polymer

VOC formation during monomer removal by post-polymerization

L. Da Cunha, P. Ilundain, R. Salazar, D. Alvarez, M.J. Barandiaran, J.M. Asua*

Institute for Polymer Materials "POLYMAT" and Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, San Sebastián-Donostia, Spain

Abstract

The formation of volatile organic compounds through secondary reactions during the post-polymerization of vinyl acetate containing latexes using organic hydroperoxides with ascorbic acid as redox initiator was investigated. It was found that such initiator systems are highly effective in reducing free vinyl acetate but organic by-products are produced. A reaction scheme consistent with the kinetic data is presented. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Residual vinyl acetate monomer; Post-polymerization; Redox initiator

1. Introduction

The polymerization of monomers rarely proceeds to completion and inevitably some amount of unreacted monomer remains in the polymer. In emulsion polymerization, the conversion of monomers at the end of the process is usually higher than 90% of conversion, and often more than 99% (the amount of unreacted monomer being typically in the parts per million, ppm, range). Due to environmental regulations, it is generally necessary to remove unreacted monomers and other volatile organic compounds (VOCs) from the latex. The market preferences also play an important role in monomer and VOC removal because monomers and VOCs often have strong (and offensive) odors, which may severely limit the range of applications of the latex.

Both post-polymerization [1–3] and devolatilization [4–8] may be used for monomer removal. Usually, post-polymerization is preferred because it is carried out either in the polymerization reactor or in the storage tank, and no additional equipment is needed. In principle, any kind of initiation system may be used for post-polymerization. However, some alternatives seem preferable. Thus, although both water-soluble and oil-soluble initiators may be used, oil-soluble initiators are difficult to feed into the reactor without adding a solvent. In addition, a high radical flux is needed to polymerize the monomer in concentrations in the ppm range. This leads to redox initiation systems. On the other hand, the monomer is located mostly in the polymer particles, and hence initiators forming hydrophobic radicals would be desirable.

Following the above discussion, water-soluble redox initiation systems producing hydrophobic radicals would be an attractive system. Organic hydroperoxides [9–15] in combination with a strong reductant such as ascorbic acid fulfil these requirements. However, organic hydroperoxides may suffer secondary reactions that would give by-products, which in turn are VOCs. This paper studies the formation of volatile organic compounds through secondary reactions during the post-polymerization of vinyl acetate containing latexes using organic hydroperoxides and ascorbic acid as the redox initiator system.

2. Experimental

2.1. Materials

The latexes to be post-polymerized were prepared by seeded semicontinuous emulsion copolymerization of vinyl acetate (VAc), butyl acrylate (BuA) and acrylic acid (AA). In order to mimic industrial latexes, the monomers were used directly as received without further purification. Potassium persulfate ($K_2S_2O_8$, Fluka) and sodium hydrogen carbonate ($NaHCO_3$, Panreac) were used as initiator and buffer, respectively, in both the preparation of the seed and the final latex. Dowfax 2A1, sodium dodecyl diphenyloxide disulfonate (Dow Chemical Co.) was the anionic surfactant used in the preparation of the seed. A mixture of anionic (Alipal Co 436, polyethoxylated nonylphenol, ammonium salt, Rhodia) and non-ionic (Arkopal N 230,

Table 1
Seed recipe

Ingredients	Initial charge (g)	Preemulsion (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
Vinyl acetate	–	110.39	–
Butyl acrylate	–	26.02	–
Acrylic acid	–	4.2	–

polyethylene glycol monononylphenyl ether, Hoescht) surfactants was used for the preparation of the final latex. Two commercial water-soluble hydroperoxides (*tert*-butyl hydroperoxide and *tert*-amyl hydroperoxide, both provided by Elf-Atochem) were used as received in combination with ascorbic acid (Fluka) in the post-polymerizations. Doubly deionized water was used throughout the work.

