymer present.

The grafting reaction can be further quantified by examining the solids content and the composition of the aqueous phase serum during the course of the polymerization.

Latexes were prepared using the standard recipe, Table 2.3.1, at 0.10% $K_2S_2O_8$ concentration, using both Vinol 205 and Vinol 107 at a 10.0% concentration. Samples were taken at three different times during the polymerization and the overall and fractional monomer conversion was determined as shown in Table 4.3.2.

TABLE 4.3.2

LATEX CONVERSIONS

Latex	Time(min)	Overall Conversion	Fractional Conversion VAc	BuA
L205/10-a	5.0	18.89	0.210	0.168
	15.0	50.73	0.242	0.773
	40.0	65.98	0.328	0.990
Final	360.0	98.96	0.976	0.990
L107/10-a	5.0	9.44	0.128	0.024
	15.0	22.48	0.156	0.270
	120.0	60.36	0.271	0.985
Final	360.0	71.03	0.420	0.990

The first sample was taken at the point where more vinyl acetate has been consumed than the butyl acrylate

monomer. The second sample was taken when the butyl acrylate monomer is consumed faster than the vinyl acetate monomer. The third sample was taken when the butyl acrylate has been completely consumed. The polymerization is complete at the 360 minute mark.

Gravimetric and FT-IR analysis to determine the percent solids and composition of the aqueous phase during the course of the polymerization is given in Table 4.3.3.

TABLE 4.3.3

PERCENT SOLIDS AND COMPOSITION OF THE THE LATEX SERUM PREPARED WITH 10.0% VINOL 205 AND VINOL 107 AS DETERMINED BY FT-IR

Latex	Reaction Time (min)	% Solids of Serum	Overall Degree of Hydrolysis	%PVAc Grafted in the Serum by FT-IR
L205/10-a	0.0	3.42	88.0	0.00
	5.0	2.98	83.0	5.02
	15.0	2.80	81.9	6.11
	40.0	2.72	81.8	6.18
Final	360.0	2.71	81.8	6.20
L107/10-a	0.0	3.23	98.0	0.00
	5.0	3.25	92.2	5.85
	15.0	3.36	85.1	13.88
	120.0	3.38	82.0	16.00
Final	360.0	3.40	81.9	16.05

The data in Table 4.3.3 show that as the polymerization progresses the overall degree of hydrolysis for the serum of the latexes prepared with both Vinol 205 and Vinol 107 approach (and end at) the 82.0 % degree of hydrolysis level

which was the value determined for water-solubility. The solids content of the serum also reflect the differences in the grafting as was first shown in Table 4.2. The serum solids of the latex using the partially hydrolyzed Vinol 205 decrease during the course of the polymerization, while, the solids content of the serum for the latex prepared with the fully hydrolyzed Vinol 107 increases during the polymerization confirming that the Vinol 107 can graft to a greater extent than the Vinol 205 and still remain water-soluble.

4.4 FT-IR Analysis of the PVAc-PBuA Copolymer Fraction

4.4.1 Introduction and Experimental

The procedure for analysis of the PVAc-PBuA copolymer composition by FT-IR was given in section 2.4.5.3.

4.4.2 Results and Discussion

The polymer fraction remaining from the centrifugation of the latexes was analyzed by FT-IR to determine the poly(vinyl acetate)/poly(butyl acrylate) ratio in the copolymer. The FT-IR data was compared to the data obtained by gas chromatography for the copolymer composition as given in Table 4.4.1. The FT-IR data shows less poly(vinyl acetate) present in the copolymer than the data by gas chromatography. Since gas chromatography measures the total

amount of monomer consumed and the FT-IR is determining the composition of the copolymer formed, it can be pointed out that this difference also shows that the vinyl acetate is involved in another reaction, namely the grafting reaction with PVOH, than with the butyl acrylate during the initial stages of the polymerization.

In the case of the latex prepared with 10.0% of the partially hydrolyzed Vinol 205 (latex L205/10) the difference between the PVAc/PBuA ratio determined by gas chromatography is less than the difference calculated by FT-IR for the latex prepared with 10.0% of the fully hydrolyzed Vinol 107 (latex L107/10). These data also show that the fully hydrolyzed PVOH can graft to a greater extent than the partially

TABLE 4.4.1

COPOLYMER COMPOSITION BY GAS CHROMATOGRAPHY AND FOURIER TRANSFORM INFRARED SPECTROSCOPY

Latex Sample	Reaction Time (min)	Overall Conv.	Ratio of PVAc/PBuA by GC		FT-IR	
L205/10-a	5.0	18.89	1.25	56/44	1.11	53/47
	15.0	50.73	0.31	24/76	0.27	21/79
	40.0	65.98	0.33	25/75	0.30	23/77
	360.0	98.96	1.00	50/50	0.87	47/53
L107/10-a	5.0	9.44	5.33	84/16	4.26	81/19
	15.0	22.48	0.58	37/63	0.47	32/68
	120.0	60.36	0.28	22/78	0.23	19/81
	360.0	71.03	0.42	30/70	0.34	25/75

hydrolyzed PVOH and consume more of the vinyl acetate in that process.

4.5 Analysis of the Latex Prepared with 20mM Sodium Lauryl Sulfate and 2-Propanol

4.5.1 Introduction and Experimental

In section 3.4, a latex was prepared using 20mM SLS and 2-propanol in order to see if the rates of individual monomer consumption would be altered by the 2-propanol acting as an aqueous phase grafting site for the VAc. From the kinetic data, the butyl acrylate reacted faster than the vinyl acetate, as to be expected but, the 2-propanol concentration decreased initially suggesting that the 2-propanol was involved in some type of reaction.

The final latex sample was destabilized by three freeze-thaw cycles and then centrifuged to separate the serum. FT-IR analysis was used to determine if any 2-propanol was present in the aqueous phase.

4.5.2 Results and Discussion

From the data presented in Figure 4.2, which shows the FT-IR adsorption spectra of the serum, it can be determined that there is an absorption band in the region from 3500-3300 cm^{-1} which is indicative of the hydroxyl group. The spectra also shows the presence of water-soluble oligomeric

PVAc, absorption peak at 1728 cm^{-1}, and possibly 2-propanol-PVAc water-soluble polymer product in the serum.

The 2-propanol, then, does participate in some type of transfer reaction with the vinyl acetate in the aqueous phase. This can be illustrated further by the examination of the copolymer fraction from the centrifugation process, Figure 4.3. The ratio of the poly(vinyl acetate)/poly(butyl acrylate), calculated according to the procedure given in section 2.4.5.3, should be 50/50 if vinyl acetate is reacting only with butyl acrylate, but, as was shown in Figure 4.2 there is vinyl acetate present in the serum as shown in the absorbance peak at 1728 cm^{-1}. The calculated copolymer ratio from Figure 4.3 was determined to be 0.71 PVAc/PBuA or a 35.5/64.5 PVAc/PBuA copolymer composition ratio. The FT-IR spectra in Figure 4.3 shows that there is no detectable 2-propanol incorporated into the copolymer by the lack of a strong absorption band in the 3300 cm^{-1} range.

The chain transfer reaction to solvent of VAc with 2-propanol, then, is not as predominate as the grafting reaction of vinyl acetate with PVOH which alters the predicted rates of vinyl acetate and butyl acrylate monomer consumption.

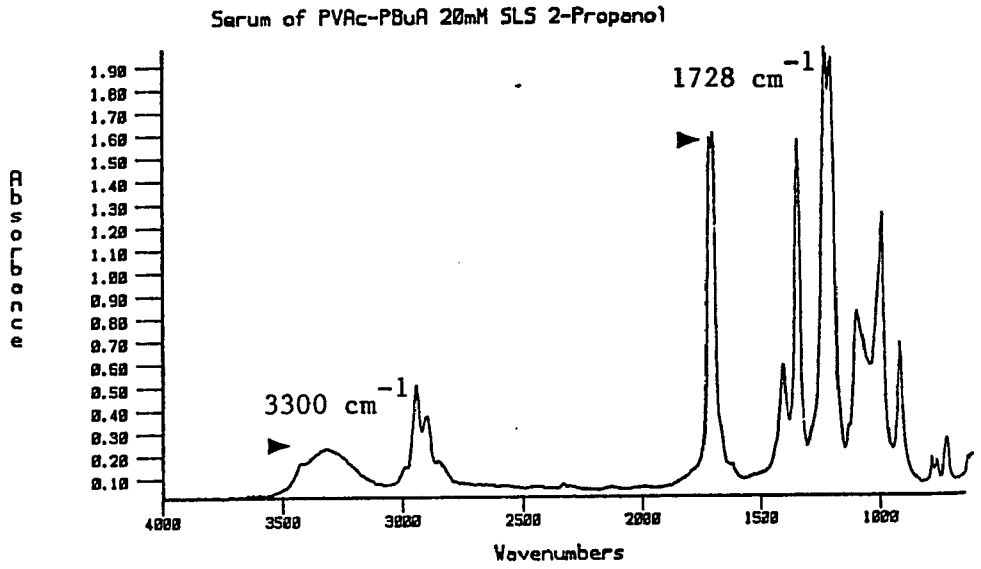


Figure 4.2: FT-IR spectra for the serum of the 50:50 (wt. ratio) VAc-BuA copolymer latex prepared with 20mM SLS and 2-propanol.

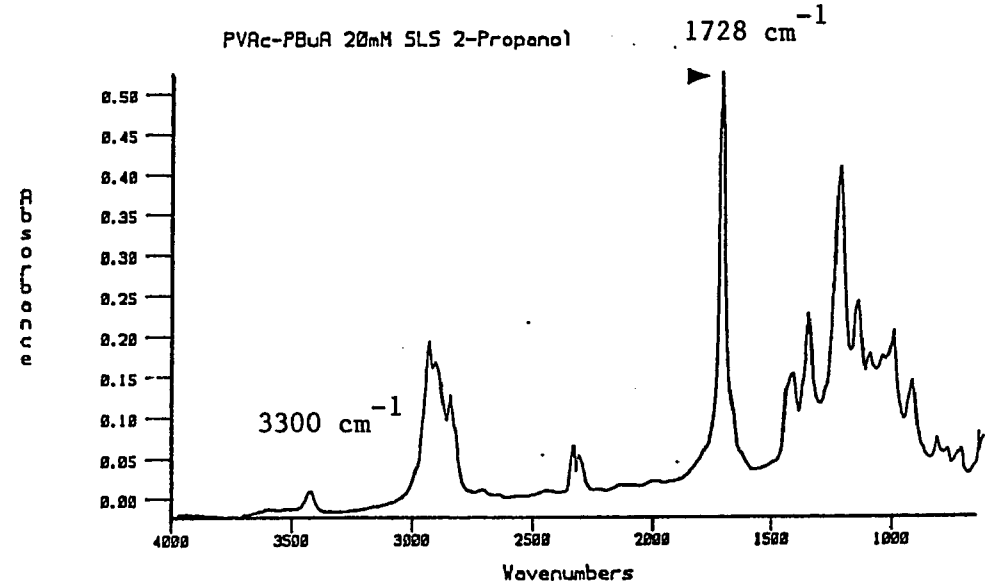


Figure 4.3: FT-IR spectra of the polymer fraction of the 50:50 (wt. ratio) VAc-BuA copolymer latex prepared using 20mM SLS and 2-propanol.

4.6 SUMMARY AND CONCLUSIONS

Fourier Transform Infrared (FT-IR) Spectroscopy was used to characterize and quantify the grafting reaction in the aqueous phase between vinyl acetate and poly(vinyl alcohol).

In the latex serum, after centrifugation, a limiting value of 82.0 % overall degree of hydrolysis of the PVOH to maintain water-solubility was determined.

The latex serum was separated from the polymer by centrifugation. The solids content of the serum was compared with the solids content of the PVOH solution before polymerization. When the fully hydrolyzed Vinol 107 was used as the emulsifier, the solids content of serum increased from the value before polymerization. The solids content of the serum decreased from the solids content before polymerization when the partially hydrolyzed Vinol 205 was used. These results indicated that the Vinol 107 can graft with the VAc more than the Vinol 205 and still remain water-soluble.

The P(VAc-BuA) copolymer particle composition was determined by both gas chromatography and FT-IR spectroscopy. The results indicated that the FT-IR data (actual copolymer composition) showed less PVAc present in the particle than the GC method (residual comonomer composition). This confirmed the reaction of VAc in the aqueous phase with the PVOH.

5. PREPARATION OF POLY(VINYL ALCOHOL) MODIFIED TO AN 82.0 % DEGREE OF HYDROLYSIS

5.1 Introduction

The modification of the two different types of poly(vinyl alcohol) to adjust the degree of hydrolysis, Vinol 205 (88.0% hydrolyzed) and Vinol 107 (98.0% hydrolyzed), is described in this chapter. The PVOH was modified through a reaction with a sufficient amount of vinyl acetate monomer to produce an overall degree of hydrolysis of the PVOH chain of 82.0%. These modified Vinol PVOHs will then be used as the emulsifiers in the emulsion copolymerization of vinyl acetate and butyl acrylate in batch and semi-continuous polymerizations.

5.2 Experimental

To achieve an 82.0% overall degree of hydrolysis, by grafting vinyl acetate to the PVOH polymer chains, the vinyl acetate monomer to be added was calculated from the initial degree of hydrolysis and concentration of the original PVOH used. The graft reaction recipe used to modify the original Vinol PVOH samples is similar to the standard latex recipe, as given in Table 2.3.1, but is altered according to the recipe given in Table 5.2.1. The product formed in the reaction will be refered to as "modified PVOH". The modified PVOH samples are prepared to give the equivalent of a 10.0% PVOH concentration when used as the emulsifier in

the emulsion copolymerization of 50:50 (by wt.) VAc/BuA.

The reactions were carried out in a magnetically stirred 75 ml sealed reactor with an N_2 blanket and a syringe sample port. The temperature of the reaction was 60°C. The monomer consumed during the reaction was determined by gas chromatography using a vinyl acetate and butyl acrylate-1,4 dioxane calibration curve. Samples were withdrawn periodically from the reactor. 0.50 grams of sample are added to 0.50 grams of a 1.00% by weight dioxane-in-water standard, and injected into the GC to determine conversion.

