Preparation of Poly(vinyl acetate) Latex with Ultrasonic and Redox Initiation

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ABSTRACT: The high water solubility of vinyl acetate (VAc) monomer increases the need for a good initiator system to speed up the polymerization and remove unreacted monomers. Ultrasonic energy can be used to initiate VAc redox emulsion polymerization in the absence of an inert gas and with sodium dodecyl sulfate as a surfactant. Combining ultrasonic energy and a redox initiator at the ambient temperature leads to a higher conversion and higher rate of polymer production in comparison with just using a redox initiator. Ultrasonic energy plays an important role in synthesizing and controlling the polymer structure. The particle size distribution is an important variable in the formulation of latex paint. Ultrasonic energy has an effect on the particle size distribution and average molecular weight of VAc poly-mer. The particle size increases with an increase in the monomer conversion for ultrasonic polymerization, whereas the particle size stays constant with the monomer conversion for redox polymerization. An ultrasonic polymer has a broader particle size distribution than a redox polymer. The average molecular weight of poly(vinyl acetate) falls with an increase in the sonication time, whereas it increases with time for a redox polymer. Ultrasonic energy also produces a stable, milky white, opaque latex. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 812–817, 2005

Key words: emulsion polymerization; particle size distribution; redox polymers

INTRODUCTION

Poly(vinyl acetate) (PVAc) is a well-known polymer used as a resin for water-borne paint. PVAc emulsion films adhere well to most surfaces, such as wood, paper, glass, and metal, and have a good binding capacity for pigments and fillers.[1] Vinyl acetate (VAc) latices find their main application in interior paints that are not exposed to high humidity conditions.[1] The particle size distribution is an important variable in latex paint formulation. Most of the problems with paint dispersions, such as low gloss, low film buildup, and low pigment loading, come from the paint stability, particle size, and film-formation process of polymer dispersions. A broad particle size distribution is often advantageous because the packing factor is strongly affected by the particle size distribution. VAc monomer has been selected because the high water solubility of VAc monomer increases the need for a good initiator system to speed up the polymerization and to remove unreacted monomers.

VAc can be polymerized by different initiators. The water-soluble ionic initiators[2] usually used for the emulsion polymerization of VAc are sodium, ammonium, and potassium persulfate. Water-soluble non-ionic initiators,[2] such as tertiary butyl hydroperoxide, and organosoluble nonionic initiators,[2] such as 2,2'-azobisisobutyronitrile (AIBN) and benzoyl peroxide, have also been used.

The aforementioned initiators require heat to produce free radicals to initiate the VAc monomers. The redox initiators[2] are commonly used to conduct VAc polymerizations at low temperatures. Tertiary butyl hydroperoxide/sodium formaldehyde sulfoxylate and potassium persulfate/sodium bisulfite/iron(II) redox systems are commonly used to initiate VAc emulsion polymerizations at the ambient temperature. In this study, PVAc latex particles were prepared with redox and ultrasonic batch emulsion polymerization processes.

EXPERIMENTAL

Apparatus

A Sonics and Materials model VC-1500 20-kHz ultrasonic generator (Newton, CT) with a standard titanium horn for use with a capacity as high as 15 L of liquid was connected to an air-cooled transducer. The oscillator power ranged on a scale of 0–100%, and the

acoustic energy corresponding to the oscillator power was measured[3] calorimetrically by the sonication of a known amount of water in a Dewar flask, the recording of the temperature change versus the time, and the calculation of the total energy released. In this work, the acoustic energy was set at 50 W (corresponding to 10 W/cm^2).

Reagents and materials

VAc from Aldrich (Gillingham, UK) was purified with three washes with 10% sodium bicarbonate, followed by three washes with distilled water to remove the hydroquinone inhibitor and drying with anhydrous sodium sulfate, and the material was then refrigerated at 10°C until use. Sodium dodecyl sulfate (SDS) from Aldrich was used as a surfactant. A mixture of ferrous sulfate heptahydrate, sodium persulfate, and sodium metabisulfite from Aldrich was used as a redox initiator without further purification. Methanol from Aldrich was used to precipitate the polymer.

