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Polymer 47 (2006) 1405–1413

polymer

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Modeling the emulsion polymerization of amino-functionalized latex particles

Jose Ramos, Jacqueline Forcada *

Departamento de Química Aplicada, Facultad de Ciencias Químicas, Institute for Polymer Materials POLYMAT and Grupo de Ingeniería Química, Universidad del País Vasco/EHU, Apdo. 1072, San Sebastián 20080, Spain

Received 19 October 2005; received in revised form 7 December 2005; accepted 9 December 2005
Available online 10 January 2006

Abstract

A mathematical model for a semicontinuous seeded cationic emulsion polymerization was developed. The model includes the most distinctive features of the copolymerization of a cationic hydrophilic monomer with a hydrophobic one, including polymerization of the hydrophilic monomer in the outer shell of polymer particles and in the aqueous phase, and the possibility of having radical concentration profiles in the polymer particles.

The reactions were carried out by means of a semicontinuous seeded cationic emulsion polymerization under starved conditions for styrene, which was the main monomer employed.

The model predicts the evolution of the fractional overall conversions, the thickness of the outer shell, the total surface charge density and the partial conversions for the semicontinuous seeded cationic emulsion polymerization of styrene and aminoethyl methacrylate hydrochloride. Furthermore, the model can distinguish between the surface charge density provided by the cationic monomer than that given by the cationic initiator. Therefore, this model can predict the best conditions to obtain well-defined latexes with specific amounts of surface amino and amidine groups useful for immunoassays.

Keywords: Cationic emulsion polymerization; Amino functionality; Modeling

1. Introduction

Functionalized latex particles with well-defined characteristics, such as uniform particle size, amount of functional groups, and location of these functional groups within the particles, are of great interest in diagnostics for the quantification of numerous biomolecules in different biological fluids. They possess a number of benefits, including ease of production, homogenous procedure and relatively high analytical sensitivity. Furthermore, immuno-reagents are more stable if functionalized particles bind proteins covalently, because the chemical attachment is very stable over time.

The use of amino-functionalized particles has several advantages over other functionalities (the binding agent, glutaraldehyde, is more stable than carbodiimide; it can be used to form spacer arms and allows a good antibody orientation) [1,2]. In order to use this kind of particles in immunoassays, monodisperse, stable particles, of known surface amino group density are required.

Up to now, almost all of the studies carried out on the synthesis of functionalized latex particles have been empirical in nature, and it is difficult to predict the best conditions to obtain functionalized latexes with a specific surface functional group density.

The prediction and attainment of the optimum process to achieve the desired product by previously specifying its characteristic can be carried out through mathematical modeling. However, current knowledge of emulsion polymerization permits only a limited understanding of the mechanisms involved by fitting experimental data in a polymerization system.

In this work, a mathematical model for the semicontinuous seeded cationic emulsion copolymerization of aminoethyl methacrylate hydrochloride (AEMH) and styrene (S) is presented. The model includes the most distinctive features of this copolymerization. It takes into consideration the polymerization and partitioning of the cationic monomer AEMH in the aqueous phase and in the outer shell of

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* Corresponding author. Tel.: +34 943 018182; fax: +34 943 015270.
E-mail address: jacqueline.forcada@ehu.es (J. Forcada).

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doi:10.1016/j.polymer.2005.12.048

the growing polymer particles, and the possibility of having radical concentration profiles in the polymer particle. Furthermore, the main effort in this model has been focused on the prediction of the outer shell thickness (δ) and total surface charge density (σ) during the reaction, and the distinction between the surface charges provided by the cationic monomer (σ_{AMINO}) from that given by the cationic initiator ($\sigma_{\mathrm{AMIDINE}}$). Moreover, polymerization-related features, such as the evolution of the partial overall conversions of S and AEMH are also predicted.

2. Experimental section

The experimental results used in this model have been described in a previous paper [3], which reported the results obtained in the semicontinuous seeded cationic emulsion polymerization of styrene and AEMH on varying the amount of cationic monomer in the feed. Six polymerizations with different amounts of cationic monomer (AEMH) were carried out. The amidine groups on the polymer particles were provided by the cationic initiator 2,2′-azobis(*N*,*N*′-dimethyleneisobutyramidine) dihydrochloride (ADIBA), and the amino groups were provided by the cationic monomer AEMH.

