Preparation of a New Polymeric Surfactant for Emulsion Polymerization

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Summary: The stability of polymeric dispersions is a property of practical importance and hence, the search for an optimized strategy to equip polymer dispersions with sufficient stability is a matter of continuous research during the last years. The kernel is to reach a sufficient stability, as it is required during polymerization, conditioning, or storage and to allow coagulation or coalescence of particles when it is needed, such as during separation of polymer from latex or during film formation. In this study, the emulsion homopolymerization system containing vinyl acetate, potassium persulfate, new polymeric surfactant, $NaHCO_3$ and water was studied in the classical glass emulsion polymerization reactor. The effects of new polymeric emulsifier on the physicochemical properties of obtained vinyl acetate latex properties were investigated depending on vinyl acetate percentage in homopolymerization.

Keywords: emulsion polymerization; lattices; stabilization; surfactants; vinyl acetate

INTRODUCTION

Surfactants are among the most versatile products used in the chemical industry, appearing in such diverse products as motor oils, pharmaceuticals and detergents. More recently, applications have been extended to such high-technology areas as electronic printing, magnetic recording, and biotechnology. [1] There are four classes of surfactants:

(a) anionic, where the head group of the molecule has a negative charge; (b) cationic, where the head group bears a positive charge; (c) zwitterionic, where both positive and negative charges are present; and (d) non-ionic, where the head group has no ionic character. Cationic surfactants, which are most relevant to the present study, usually fall into one of the following categories: long-chain amines or polyamines and their respective salts, quaternary ammonium salts (e.g. hexadecyltrimethyl ammonium bromide), oligo(ethylene oxide) amines and their quaternized derivatives, and amine oxides. Cationic surfactants are used in many applications from fabric softeners and toiletries to adhesion promoters in asphalt and corrosion inhibitors. [2]

Heterophase polymerizations, especially emulsion polymerizations, are important industrial technologies yielding synthetic elastomers, paints, paper coatings, adhesives, etc. In emulsion polymerizations, the use, or in situ production, of surfactants is necessary in order to achieve stabilization of the latex particles produced during polymerization and indeed later on in the derived products.[3]

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The stability of polymeric dispersions is a property of practical importance and hence, the search for an optimized strategy to equip polymer dispersions with sufficient stability is a matter of continuous research during the last years. The kernel is to reach a sufficient stability, as it is required during polymerization, conditioning, or storage and to allow coagulation or coalescence of particles when it is needed, such as during separation of polymer from latex or during film formation. Stability is an important topic in the field of polymer colloid research such as under the conditions of the polymerization process.[4]

In general, particle stabilization is achieved by the use of various emulsifiers which are employed in emulsion polymerization formulations. The anionic and nonionic emulsifiers are the most widely utilized because of enhanced compatibility with negatively charged latex particles (usually as a result of persulfate initiator fragments) as compared to other emulsifier's.[5–7] Recent years, particle stabilization can achieved via novel surfactants.

There has been published the numbers of studies regarding with the influence of initiator type [8] and of the chain length of emulsifier[9–11] on the emulsion homopolymerization of vinyl acetate (VAc) and copolymerization VAc-acrylic monomers (butyl acrylate, 2-ethylhexyl acrylate, methyl metacrylate, etc.) and latex properties.[5–8] Cationic surfactants are only infrequently used in VAc emulsion polymerization because they are not compatible with anionic emulsifiers or negatively charged latex particles.[7]

In the present work, a new polymeric surfactant was prepared and used in the emulsion homopolymerization of VAc in the presence of potassium persulfate as an initiator, $NaHCO_3$ and water in the classical glass emulsion polymerization reactor. The effects of new polymeric emulsifier on the physico-chemical properties of obtained VAc latex properties were investigated depending on vinyl acetate percentage in homopolymerization.

