Postpolymerization of Vinyl Acetate-Containing Latexes

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ABSTRACT: The postpolymerization of vinyl acetate (VAc)-containing latexes with *tert*-butyl hydroperoxide (TBH)/ascorbic acid (AsA) as a redox initiation system was investigated. Volatile organic compounds (VOCs) such as acetone and *tert*-butyl alcohol were produced in this process. The influence of the TBH/AsA ratio, initiator concentration, reaction temperature, and feeding time on the reduction of residual VAc and VOC formation during the postpolymerization was investigated. A total reduction of residual VAc monomer was achieved, with the formation of VOCs kept within acceptable limits. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 923–928, 2002

Key words: residual vinyl acetate monomer; postpolymerization; redox initiators; *tert*-butyl hydroperoxide; ascorbic acid; emulsion polymerization

INTRODUCTION

Emulsion polymerization is the chief process used to produce a wide range of products, such as paints, adhesives, binders for nonwoven fabrics, synthetic rubbers, additives in paper and textiles, leather-treatment materials, impact modifiers for plastic matrices, and additives for construction materials.[1] In emulsion polymerization, the conversion of monomers at the end of the process is usually higher than 90% and often more than 99% (the amount of unreacted monomer typically being in the range of parts per million). Because of environmental regulations, it is generally necessary to remove unreacted monomers and other volatile organic compounds (VOCs) from latex. Market preferences also play an important role in

monomer and VOC removal because monomers and VOCs often have strong (and offensive) odors that may severely limit the range of applications of the latex. Both postpolymerization[2–5] and devolatilization[6–10] are used to reduce free monomer content. Postpolymerization is preferred because it is carried out either in the polymerization reactor or in the storage tank, and no additional equipment is needed. Postpolymerization mostly employs redox initiation systems that are based on the ability of adequate reducing agents to accelerate the rate of decomposition of highly oxidizing agents.

In this article, the postpolymerization of vinyl acetate (VAc)-containing latexes is investigated. VAc is a common component of emulsion polymerization formulations and presents a low reactivity ratio with respect to many monomers [e.g., (meth)acrylates]. Therefore, in latexes including VAc in the formulation, this monomer is the main (and, in many cases, only) residual monomer. Postpolymerizations were carried out with a *tert*-butyl hydroperoxide (TBH)/ascorbic acid (AsA) redox system. The effects of the TBH/AsA ratio,

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Table I   Seed Recipe and Formulation Used for the Seeded Semicontinuous Emulsion Polymerization

Seed Recipe			
Ingredient	Initial Charge (g)	Pre-Emulsion (g)	Initiator Solution (g)
Dowfax 2A1	15.16	1.76	—
NaHCO$_3$	1.5	—	—
K$_2$S$_2$O$_8$	0.66	—	1.34
Water	1350	87.85	75
VAc	—	110.39	—
BuA	—	26.02	—
Acrylic acid	—	4.2	—

Formulation			
Ingredient	Initial Charge (g)	Stream I (g)	Stream II (g)
Alipal Co 436	6.13	6.13	—
Arkopal N 230	6.13	6.13	—
NaHCO$_3$	1.75	—	—
K$_2$S$_2$O$_8$	1.63	—	—
Water	99.53	99.53	—
Seed[a]	527	—	—
VAc	—	—	600
BuA	—	—	141.4
Acrylic acid	—	—	22.93

[a] Solids content = 9.6 wt %.

total initiator concentration, temperature, and feeding time on the polymerization of VAc were investigated.