3. Model description

In this work, the most important colloidal feature to predict is the density of surface functional groups on the latex particles. Therefore, a mathematical model, which is based on that of de la Cal and Asua [4] for seeded emulsion polymerization stabilized by polymerizable surfactants, was developed. The model presented here considers the fact that the polymeric particles synthesized are also charged polymeric colloids.

The model incorporates the following features and assumptions:

First, a seeded semicontinuous emulsion copolymerization of a hydrophobic monomer (styrene, S) and a hydrophilic-cationic one (AEMH, A) is considered.

Second, styrene homopolymerizes in the core and copolymerizes in the outer shell of polymer particles, and AEMH copolymerizes with styrene in the outer shell and homopolymerizes in the aqueous phase.

Third, from a kinetic point of view, the polymer particles are monodisperse in size.

Fourth, the thickness of the outer shell (δ) increases by copolymerization of styrene and AEMH, and is calculated as

$$\delta = r_{\mathrm{p}} - r_{\mathrm{pcore}} \tag{1}$$

where r_{p} is the particle radius and r_{pcore} is the core radius.

Fifth, when water-soluble initiators are used, surface anchoring of the hydrophilic entering radicals may yield a radical profile in the polymer particles. With this radical profile in the polymer particles the average concentration of radicals, as well as the consumption of each monomer (S and A), in the core and in the outer shell can be quantified separately. Methods to calculate this concentration profile have been proposed [5,6], but for the purposes of the present work, the arbitrary profile used by de la Cal and Asua [4] is used:

$$[R] = a + b\left(\frac{r}{r_{\mathrm{p}}}\right)^2 \tag{2}$$

where r is the radial distance, r_{p} is the particle radius, b is a parameter that determines the steepness of the radical concentration profile, and a is a parameter that takes into account the average number of radicals per particle (calculated by means of Eq. (10)).

Sixth, monomer partitioning follows thermodynamic equilibrium.

Seventh, the gel effect was taken into account for the termination kinetic constant in polymer particles.

Eighth, the amount of surface amidine groups on the polymer particles is a function of the ratio AEMH/Styrene feed.

Ninth, all the cationic amino monomer polymerized in the particles contributes to the surface charge density. This means that there are no buried amino groups provided by the cationic monomer inside the particles.

3.1. Monomer material balances

The material balance for styrene (S) is the following:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -k_{\mathrm{pSS}}[\bar{R}]_{\mathrm{core}}V_{\mathrm{core}}[S]_p\frac{N_p}{N_A} - \left(k_{\mathrm{pSS}}P_{\mathrm{S}}^{\mathrm{shell}} + k_{\mathrm{pAS}}P_{\mathrm{A}}^{\mathrm{shell}}\right)[\bar{R}]_{\mathrm{shell}}V_{\mathrm{shell}}[S]_{\mathrm{p}}\frac{N_{\mathrm{p}}}{N_{\mathrm{A}}} + F_{\mathrm{S}} \tag{3}$$

In this equation, the first term of the right-hand side member represents the homopolymerization of styrene in the core, and the second, the copolymerization with the cationic monomer (A) in the outer shell; S is the total number of moles of styrene in the reactor; $k_{\mathrm{p}ij}$ are the propagation rate constants; P_i^j are the probabilities of having a radical with an ultimate unit of type i in the phase j; $[\bar{R}]_{\mathrm{core}}$ and V_{core} are the average concentration of radicals in the core and the volume of the core; $[\bar{R}]_{\mathrm{shell}}$ and V_{shell} are the average concentration of radicals in the shell and the volume of the shell; $[S]_{\mathrm{p}}$ is the concentration of styrene in the polymer particles; N_{p} is the total number of polymer particles in the reactor; N_{A} is Avogadro's number; and F_{S} is the molar feed rate of styrene.