TABLE 5.2.1

RECIPE USED TO PREPARE MODIFIED PVOH

Component	Weight (grams)
DDI H_2O	36.25
PVOH	1.25
$NaHCO_3$	*
$K_2S_2O_8$	*
Vinyl Acetate when modifying:	
Vinol 205	0.1382
Vinol 107	0.2816

* 1.0% of the vinyl acetate weight in grams

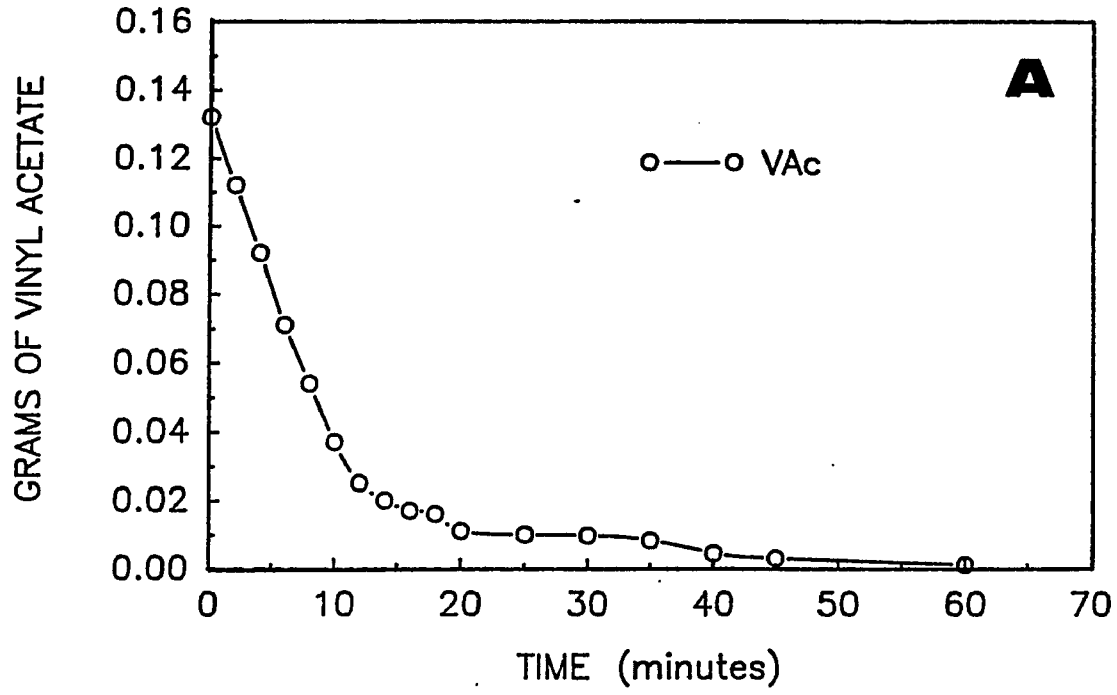
For the reactions with both the partially hydrolyzed Vinol 205 and the fully hydrolyzed Vinol 107, the amount of vinyl acetate added to the reaction is less than the limit of water-solubility (VAc water-solubility 2.50g/100g H_2O).

It could then be assumed that all the vinyl acetate monomer is dissolved in the aqueous phase and is not present in the form of monomer droplets.

5.3 Results and Discussion

Data showing the consumption of vinyl acetate versus time for the reactions run with the Vinol 205 and Vinol 107 are shown in Figure 5.1. For both the Vinol 205 and the Vinol 107 PVOHs, approximately 80.0% of the vinyl acetate monomer was consumed within the first 10 minutes of the reaction. The remaining vinyl acetate was then consumed over a period of 50 minutes. These data would suggest that the grafting reaction in the aqueous phase during the copolymerization proceeds very rapidly. This rapid grafting reaction in the aqueous phase between the vinyl acetate and poly(vinyl alcohol) would be preferred compared with the VAc-BuA reaction and would cause a faster consumption of the VAc monomer, which was observed in the fractional monomer versus overall conversion data given in section 3.1.4.

To demonstrate the dominance of the aqueous phase grafting reaction even further, butyl acrylate was added to the recipe as given in Table 5.2.1 in the same weights as the vinyl acetate. In these reactions, the butyl acrylate is



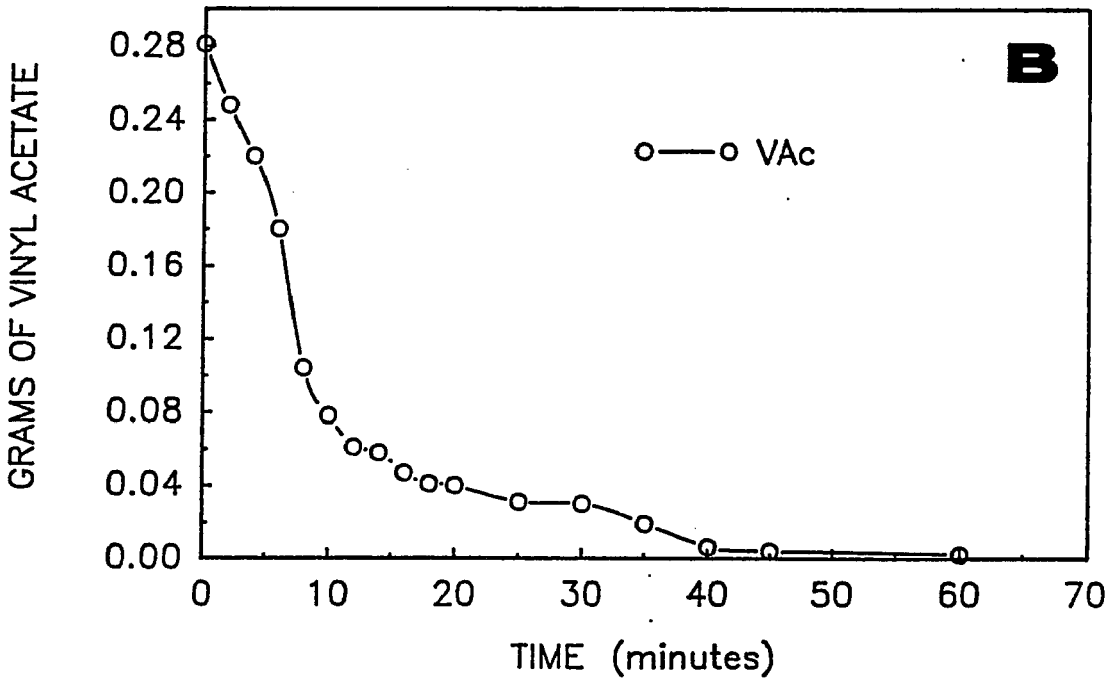


Figure 5.1: Consumption of vinyl acetate (in grams) versus time when polymerized using 10.0%:
(A) Vinol 205
(B) Vinol 107

well above it's water-solubility limit (BuA water-solubility = 0.14 g/100 g H_2O) [39] and should be in the form of monomer droplets dispersed in the aqueous phase. The vinyl acetate, as mentioned earlier, is dissolved in the aqueous phase. The consumption of vinyl acetate and butyl acrylate with time in the presence of Vinol 205 and 107 is given in Figure 5.2. As with Figure 5.1, approximately 80.0% of the vinyl acetate was consumed within the first 10 minutes of the reaction for both of the Vinol PVOHs used. The butyl acrylate, on the other hand, reacts very slowly until the vinyl acetate is almost consumed, at which point the butyl acrylate then reacts at a very rapid rate until exhausted. When comparing the rates of disappearance of vinyl acetate versus time in the first 10 minutes for the reactions with and without butyl acrylate, as given in Table 5.3.1, the rates for the vinyl acetate are slightly increased by the presence of the butyl acrylate monomer.

TABLE 5.3.1

RATES OF VINYL ACETATE CONSUMPTION DURING THE MODIFICATION OF VINOL 205 AND VINOL 107

Sample	Rate of Vinyl acetate Consumption (grams / minute)
Modified PVOH-205	9.57×10^{-3}
Modified PVOH-107	9.74×10^{-3}
Modified PVOH-205/ BuA	10.50×10^{-3}
Modified PVOH-107/ BuA	10.21×10^{-3}

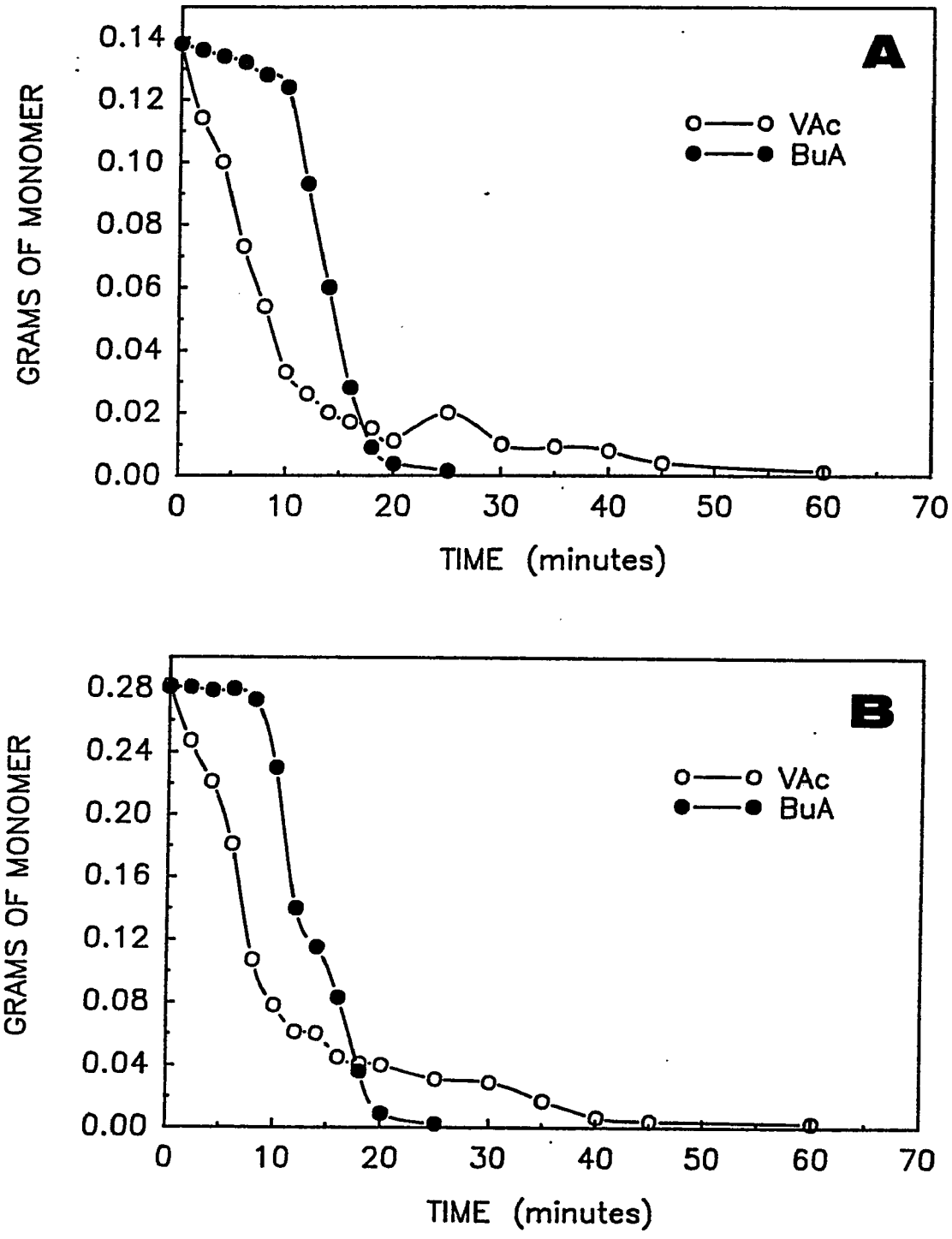


Figure 5.2: Consumption of vinyl acetate (in grams) versus time in the presence an equal weight (in grams) of butyl acrylate when polymerized using 10.0%:
(A) Vinol 205
(B) Vinol 107

These data would suggest that during the course of the polymerization the aqueous phase reaction is independent of the butyl acrylate and that the butyl acrylate polymerization is dependent upon the grafting reaction of the PVOH-VAc to generate loci for particle nucleation.

The solids content of the modified PVOH formed in the reaction was determined by gravimetric analysis. The modified PVOH was then centrifuged, using the procedure as given in section 2.4.4., and the solids content of the serum was determined. The percent solids results, as given in Table 5.3.2, compare the modified PVOH before and after centrifugation for the reactions with only VAc and the reactions with both VAc and BuA. The serum solids for the reaction with VAc alone, show that there is only a minimal loss of material due to the centrifugation process, which means that the modified PVOH graft copolymer formed is predominately water-soluble. In the cases where butyl acrylate was added to the recipe, the percent solids difference before and after centrifugation is considerably larger. This is probably due to the formation of primarily butyl acrylate homopolymer particles that have either physically adsorbed modified PVOH on the surface or modified PVOH that has been incorporated into the particles.

Using FT-IR spectroscopy, according to the procedure as

given in section 2.4.5.2, the increase in the acetate content of the PVOH due to the grafted vinyl acetate was determined. The overall degree of hydrolysis of the original PVOH sample and the modified PVOH is given in Table 5.3.3.

TABLE 5.3.2

SERUM SOLIDS OF MODIFIED PVOH GRAFT COPOLYMERS

Sample	Solids, before Centrifugation	Solids, after	% Difference
Modified PVOH-205	3.83	3.78	1.31
Modified PVOH-107	4.22	4.19	0.71
Modified PVOH-205/BuA	4.11	3.79	7.79
Modified PVOH-107/BuA	4.83	4.17	13.66

TABLE 5.3.3

FT-IR SPECTROSCOPY RESULTS FOR THE OVERALL DEGREE OF HYDROLYSIS OF THE MODIFIED PVOH

Sample	% OH, original PVOH Sample	% OH, after modification
Modified PVOH-205	88.0	82.96
Modified PVOH-107	98.0	83.41
Modified PVOH-205/BuA	88.0	83.17
Modified PVOH-107/BuA	98.0	82.91

All of the modified PVOH samples achieved values close to the 82.0 % degree of hydrolysis limit for water-solubility of the PVOH-PVAc graft copolymer. The presence of the BuA in the modified PVOH-205/BuA and modified PVOH-107/BuA samples did not seem to affect the final degree of hydrolysis of the modified PVOH when compared to the samples prepared with VAc alone.

5.4 Preparation of PVAc-PBuA Latexes using Modified PVOH as the Emulsifiers

The modified PVOH samples (modified PVOH-205 and modified PVOH-107) were used as the emulsifiers for the emulsion copolymerization of 50:50 (by wt.) vinyl acetate/ butyl acrylate using the standard recipe, Table 2.3.1. The latexes were characterized using the procedures given in section 2.4.

The modified PVOH solutions where adjusted by the addition of DDI water to a 3.35% solids content, which would correspond to a 10.0% PVOH concentration based on total monomer weight. The actual serum solids were determined by gravimetric analysis and were found to be: 3.38% for the modified PVOH-205 and 3.36% for the modified PVOH-107.