EXPERIMENTAL

Materials

The latexes to be postpolymerized were prepared by the seeded semicontinuous emulsion copolymerization of VAc, butyl acrylate (BuA), and acrylic acid. To mimic industrial latexes, technical monomers, that is, monomers containing inhibitors, were used as received without further purification. Potassium persulfate (K$_2$S$_2$O$_8$, Fluka, Neu-Ulm, Switzerland) and sodium hydrogen carbonate (NaHCO$_3$, Panreac, Barcelona, Spain) were used as the initiator and buffer, respectively, in both the preparation of the seed and the final latex. Sodium dodecyl diphenyloxide disulfonate (Dowfax 2A1, Dow Chemical Co., Rotterdam, The Netherlands) was the anionic surfactant used in the preparation of the seed. A mixture of anionic [Alipal Co 436, Paris, France (poly-

ethoxylated nonylphenol and ammonium salt), Rhodia] and nonionic [Arkopal N 230 (polyethylene glycol monononylphenyl ether), Hoescht, Barcelona, Spain] surfactants was used for the preparation of the final latex. A commercial water-soluble hydroperoxide (TBH, Atofina, Serquigny, France) was used as received in combination with AsA (Fluka, Steinheim, Switzerland) in the postpolymerizations. Doubly deionized water was used throughout the work.

Seed Preparation

Table I presents the formulation used to prepare the seeds. Polymerizations were carried out in a 2-L jacketed glass reactor equipped with a reflux condenser, a thermocouple, a stainless steel stirrer at 200 rpm, a nitrogen inlet (12–15 mL/min nitrogen flow), and two feed inlet tubes. The reactor containing the initial charge was heated to 70°C, the boiling point of VAc. Then, the pre-emulsion (monomers, surfactant, and water) and the initiator solution were simultaneously added to the reactor in two separate streams over a period of 4 h.

Table II Formulation Used in the Postpolymerizations

Run	VAc/TBH/AsA Molar Ratio[a]	Temperature (°C)	Feeding Time (min)
1	1/0.25/0.125	70	60
2	1/0.375/0.0625	70	60
3	1/0.125/0.189	70	60
4	1/2/1	70	60
5	1/0.5/0.25	70	60
6	1/0.125/0.0625	70	60
7	1/0.25/0.125	30	60
8	1/0.25/0.125	50	60
9	1/0.25/0.125	60	60
10	1/0.25/0.125	80	60
11	1/0.25/0.125	70	45
12	1/0.25/0.125	70	90

[a] Based on total solid concentration.

After the addition period, the residual initiator was decomposed by the heating of the seed for 20 h at 70°C. Then, the seeds were filtered (138-μm mesh). No coagulum was found after filtration. The final characteristics of the seed were the following: solid content, 9.6 wt %; particle diameter, 40–50 nm (dynamic light scattering, Coulter N4 Plus, Miami, FL); and pH, 4.

Final Latex

VAc/BuA/acrylic acid latexes were synthesized by seeded semicontinuous emulsion polymerization under monomer-starved conditions, reaching a 55 wt % final latex solid content. The formulation is given in Table I. The water, seed latex, initiator ($K_2S_2O_8$), buffer ($NaHCO_3$), and mixture of anionic and nonionic surfactants (Alipal Co 436 and Arkopal N 230) were charged into the aforementioned reactor and maintained at 70°C with continuous stirring at 200 rpm. The aqueous solution of the surfactants was fed concurrently with the mixture of pure monomers for 4 h. Then, the reactor was kept at 70°C for 1 h. The remaining persulfate was decomposed by the heating of the latex for 20 h at 80°C.

The final characteristics of the latexes were the following: solid content, 55 wt % (no coagulum found after filtration); particle diameter, 220–230 nm (dynamic light scattering, Coulter N4 Plus); and pH, 4.2.

Residual monomers and VOCs were measured by headspace gas chromatography (HSGC, Hewlett-

Packard, Wilmington, DE) with the full evaporation technique. In this technique, the sample is thermostated in a closed vessel at a temperature that makes the volatile compounds gaseous. The amount of the sample must be small enough to avoid retention of the volatile compounds in the matrix but large enough to allow accurate measurements. The analyses were performed with a Hewlett–Packard HP 7694E headspace sampler interfaced to a Hewlett–Packard HP 6890 GC system with an electronic pneumatic control and a flame ionization detector. 4-Methyl-2-pentanone was used as an internal standard.