In the shell, the probabilities are those of an emulsion copolymerization [7]

$$P_{\mathrm{S}}^{\mathrm{shell}} = \frac{k_{\mathrm{pAS}}[S]_{\mathrm{p}}}{k_{\mathrm{pAS}}[S]_{\mathrm{p}} + k_{\mathrm{pSA}}[A]_{\mathrm{p}}} \tag{4}$$

$$P_{\mathrm{A}}^{\mathrm{shell}} = 1 - P_{\mathrm{S}}^{\mathrm{shell}} \tag{5}$$

The material balance for the cationic monomer AEMH (A) is:

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -\left(k_{\mathrm{pSA}}P_{\mathrm{S}}^{\mathrm{shell}} + k_{\mathrm{pAA}}P_{\mathrm{A}}^{\mathrm{shell}}\right)[\bar{R}]_{\mathrm{shell}}V_{\mathrm{shell}}[A]_{\mathrm{p}}\frac{N_{\mathrm{p}}}{N_{\mathrm{A}}} - k_{\mathrm{pAA}}[R]_{\mathrm{w}}V_{\mathrm{w}}[A]_{\mathrm{w}} + F_{\mathrm{A}} \tag{6}$$

In this equation, the subscript w refers to the aqueous phase; the first term of the right-hand side member represents the copolymerization of A with styrene, and the second term expresses the homopolymerization of AEMH in the aqueous phase; A is the total number of moles of AEMH in the reactor; $[A]_{\mathrm{p}}$ is the concentration of AEMH in the shell of the polymer particles; $[R]_{\mathrm{w}}$ and V_{w} are the concentration of radicals in the aqueous phase and the volume of water; and F_{A} is the molar feed rate of AEMH.

3.2. Initiator and water material balances

The material balances for initiator and water are:

$$\frac{\mathrm{d}I}{\mathrm{d}t} = -k_{\mathrm{I}}I + F_{\mathrm{I}} \tag{7}$$

$$\frac{\mathrm{d}w}{\mathrm{d}t} = F_{\mathrm{W}} \tag{8}$$

where I is the total number of moles of cationic initiator; k_{I} is the rate coefficient for initiator decomposition; F_{I} is the molar feed rate of the cationic initiator; w is the total number of moles of water; and F_{W} is the molar feed rate of the water.

3.3. Balance of radicals

In order to calculate the values of the average concentration of radicals in the core $[\bar{R}]_{\mathrm{core}}$ and in the shell $[\bar{R}]_{\mathrm{shell}}$, and the concentration of radicals in the aqueous phase $[R]_{\mathrm{w}}$ required in the monomer material balances, two steps are required: (i) calculate the average number of radicals per particle ($\tilde{n}$), and (ii) apply the radical profile in the polymer particles.

The balance of radicals in the aqueous phase is:

$$2k_{\mathrm{tw}}[R]_{\mathrm{w}}^{2}V_{\mathrm{w}} + k_{\mathrm{a}}[R]_{\mathrm{w}}\frac{N_{\mathrm{p}}}{N_{\mathrm{A}}} = 2fk_{\mathrm{I}}I + k_{\mathrm{d}}\bar{n}\frac{N_{\mathrm{p}}}{N_{\mathrm{A}}} \tag{9}$$

where k_{tw} is the average termination rate constant in the aqueous phase; k_{a} and k_{d} are the radical entry and exit rate coefficients, which will be calculated later; f is the efficiency factor for initiator decomposition; and $\bar{n}$ is the average number of radicals per particle given by Ref. [8]

$$\bar{n} = \frac{2k_{\mathrm{a}}[R]_{\mathrm{w}}}{k_{\mathrm{d}} + \sqrt{k_{\mathrm{d}}^{2} + 4k_{\mathrm{a}}[R]_{\mathrm{w}}\varphi(k_{\mathrm{tp}}/v_{\mathrm{p}}N_{\mathrm{A}})}} \tag{10}$$

$$\varphi = \frac{2(2k_{\mathrm{a}}[R]_{\mathrm{w}} + k_{\mathrm{d}})}{2k_{\mathrm{a}}[R]_{\mathrm{w}} + k_{\mathrm{d}} + (k_{\mathrm{tp}}/v_{\mathrm{p}}N_{\mathrm{A}})} \tag{11}$$

where k_{tp} is the average termination rate constant in the polymer particles and will be calculated later; and v_{p} is the volume of the polymer particle. Once $\bar{n}$ is known, the value of a in Eq. (2) for each (a/b) value can be calculated using the following expression:

$$\bar{n} = \int_{0}^{r_{\mathrm{p}}}\left[a + b\left(\frac{r}{r_{\mathrm{p}}}\right)^{2}\right]4\pi r^{2}\mathrm{d}r \tag{12}$$