Figure 5.3 shows the fractional conversion for each monomer versus the overall conversion for latexes made with the VAc modified Vinol PVOH 205 and 107. The most significant observation evident in Figure 5.3 is that in the

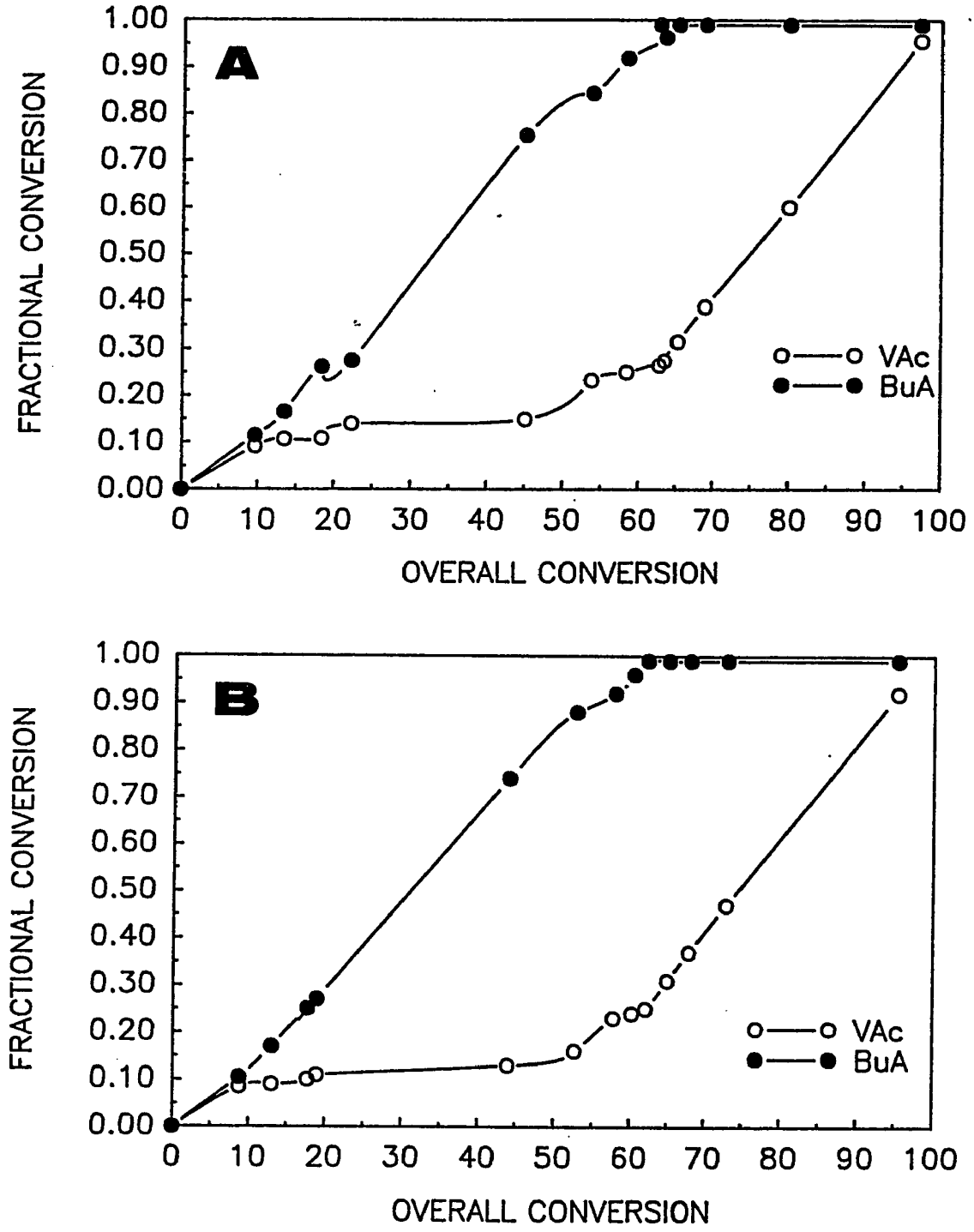


Figure 5.3: Fractional conversion versus overall conversion for the emulsion copolymerization of 50:50 (by wt.) VAc/BuA using 10.0% (based on total monomer wt.) of:
(A) Modified PVOH-205
(B) Modified PVOH-107

initial region of polymerization (less than 30% overall conversion) the vinyl acetate monomer is not consumed faster than the butyl acrylate monomer, which was observed when the original Vinol 205 and Vinol 107 were used as the emulsifiers for similar polymerizations, shown previously in Figures 3.5 and 3.6.

This data supports previous results that show that the vinyl acetate is being consumed at a faster rate at the early stages of the polymerization because of the grafting reaction in the aqueous phase between the vinyl acetate and the poly(vinyl alcohol). The grafting reaction continues until the degree of hydrolysis of the grafted PVOH chain reaches the 82.0 % OH level. After this point, the PVOH-PVAC graft copolymer becomes water-insoluble and then precipitates from the aqueous phase. The precipitating water-insoluble PVOH-PVAc graft copolymer can then begin to act as a site for particle nucleation. By preparing a PVOH-PVAc copolymer with an 82.0% degree of hydrolysis, the grafting reaction produces more water-insoluble copolymer faster, consuming less vinyl acetate.

The initial rates of polymerization (calculated from the initial slope of the overall conversion versus time curves, to 60.0 % conversion) for the emulsion copolymerization of 50:50 (wt. ratio) VAc-BuA using 10.0% (based on monomer) of the modified PVOH-205 and the modified

PVOH-107 poly(vinyl alcohol) have similar initial rate values when using the same initiator concentration. The initial rate of polymerization using the original Vinol 205 under similar conditions was slighlty higher than the latexes prepared with the modified PVOH-205 and modified PVOH-107, as given in Table 5.4.1.

TABLE 5.4.1

COMPARISON OF INITIAL RATES OF POLYMERIZATION AT A 0.10% POTASSIUM PERSULFATE CONCENTRATION

Latex	Rate of Polymerization, initial
10.0 % Vinol 205 (Latex L205/10)	5.76×10^{-3} g/l-min
10.0 % Vinol 107 (Latex L107/10)	2.23×10^{-3} g/l-min
10.0 % Modified PVOH-205 (Latex Mod-205/10)	5.48×10^{-3} g/l-min
10.0 % Modified PVOH-107 (Latex Mod-107/10)	5.32×10^{-3} g/l-min

The initial rates of polymerization for both of the latexes prepared with the modified PVOH samples are faster than the initial rate of polymerization determined for the latex prepared with the fully hydrolyzed Vinol 107 under the same conditions.

The particle size data of Figure 5.4(B) show that the latex prepared with the modified PVOH-205 were similar in particle size to the latex prepared with the Vinol 205.

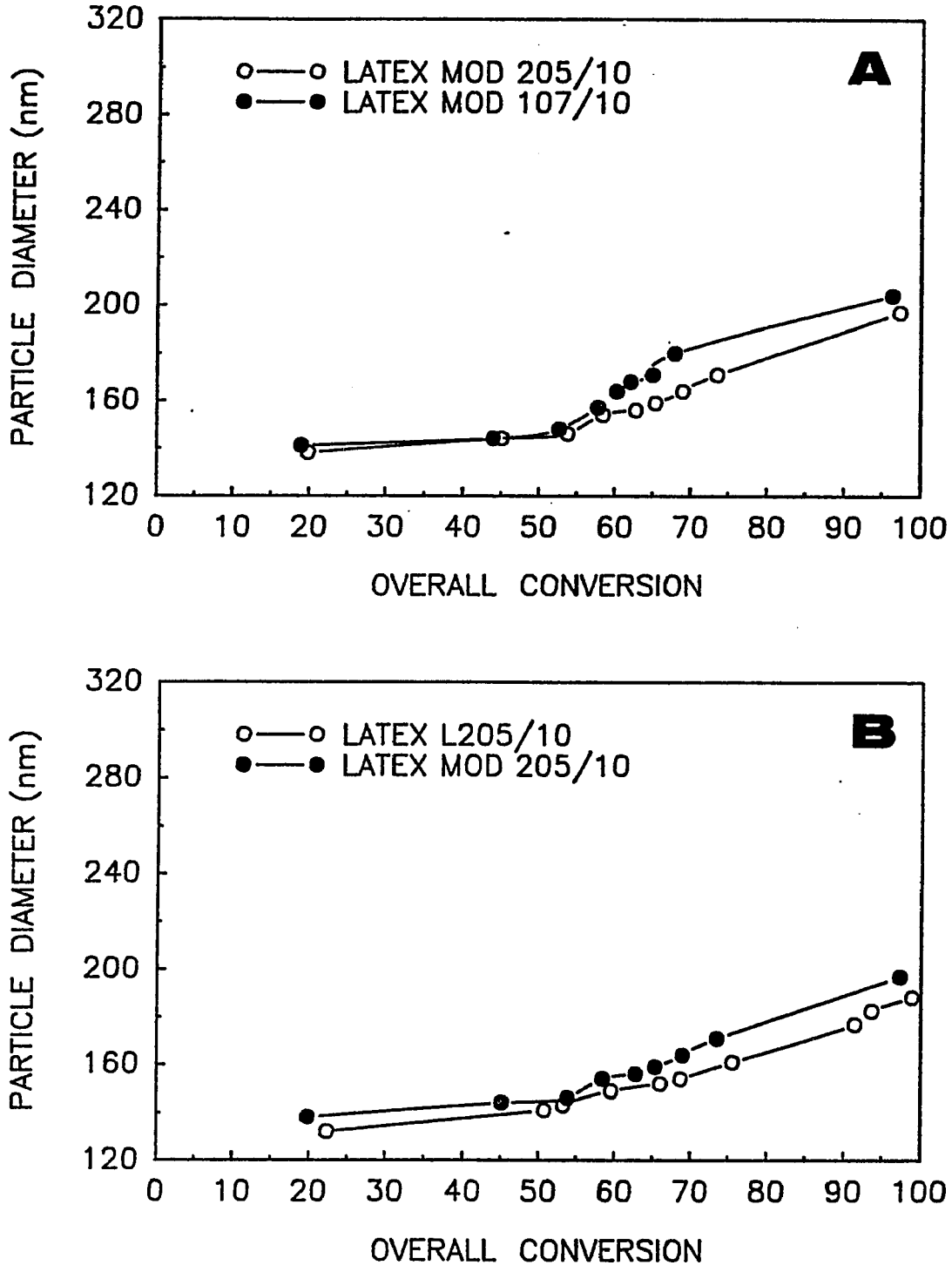


Figure 5.4: Particle diameter (nm) versus conversion for 50:50 (by wt.) VAc/BuA latexes (0.1% $K_2S_2O_8$) using 10.0% emulsifier (based on monomer) for:
(A) Latexes prepared with Modified PVOH
(B) Latexes prepared with Vinol 205 and Modified PVOH-205

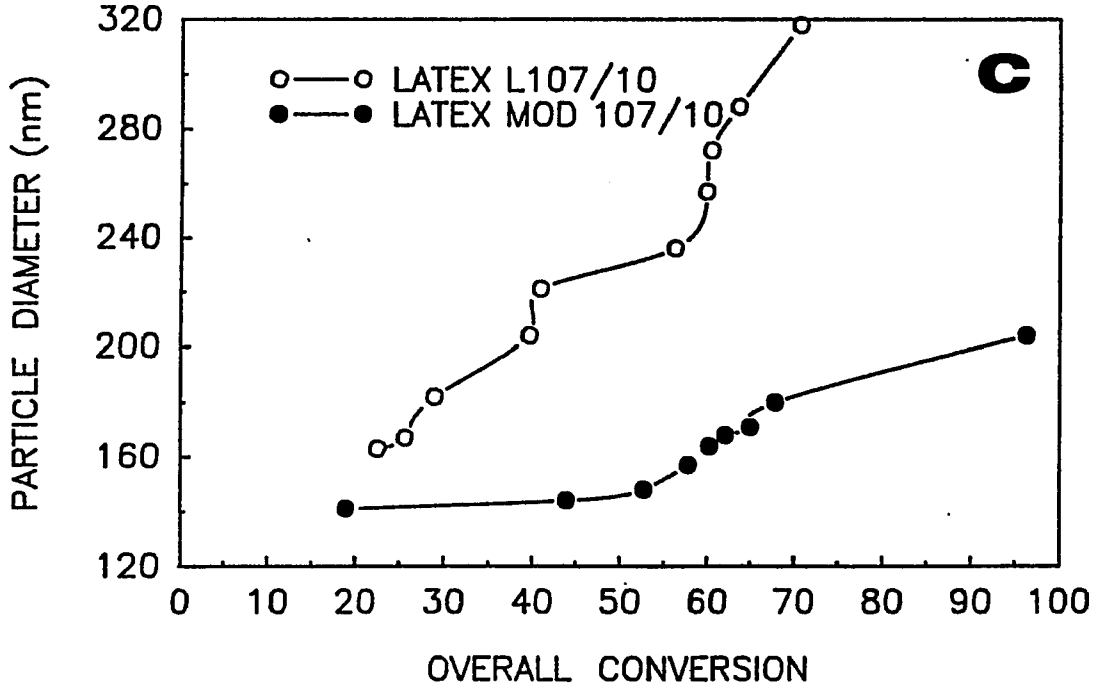


Figure 5.4 cont.: Particle diameter (nm) versus conversion for 50:50 (by wt.) VAc/BuA latexes (0.1% $K_2S_2O_8$) using 10.0% emulsifier (based on monomer) for:
(C) Latexes prepared with Vinol 107 and Modified PVOH-107

On the other hand, the particle size of the latex prepared with the modified PVOH-107 is drastically smaller than the latex prepared with the original Vinol 107, as shown in Figure 5.4(C). Figure 5.4(A) shows that the latex particle size is similar when the modified PVOH-205 or modified PVOH-107 is used as the emulsifier.

When the particle size data obtained by transmission electron microscopy (TEM) was compared with the data from the Coulter N4M, the TEM data also showed that the latexes prepared with the modified PVOH-205 and the modified PVOH-107 have similar particle diameters to the the latex prepared with the original Vinol 205, Table 5.4.2.

TABLE 5.4.2

PARTICLE SIZE COMPARISON OF LATEXES PREPARED WITH MODIFIED PVOH EMULSIFIER

	Particle Diameter (nm)			
Latex	Coulter N4M	TEM		
		D_N	D_W	D_V
Mod PVOH-205	191.2	136.3	143.4	138.7
Mod PVOH-107	196.4	138.9	147.7	141.8
L205/10	188.0	132.5	150.2	138.0

The particle size distributions determined using the TEM data for the latexes prepared with the modified PVOH-205 and PVOH-107 were broad, as shown in Figure 5.5.