VAc was the only unreacted monomer found in a significant amount in the latex after the regular semicontinuous emulsion polymerization process. In addition, acetaldehyde, 1-butanol, butyl acetate, and a mixture of acids (mostly acetic acid with traces of acrylic acid) were identified by mass spectrometry and quantified by HSGC with the full evaporation technique. These byproducts resulted from the hydrolysis of the monomers during the reaction.[11]

Postpolymerizations

The postpolymerizations were performed in a 500-mL glass reactor equipped with a reflux condenser, a mechanical stirrer, a thermocouple, a sampling device, and two feed inlet tubes. After the introduction of the latex into the reactor (ca. 500 g), the latex was brought to the desired temperature by a thermostatic bath. Then, the aqueous solution of the oxidizing agent and the reducing agent were separately fed into the reactor with feeding times ranging from 45 to 90 min. After feeding, the reactor was kept at the reaction temperature for 2 h without a negative effect on
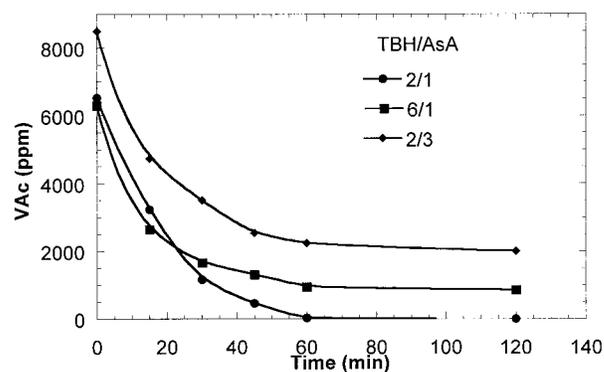
Figure 1   Effect of the TBH/AsA molar ratio on VAc removal at 70°C.
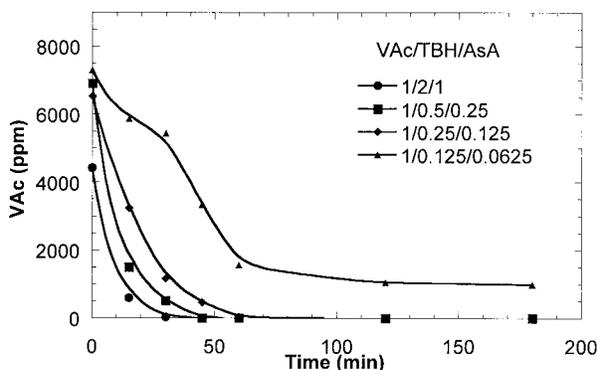
Figure 2 Effect of the initiator concentration on VAc polymerization at 70°C.

the final characteristics of the latex. Table II summarizes the reactions performed.

RESULTS

Effect of the Oxidant/Reductant Ratio

Very recently, we proposed that the reduction of TBH with AsA follows a mechanism with two-electron transfer, which involves the formation of *tert*-butoxyl radicals as reaction intermediates.[11] According to this mechanism, the optimal stoichiometric TBH/AsA ratio should be 2/1.

To validate experimentally the mechanism of reduction of TBH with AsA, we performed runs at different TBH/AsA ratios. In these experiments, the total amount by weight of the total redox initiator was kept constant, and the TBH/AsA molar ratio was varied from 2/3 to 6/1 (runs 1–3). The two components of the initiator system were fed separately over 60 min. Figure 1 presents the effect of the TBH/AsA molar ratio on VAc consumption. The best results were obtained with a 2/1 molar ratio. In this case, a complete polymerization of VAc was achieved after 1 h. However, substantial amounts of VAc remained in the latex when TBH/AsA molar ratios other than 2/1 were used. This supports the hypothesis that the reaction of TBH and AsA follows a mechanism with two-electron transfer, which involves the formation of *tert*-butoxyl radicals as reaction intermediates.[11]

Effect of the Initiator Concentration

Figure 2 presents the effect of the initiator concentration on the kinetics of VAc postpolymerization. These polymerizations were carried out at

70°C with a TBH/AsA molar ratio of 2/1. The amount of initiator refers to the moles of unreacted VAc at $t = 0$. Figure 2 shows that the VAc polymerization rate increased with the initiator concentration. In addition, a complete conversion of the residual monomer was achieved in less than 1 h for initiator concentrations equal or higher than VAc/TBH/AsA = 1/0.25/0.125. This corresponds to a total initiator amount of about 0.24 wt % with respect to the latex.

