Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

ELSEVIER

Reactive & Functional Polymers 66 (2006) 247–254

REACTIVE
&
FUNCTIONAL
POLYMERS

www.elsevier.com/locate/react

The comparison between initial charge, shot and modified shot processes and their effects on macrostructure of particles in emulsion copolymerization of styrene–butadiene–acrylic acid

Ali Reza Mahdavian *, Mahdi Abdollahi

Polymer Science Department, Iran Polymer & Petrochemical Institute, P.O. Box 14965/115, Tehran 14967, Iran

Received 3 August 2005; accepted 4 August 2005

Abstract

Carboxylated styrene–butadiene latexes with 30% solid content were prepared by emulsion copolymerization technique with initial charge and shot-addition methods. The distribution of carboxylic groups in different locations of latex system, i.e., interior and surface of particles and aqueous phase during polymerization reaction was studied by conductometric back titration method (Hen method). The obtained results from shot process show that addition of acrylic acid with some water in interval III of emulsion polymerization will decrease the amount of surface bound carboxylic acids relative to initial charge method. So the process of shot addition was modified by addition of styrene, emulsifier and initiator accompanied with acrylic acid and water in conversions above 80% in the second stage. The analysis of the obtained latex shows that the amount of surface bound acid was raised from 58% for initial charge method to 72% for this modified technique.

Keywords: Emulsion polymerization; Carboxylated SBR; Surface bound acid; Conductometric back titration; Initial charge process; Shot-addition process

---

1. Introduction

Carboxylated styrene–butadiene latexes are among the most important emulsion polymers due to their wide applications. These are used as binders in paper coating, carpet backing and paints [1–5]. Incorporation of carboxylic acid groups into the particle surface even in low amounts has great advantages. These groups could improve the compatibility of the latex with pigments, film strength and adhesion of the film to polar substrates. They would expose new sites for cross-linking reactions, modify water resistancy of papers and textiles and also develop aging of the substrate. The presence of carboxylic groups chemically bonded to the particles' surface produces some electrostatic repulsion and induces colloidal and mechanical stability to the corresponding latexes too [1,2,6,7].

The characteristics of the water–particle interface are one of the determining factors in colloidal properties and applications of emulsion polymers. Chemical and mechanical stability, adhesion and

---

* Corresponding author. Tel.: +9821 458 0000; fax: +9821 458 0021.

E-mail address: a.mahdavian@ippi.ac.ir (A.R. Mahdavian).

1381-5148/$ - see front matter
doi:10.1016/j.reactfunctpolym.2005.08.014

rheology are among the parameters that depend directly on the interaction of particles' surface with surrounding media. In contrast with bulk properties, surface phenomena are affected remarkably by small changes in colloid composition of the system. Any success in preparation of a stable emulsion could depend on the presence of a component in the water–particle interface [7]. This component may be the neutralized carboxylic acid group that has been copolymerized at the surface of latex particles and in the case of neutralization; the anionic groups could stabilize them. Addition of carboxylic acid monomers at the near end of emulsion polymerization (shot process) results in increases in the concentration of carboxylic acid groups incorporated in the particles' surface [8,9]. Greene [10,11] have studied the effect of monomers bearing carboxylic acid groups on their distribution in seeded emulsion polymerization of styrene, butadiene and carboxylic acid monomers extensively.

In this work, the effects of shot process and added components on the distribution of carboxylic groups have been studied in styrene–butadiene–acrylic acid emulsion polymerization. Meanwhile, a modified shot process is presented in order to increase the concentration of carboxylic acid groups on the surface of particles.

2. Materials and methods

Styrene (St) was purchased from Merck Chemical Co. It was washed twice with NaOH solution (5% W/V) and dried over anhydrous calcium chloride and stored at 0 °C in dark bottles. Acrylic acid (AA) from BASF, potassium persulfate (KPS) from Merck, sodium lauryl sulfate (SLS) from Aldrich and butadiene (Bu) from Bandar Imam Petrochemical Co. (Iran) were used without further purification. Double distilled water was used in each polymerization recipe.

Conductometer model CG855 and pH meter model CG825 both from Schott Co. were used in determination of carboxylic groups' distribution in latex systems. Conductometric back titration was performed according to the Hen method [12] in order to determine the position of polymerized carboxylic acid and measuring its amount.

Solid content at each time (SC(t)) was calculated by gravimetry method. Sampling was performed and polymerization of each sample was stopped by hydroquinone solution in methanol (15% W/V). Then it was dried at 60 °C under reduced pressure and the solid content was calculated. Overall conversion by weight ($X_{\mathrm{ov}}(t)$) was obtained by calculating solid content at initiation time (SC(initial)) and at the end of reaction (SC(final)). Both could be found theoretically from recipe and measurement of solid content at any time (SC(t)) by using the following equation:

$$X_{\mathrm{ov}}(t) = \frac{\mathrm{SC}(t) - \mathrm{SC(initial)}}{\mathrm{SC(final)} - \mathrm{SC(initial)}}. \tag{1}$$

3. Emulsion copolymerization

Emulsion copolymerization reactions were carried out in a Buchi reactor equipped with a mechanical stirrer (U-shape with stirring speed of 350 rpm) and circulator of silicone oil. All of the reactions were performed at 70 °C under N_2 atmosphere. The scheme of the reactor and their accessories has been shown in Fig. 1.

Three methods (initial charge, shot-addition and modified shot-addition techniques) were used for these polymerization reactions. The amount of components in each technique has been listed in Tables 1–3.

In shot-addition and modified shot-addition techniques, the amounts of monomers were set such that total solid contents of stage I and stage II would be the same.

4. Results and discussion

We applied a gravimetric technique in order to follow the conversion versus time. These data were used in each experiment when we needed conversion data. Initial charge addition technique was used to prepare carboxylated styrene–butadiene latex (XSBR) according to Table 1. The obtained latex was analyzed in order to find out the location of polymerized acrylic acid during the process. Shot addition was the next method, which was used in this emulsion copolymerization. In the second stage of this method, acrylic acid and an appropriate amount of water were added to the reaction after 65–70% conversion of the first stage (Table 2). Different amounts of acrylic acid were added whilst keeping the concentration of other components constant and the effect of acrylic acid concentration on its distribution was studied.

In the shot process, carboxylic acid monomer is often added to the reactor in interval III of emulsion polymerization (total conversion is more than 50%).