2.2. Seed preparation

Table 1 presents the formulation used to prepare the seeds. The 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 (nitrogen flow at 12–15 ml/min) and two feed inlet tubes. The reactor containing the initial charge was heated to 70°C, the boiling point of vinyl acetate. Then, the preemulsion (monomers, surfactant and water) and the initiator solution were simultaneously added into the reactor in two separate streams, during a period of 4 h.

After the addition period, the residual initiator was decomposed by heating the seed for several hours (20 h) at 70°C. Then, the seeds were filtered (mesh of 138 μm). No coagulum was found after filtration. The final characteristics of the seed were: solids content, 9.6%; particle diameter, 40–50 nm (Dynamic Light Scattering, Coulter N4 Plus); pH, 4.

Table 2
Formulation used for the seeded semicontinuous emulsion polymerization

Ingredients	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	–	–
Vinyl acetate	–	–	600
Butyl acrylate	–	–	141.4
Acrylic acid	–	–	22.93

[a] Solids content = 9.6%.

2.3. Final latex

Fifty-five percent high solids content VAc/BuA/AA seeded emulsion polymerizations were carried out following the recipe in Table 2. The polymerizations were carried out at 70°C, in a 2-l glass reactor fitted with a reflux condenser, a thermocouple, a stainless-steel stirrer at 200 rpm, a sampling device, a nitrogen inlet (nitrogen flow at 12–15 ml/min) and two feed inlet tubes. The initial charge of the reactor (see Table 2) was formed by the seed, the buffer (sodium hydrogen carbonate), the initiator (potassium persulfate), water and the mixture of anionic and non-ionic surfactants (Alipal Co 436 and Arkopal N 230). The feed was divided into two streams. The first was an aqueous solution of the surfactants and the second was a mixture of pure monomers. The feeding lasted 4 h. Then, the reactor was kept at 70°C for 1 h. After that, the residual persulfate was decomposed by heating the latex for 20 h at 80°C. The final characteristics of the latexes were: solids content, 55% (no coagulum found after filtration); particle diameter, 220–230 nm (Dynamic Light Scattering, Coulter N4 Plus); pH, 4.2.

Residual monomers and VOCs were measured by Head-Space Gas Chromatography (HS-GC) using the full evaporation technique. In this technique the sample is thermostatted in a closed vessel at a temperature that makes the volatile compounds to be in the gas phase. The amount of sample must be small enough to avoid retention of the volatile compounds in the matrix, but large enough to allow accurate measurements.

The analysis were performed using a Hewlett Packard HP 7694E Headspace Sampler interfaced to a Hewlett Packard HP 6890 GC System with electronic pneumatic control and a flame ionization detector. 4-Methyl-2-pentanone was used as internal standard.

Vinyl acetate was the only unreacted monomer found in a significant amount in the latex after the regular semicontinuous emulsion polymerization process. This was somehow expected as acrylates are much more reactive than VAc. 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. These by-products resulted from the hydrolysis of the monomers during the regular reaction.

Vinyl acetate can be hydrolyzed by acidic catalysis forming acetic acid and vinyl alcohol. The expected alcohol is

Table 3
Formulation used in the post-polymerizations

Run	Redox system	Latex (g)	Initiator[a]	
			Oxidant (g)	VIT C (g)
1	TBH–VIT C	500.02	2.35	2.29
2	TAH–VIT C	500.01	2.70	2.29
3	TBH–VIT C	500.01	2.35	2.29

[a] Feeding time: 1 h.

Fig. 1. Evolution of the residual VAc monomer and VOC concentrations formed during the post-polymerization carried out with *tert*-butyl hydroperoxide–ascorbic acid. Legend: (a) VAc and VOCs formed during the post-polymerization; (b) VOCs formed during the latex production.