Polymerization procedure

Different polymerization conditions were studied with ultrasonic and redox initiation. The emulsion polymerizations were performed in a 500-mL, three-necked, round-bottom flask for the redox polymerization and in a 400-mL plastic beaker for the ultrasonic polymerization. The ingredients for the polymerization were 60 g of the total monomer, 0.5 g of the surfactant, and 90 g of water. A mixture of the initiators (0.1 g of ferrous sulfate heptahydrate, 0.2 g of sodium persulfate, and 0.2 g of sodium metabisulfite) was added at the beginning of the polymerization to the rest of the ingredients. Mechanical stirring was used for redox polymerization at 500 rpm, and there was no additional mechanical stirring for ultrasonic polymerizations. The tip of the horn was placed in the emulsion 1.0 cm from the bottom of the beaker. The output of ultrasonic energy was fixed at 50% (corresponding to an acoustic intensity[3] of 10 W/cm^2) for all experiments. The top of the beaker was covered with aluminum foil around the horn. The final conversion percentage was obtained by gravimetric analysis.

Particle size measurement

The average diameter of the polymer particles was measured with a Mastersizer 2000 model analyzer (Malvern Instruments Ltd., Malvern, UK) with the Hydro 2000S accessory.

Molecular weight analysis

The average molecular weights were measured by gel permeation chromatography (Cirrus software, version
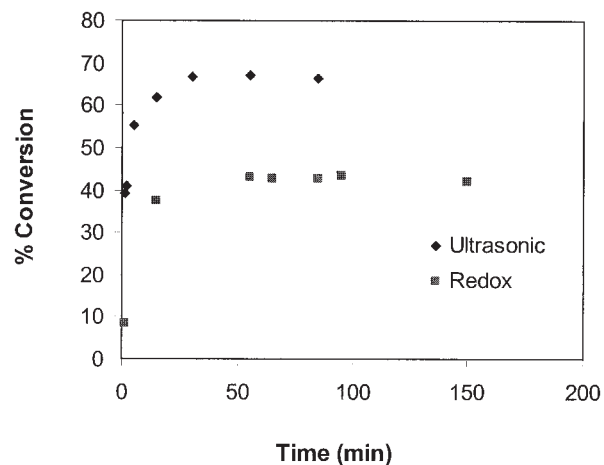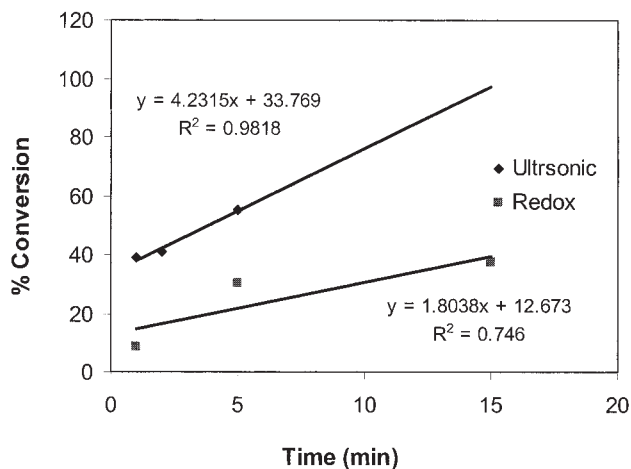

Figure 1 Conversion percentage of the VAc monomer at the ambient initial temperature (60 g of VAc, 90 g of H$_2$O, 0.5 g of SDS, 0.1 g of ferrous sulfate heptahydrate, 0.2 g of sodium persulfate, 0.2 g of sodium metabisulfate, and ultrasonic final temperature of 50°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

2.0, Polymer Labs, Amhyrst, MA) with mixed bed B columns from Polymer Labs (300 × 7.8 mm i.d., 10-um particle size). The flow rate was 0.9 mL/min; tetrahydrofuran was used as the eluting solvent at room temperature. Four calibration broad-molecular-weight polystyrene standards were used. A Hamielec calibration (linear) model supplied by Polymer Labs (Amhyrst, MA) was used for the evaluation.

RESULTS AND DISCUSSION

Thermal initiators require heat to produce free radicals to initiate polymerization. The redox initiators offer a further degree of freedom, in that they allow free-radical polymerization without the use of a significant quantity of heat. The high water solubility of the VAc monomer (2.0 g/100 g at 20°C) requires a good initiator system to speed up the polymerization at a low temperature and to remove unreacted monomer. Also, the hydrolysis of acetate groups in PVAc to alcohol groups at high temperatures increases the need for an effective method to carry out the polymerization at low temperatures. A sodium persulfate/sodium bisulfite/iron (II) redox system allows polymerization to proceed at the ambient temperature, and it was used in this work. Ultrasonic energy, combined with a redox initiator, was used to initiate the emulsion polymerization of VAc monomers at a low temperature (the ambient temperature). The polymerization was faster and gave a higher conversion (65%) than that with the redox initiator (40%), as shown in Figures 1 and 2. This method is a promising way for the synthesis of VAc and acrylate polymers at low