EXPERIMENTAL

Materials

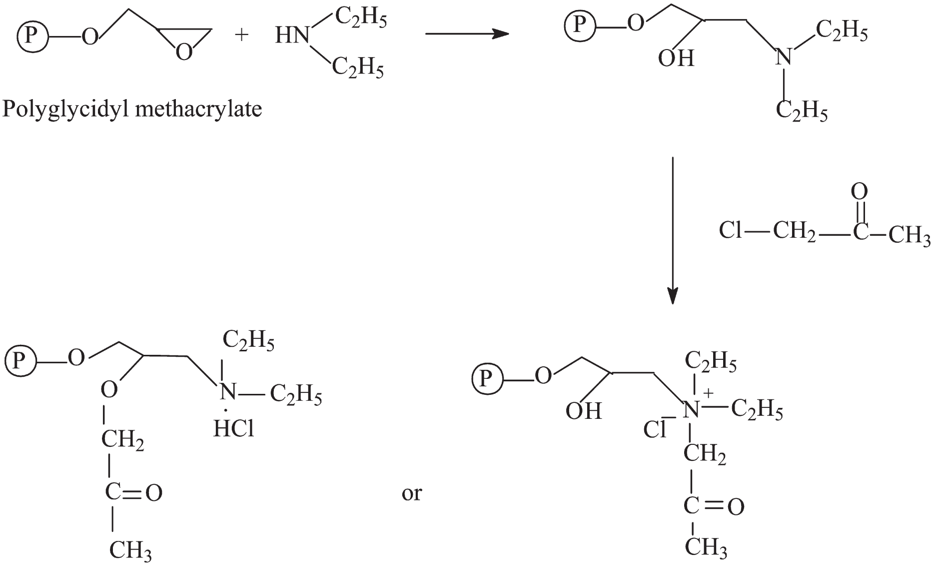
Argon Chemistry Inc. (Turkey) VAc monomer was used as commercial product. The stability of the latexes was achieved by polymeric surfactant consisting of poly(glycidiyl methacrylate) (polyGMA) which its chemical structure was given in Scheme 1. This substance was acted like a protective colloid because of given viscose solution even very low concentration, potassium persulfate (PPS) (Merck) was used as thermal initiator, Nopco 1497-V (nonsilicone antifoam agent based on octyl alcohol and tributyl phosphate) was used as an antifoam agent, and sodium bicarbonate (Merck) was used for adjusting the pH value of the polymerization media. All substances were used as received. Deionized water was used in all studies.

Modification of PolyGMA with Diethylamine

PolyGMA ($\overline{M}_n = 43000$) (8 g) was dissolved in 2-methyl-1-pyrrolidone 30 mL and then this solution was put in 25 ml of diethylamine in a 100 ml of flask. The mixture was stirred for 24 h at room temperature. While stirring, it was heated at 80 °C in a termostated oil bath for 3 h. After chilling the mixture was poured into 250 ml of distilled water and washed with the excess of water (1 L), 25 ml alcohol and dried overnight under vacuum for 24 h. The yield was found 9.3 g.

Quaternization of Amine Modified PolyGMA with Chloroacetone

5 g of the amin e modified polyGMA was dissolved in 2-methyl-1-pyrrolidone 20 mL and 3.3 g (35.7 mmol) chloroacetone was placed in this solution. The mixture was stirred for 3 days at room temperature. After reaction, the mixture was poured into diethyl ether. The precipitated polymer was filtered and washed with ether. The product was dried under vacuum at room temperature for 24 h.



Scheme 1.
The structure of the new polymeric surfactant.

Determination of the Chlorine Contents

The chlorine content of the quaternary polymer was determined as follows:

0.2 g of the polymer was mixed with 3 g powdered $NaOH\text{-}Na_2CO_3$ (1:1) mixture in a porcelain pot. The mixture was heated and fused by a naked flame of a Bunsen burner. After cooling to the room temperature, the mixture was digested in distilled water and filtered. The filtrate and washings were combined and neutralized with 2 M HNO_3 solution. The solution was diluted accordingly. Chloride content of the polymer was calculated by using mercuric thiocyanate method as described in the literature [12] and was found as 3.20 mmol per polymer.

Determination of the Critic Micel Concentration (CMC)

For this purpose, 0.1142 g polymer sample was dissolved in 100 mL water. This solution was placed in thermostat bath at 25 °C. After adding 1 mL of water in each time to polymer solution, conductances of this solution were measured by using conductometry. CMC of the polymer was found from Figure 1 and was calculated as 5.71×10^{-2} g/mL.

Emulsion Polymerization Procedure of VAc

Semicontinuous emulsion polymerizations were carried out in a 1 L five neck glass reactor equipped with a condenser, a thermometer, two dropping funnels, and a mechanical stirrer having a constant speed of 200 rpm and a reflux condenser in a total batch period of 3 h. Only 10% of the total monomer was introduced at the beginning of the reaction at 60 °C and the remaining monomer was added dropwise at 71 ± 2 °C from dropping funnels during the remaining time. Initiator was dissolved in a small amount of water and these freshly prepared initiator portions were added at 30 minute intervals throughout the reaction.