During the postpolymerization reactions, the formation of VOCs (acetone and *tert*-butyl alcohol) was observed. Figure 3 presents the evolution of these compounds during the process. Both acetone and *tert*-butyl alcohol increased during postpolymerization and remained constant after it. Figure 3 also shows that the concentrations of the VOCs increased with the initiator concentration. In addition, a concave shape of the concentration–time curve can be observed. These find-

a)

b)
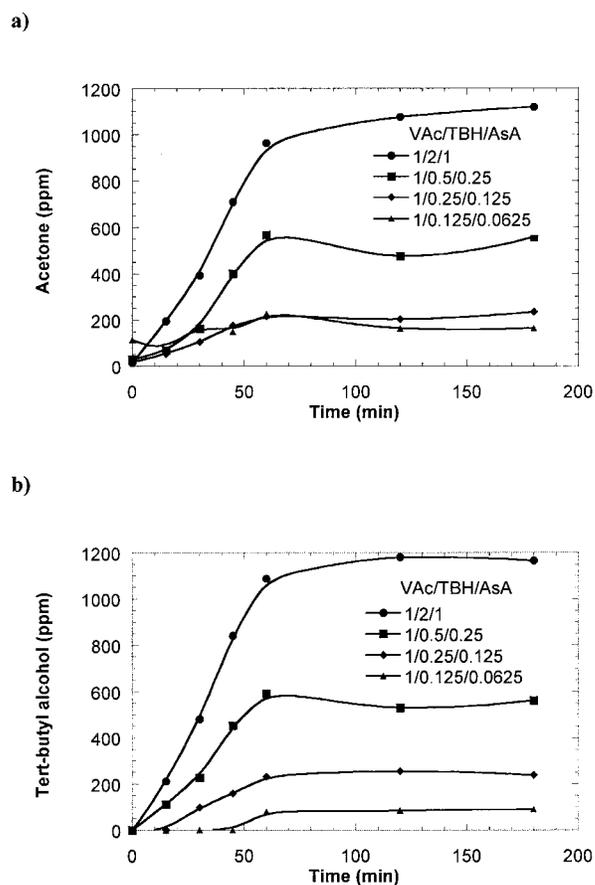
Figure 3 Effect of the initiator concentration on VOC formation at 70°C: (a) acetone and (b) *tert*-butyl alcohol.
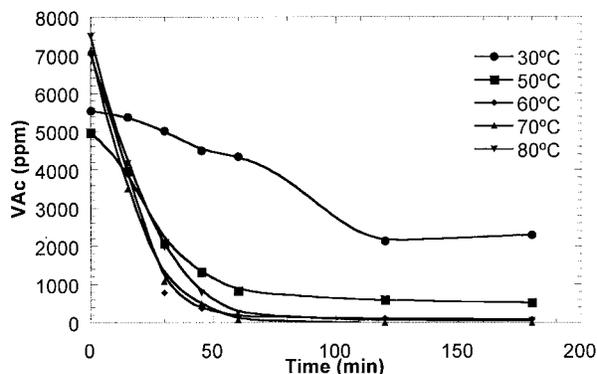
Figure 4 Effect of the postpolymerization temperature on VAc removal (VAc/TBH/AsA = 1/0.25/0.125).