Fig. 2. Evolution of the residual VAc monomer and VOC concentrations formed during the post-polymerization carried out with *tert*-amyl hydroperoxide–ascorbic acid. Legend: (a) VAc and VOCs formed during the post-polymerization; (b) VOCs formed during the latex production.

unstable and acetaldehyde instantaneously forms by tautomeric rearrangement [16]:

Hydrolysis of butyl acrylate leads to the formation of 1-butanol and acrylic acid:

Butyl acetate results from the esterification reaction between acetic acid and 1-butanol:

Some amount of ethanol was also detected in the latex, but this compound appeared because the Alipal Co 436 non-ionic surfactant is commercialized as a viscous alcoholic solution.

2.4. Post-polymerizations

Because VAc was the only unreacted monomer found in a significant amount in the latex after the regular polymerization process, only post-polymerizations of VAc were considered.

Table 3 presents the formulations used in the post-polymerizations, that were performed in a 0.5-l jacketed glass reactor equipped with a reflux condenser, a stainless-steel stirrer at
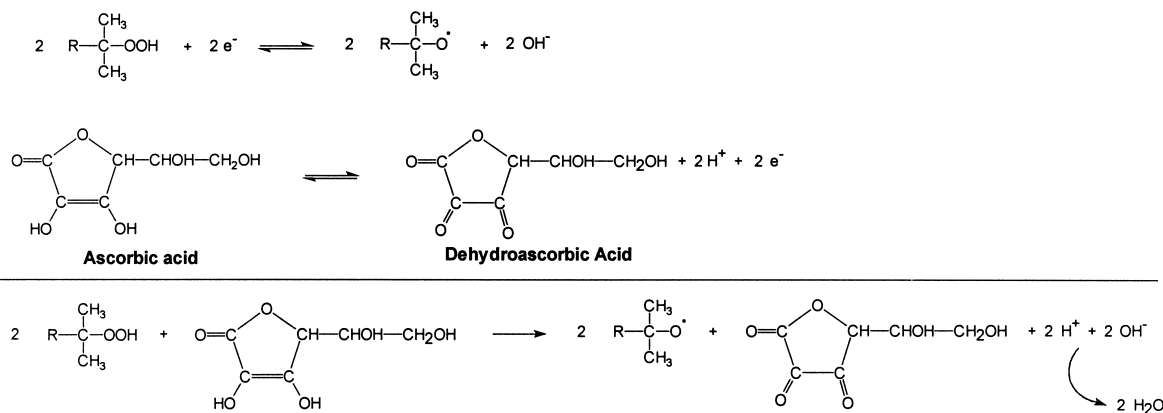
180 rpm, a thermocouple, a sampling device, a nitrogen inlet (nitrogen flow at 3–4 ml/min) and two feed inlet tubes.

After charging the latex (500 g) into the reactor, the temperature was increased to 70°C. Then, aqueous solutions of the oxidizing agent and the reducing agent were separately fed during 1 h to the reactor. Precautions were taken to place the feed tubes far from each other. After feeding, the reactor temperature was held at 70°C for 2 h.

3. Results and discussion

Figs. 1 and 2 present the evolution of monomer and VOC concentrations in the post-polymerizations carried out with *tert*-butyl hydroperoxide–ascorbic acid (TBH-VIT C; run 1) and *tert*-amyl hydroperoxide–ascorbic acid (TAH-VIT C; run 2), respectively. It can be seen that both initiator systems were effective in completely polymerizing the VAc in a

Figs. 1a and 2a suggest that acetone and *tert*-butyl alcohol (*tert*-amyl alcohol for TAH-VIT C) were produced while the initiator system was active. Thus, these VOCs were produced from the very beginning of the post-polymerization when TBH-VIT C, which did not suffer inhibition, was used. On the other hand, no VOCs were produced during the first 15 min of the post-polymerization using TAH-VIT. Fig. 2a shows that almost no reaction of VAc was observed during this period, indicating that there were no radicals available in the system. In addition, the formation of VOC ended when the initiator feed was stopped.