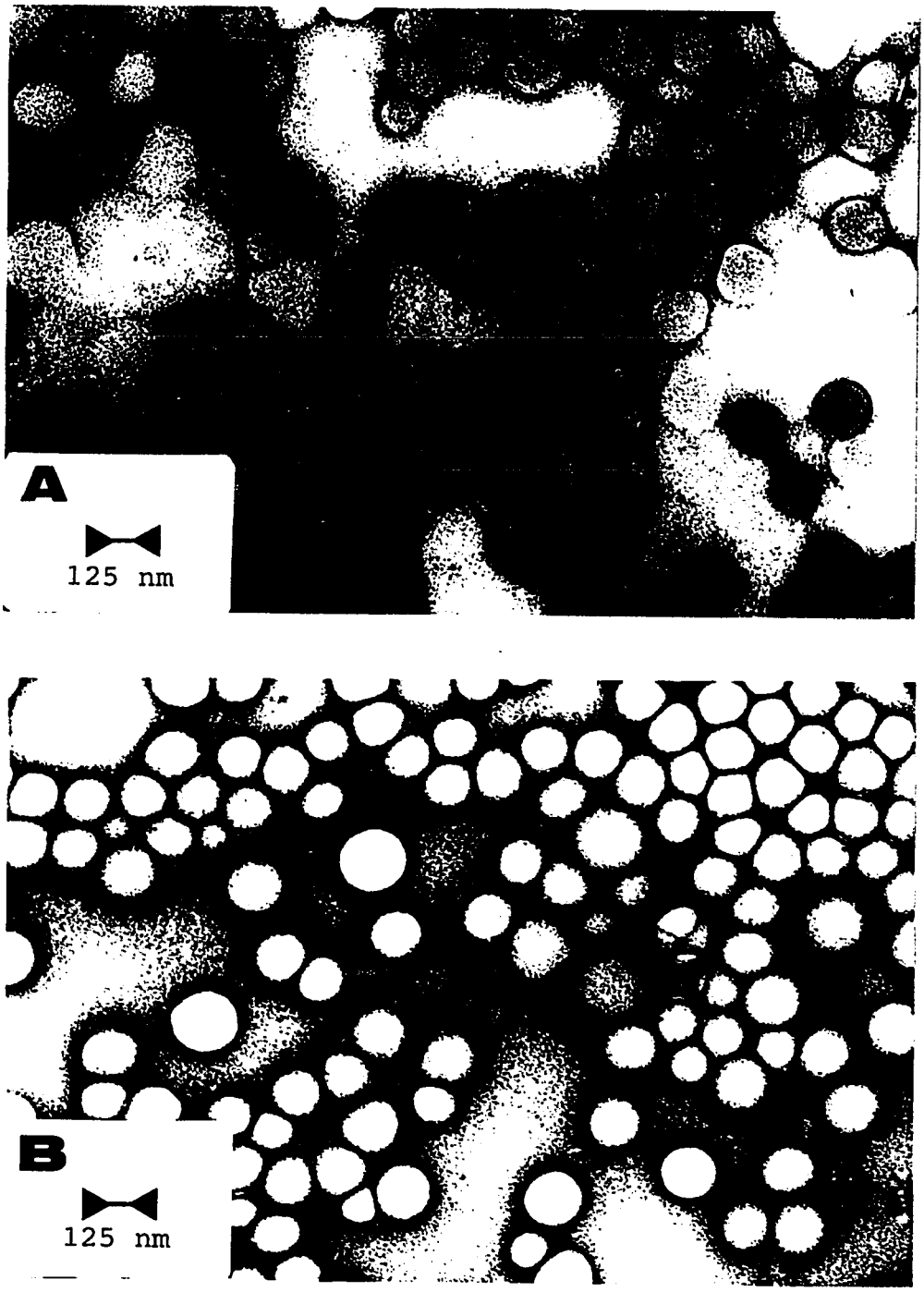


Figure 5.5: Electron micrographs of 50:50 (by wt.) VAc-BuA copolymer latexes prepared with 10.0% (based on monomer) of:
(A) Modified PVOH-205
(B) Modified PVOH-107

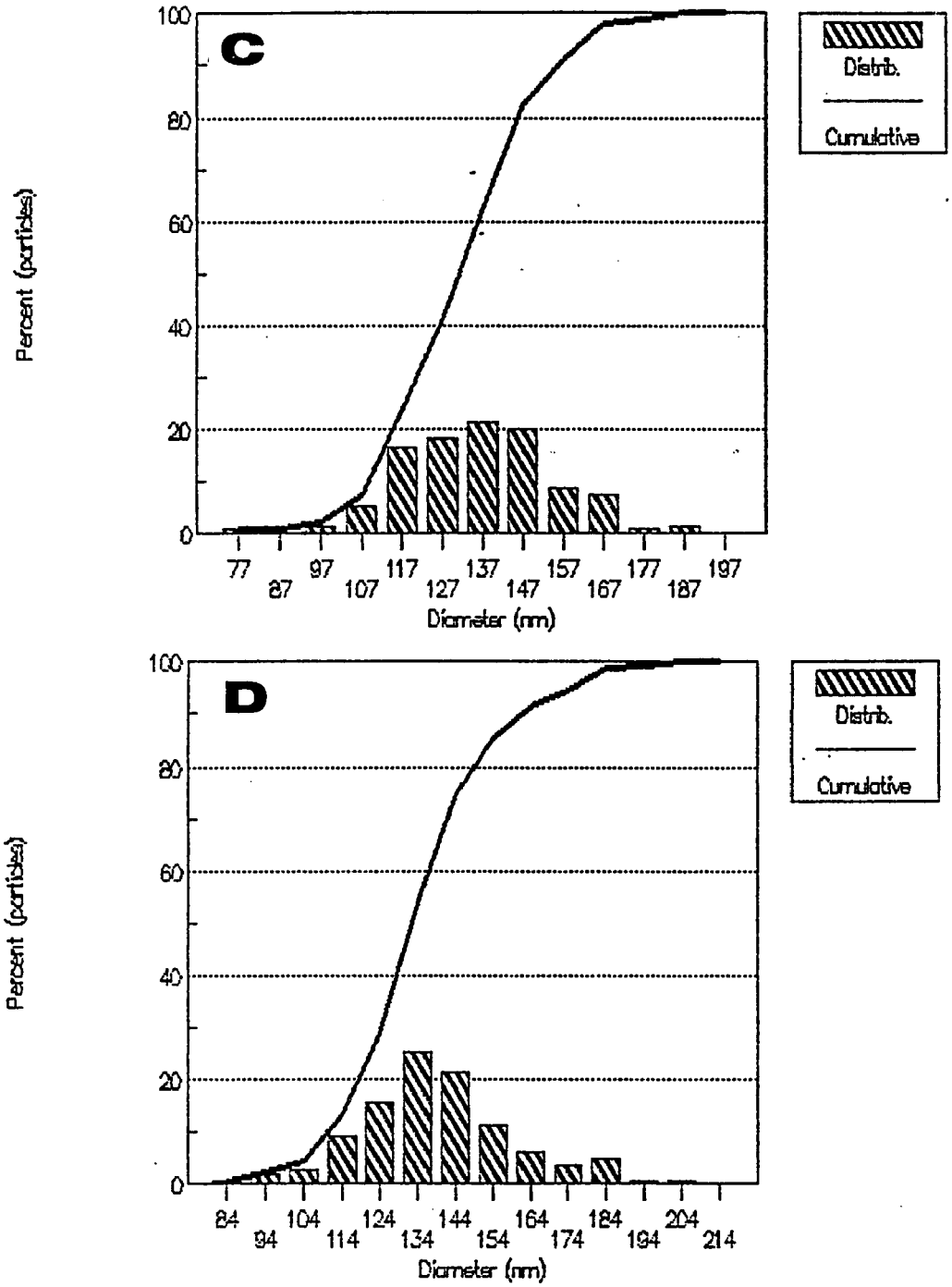


Figure 5.5 cont.: Particle size distribution analysis data for 50:50 VAc-BuA copolymer latexes prepared with 10.0% (based on monomer):
(C) Modified PVOH-205
(D) Modified PVOH-107

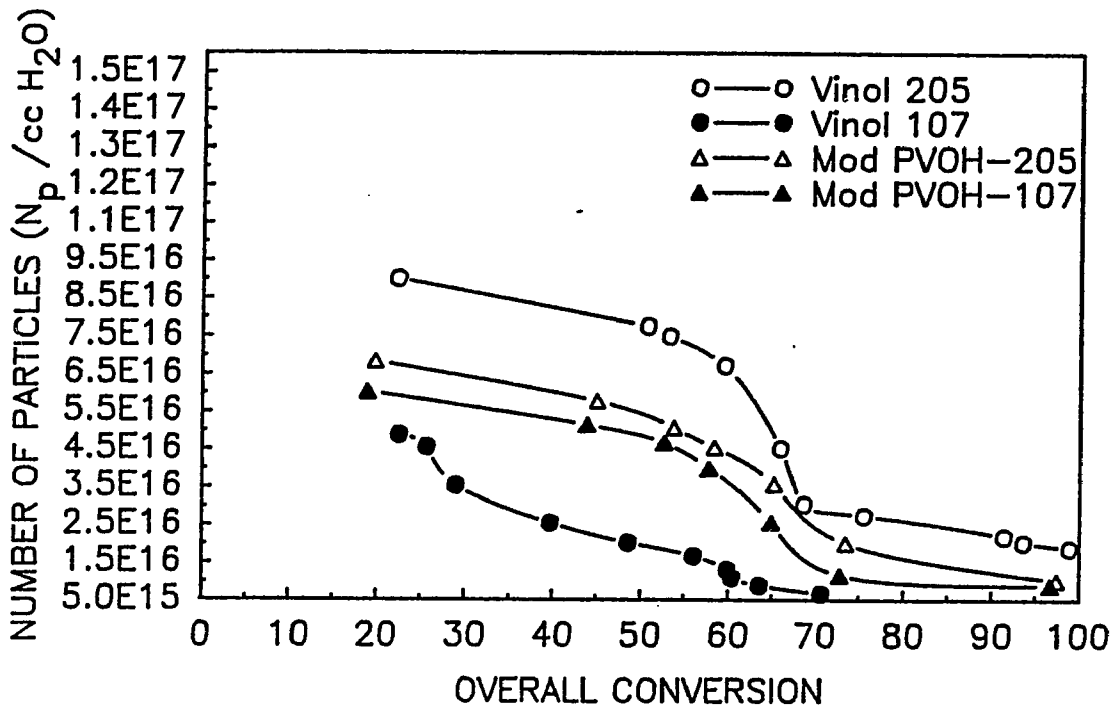


Figure 5.6: Particle Number density (N_p cc/H_2O) for 50:50 (by wt.) VAc/BuA latexes using 10.0% (based on total monomer wt.) of Vinol 205, Vinol 107, modified PVOH-205, and modified PVOH-107.

The particle number density, as shown in Figure 5.6, for the latexes prepared with the modified PVOH samples was found to be larger than the particle number density for the latex prepared with the Vinol 107. But, the particle number density of the latexes prepared with the modified PVOH samples is comparable to the particle number density for the latex prepared with the Vinol 205.

The kinetic data, in terms of the initial rates of polymerization, for the latexes prepared with the modified PVOH samples should be faster than for the latex prepared

with the Vinol 205, since the modified PVOH samples are grafted to the 82.0% degree of hydrolysis water-solubility limit, but this is not the case. The particle size and number density data also reflect the kinetic similarities between the latexes prepared with the modified PVOH samples and the latex prepared with the Vinol 205.

One possible explanation for the latexes prepared with the modified PVOH samples not having a faster rate of polymerization, and thus a smaller particle size, than the latex prepared with the Vinol 205 is that the modified PVOH have an increased level of VAc branching due to the grafting reaction. The modified PVOH samples consist of the original Vinol PVOH polymer chains which have been grafted onto in branches by the vinyl acetate. This branching of the modified PVOH chain could decrease the rate of grafting with the vinyl acetate in the aqueous phase when the modified PVOH samples are used as the emulsifiers in an emulsion copolymerization by reducing the availability of grafting sites on the original PVOH chain.

The solids content of the final serum of the PVAc-PBuA latexes prepared using the modified PVOH decrease from solids before the polymerization as shown in Table 5.4.3.

TABLE 5.4.3

COMPARISON OF SERUM SOLIDS FOR LATEXES PREPARED WITH VINOL 205 AND MODIFIED PVOH-205 AND MODIFIED PVOH-107

Sample	Solids, before Polymerization	Solids, after	% Difference
L205/10 (10.0% Vinol 205)	3.58	2.89	19.23
L205/5 (5.0% Vinol 205)	1.52	1.19	21.32
Mod-205/10 (10.0% Modified PVOH-205)	3.38	2.39	29.43
Mod-107/10 (10.0% Modified PVOH-107)	3.36	2.33	30.58

The decrease of the solids content from the initial to the final value is 29.43% for the latex made with the modified PVOH-205 and 30.58% for the latex made with the modified PVOH-107. The percent decrease in solids content determined for the latex prepared with the original Vinol 20 is less that the value obtained for the latex prepared with the modified PVOH-205 and modified PVOH-107. These data show that the greater final solids content of the latex prepared with the 10.0% Vinol 205 is due to more water-soluble graft copolymer in the aqueous phase. Since the modified PVOH are already at the 82.0% hydrolysis level a smaller degree of grafting is necessary for the graft copolymer to become

water-insoluble.

FT-IR analysis shows a slight decrease in the degree of hydrolysis of the final serum of the latexes prepared using the modified PVOH-205 and modified PVOH-107 compared to the overall degree of hydrolysis of the modified PVOH before polymerization, as shown in Table 5.4.4.

TABLE 5.4.4

FT-IR ANALYSIS OF THE LATEX SERUM PREPARED USING MODIFIED PVOH

Sample	Degree of Hydrolysis	
	Initial	Final
Modified PVOH-205	82.96	82.64
Modified PVOH-107	83.41	82.08

The FT-IR data show that both of the modified PVOH can undergo more grafting with the VAc and still remain water-soluble.

5.5 Semi-Continuous Polymerization of Vinyl Acetate Using Modified PVOH as the Emulsifier

5.5.1 Introduction

In this section, the partially hydrolyzed (88.0% OH) Vinol 205 and the fully hydrolyzed (98.0% OH) Vinol 107 will be modified by reacting with vinyl acetate to produce an

82.0% overall degree of hydrolysis of the PVOH-PVAc graft copolymer. The modified PVOH's will then be used as the emulsifier in the semi-continuous polymerization of vinyl acetate. The objective of the section is to monitor particle growth during the course of the polymerization as a function of conversion and monomer feed rates.

5.5.2 Experimental

The poly(vinyl alcohol) was modified, in batch, using the procedure given in section 5.2. In these experiments, 150.00 grams of the modified PVOH was prepared using the reactor set-up described in section 2.2.1 and recipe as given in Table 5.5.1. The reaction was carried out at 60^{o}C for 2 hours. The solids contents of the modified PVOH solutions were determined by gravimetric analysis. The overall degree of hydrolysis was determined by FT-IR following the procedure given in section 2.4.5.2.