ings are consistent with the following reaction scheme:[11]
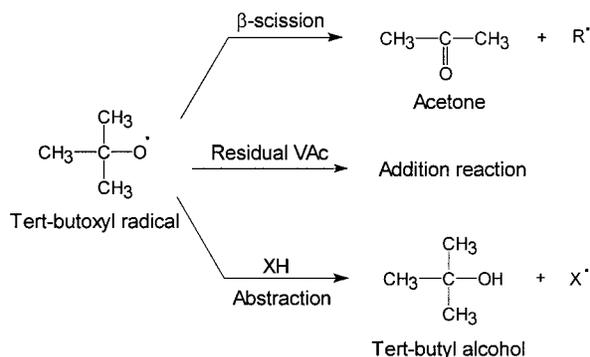
(XH: Solvent, monomers, polymer or impurity)

Effect of the Temperature

An increase in temperature might increase the postpolymerization rate and shorten the process time. However, the TBH/AsA redox system produced very active hydrophobic radicals that generated additional VOCs (acetone and *tert*-butyl alcohol) by two competitive reactions, the kinetics of which could have different temperature dependencies. Therefore, the effect of the temperature on the unreacted VAc monomer and VOCs was studied from 30 to 80°C (runs 1, 7, 8, 9, and 10).

Figure 4 shows that the kinetics of the VAc postpolymerization were not affected by temperatures greater than 60°C. However, at 50°C, a rather high concentration of unreacted monomer remained after the postpolymerization. The unreacted amount was even higher at lower temperatures. These results suggest that a minimum tem-

a)

b)
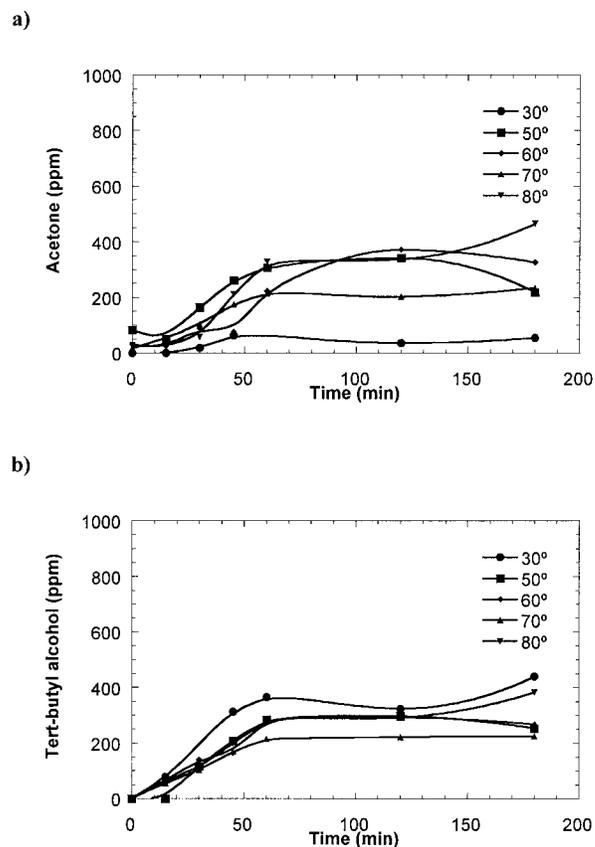
Figure 5 Effect of the temperature on VOCs formed during postpolymerization (VAc/TBH/AsA = 1/0.25/0.125): (a) acetone and (b) *tert*-butyl alcohol.

perature (ca. 60°C) is required for the efficient postpolymerization of VAc. Figure 5 shows that temperature had no significant effect on VOC formation from 60 to 70°C.
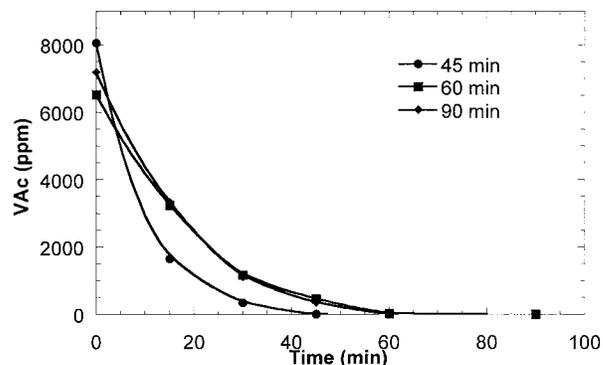
Figure 6 Effect of the feeding time on VAc consumption (temperature = 70°C; VAc/TBH/AsA = 1/0.25/0.125).