y = 4.2315x + 33.769
R² = 0.9818

y = 1.8038x + 12.673
R² = 0.746

Figure 2 Rate of polymer production at the ambient initial temperature (60 g of VAc, 90 g of H₂O, 0.5 g of SDS, 0.1 g of ferrous sulfate heptahydrate, 0.2 g of sodium persulfate, 0.2 g of sodium metabisulfate, and ultrasonic final temperature of 50°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperatures and saves energy. In previous work,[3–5] an inert gas was an important factor to allow ultrasonic polymerization to proceed. An inert gas functions as nucleus sites (weak spots) present in the liquid for bubble collapse to occur for larger sonochemical effects. It has been reported[6] that the initiation of styrene polymerization occurs primarily only when there is sufficient gas present to form a field of bubbles undergoing stable cavitation. In the absence of the gas, transient cavitation occurs, resulting in depolymerization and the formation of colored compounds similar to a pyrolysis product. However, in this work, no inert gas was used to allow ultrasonic polymerization to proceed because a redox initiator starts the polymerization at room temperature and the function of ultrasonic energy probably is to speed up the polymerization rate and the conversion. Ultrasonic polymerization will not occur at room temperature if a redox initiator is not used.

The combination of ultrasonic energy and an initiator can give a low residual monomer,[5] which is of prime concern for many latex producers. The high solubility of VAc in water may lead to difficulties in copolymerization with more hydrophobic monomers because the relative concentrations of the copolymerizing monomers in the polymer and water phases are different. Also, the type of the initiator will affect the latex properties. The homopolymerization of VAc and copolymerization with *n*-butyl acrylate (BA) were studied[7] with a new redox initiator, potassium persulfate and acetone sodium bisulfite. A good conversion was reported at 50°C, although the reaction rates decreased with an increase in the BA content. The effects of other bisulfite adducts on the polymerization of

VAc with potassium persulfate through the addition of sodium bisulfite to the carbonyl functionality on benzaldehyde, acetaldehyde, octyl aldehyde, methyl propyl ketone, and acetone were studied.[8] The rate of polymerization in the presence of these bisulfite adducts was a function of the initiator concentration, to the 0.54, 0.66, 0.95, 1.0, and 1.1 powers, respectively, for the surfactant-free emulsion polymerization at 40°C.

The rate of polymer production was determined from the slope of the first linear part of the curve of the conversion percentage versus the time (min), as shown in Figure 2, which occurs between 5 and 70% conversion for ultrasonic polymerization. This period may represent interval II in the curve of the emulsion polymerization rate versus time.[9] Combining ultrasonic energy and a redox initiator at 25°C always leads to a faster rate of polymer production (almost 2–3 times) in comparison with just using a redox initiator, as shown in Figure 2.

Effect of ultrasonic energy on the particle size distribution

There are three types of emulsion polymerizations: conventional emulsion system, miniemulsion system, and microemulsion system. The differences between them lie in the monomer droplet size and droplet size distribution before polymerization. A conventional emulsion has a monomer droplet size of 0.3–10 μm, and the polymerization mainly occurs in monomer-swollen micelles. A miniemulsion has a monomer droplet size (0.05–0.2 μm) and is less polydisperse in size, whereas a microemulsion has a monomer droplet size less than 20 nm and is homogeneously dispersed in the emulsion system.[10] For miniemulsion and microemulsion systems, the polymerization occurs inside the monomer droplets, although it is believed that a small fraction of these monomer droplets are initiated. This will lead eventually to a larger final particle size than the initial monomer droplet and a high polymerization rate.[10]

A batch process was used in this work to study the particle size and its distribution. This process involves an initial charge of deionized water, monomers, surfactants, and initiator mixtures into the reaction container, and then the reaction is continued at the ambient temperature. This is important because with batch processes, a monoparticle size distribution or narrower molar mass distribution is expected.[11] However, under dispersion by ultrasonic energy, broader particle size distributions occur.