5.5.3 Results and Discussion

The conversion of the modified PVOH samples was determined by gravimetric analysis and was found to be: 99.14% conversion for the modified PVOH-205 and 99.23%

TABLE 5.5.1

RECIPE FOR MODIFICATION OF VINOL 205 AND VINOL 107 FOR IN SEMI-CONTINUOUS POLYMERIZATION

Component	Weight (in grams)
DDI Water	150.00
PVOH	5.00
Vinyl Acetate when modifying:	
Vinol 205	0.5528
Vinol 107	1.1264
Potassium Persulfate when modifying:	
Vinol 205	0.0055
Vinol 107	0.0113
Sodium Bicarbonate when modifying:	
Vinol 205	0.0055
Vinol 107	0.0113

conversion for the modified PVOH-107.

The serum solids of the modified PVOH solutions was determined, before and after centrifugation for 2 hours at 18,000 rpm at $4^{o}C$, and shown in Table 5.5.2. The modified PVOH solutions were centrifuged to remove any water-insoluble products that might have formed.

The overall degree of hydrolysis as determined by FT-IR of the modified PVOH samples is shown in Table 5.5.3.

The solids content of the modified PVOH solutions and

the FT-IR data show that the modified PVOH-205 and modified PVOH-107 are water-soluble graft copolymers.

TABLE 5.5.2

SOLUTION SOLIDS OF MODIFIED PVOH BEFORE AND AFTER CENTRIFUGATION

Sample	Solids, before Centrifugation	Solids, after Centrifugation	% Difference
Modified PVOH-205	3.87	3.81	1.55
Modified PVOH-107	4.29	4.25	0.93

TABLE 5.5.3

FT-IR SPECTROSCOPY DETERMINATION OF THE OVERALL DEGREE OF HYDROLYSIS OF THE MODIFIED PVOH SAMPLES FOR USE IN SEMI-CONTINUOUS POLYMERIZATION

Sample	% OH, original PVOH sample	% OH, after modification
Modified PVOH-205	88.0	83.01
Modified PVOH-107	98.0	83.37

5.5.4 Semi-continuous Polymerization

The modified PVOH solutions were then used in the semi-continuous polymerization of vinyl acetate. The modified

PVOH solutions were diluted with DDI water to a solids content of 3.35% to have a 10.0% by weight based on the VAc monomer used in the recipe. The initiator and buffer each had a concentration of 0.10% based on monomer weight. The recipe used for the semi-continuous polymerization is given in Table 5.5.4.

TABLE 5.5.4

RECIPE FOR THE SEMI-CONTINUOUS POLYMERIZATION OF VAc USING MODIFIED PVOH AS EMULSIFIER

Component	Weight (grams)
Modified PVOH Solution	100.00 (96.65g water, 3.35g modified PVOH)
Vinyl Acetate	33.50
Potassium Persulfate	0.0335
Sodium Bicarbonate	0.0335

The latex recipe gives a latex solids content of 27.63 percent.

The polymerization was carried out in the reactor described in section 2.2.1. One side-neck of the reactor flask was equipped with the monomer feed line. A Harvard Apparatus Model 975 Infusion syringe pump and a 50ml glass syringe were used to feed the monomer into the reactor. The feed rates of the monomer were controlled by adjusting the gear ratios of the motor in the syringe pump. All of the components, except the vinyl acetate, were added in batch

to the reactor. The polymerization conditions were described in section 2.4.1. The vinyl acetate monomer was added continuously at a preselected feeding rate. The polymerization was started when the VAc monomer feed was introduced into the reactor.

During the course of the polymerization 3.00 gram samples were withdrawn and used to determine monomer conversion, particle size and serum solids. Each sample withdrawn from the reaction was weighed. The overall conversion was determined by gravimetric analysis taking into account the amount of emulsion previously removed for each sample.

Two flow rates were selected for the vinyl acetate feed into the reactor: 0.15ml/min and 0.59ml/min. When converting the flow rates from ml/min to g/min, flow rate is multiplied by the density of VAc (0.9317 g/ml at 20^{o}C). The flow rates in grams/minute then correspond to 0.14g/min and 0.51g/min. The two feed rates selected added the 33.50 grams of vinyl acetate over time periods of 240 minutes and 66 minutes, respectively.

The feed rates selected provided two different polymerization schemes, as shown in the conversion versus time data in Figure 5.7. The conversion data for the feed rate of 0.14 g/min shows a starved polymerization scheme for both the modified PVOH-205 and PVOH-107, since the

continuously added VAc monomer is instantaneously being converted to polymer as illustrated by the near 100% conversion throughout the polymerization.

The feed rate of 0.51g/min for the modified PVOH-205 and modified PVOH-107 showed a flooded polymerization scheme. The rate of polymerization of the vinyl acetate was not rapid enough to convert the monomer to polymer as it was

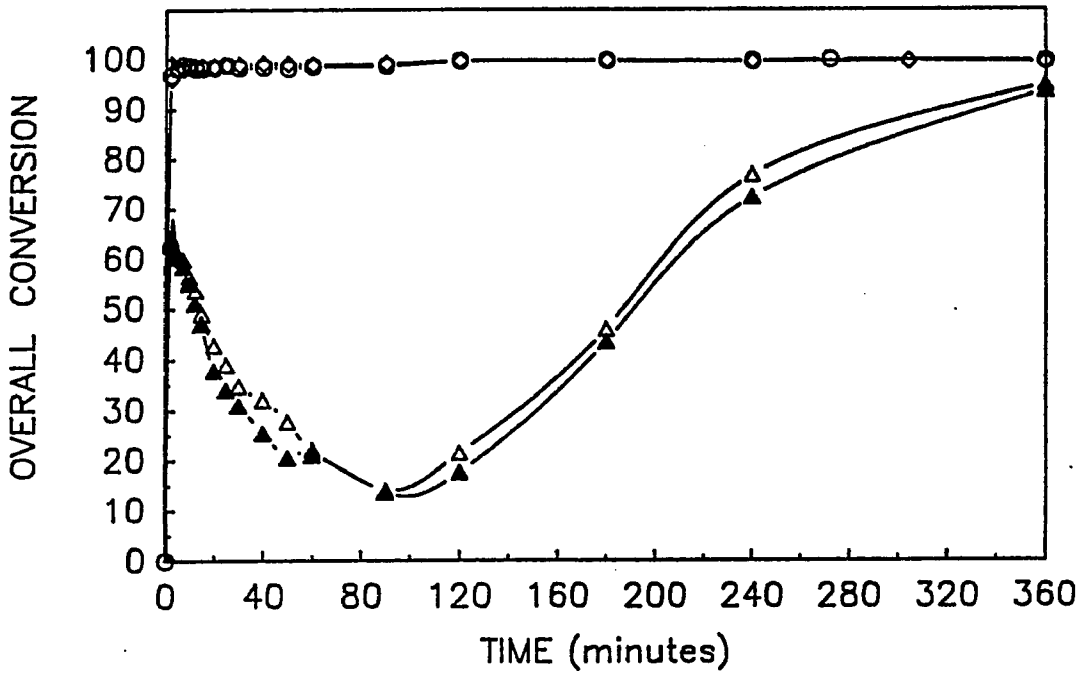


Figure 5.7: Overall Conversion Versus Time (minutes) for VAc Latexes prepared Semi-Continuously using Modified PVOH-205 and Modified PVOH 107 at a 10.0% Concentration (based on total monomer wt.) at 2 Different Feed Rates:
(○) Modified PVOH-205: 0.14g/min
(◇) Modified PVOH-107: 0.14g/min
(△) Modified PVOH-205: 0.51g/min
(▲) Modified PVOH-107: 0.51g/min

fed into the reactor and the monomer then forms a reservoir of droplets dispersed in the aqueous phase. This is illustrated in Figure 5.7 for the recipes that used the 0.51g/min flow rate in the overall conversion decreases with time until all of the monomer has been added to the polymerization reactor (approx. 66 min.) at which point the conversion begins to increase until the reaction is complete.

When comparing the 2 feed rates, the 0.14 g/min feed rate achieved maximum conversion (approx. 98.5%) at the first sample time of 2.5 minutes and maintained that value through the 360 minute polymerization time. The recipes using the 0.51g/min feed rate achieved approximately 94% overall conversion at the end of the 360 minute polymerization cycle, but only an average 64.5% overall conversion at the 2.5 minute sample time. This data would suggest that either the VAc was still polymerizing at the 360 minute mark and the reaction was not complete or the added monomer which in the rapid feed rate created monomer droplets in which the excess VAc could have been volatilized out of the reactor through the reflux condenser, stirring shaft gland, or joint fittings.

5.5.5. Particle Size and Number Density Determination

The latex particle diameter and the particle number

density were determined by the methods described in section 2.4.3.

The PVAc latexes prepared with modified PVOH-205 and modified PVOH-107 at the 0.14g/min monomer feed rate showed an increase in particle size with time, while the particle density (N_p/cc H_2O) remained relatively constant, as shown in Figure 5.8 and Table 5.5.5.

TABLE 5.5.5

PARTICLE DIAMETER AND NUMBER DENSITY FOR PVAC LATEXES PREPARED USING MODIFIED PVOH AT A 0.14 GRAM/MINUTE MONOMER FEED RATE

Latex Prepared with Modified PVOH-205 / Modified PVOH-107		
Time (min)	Diameter (nm)	Number (N_p/ cc H_2O) x 10^{16}
15	72.3 / 76.6	1.30 / 1.06
20	79.2 / 80.7	1.28 / 1.27
25	83.4 / 85.2	1.17 / 1.29
30	91.4 / 90.7	1.21 / 1.28
40	100.1 / 102.4	1.27 / 1.19
50	124.2 / 115.6	1.35 / 1.17
70	126.4 / 125.9	1.15 / 1.18
90	129.7 / 134.8	1.32 / 1.28
120	138.8 / 137.7	1.33 / 1.35
240	162.3 / 171.2	1.40 / 1.37
360	168.2 / 172.3	1.38 / 1.36

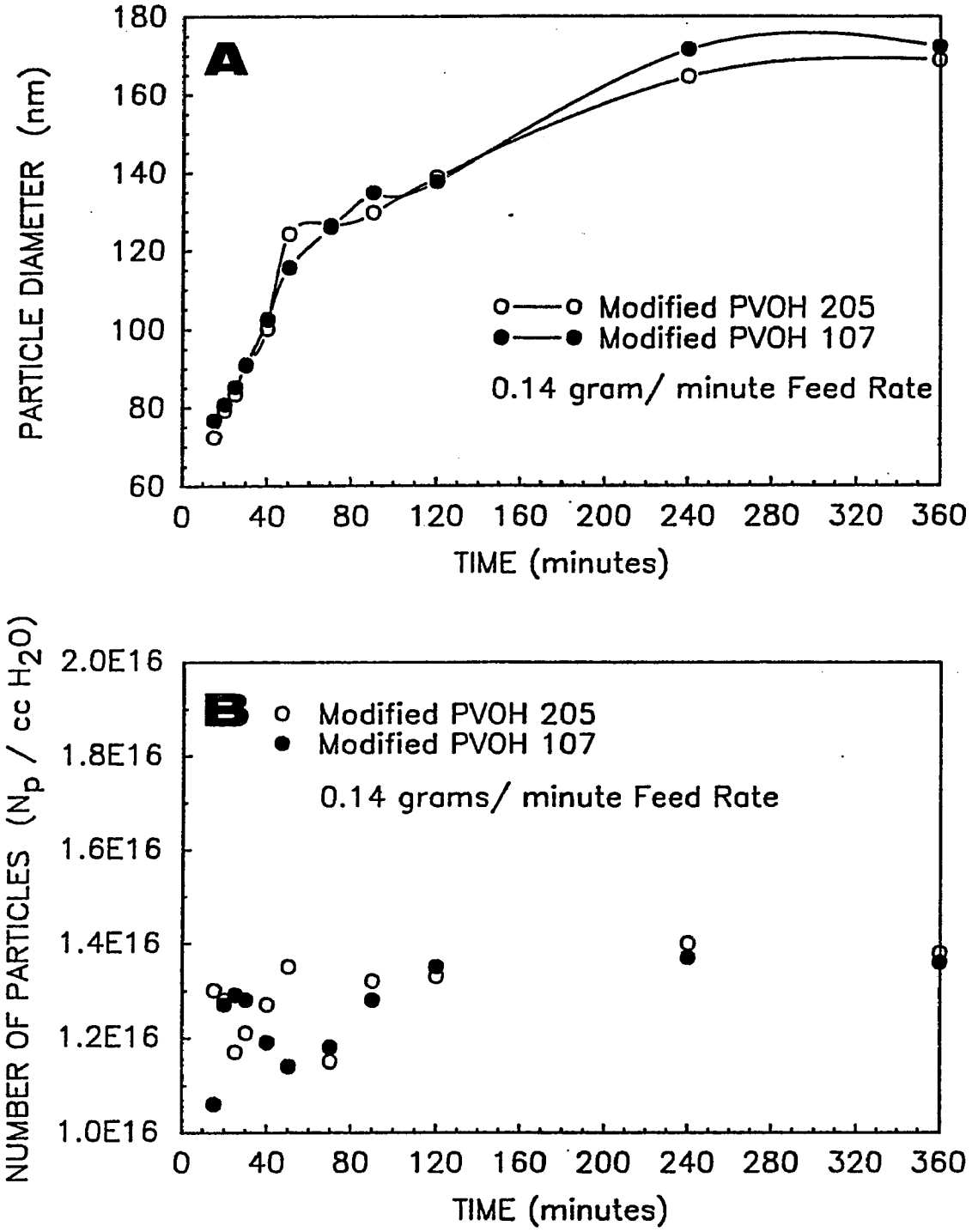


Figure 5.7: Particle Diameter (A) and Particle Number Density (B) for PVAc latexes prepared semi-continuously at a 0.14g/min feed rate using 10.0% Modified PVOH-205 and Modified PVOH-107.

The first particles that were detectable using the Coulter Electronics N4M appeared at the 15 minute mark into the polymerization. The particle size and conversion data would then show that the vinyl acetate monomer was being consumed instantaneously upon addition to the polymerization. As the particles are formed, the monomer that is fed into the system is being consumed by the growing particles rather than reacting in the aqueous phase with the PVOH. This was confirmed by the determination of the serum solids content of each sample withdrawn from the reactor and plotting the data as a function of time as shown in Figure 5.9.