In the case of organic peroxides in combination with metal ions as the reducing agent, a *tert*-alkoxyl radical $RC(CH_3)_2O^{\cdot}$ is produced by single-electron transfer and cleavage of the −O−O− bond [12]. When ascorbic acid is used as the reducing agent a similar mechanism may occur, but involving two-electron transfer, with the formation of dehydroascorbic acid [18–20] and *tert*-alkoxyl radicals:

rather short period of time. TBH-VIT C seems to be more efficient than TAH-VIT C but the differences in monomer consumption observed in Figs. 1a and 2a may be due to traces of oxygen [17] that caused some inhibition when the system TAH-VIT C was used.

Fig. 1a shows that a significant amount of *tert*-butyl alcohol and acetone was produced during the post-polymerization when TBH-VIT C was used. Similarly, Fig. 2a shows that *tert*-amyl alcohol and acetone were produced in the case of the post-polymerization initiated with TAH-VIT C. In addition, Figs. 1b and 2b showed that the concentrations of the VOCs formed during latex production (butyl acetate, 1-butanol, acetaldehyde) or contained in the components of the formulation (ethanol) did not vary during post-polymerization.

Figs. 1a and 2a show that the high efficiency of the organic hydroperoxides (in combination with ascorbic acid) was counteracted by the fact that large amounts of VOCs were produced. The knowledge of the mechanisms involved in the formation of these VOCs is a requirement for the development of optimal strategies aiming at minimizing the amounts of both residual monomer and VOC.

β-Scission of the *tert*-alkoxyl radicals yields acetone, and hydrogen abstraction the *tert*-alkyl alcohol [21–33]. These two reactions occurred in parallel with the initiation of the residual VAc according to the following mechanism:
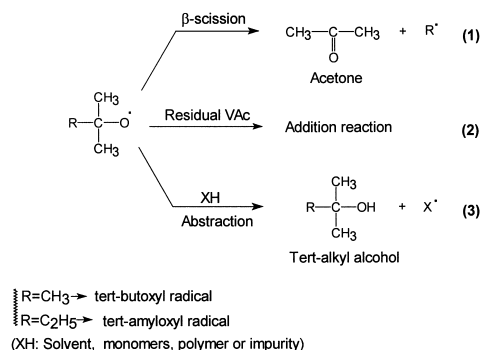
The reaction scheme presented in Eqs. (1)–(3) is consistent with the kinetic data shown in Figs. 1a and 2a. Thus, in the post-polymerization carried out using TAH-VIT C, no VOCs were formed during the first stages of the process where no radical activity was observed (Fig. 2a). According
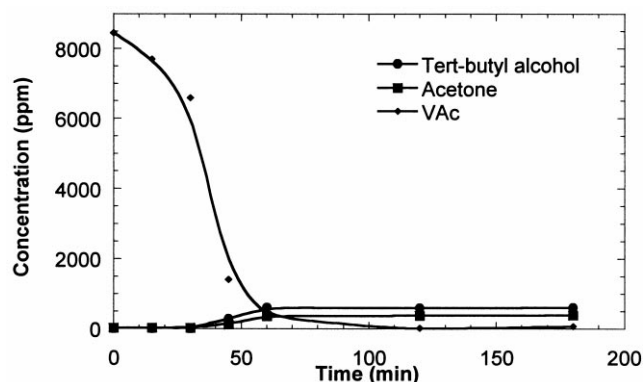
Fig. 3. Evolution of the monomer and VOC concentrations in run 3.

to the reaction scheme, the higher the monomer concentration the lower the rate of production of acetone and *tert*-alkyl alcohol. This agrees with the results showed in Figs. 1a and 2a, where the production rate of VOCs accelerated during the process as the concentration of VAc decreased. This is further illustrated in Fig. 3 where the evolution of residual VAc, acetone and *tert*-butyl alcohol for a post-polymerization (run 3) using the same amount of initiators than in run 1, but with a higher amount of initial VAc is presented. Comparison with Fig. 1a shows that a substantially lower amount of VOC was produced when the monomer concentration increased.