The ultrasonic polymerization of VAc at 25°C shows a broader size distribution, and the particle size gets larger with an increase in the monomer conversion. It increases from 227 nm at 1 min to 452 nm at 30 min, as shown in Table I and Figure 3. This happens even in

TABLE I
Average Particle Sizes of the Redox and Ultrasonic Polymers

Time (min)	Redox polymer $d_{0.5}$ (μm)	Ultrasonic polymer $d_{0.5}$ (μm)
1	0.110	0.227
5	0.104	0.259
10	0.118	0.310
20	0.119	0.354
30	0.119	0.452

Figure 4 Particle size distribution of redox PVAc latex. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the absence of a cosurfactant as in the miniemulsion case. This increase gives additional confirmation of a high rate of particle formation. Biggs and Grieser[10] found that the ultrasonic polymerization of polystyrene with SDS as a surfactant showed a general shift toward a larger particle size with increased monomer conversion. Also, they found that the monomer-swollen micelles were the main locus of polymerization, and this was consistent with conventional emulsion polymerization. In this work, the polymerization may have occurred not only inside the micelle but also inside the monomer droplet and aqueous phase. Under the ultrasonic dispersion, the size of the monomer droplets became smaller, and they competed in number and surface area with the micelle, which then gave ab additional place for the emulsion polymerization to occur. This may give an explanation for particle size broadening. El-Aasser et al.[12] reported a broad particle size distribution and dual nucleation in droplets and micelles for the miniemulsion polymerization of BA and VAc with sodium hexadecyl sulfate as a surfactant, hexadecane as a cosurfactant, and ammonium persulfate as an initiator. Biggs and Grieser[10] suggested that the small latex diameter in the final sam-

ples meant little particle coagulation during the polymerization process, which would lead to a larger final particle size. The lack of coagulation may be explained by the formation of a surface charge on the primary particles, which confers on them electrostatic stabilization. The driving force for particle size coagulation is their instability in comparison with larger particles. Once the particles reach a large size with high colloidal stability, there is no longer a driving force for coagulation, and further growth occurs only by polymerization.[9] A broad particle size distribution for styrene miniemulsion polymerization was reported[13] at 125°C with cetyl alcohol as a cosurfactant and sodium laryl sulfate as a surfactant. The main reason for this broadening was particle coagulation.

The redox polymerization of VAc, for example, shows a monomodal distribution with an almost constant particle size of $d_{0.5}$ = 119 nm, as shown in Table I and Figure 4. This suggests that the polymerization takes place almost only in the micelle, with a constant diffusion from the monomer droplet[9] to the monomer-swollen micelle. A monomodal particle size distribution of a conventional emulsion polymerization of methyl methacrylate (MMA) and BA at 70°C (55 nm) and a bimodal particle size distribution of an ultrasonic emulsion polymerization of MMA and BA at 25°C (56 and 211 nm) with SDS as a surfactant and ammonium persulfate as an initiator have been reported.[14]
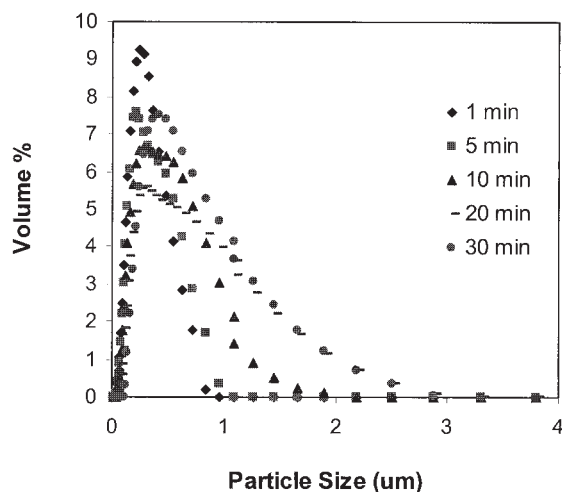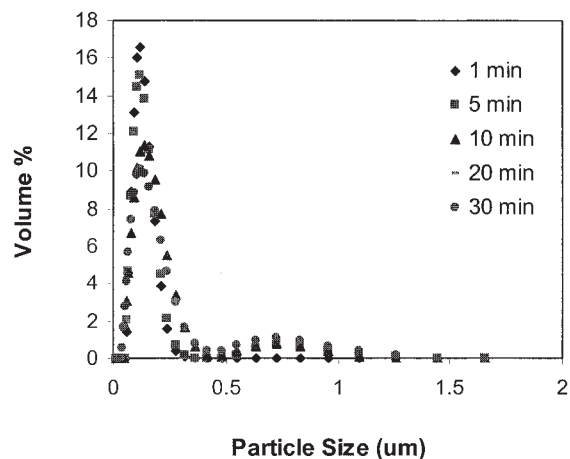