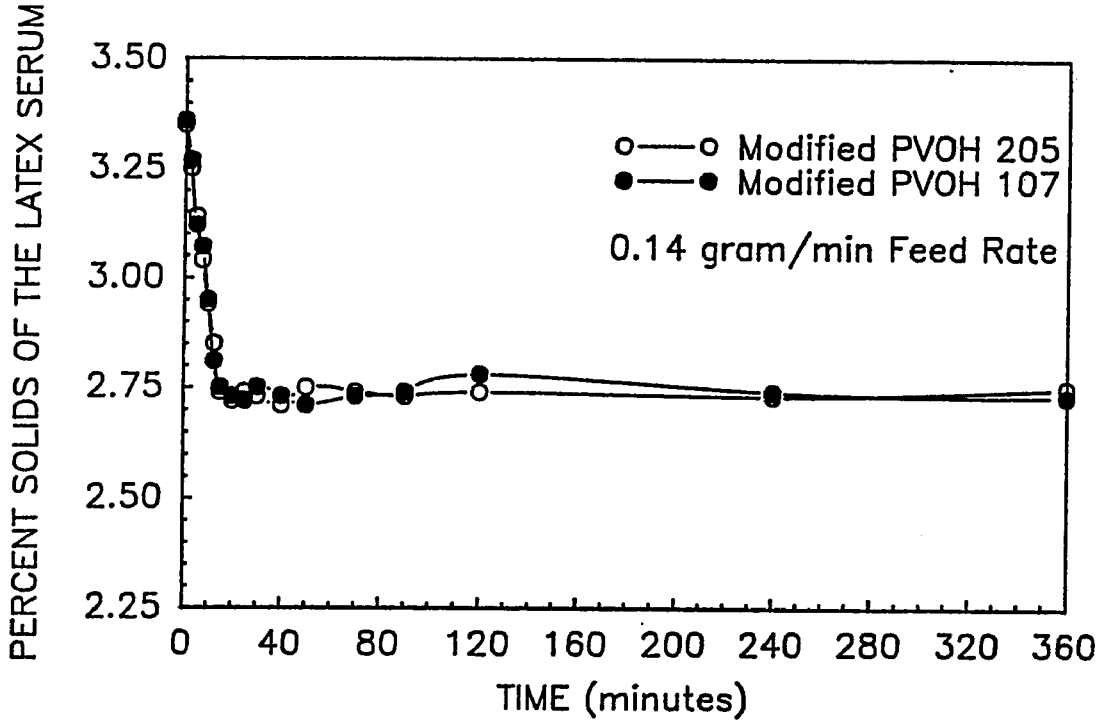


Figure 5.9: Serum Solids Versus Time for PVAc Latexes Prepared with 10.0% Modified PVOH-205 and Modified PVOH-107 at a 0.14g/min Monomer Flow Rate.

The data in Figure 5.9 show that there was a sharp initial decrease of the solids content of the latex serum during the course of the polymerization. The decrease in the serum solids began to level off to a constant value at approximately the 15 minute mark during the polymerization. This leveling off point in the curve coincides with the time at which particles were first detected.

In this semi-continuous polymerization, the VAc added was reacting with the aqueous phase modified PVOH until the graft copolymer becomes water-insoluble. When the graft copolymer precipitated from the aqueous phase, a loci for particle nucleation was formed by the hydrophobic acetate blocks or branches, the VAc monomer being added to the reaction will then enter this hydrophobic region and was initiated by the precipitated macroradicals and polymer particles began to form. The constant serum content after the 15 minute mark in the polymerization also shows that the amount of emulsifier needed to form the particles initially was also a sufficient amount to stabilize the particles against coalescence during the course of the polymerization. Particle coalescence was seen when PVAC-PBuA copolymer latexes made in batch using the original Vinol 205 and Vinol 107, section 3.1.3, and the modified PVOH 205 and modified PVOH 107 in section 5.4.

When using the modified PVOH-205 and modified PVOH-107

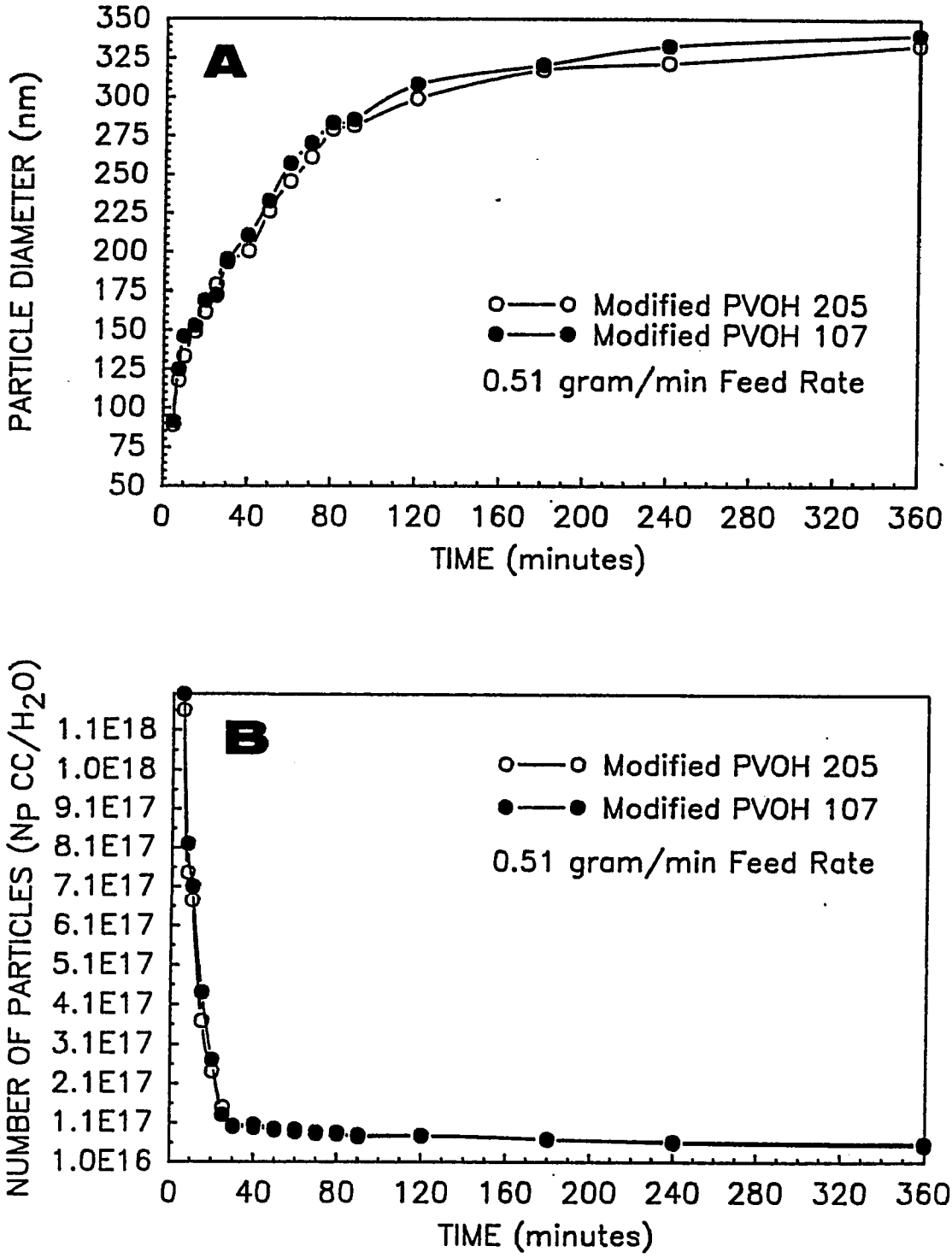


Figure 5.10: Particle Diameter (A) and Particle Number Density (B) for PVAc Latexes Prepared Semi-Continuously at a 0.51g/min Feed Rate using 10.0% Modified PVOH-205 and Modified PVOH-107.

at the 0.51 gram/minute VAc monomer flow rate, the results are very different when compared to the 0.14 gram/minute Vac feed rate. The particle diameter increased with time during the course of the polymerization, while the particle density (N_p /cc H_2O) decreased significantly in the first 40 minutes of the polymerization, as shown in Figure 5.10 and Table 5.5.6. The number of particles, in the 0.51g/min feed rate

TABLE 5.5.6

PARTICLE DIAMETER AND NUMBER DENSITY FOR PVAc LATEXES PREPARED USING MODIFIED PVOH AT A 0.51 GRAM/MINUTE MONOMER FEED RATE

Latex Prepared with Modified PVOH-205 / Modified PVOH-107			
Time (min)	% Conversion	Diameter (nm)	N_p / cc H_2O x 10^{15}
5	61.2 / 60.9	88.09 / 91.2	11.6 / 12.0
7.5	56.5 / 55.8	117.5 / 124.6	7.45 / 8.20
10	53.6 / 51.1	133.1 / 145.7	6.74 / 7.10
15	48.9 / 47.1	148.9 / 152.6	3.68 / 4.40
20	42.7 / 41.9	161.3 / 168.7	2.41 / 2.72
25	38.9 / 37.3	178.4 / 172.0	1.49 / 1.31
30	34.7 / 34.0	194.6 / 192.8	1.20 / 1.00
40	32.0 / 31.5	200.3 / 210.5	0.97 / 0.99
50	27.6 / 25.4	226.3 / 232.7	0.91 / 0.94
60	22.1 / 20.9	245.4 / 257.4	0.86 / 0.92
90	14.0 / 13.7	281.4 / 285.0	0.74 / 0.78
120	21.0 / 10.5	298.9 / 308.3	0.76 / 0.77
180	46.3 / 44.9	317.4 / 320.5	0.67 / 0.69
240	76.2 / 74.6	321.6 / 332.6	0.62 / 0.59
360	94.7 / 93.8	333.4 / 340.2	0.57 / 0.52

continued to decrease after the 40 minute mark but not as

significantly. In contrast, the number of particles for the PVAc latex prepared at the 0.14 g/min feed rate stayed relatively constant throughout the polymerization for both the modified PVOH-205 and the modified PVOH-107. The first particles detected by the Coulter N4M when using the 0.51 g/min feed rate was at 5.0 minute mark into the polymerization as compared to the PVAc latex made at the 0.14 g/min feed rate, where the first particles appeared at the 15 minute mark. This difference is due to the faster addition of the VAc allowing for particles to be generated earlier into the polymerization.

When examining the solids content of the latex serum versus time for the PVAc latexes prepared at the 0.51 g/min feed rate, the solids content decreases sharply up to approximately the 60 minute mark into the polymerization. The 60 minute mark is also the time when almost all of the VAc monomer has been added to the reaction (65.68 minutes for complete monomer addition) and the overall conversion of the reaction is near the minimum, 22.00 % monomer converted. The solids content then increases for the duration of the polymerization, Figure 5.11.

In this polymerization scheme using the 0.51 gram/min flow rate, as the vinyl acetate monomer is added the feed rate is too rapid to be converted instantaneously. The monomer then swells existing particles and also forms

monomer droplets. At 66 minute point into the polymerization the maximum amount of unreacted monomer is in the system and the amount of modified PVOH adsorbed onto the particle surface or monomer droplets is also at a maximum. As the polymerization progresses, the particles begin to coalesce as demonstrated by the increase in particle diameter and the decrease in the particle number density. As the particles coalesce the amount of protective colloid needed to

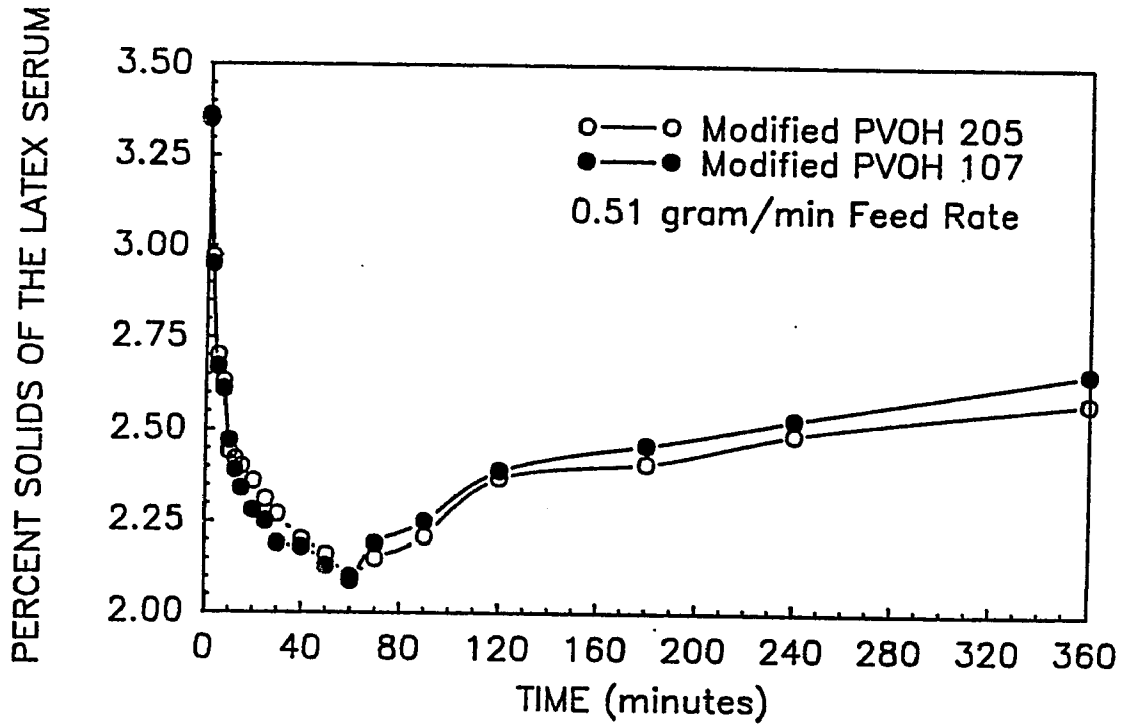


Figure 5.11: Serum solids Content as a Function of Time for PVAc Latexes Made Semi-Continuously Using 10.0% Modified PVOH at a Monomer Feed Rate of 0.51 gram/minute.

stabilize the particles is less, thus, the increase in the serum solids of the latex past the 66 minute mark of the polymerization.

5.6 SUMMARY AND CONCLUSIONS

In this chapter, the original PVOH samples, Vinol 205 and Vinol 107, where modified to an overall degree of hydrolysis of 82.0% by reacting with vinyl acetate monomer. The modified PVOH samples were then used in the batch polymerization of VAc and BuA and in the semi-continuous polymerization of VAc.

The results from the batch polymerizations indicate that the modified PVOH-205 and modified PVOH-107 performed similarly in terms of rates of polymerization and particle size data to the original Vinol 205 at the 10.0% PVOH concentration and a 0.10% initiator concentration (based on total monomer weight). The most significant difference between the latexes prepared with the modified PVOH samples and the original Vinol samples was found at the initial stages of polymerization. When the original Vinol 205 and 107 were used the VAc consumption was more rapid than the BuA in the initial stages of the polymerization, due to a grafting reaction with the aqueous phase PVOH. When the modified PVOH-205 and PVOH-107 are used the VAc is not consumed faster then the BuA, since the PVOH have already

been grafted to their water-solubility limit. The latexes prepared with the Vinol 205 were found to have a slightly faster rate of polymerization than the modified PVOH which was unexpected, but is probably caused by a higher degree of branching due to the modification of the PVOH samples.