Measurements

New synthesized polymeric surfactant was characterized by FT-IR and critic micel concentration. Latexes were characterized by measuring Brookfield viscosity, average molecular weights ($\overline{M}_n, \overline{M}_w$), and surface tension of VAc latexes to air. Conversion was monitored gravimetrically. The viscosities of the homopolymer latexes were determined by Brookfield Programmable DV-II model viscometer with spindle

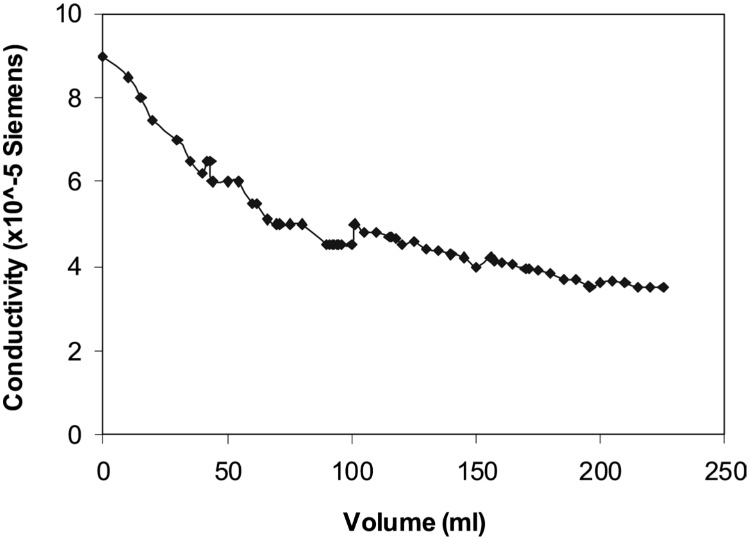


Figure 1.
Determination of critic micel concentration by conductometry.

number 4 at 23 °C. Number average molecular weights ($\overline{M}_n$) and weight average molecular weights ($\overline{M}_w$) of polymers were determined by the GPC Agilent model 1100 type instrument with a refractive index detector and calibrated with polystyrene standarts consist of three Waters styragel colums (HR 4, HR 3, and HR 2). THF was diluent solvent at a flow rate of 0.3 mL/min at 30 °C. The surface tension measurements were done with ring-detachment method by torsion tensiometer and a platinium ring at 23 °C.

RESULTS and DISCUSSION

Glycidyl methacrylate (GMA) based cross-linked polymers have advantages over other polymer supports due to ease of functionalization through the epoxide groups involved. Reaction with excess diethyl amine gives a tertiary amine containing functions. Reaction of amine function polymer in N-methyl pyrrolidone with excess of 2-Chloro acetone gives a product with a quaternized amine functions with 3.2 mmol.g^{-1} chloride content. (Scheme 1). This corresponds to about 98% quaternization. However, quaternization of ethanol amines have been reported to rearrange to diethyl amino ether moieties spontaneously.[13]

In the FT-IR spectra of the amine modified polymeric surfactant, the stretching band of the C-O group in the epoxy ring is disappeared, and the stretching band of the aliphatic hydroxyl group is appeared 3431 cm^{-1}. This situation confirms that tertiary amine modified group, and is formed. In the FT-IR spectra of the quaternized amine modified polymeric surfactant, the stretching vibration band of the aliphatic C-O group in the starting compound disappeared at the end of the reaction. This can be ascribed to ether formation during quaternization.

The emulsifier was used in a constant weight ratio (0.75%) in the polymerization recipe and VAc percentage was varied. Thus, by increasing the monomer ratio, the molar concentration of the emulsifier was decreased. A regular latex viscosity decrease is seen with an increase of VAc percentage in the polymerization for the lattices having a constant emulsifier weight

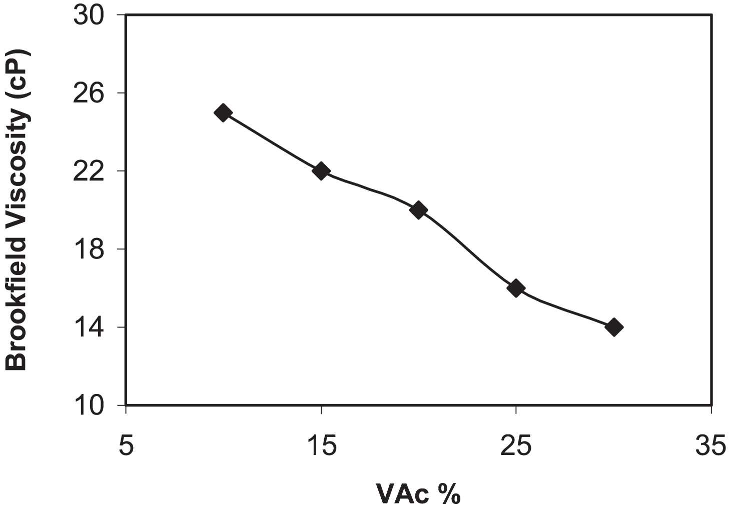


Figure 2.
Brookfield viscosity versus VAc % in the polymerization.

percent in Figure 2. It is expected that the number of initial polymer particles should decrease, thus increasing the size of the particles at the end of the polymerization.