The average concentration of radicals in the core of the particle is:

$$[\bar{R}]_{\mathrm{core}} = \frac{\int_{0}^{r_{\mathrm{pcore}}}\left[a + b(r/r_{\mathrm{p}})^{2}\right]4\pi r^{2}\mathrm{d}r}{4/3\pi r_{\mathrm{pcore}}^{3}} \tag{13}$$

The average concentration of radicals in the outer shell is:

$$[\bar{R}]_{\mathrm{shell}} = \frac{\int_{r_{\mathrm{pcore}}}^{r_{\mathrm{p}}}\left[a + b(r/r_{\mathrm{p}})^{2}\right]4\pi r^{2}\mathrm{d}r}{4/3\pi\left(r_{\mathrm{p}} - r_{\mathrm{pcore}}^{3}\right)} \tag{14}$$

This model differs from that proposed by de la Cal and Asua [4] in the thickness of the shell in which the copolymerization takes place. For de la Cal and Asua, the surfmer polymerization occurs in the outer shell with a constant value of thickness, and in this work the value of the thickness changes as copolymerization proceeds, increasing together with the copolymer formed.

3.4. Entry and exit of radicals into particles constants

The rate coefficient for radical absorption into the particles depends on the particle size. It has been proposed that this dependence may be taken into account by means of the following equation [9]:

$$k_{\mathrm{a}} = k_{\mathrm{a}}^{*}\mathrm{d}p^{\alpha_{1}} \tag{15}$$

Where k_{a}^{*} includes all the terms of the absorption kinetic constant except for the particle size dependence, and α_1 is a constant that depends on the particle size. Lopez de Arbina et al. [10] studied the emulsion polymerization of styrene over a wide range of experimental conditions, finding that radical entry was consistent with the diffusional entry mechanism [11], that is $\alpha_1 = 1$. In the present work, the values of α_1 and k_{a}^{*} obtained by Lopez de Arbina et al. [10] and Mendoza et al. [12], respectively, were used.

The radical desorption rate constant is assumed to be the sum of the rate coefficients in the core and in the shell:

$$k_{\mathrm{d}} = k_{\mathrm{dcore}} + k_{\mathrm{dshell}} \tag{16}$$

For the core, the desorption rate constant is given by the new model recently proposed by Asua [13], taking into account the radius of the core and the variable value of the thickness of the shell (δ).

$$k_{\mathrm{dcore}} = \lambda_{\mathrm{core}}\frac{\gamma_{\mathrm{core}}N_{\mathrm{A}}}{\eta_{\mathrm{core}}m_{\mathrm{S}}}\left(1 - \frac{\lambda_{\mathrm{core}}N_{\mathrm{p}}}{\lambda_{\mathrm{core}}N_{\mathrm{p}} + k_{\mathrm{pSS}}[S]_{\mathrm{w}} + 2k_{\mathrm{tw}}[R]_{\mathrm{w}}}\right) \tag{17}$$

Where $[S]_\mathrm{w}$ is the concentration of styrene in the aqueous phase. Other parameters appearing in Eq. (17) are:

$$\gamma_\mathrm{core} = \frac{k_\mathrm{fSS}[S]_\mathrm{p}}{v_\mathrm{p} N_\mathrm{A} D_\mathrm{p}} \tag{18}$$

$$\eta_\mathrm{core} = \frac{k_\mathrm{pSS}[S]_\mathrm{p}}{D_\mathrm{p}} \tag{19}$$

$$\lambda_\mathrm{core} = \frac{4\pi D_\mathrm{w} r_\mathrm{pcore}}{1 + \frac{D_\mathrm{w}}{D_\mathrm{h}} \frac{\delta}{r_\mathrm{pcore}} + \frac{D_\mathrm{w}}{D_\mathrm{p} m_\mathrm{S}} \frac{1}{r_\mathrm{pcore}\sqrt{\eta_\mathrm{core}}\, \coth\left(r_\mathrm{pcore}\sqrt{\eta_\mathrm{core}}\right) - 1}} \tag{20}$$

Where k_fSS is the transfer rate kinetic constant of styrene; v_p is the volume of the polymer particle; D_p, D_h and D_w are the diffusion rate coefficient in the polymer particles, hairy layer, and in the aqueous phase, respectively; and m_S is the partition coefficient of styrene radicals in the shell [13].