In the semi-continuous polymerization of VAc using the modified PVOH the starved polymerization scheme showed a constant number of particles and instantaneous conversion of the VAc being feed into the reactor. The flooded polymerization scheme showed a decrease in the particle number with time and decreasing monomer conversion with time. This suggested that in the starved polymerization the particle nucleation loci was established initially, noted by the sharp drop in the solids content of the serum, followed by the VAc being fed into the reactor is being consumed in the polymer particles rather than reacting in the aqueous phase with the PVOH. In the flooded polymerization scheme, the VAc which is added cannot all be converted so it swells the forming polymer particle and/or forms monomer droplets until it is consumed. This was demonstrated by the initial decrease in the serum solids content followed by an increase until the end of the polymerization.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The following section represents a summary of the conclusions from the experimental investigation of the grafting reactions of poly(vinyl alcohol) during the emulsion copolymerization of vinyl acetate and butyl acrylate.

The experimental copolymerization kinetic data presented in chapter 3 has shown that the vinyl acetate monomer is involved in another reaction besides the copolymerization with n-butyl acrylate. The vinyl acetate has been shown to react in the aqueous phase with the poly(vinyl alcohol) emulsifier. This grafting reaction in the aqueous phase between the PVOH and VAc causes a faster initial consumption of the VAc which was not predicted by the copolymerization reactivity ratios. According to the prediction of the reactivity ratios the butyl acrylate, being the more reactive monomer, should react faster than the vinyl acetate. This was illustrated when sodium lauryl sulfate was used as an emulsifier in the copolymerization of VAc and BuA.

The effect of poly(vinyl alcohol) on the water-solubility of VAc and BuA was determined and was found to

not to alter the water-solubilities of either monomer. The high water-solubility of the vinyl acetate compared to the butyl acrylate was shown not to cause the VAc to be consumed faster than the BuA in the initial stages of polymerization. An emulsifier-free copolymerization of VAc and BuA was carried out and the consumption of each monomer reflected the difference in reactivity ratios.

In chapter 4 the aqueous phase graft copolymer of PVOH and VAc was analyzed using Fourier Transform (FT-IR). The data showed that there is a minimum degree of hydrolysis of the PVOH-PVAC graft copolymer needed to maintain water-solubility and that value was found to approximately 82.0 %. The grafting reaction of vinyl acetate with PVOH was further illustrated by the examination of the PVAc-PBuA copolymer by FT-IR. The FT-IR data showed that there was less PVAc in the copolymer particle than calculated by gas chromatography. The GC determined the monomer consumed while the FT-IR determined the composition of the copolymer.

In chapter 5, the poly(vinyl alcohol) used in the chapters 3 and 4 was modified by reacting with vinyl acetate to an overall degree of hydrolysis of 82.0%. The modified PVOH's were then used as the emulsifier in batch polymerization of VAc and BuA and semi-continuous polymerization of VAc. Results from the batch polymerization showed that when the modified PVOH's were used as the

emulsifiers the vinyl acetate was not consumed faster than the butyl acrylate in the initial stages of polymerization. Showing that the grafting reaction of the vinyl acetate with the PVOH is the cause of the faster VAc consumption. The modification reaction grafted the VAc to the water-solubility limit. When the modified PVOH were used in the batch polymerizations, only a small amount of grafting was necessary to cause the PVOH-PVAc graft copolymer to become water-insoluble. Thus less initial vinyl acetate consumption.

The particle nucleation mechanism can be illustrated as follows: The poly(vinyl alcohol)-poly(vinyl acetate graft copolymers are acting as the particle nucleation site. The potassium persulfate is initiating the poly(vinyl alcohol) chains by the abstraction of a hydrogen. The PVOH radicals then will add the vinyl acetate monomer present in the aqueous phase and create a water-soluble PVOH-PVAC graft copolymers. Particle nucleation occurs in two manners: The grafting process continues until the PVOH-PVAc graft copolymer becomes water-insoluble and precipitates from the aqueous phase. Upon precipitation the water-insoluble PVOH-PVAc graft copolymer is adsorbed by the dispersed monomer droplets. Initiation of the droplets then takes place. The second mechanism of particle nucleation is the PVOH grafts with the vinyl acetate until the chains begin to exhibit a

hydrophobic/hydrophilic balance due to the grafted water-insoluble vinyl acetate. At this point the butyl acrylate and vinyl acetate, in the form of monomer droplets, begin to diffuse from the droplets into the hydrophobic regions of the grafted PVOH-PVAc copolymer and particles are nucleated. The grafting reaction has to occur first which is the cause of the faster initial consumption of the vinyl acetate monomer. As the particles begin to form, the more reactive butyl acrylate polymerizes faster than the vinyl acetate until it is exhausted. At that point the vinyl acetate begins to react at a faster rate and polymerizes until it is completely consumed and the polymerization is complete.

6.2 RECOMMENDATIONS

(1) The effect of shear rate due to agitation should be studied. Different agitation speeds can affect the kinetics of polymerization, particle formation, size and number. Experiments should have a standard emulsion recipe and reactor design. Effects of variation of the stirring blade dimensions and design and the stirring rate on the latex properties would be studied.

(2) The temperature of polymerization could be raised and lowered to examine temperature effects on the grafting reaction in the aqueous phase between PVOH and VAc. In this dissertation the degree of hydrolysis of the PVOH-PVAc graft

copolymer for water-solubility was found to be 82.0% at 60°C. Future studies could examine whether or not the 82.0% degree of hydrolysis limit for water-solubility is valid at different temperatures.

(3) Extend the semi-continuous monomer addition experiments to the VAc-BuA comonomer system. Examine the effects of feed rate on the grafting reactions of PVOH and VAc in the aqueous phase and in the polymer particle. Also examine the copolymer composition as a function of the comonomer feed rate to determine how the PVOH will graft with the polymer particle formed.

(4) Further characterize the aqueous phase PVOH-PVAc graft copolymer by Nuclear Magnetic Resonance (NMR) using either H^1 or C^{13} or both. NMR can be used to determine the grafting sites, acetyl group "blockiness", and the branch lengths. NMR could follow the grafting reaction with time at 60°C and monitor the growth of the aqueous phase graft copolymer.

(5) The development of a mathematical model that predicts the experimental data for VAc and BuA monomer consumption. The model should take into account the aqueous phase grafting reaction between the VAc and the PVOH and its role in particle nucleation. Predictions for the aqueous phase graft copolymer and water-insoluble copolymer compositions should be provided by the model.

(6) To study the adsorption-desorption behavior of poly(vinyl alcohol) on the surface of PVAc and P(VAc-co-BuA) particles. The degree of hydrolysis, molecular weight, and the concentration of the PVOH should be varied to determine their effect on the adsorption behavior. The adsorption behavior should be examined for the final latex particles as well as throughout the course of the polymerization.

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APPENDIX A

SELECTED CONVERSION-TIME DATA

Latex NJE-SLS

50:50 (wt. ratio) VAc-BuA
0.10% (based on monomer wt.) $K_2S_2O_8$
20mM (aqueous concentration) Sodium Lauryl Sulfate (SLS)

Time (min)	Overall Conversion	X_{VAc}	X_{BuA}
0.00	0.00	0.000	0.000
5.00	12.11	0.088	0.154
10.00	18.98	0.113	0.267
15.00	43.17	0.151	0.713
20.00	52.31	0.203	0.829
25.00	56.15	0.204	0.914
30.00	58.91	0.217	0.964
40.00	60.95	0.219	0.990
50.00	61.59	0.232	0.990
60.00	62.77	0.256	
90.00	66.77	0.334	
120.00	71.31	0.422	
150.00	76.11	0.503	
240.00	83.24	0.661	
360.00	96.30	0.976	

Latex NJE-Emulsifier-Free

50:50 (wt. ratio) VAc-BuA
0.50% (based on monomer wt.) $K_2S_2O_8$

Time (min)	Overall Conversion	X_{VAc}	X_{BuA}
0.00	0.00	0.000	0.000
2.00	0.61	0.002	0.010
4.00	1.27	0.003	0.023
6.00	2.23	0.009	0.035
8.00	3.64	0.024	0.049
10.00	4.43	0.027	0.061
12.00	5.52	0.036	0.074
14.00	12.08	0.090	0.152
16.00	16.35	0.108	0.219
18.00	26.92	0.126	0.412
20.00	38.24	0.147	0.618
25.00	45.28	0.181	0.724
30.00	48.26	0.201	0.765
40.00	50.66	0.221	0.792
50.00	53.72	0.244	0.830
60.00	58.98	0.261	0.918
90.00	69.21	0.344	0.983
120.00	75.37	0.524	0.983
180.00	83.27	0.682	
240.00	90.83	0.834	
360.00	94.76	0.912	

Latex L205/10

50:50 (wt. ratio) VAc-BuA
0.10% (based on monomer wt.) $K_2S_2O_8$
10.0% (based on monomer wt.) Vinol 205

Time (min)	Overall Conversion	X_{VAc}	X_{BuA}
0.00	0.00	0.000	0.000
2.50	10.07	0.134	0.061
5.00	18.89	0.192	0.170
10.00	22.29	0.211	0.243
15.00	50.73	0.245	0.682
20.00	53.21	0.283	0.774
25.00	54.52	0.296	0.893
30.00	65.50	0.311	0.985
40.00	65.98	0.323	0.991
50.00	66.69	0.333	0.991
60.00	68.65	0.375	
70.00	69.73	0.394	
80.00	73.09	0.462	
90.00	75.52	0.516	
120.00	84.23	0.687	
150.00	91.38	0.834	
180.00	92.11	0.850	
240.00	93.60	0.878	
300.00	96.76	0.934	
360.00	98.42	0.981	

Latex L107/10

50:50 (wt. ratio) VAc-BuA
0.10% (based on monomer wt.) $K_2S_2O_8$
10.0% (based on monomer wt.) Vinol 107

Time (min)	Overall Conversion	X_{VAc}	X_{BuA}
0.00	0.00	0.000	0.000
2.50	3.21	0.080	0.011
5.00	9.44	0.127	0.024
10.00	10.43	0.132	0.080
15.00	22.48	0.156	0.270
20.00	25.61	0.164	0.321
25.00	28.93	0.175	0.422
30.00	39.65	0.183	0.613
40.00	40.88	0.188	0.705
50.00	48.54	0.198	0.771
60.00	56.20	0.222	0.833
70.00	56.67	0.230	0.914
80.00	57.66	0.247	0.967
90.00	59.83	0.263	0.985
120.00	60.36	0.271	0.985
150.00	63.54	0.342	0.985
180.00	67.01	0.351	
240.00	68.27	0.362	
300.00	69.80	0.394	
360.00	70.64	0.423	

Latex Mod205/10

50:50 (wt. ratio) VAc-BuA
0.10% (based on monomer wt.) $K_2S_2O_8$
10.0% (based on monomer wt.) Modified PVOH-205

Time (min)	Overall Conversion	X_{VAc}	X_{BuA}
0.00	0.00	0.000	0.000
2.50	9.67	0.092	0.115
5.00	13.48	0.106	0.164
7.50	18.41	0.108	0.261
10.00	22.36	0.139	0.274
15.00	45.08	0.149	0.753
20.00	53.78	0.233	0.843
25.00	58.40	0.250	0.918
30.00	63.47	0.274	0.963
45.00	62.73	0.265	0.990
60.00	65.27	0.315	0.990
90.00	68.93	0.358	0.990
120.00	80.87	0.634	
360.00	97.31	0.956	

Latex Mod107/10

50:50 (wt. ratio) VAc-BuA
0.10% (based on monomer wt.) $K_2S_2O_8$
10.0% (based on monomer wt.) Modified PVOH-107

Time (min)	Overall Conversion	X_{VAc}	X_{BuA}
0.00	0.00	0.000	0.000
2.50	8.73	0.085	0.105
5.00	12.97	0.092	0.169
7.50	17.66	0.108	0.251
10.00	18.92	0.113	0.270
15.00	43.91	0.132	0.741
20.00	52.66	0.223	0.834
25.00	57.74	0.237	0.922
30.00	60.72	0.240	0.963
45.00	62.03	0.253	0.990
60.00	64.93	0.311	0.990
90.00	67.84	0.374	
120.00	72.03	0.473	
360.00	95.78	0.926	

APPENDIX B

DETERMINATION OF THE INDIVIDUAL MONOMER CONVERSIONS BY GAS CHROMATOGRAPHY

The fractional monomer conversion of VAc (X_{VAc}) and BuA (X_{BuA}) can be calculated from the overall conversion X_T as determined by gas chromatography and gravimetric analysis by the following equations:

$$X_{VAc} = \frac{W_{VAc,0} - W_{VAc}(1 - X_T)}{W_{VAc,0}}$$

$$X_{BuA} = \frac{W_{BuA,0} - W_{BuA}(1 - X_T)}{W_{BuA,0}}$$

where:

$$W_{VAc} = \frac{1}{1 + \frac{G_{BuA}}{G_{VAc}}}$$

$$W_{BuA} = \frac{1}{1 + \frac{G_{VAc}}{G_{BuA}}}$$

$W_{VAc,0}$ and $W_{BuA,0}$ are the initial monomer weight ratios.

W_{VAc} and W_{BuA} are determined by the GC calibration curve plotting the ratio of peak areas of VAc and BuA versus the ratio of monomer weights.

X_T is the overall fractional monomer conversion (in grams) determined by gravimetric analysis.

To determine fractional monomer conversion independent of gravimetric analysis 1,4-diozane is used as an external reference. Calibration curves are generated for VAc/dioxane and BuA/dioxane. The equations of the lines defined by the data points are:

VAc/dioxane	$y = 0.2108x + 0.0023$	$(R^2 = 0.9842)$
BuA/dioxane	$y = 0.4761x + 0.0061$	$(R^2 = 0.9903)$

The monomer/dioxane peak ratios are inserted into the above equations. The value obtained from the relative equations for the weight ratio can then be used to determine the amount of monomer present and subsequently the fractional monomer conversion.

APPENDIX C

COPOLYMERIZATION REACTIVITY RATIO DETERMINATION FOR PVOH AND PVAc

Introduction

When two or more monomers enter into an emulsion polymerization, the resultant copolymer composition is determined by the relative concentration of each monomer, the copolymerization reactivity ratios and water-solubilities.