Latexes usually show Newtonian fluid behavior at very low concentrations, and surface layers can significantly increase the effective volume of latex particles. Such layers may be due to the adsorbed surfactants; adsorbed or reacted polymeric stabilizers and surface charges on the polymer particle. The smaller the particle size is, the greater will be the contribution of a surface layer of given thickness to the effective volume of the particle. The greater viscosity is the greater will be the contribution of a surface layer of given thickness to the effective volume of the particle. That effect can be explained by the fact that the viscosity depends on an effective particle volume.[6]

Napper and Alexander examined the effect of different types of emulsifiers in the emulsion polymerization of VAc. [14] The concentration of all the emulsifiers (anionic, nonionic, and cationic) was kept so low that they did not allow the formation of micelles in the aqueous phase. Nonionic emulsifiers were found to have little effect on the polymerization reaction. Anionic emulsifiers accelerated the reaction, the effect increasing with the length of the hydrophobic part of the emulsifier, whereas cationic emulsifiers retarded the reaction and there was no effect of the chain length of the emulsifier on this retardation behavior. Additionally, anionic emulsifiers increased the number of particles, whereas cationic emulsifiers caused a decrease and gave a very broad distribution of sizes. [14] Cationic emulsifier cause to increase particle size, thus decreasing viscosity. Our viscosity results are agreed well with Napper et al[14] data. In general, initiator is also affected the stabilization of latex particles, if there is no emulsifier in the polymerization media, the sulfate end groups introduced by the persulfate initiator are often sufficient to stabilize latex particles at relatively low monomer-water ratios to produce a monodisperse latex. If emulsifier is present, the lower its concentration, the higher the tendency to obtain monodisperse latex. [7]

The number average molecular weights ($\overline{M}_n$) and the weight average molecular weights ($\overline{M}_w$) of polyVAc were determined by GPC. In Figure 3 and Figure 4 it was seen that $\overline{M}_n$ s and $\overline{M}_w$s of latexes changed regularly with the increasing VAc percent

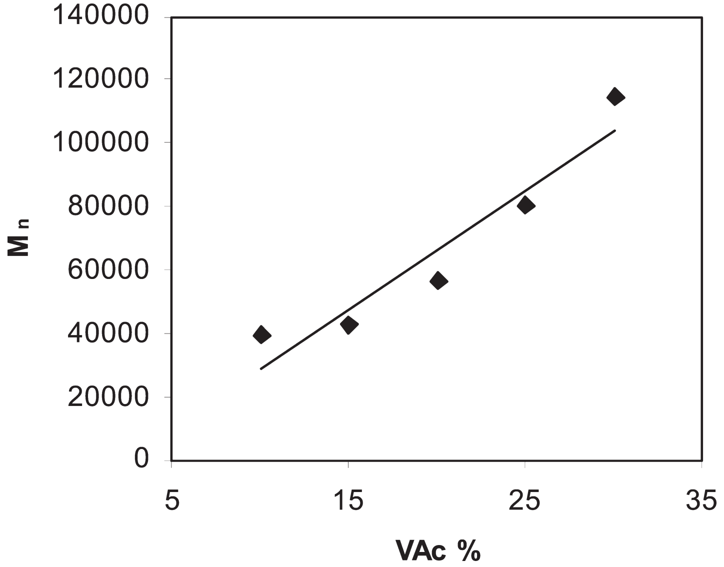


Figure 3.
Number average molecular weight of latexes versus VAc % in the polymerization.

of the polymer composition. $\overline{M}_n$ and $\overline{M}_w$ results give some information about reaction kinetics, so it can be understand that copolymerization is taken under control and keep going low rate. Due to high amounts of emulsifier in the polymerization low $\overline{M}_n$ but high $\overline{M}_w$ of latexes were found. Those were expected results for new oligomeric surfactant, because of that reason and they have agreed well for familiar with stabilizator by literature.[15]