4. Conclusions

In the present work, it was found that *tert*-alkyl hydroperoxides–ascorbic acid redox systems were highly effective in reducing free VAc in latexes. However, these systems produced very active hydrophobic radicals that also generated VOCs (acetone and *tert*-alkyl alcohol). Acetone was produced by β-scission of the *tert*-alkoxyl radicals whereas hydrogen abstraction yielded *tert*-alkyl alcohol. This reaction scheme is consistent with the kinetic data available, namely that the production rate of these new VOCs accelerated during the post-polymerization as the concentration of VAc decreased.

Acknowledgements

References

[1] Moore JD, Feast AAJ. United States Patent application US 4301264, 1981.
[2] Straub F, Spoor H, Schenck H-U, Schwarz W. United States Patent application US 4182851, 1980.
[3] Olivares MA, Archundia FJ, Ramos F. United States Patent application US 5886140, 1999.
[4] Kelly P. European Patent application EP 065977 A1, 1995.
[5] Uchida S, Kurazono T, Ishibashi S, Matsuda E. European Patent application EP 0668134 A2, 1995.
[6] Chandra BP, Greaves JC, Lovelock VG. United States Patent application US 4283526, 1981.
[7] Chen SL, Wong TH, Gujarathi RN. Canadian Patent application CP 2134839, 1996.
[8] Govoni G, Guardigli P, Rubichi G. European Patent application EP 0035661 A3, 1981.
[9] Anderson LL, Brouwer WM. J Coat Tech 1996;68:75 (and references therein).
[10] Kamath VR, Sargent JD. J Coat Tech 1987;59:51.
[11] Misra GS, Bajpai UDN. Prog Polym Sci 1982;8:61–131.
[12] Moad G, Solomon DH. The chemistry of free radical polymerization. Amsterdam: Elsevier, 1995 (p. 78 and references therein).
[13] Sempio C, Saija LM, Novellara RE, Montessoro E. European Patent application EP 0767180 A1, 1997.
[14] Dolgoplosk BA, Tiniakova EI. J Polym Sci 1958;30:315.
[15] Pattnaik S, Roy AK, Baral N, Nayak PL. J Macromol Sci Chem 1979;6:797.
[16] Othmer K. Encyclopedia of chemical technology. 3rd ed.. New York: Wiley, 1979 (p. 927).
[17] López de Arbina L, Gugliotta LM, Barandiaran MJ, Asua JM. Polymer 1998;39(17):4047.
[18] Grinstead RR. J Am Chem Soc 1960;82:3464.
[19] Weissberger A, LuValle JE, Thomas DS. J Am Chem Soc 1943;65:1934.
[20] Deutsch JC. Anal Biochem 1998;255:1.
[21] Walling C, Padwa A. J Am Chem Soc 1963;85:1593.
[22] Walling C, Wagner PJ. J Am Chem Soc 1964;86:3368.
[23] Walling C. Pure Appl Chem 1967;15:69.
[24] Kochi JK. J Am Chem Soc 1962;84:1193.
[25] Bacha JD, Kochi JK. J Org Chem 1965;30:3272.
[26] Ingold KU. Pure Appl Chem 1967;15:49.
[27] Hiatt R, Mill T, Mayo FR. J Org Chem 1968;33:1417.
[28] Hiatt R, Mill T, Irwin KC, Castleman JK. J Org Chem 1968;33:1421.
[29] Hiatt R, Mill T, Irwin KC, Castleman JK. J Org Chem 1968;33:1428.
[30] Encina MV, Rivera M, Lissi EA. J Polym Sci 1978;16:1709.
[31] Griffiths PG, Rizzardo E, Solomon DH. J Macromol Sci Chem 1982;1:45.
[32] Grant RD, Griffiths PG, Moad G, Rizzardo E, Solomon DH. Aust J Chem 1983;36:2447.
[33] Avila DV, Brown CE, Ingold KU, Lusztyk J. J Am Chem Soc 1993;115:466.