A quantitative treatment of a steady-state terpolymerization scheme was first quantified by Alfrey and Goldfinger [54]. Their treatment was quite complex since it involved 9 propagation reactions and 6 monomer reactivity ratios of the 3 monomers. Combination of the rates of disappearance of each of the 3 monomers, an assumption of steady-state concentrations for $M_1^{\bullet}$, $M_2^{\bullet}$, and $M_3^{\bullet}$ radicals, and the use of appropriate rate expressions , the terpolymer composition can be calculated by the following equations:

$$d[M_1]:d[M_2]:d[M_3] = \qquad \text{(C.1)}$$

$$[M_1]\left\{\frac{[M_1]}{r_{31}r_{21}}+\frac{[M_2]}{r_{21}r_{32}}+\frac{[M_3]}{r_{31}r_{23}}\right\}\left\{[M_1]+\frac{[M_2]}{r_{12}}+\frac{[M_3]}{r_{13}}\right\}$$

$$:[M_2]\left\{\frac{[M_1]}{r_{12}r_{31}}+\frac{[M_2]}{r_{12}r_{32}}+\frac{[M_3]}{r_{32}r_{13}}\right\}\left\{[M_2]+\frac{[M_1]}{r_{21}}+\frac{[M_3]}{r_{23}}\right\}$$

$$:[M_3]\left\{\frac{[M_1]}{r_{13}r_{21}}+\frac{[M_2]}{r_{23}r_{12}}+\frac{[M_3]}{r_{13}r_{23}}\right\}\left\{[M_3]+\frac{[M_1]}{r_{31}}+\frac{[M_2]}{r_{32}}\right\}$$

The terpolymerization composition equations are generally valid only when all of the reactivity ratios have a finite value. If one or more of the monomers cannot homopolymerize, the equations become indeterminate [56].

Skeist [55] derived equations to predict the copolymer composition from the equations of Alfrey and Goldfinger which makes it possible to determine the proportion of the original monomer which is still unreacted.

The above calculations were derived to determine the terpolymer composition at an instantaneous monomer feed. Using known monomer reactivity ratios and initial monomer concentrations.

6.2 Calculation of the Reactivity Ratios Between PVOH and VAc

To calculate the reactivity ratios between PVOH and VAc in the emulsion copolymerization of VAc and BuA using PVOH as an emulsifier several assumptions were made:

(1) There is no reaction between the PVOH and the BuA.

(2) The polymerization system is homogeneous with the PVOH, VAc, and BuA coexisting as a single phase.

(3) The PVOH is considered to be a monomer and is completely consumed in the reaction when the vinyl acetate is no longer reacting faster than the butyl acrylate.

The equation (C.1) is then simplified by removing terms that have r_{32} or r_{23}, where r_1 is VAc, r_2 is BuA, and r_3 is

PVOH. The VAc and BuA fractional conversion versus time data from the latex L107/5 (5.0% Vinol 107) at a 0.1% initiator concentration, Appendix A, are used up to the 15 minute mark. At the 15 minute mark, the initial number of moles of PVOH is assumed to be consumed in a reaction with the VAc. This is illustrated by:

Time (min)	X_{VAc}	X_{BuA}	X_{PVOH}
2.5	0.0512	0.0144	0.1667
5.0	0.1062	0.0273	0.3335
7.5	0.1144	0.0478	0.5003
10.0	0.1205	0.0642	0.6670
15.0	0.1462	0.1304	1.0000
20.0	0.1631	0.2113	

From the hypothetical PVOH consumption as outlined above, using the initial moles of monomer and the final moles of the terpolymer formed at the 15 minute mark the reactivity ratios between the PVOH and the vinyl acetate can be calculated from equation C.1. The literature values for VAc r_1 and BuA r_2 [39] are used. The values determined are $r_{31} = 15.9968$ and $r_{13} = 0.0625$ These calculated values suggest that the PVOH will preferentially add VAc monomer than to itself. These values are somewhat representative of the actual situation if they are compared with the transfer rate constants of monomer to polymer for VAc, PVAc and PVOH as determined by Okamura [23]:

VAc to PVAc $C_{p(AC)} = 1.5 \times 10^{-4}$

VAc to PVOH $C_{p(OH)} = 35 \times 10^{-4}$

The reactivity ratios would predict a higher rate of VAc adding to PVOH rather than to PVAc.

The VAc r_1 and the BuA r_2 values found in the literature were compared to the reactivity ratios calculated from experimental data of latex NJE-SLS found in Appendix A. The experimental VAc r_1 and BuA r_2 were determined using the equations derived by Behnken [57] and the reactivity ratios were estimated using the Nelder-Mead [58] simplex algorithm for minimizing a nonlinear function of several variables. The polymerization was treated as a bulk system. The results of the mathematical determination are show in Table AC.1.

TABLE AC.1

MATHEMATICAL ESTIMATION OF REACTIVITY RATIOS

Latex System	r_1 VAc	r_2 BuA	% error	# points
NJE-SLS	0.076	6.24	4.71	12
Literature [16,52]	0.04	5.50		

The reactivity ratios determined mathematically for the VAc and BuA in the latex system NJE-SLS are slighty higher than the literature values, but are still within the acceptable range of values.

In order to give a more thorough evaluation of the reactivity ratios in this system several considerations must be taken into account: The water-solubility of each monomer,

n-bar, and the monomer partitioning between the phases. Treat the system as heterogeneous rather than homogeneous.

Comparison of the Fractional Conversion versus Overall Conversion Curves

The fractional conversion of VAc and BuA versus overall conversion curves were compared for latex recipes: NJE-SLS, L205/10, L107/10, Mod205/10, Mod107/10, and NJE/Emulsifier-free.

The VAc fractional conversion curve for each latex recipe was divided into 3 regions (A,B, and C) as shown in Figure C.1. The dimensionless slopes of each VAc fractional conversion region and the BuA fractional conversion curve are calculated and compared in Table AC.2.

TABLE AC.2

COMPARISON OF SLOPES FRACTIONAL CONVERSION CURVES

Latex	Slope VAc (x 10^{-2})			Slope BuA (x 10^{-2})
	A	B	C	
NJE-SLS	0.727	0.263	2.10	1.67
NJE-Em. Free	0.766	0.272	2.17	1.54
L205/10 (10.0% Vinol 205)	1.22	0.221	2.03	1.58
L107/10 (10.0% Vinol 107)	1.73	0.159	1.28	1.74
Mod205/10 (10.% Mod-PVOH 205)	0.951	0.297	2.02	1.62
Mod107/10 (10.0% Mod-PVOH 107)	0.974	0.301	1.99	1.64

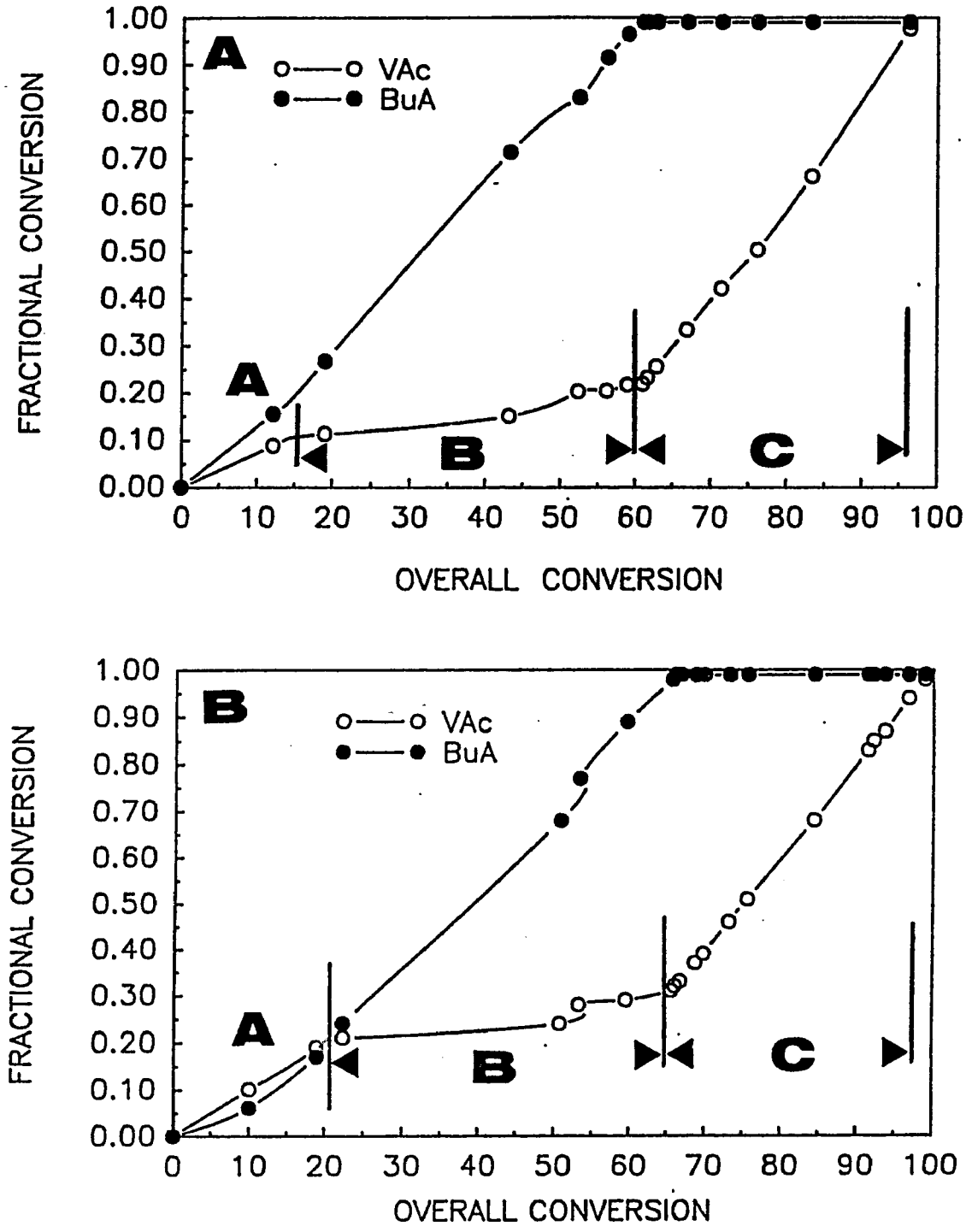

Figure C.1: VAc fractional conversion curves divided into 3 regions for:
(A) 20mM SLS, 0.1% $K_2S_2O_8$ Latex NJE-SLS
(B) 10.0% Vinol 205, 0.1% $K_2S_2O_8$ Latex L205/10

For each polymerization recipe the slopes of the BuA fractional conversion curve are similar in value. This data shows that the BuA reaction is unaffected by the type of emulsifier used in the polymerization. The data for the VAc fractional conversion curves in regions B and C are similar in numerical value. These would suggest that the vinyl acetate reaction with the PVOH has slowed down and only VAc homopolymerization is taking place. This is illustrated by examining region A, were the slopes of the latexes prepared with Vinol 205 and Vinol 107 show a faster consumption of the VAc due to the grafting reaction with the PVOH. After the initial grafting reaction is completed, VAc homopolymerization as a branch onto the PVOH graft backbone continues and is observed as VAc homopolymerization which is shown in the slope calculations. Superposition, Figure C.2, of the fractional conversion versus overall conversion curves for the latexes prepared with 20mM SLS (latex NJE-SLS) and 10.0% Vinol 205 (latex 107/10) show the similarities in the fractional conversion curves for BuA and VAc, regions B and C, and the difference in VAc region A due to the VAc-PVOH grafting reaction in the initial stages of the polymerization.

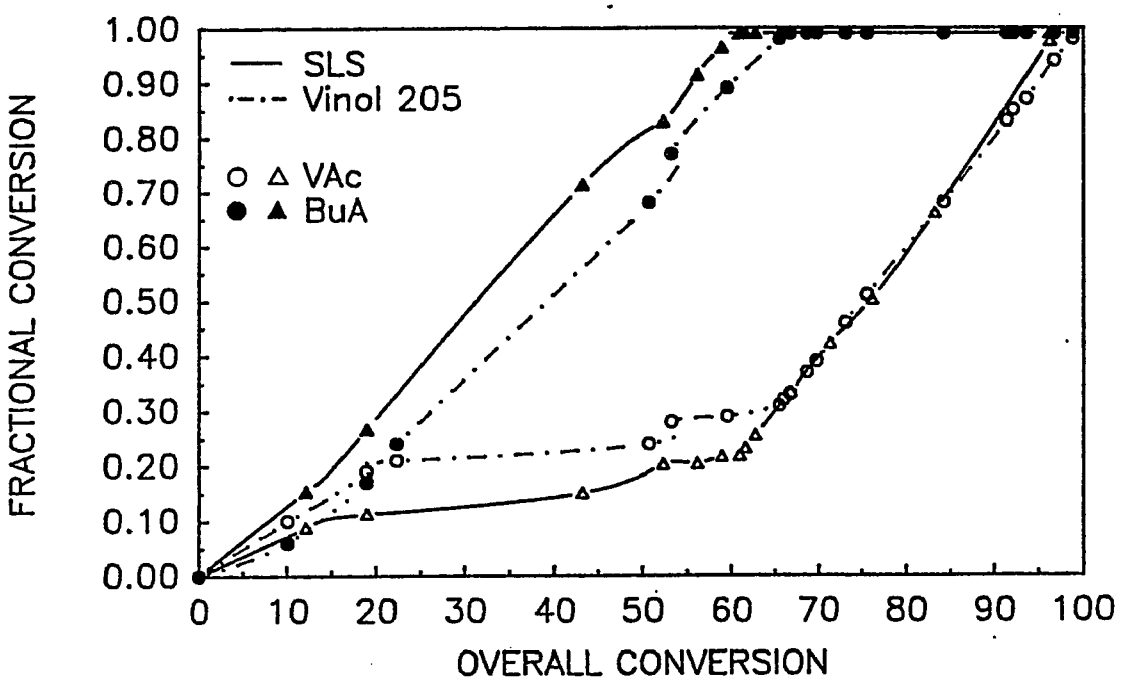

Figure C.2: Superposition of latex NJE-SLS and latex L205/10 fractional conversion versus overall conversion data

VITA

Neal Joseph Earhart was born on March 11, 1958 in Louisville, Kentucky. Forces not understood by him in his early years caused him to be moved to Allentown, Pennsylvania at the age of 6. Being the typical west-end Allentown teen-youth, he attended William Allen High School and graduated in the glorious bicentennial year of our country, 1976. He attended Allentown College of St. Francis de Sales, the Lehigh Valleys' only catholic college and thank God for that! During his stay at Allentown College, he befriended another crazy person and together they were called Torch and Bomb, Inc. He graduated from Allentown College in 1980 with a B.S. in Chemistry. The educational lifestyle had it's benefits, so he went to Lehigh University to graduate school. He was admitted into the Chemistry department and subsequently convinced to become a member of the illustrious Emulsion Polymers Institute for what he thought was going to be a brief stay. He received his Master's degree in Polymer Science and Engineering in 1983. Due to low salary offers from potential employers, he decided to stay for a PH.D. In 1985 he left graduate school and sought a career in the world of four-star french restaurants. Through times of customer stupidity and general ignorance (but good food, however), he decided that being a

maitre'd was not for him. He wanted to keep his sanity so he sought graduate school once again. He was admitted back into the EPI in 1987 and started work, once again, on his Ph.D. research. He had made many friends during his lengthy career with the EPI and he will remember some more than others for one reason or another.