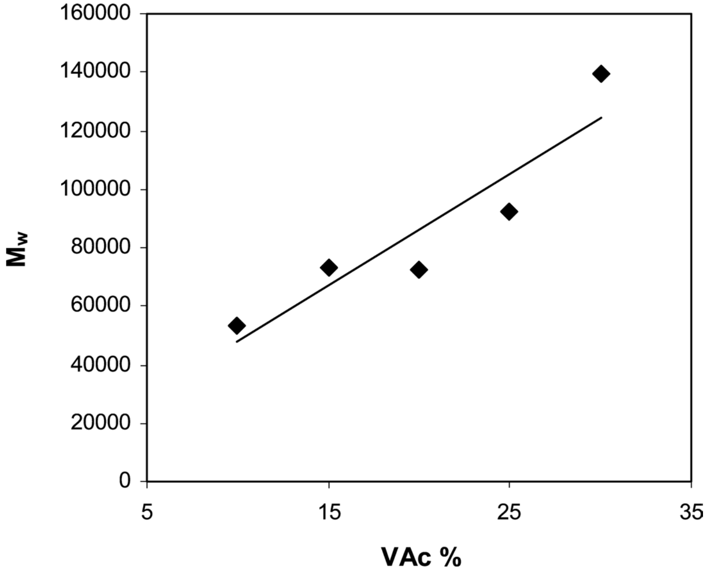


Figure 4.
Weight average molecular weight of latexes versus VAc % in the polymerization.

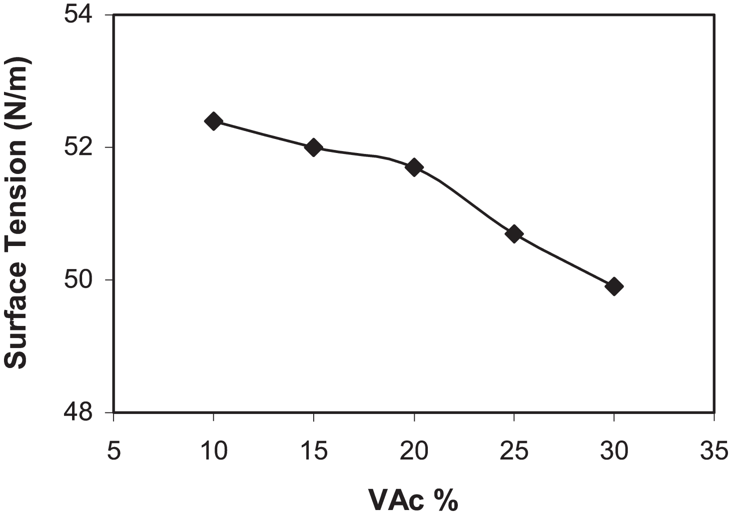


Figure 5.
Surface tension versus VAc % in the polymerization.

The method of monomer addition into the emulsion polymerization medium determine the homogeneity of the copolymer, molecular, surface and colloidal properties of copolymers, which have different reactivity ratio and mainly different water solubility, and those characteristics of monomers also affect physical and mechanical properties of polymers. Semi-batch or semi-continuous process is mainly used in synthesizing of VAc polymers. Latex heterogeneity obtaining from batch process is much bigger than semicontinuous process and also increases the increasing of VAc % in the polymer composition.[5] The obtaining low value is the indication of the presence of a large quantity of low molecular weight oligomers, which are initiated in the aqueous phase. The high molecular weight fraction is caused by long-chain branching.

The surface tensions of polymer changed regularly with the increasing VAc percentage in the polymerization. Surface tension depends on free emulsifier amounts in the latex, and the raising of this amount leads to the tendency of surface tension to decrease. But emulsifier adsorption onto polymer particles cause to decrease free emulsifier concentration in latex, the increasing adsorption cause to increase surface tension of latexes. The increasing hydrophobic character into polymer causes to increasing emulsifier adsorption onto polymer particles. Thus the increasing of free emulsifier concentration in latex by blocking of emulsifier adsorption and the decreasing of polarity differences between interfaces cause to decrease the surface tension, especially for VAc latexes. It was determined that increase of the monomer percentage in the homopolymerization of VAc initiated by a persulfate does not affect the surface tension of the final latex very seriously, but small changes were seen in Figure 5.

CONCLUSION

In this work, poly(VAc) homopolymer lattices were prepared in the presence of an potassium persulfate initiator, new polymeric surfactant by applying semicontinuous emulsion polymerizations. It was determined that when the weight ratio of the emulsifier in the recipe was kept constant the resultant latex viscosity decreases. Increase of the VAc does not affect the surface tension of the latex very seriously.

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