Figure 3 Particle size distribution of ultrasonic PVAc latex. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Source of free radicals in ultrasonic polymerization versus redox polymerization and its effect on the molecular weight distribution

The use of ultrasonic energy in initiating an emulsion polymerization will produce a high concentration of free radicals as a result of a high local temperature and pressure produced when the bubble

TABLE II
Average Molecular Weights of the Redox and Ultrasonic Polymers

Tim (min)	Redox Polymer			Ultrasonic Polymer		
	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
1	58,750	184,500	3.14	88,000	365,000	4.14
5	86,000	341,000	3.96	112,000	607,000	5.52
20	83,500	351,000	4.20	93,600	342,000	3.65
30	83,650	386,000	4.61	76,100	284,000	3.73

The results are averages of two measurements. M_w = weight-average molecular weight.

collapses. The source of free radicals[3,9,15] not only comes from the initiator but also may come from the aqueous phase, the monomers, and the surfactant. Similar rates[16] of initiation were found for ultrasonic energy alone at 25°C and the thermally initiated polymerization of MMA with AIBN as an initiator. Price[16] also found that the sonochemical rates were three orders of magnitude higher than the corresponding values for the thermal polymerization of initiator AIBN in MMA. Moreover, the rate of polymerization was proportional to the monomer concentration and depended on the square root of the ultrasonic intensity, and the final molecular weight varied inversely with the monomer concentration and the square root of the ultrasonic intensity $(I_{us})^{-0.5}$.[16] In this work, the average molecular weight of the polymer produced by ultrasonic energy at 25°C was found to be different than the one produced by the conventional redox process. The ultrasonic polymerization of VAc at 25°C with a redox initiator showed a high number-average molecular weight (M_n) at an early time, and then it decreased with an increase in the time of polymerization. M_n was 88,000 with a molecular weight

distribution of 4.1 at 1 min of the polymerization reaction, and it fell to 76,100 with a molecular weight distribution of 3.7 at 30 min of the polymerization reaction, as shown in Table II and Figure 5. This may be due to the high concentration of free radicals produced by ultrasonic energy as the polymerization time proceeded. On the other hand, M_n of the pure redox polymerization of VAc at 25°C was 58,750 with a molecular weight distribution of 3.1 at 1 min of the polymerization reaction, and M_n was 83,650 with a molecular weight distribution of 4.6 at 30 min of the polymerization reaction, as shown in Table II and Figure 5. It has been shown[16] that a high-molecular-weight polymer is formed during the early stages of acrylate monomer polymerization but falls at longer times under ultrasonic irradiation. This is not the case with the thermally initiated radical polymerization, and the reason for this is that the degradation process occurs in parallel with the polymerization once long chains are formed. Also, it was found[17] that the initial molecular mass of poly(methyl methacrylate) in benzene was reduced from 430,000 to 83,000 after 200 min of ultrasonic irradiation.

CONCLUSIONS

Ultrasonic energy can be used to initiate VAc redox emulsion polymerization in the absence of an inert gas. Combining ultrasonic energy and a redox initiator provides a good initiation system to produce a high polymer conversion and a high rate of polymer production in comparison with just using a redox initiator. Ultrasonic energy is a good tool for controlling the particle size and molecular weight of VAc polymer. Ultrasonic energy also produces a stable, milky white, opaque emulsion.

Figure 5 M_n distribution of ultrasonic and redox VAc polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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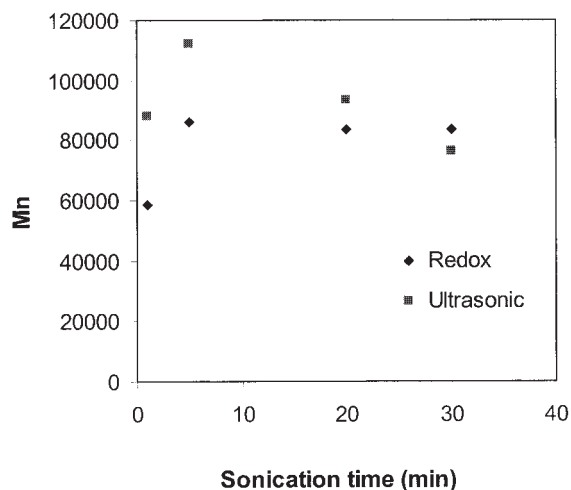
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