a)

b)
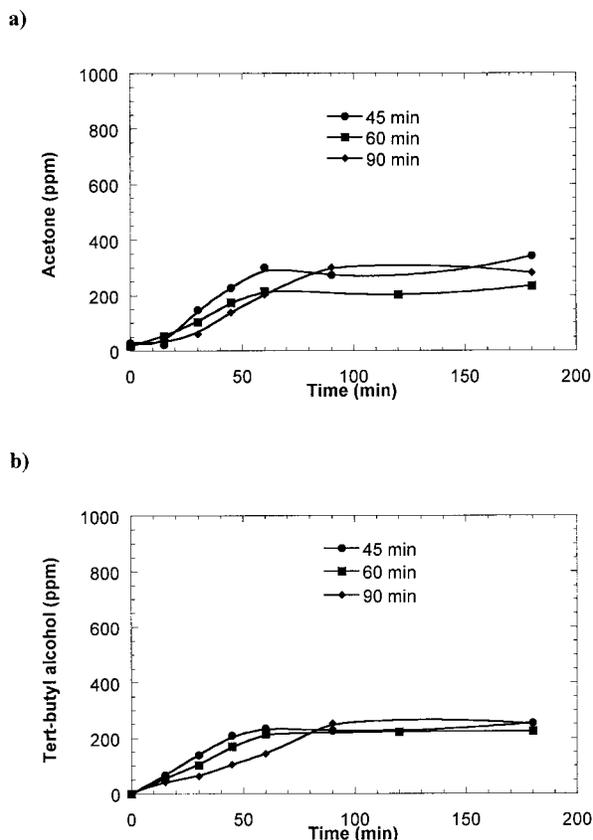
Figure 7 Effect of the feeding time on VOC formation (temperature = 70°C; VAc/TBH/AsA = 1/0.25/0.125): (a) acetone and (b) *tert*-butyl alcohol.

Effect of the Feeding Time

Three experiments were carried out at 70°C, with the feeding time varied from 45 to 90 min (run 11, 45 min; run 1, 60 min; and run 12, 90 min). Figure 6 shows that total elimination of the monomer was achieved in all cases. These results show that a postpolymerization process shorter than 1 h is feasible.

In addition, the results obtained in run 12 suggest that a initiator concentration lower than 1/0.25/0.125 may be enough to completely eliminate the monomer because the amount of initiator fed into the system in the 1st h of this run (when complete elimination of VAc was achieved) was 1/0.167/0.083.

Figure 7 shows that the total amount of VOCs was not significantly affected by the feeding time.

CONCLUSIONS

The TBH/AsA redox system is effective in reducing residual VAc monomer in latex. This initiation system produces very active radicals, which are able to totally eliminate residual VAc, but it generates byproducts, which in turn are VOCs. Fortunately, it was possible to reduce the VOC formation by minimization of the amount of the redox initiator system added during the chemical posttreatment. In fact, a formulation that allowed total VAc monomer elimination generated less than 500 ppm of new VOCs was obtained. The optimal TBH/AsA ratio was 2/1. This supports the hypothesis that the reaction of TBH and AsA follows a mechanism with two-electron transfer forming *tert*-butoxyl radicals. The minimum amount of initiator required to completely eliminate the residual VAc was 0.2–0.25 wt % with respect to the latex. In addition, the kinetics of postpolymerization were not influenced by the reaction temperature in the range 60–80°C, but lower temperatures could not be used to efficiently reduce residual VAc. Complete removal of the residual monomer was achieved in 45 min.

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