For the shell, the desorption rate constant is the sum of the desorption rate coefficients for styrene and cationic monomeric radicals.

$$k_\mathrm{dshell} = k_\mathrm{dshellS} + k_\mathrm{dshellA} \tag{21}$$

$$k_{\mathrm{dshell}i} = \lambda_{\mathrm{shell}i} \frac{\gamma_{\mathrm{shell}i} N_\mathrm{A}}{\eta_{\mathrm{shell}i} m_i} \left(1 - \frac{\lambda_{\mathrm{shell}i} N_\mathrm{p}}{\lambda_{\mathrm{shell}i} N_\mathrm{p} + \left(k_\mathrm{pii} P_i^\mathrm{w} + k_\mathrm{pji} P_j^\mathrm{w}\right)[i]_\mathrm{w} + 2k_\mathrm{tw}[R]_\mathrm{w}}\right) \tag{22}$$

Where $k_{\mathrm{p}ji}$ and $k_{\mathrm{p}ji}$ are the propagation rate kinetic constants for homopolymerization and copolymerization of AEMH and styrene; $[i]_\mathrm{w}$ is the concentration of monomer i in the aqueous phase, and m_i is the partition coefficient of i radicals in the shell [13].

$$\gamma_{\mathrm{shell}i} = \frac{\left(k_{\mathrm{f}ii} P_i^\mathrm{shell} + k_{\mathrm{f}ji} P_j^\mathrm{shell}\right)[i]_\mathrm{p}}{v_\mathrm{p} N_\mathrm{A} D_\mathrm{p}} \tag{23}$$

Where, $k_{\mathrm{f}ij}$ are the chain transfer kinetic constants of i radicals to j monomer. In Eq. (22), there are two more parameters, defined as follows:

$$\eta_{\mathrm{shell}i} = \frac{\left(k_{\mathrm{p}ii} P_i^\mathrm{shell} + k_{\mathrm{p}ji} P_j^\mathrm{shell}\right)[i]_\mathrm{p}}{D_\mathrm{p}} \tag{24}$$

$$\lambda_{\mathrm{shell}i} = \frac{4\pi D_\mathrm{w} r_\mathrm{pcore}}{1 + \frac{D_\mathrm{w}}{D_\mathrm{h}} + \frac{D_\mathrm{w}}{D_\mathrm{p} m_i} \frac{1}{r_\mathrm{pcore}\sqrt{\eta_{\mathrm{shell}i}}\, \coth\left(r_\mathrm{pcore}\sqrt{\eta_{\mathrm{shell}i}}\right) - 1}} \tag{25}$$

3.5. Gel effect inside latex particles

The decrease in termination rate constant with increasing polymer fraction is one of the major factors influencing polymerization kinetics (gel effect) [14]. The termination rate constant in the particle is obtained from the termination kinetic constant modified by a gel effect parameter (g^2):

$$k_\mathrm{tp} = k_\mathrm{tSS} g^2 \tag{26}$$

where k_tp is the termination rate constant in the particle; k_tSS is the termination kinetic constant for styrene homopolymerization; and g^2 is the gel effect parameter.

The empirical correlation proposed by Friis and Hamielec [15] for styrene polymerization at 70 °C did not fit well our experimental data. Gilbert [16] stated that the termination constant found for one system or conversion cannot generally be used in analyzing the kinetic of another. Therefore, in this work the experimental relationship between gel effect and conversion used for styrene is:

$$g^2 = \exp\left[-BX_\mathrm{p}\right] \tag{27}$$

where B is an adjustable parameter and X_p is the conversion in the particle.

3.6. Monomer partitioning

In order to calculate the monomer concentrations in the different phases, it was assumed that:

(i) Monomer partitioning was given by thermodynamic equilibrium.
(ii) The concentrations of the monomers in the polymer particles were homogeneous throughout the particle radius.
(iii) There were no monomer droplets in the reactor because semicontinuous emulsion polymerizations under starved conditions were carried out.

The concentrations of the monomers in aqueous phase and polymer particles can be calculated by solving the following equations:

$$K_\mathrm{wp}^i = \frac{V_i^\mathrm{p}/V_\mathrm{p}}{V_i^\mathrm{w}/V_\mathrm{w}}; \quad i = S, A \tag{28}$$

$$V_i = V_i^\mathrm{p} + V_i^\mathrm{w}; \quad i = S, A \tag{29}$$

$$V_\mathrm{w} = W + V_\mathrm{S}^\mathrm{w} + V_\mathrm{A}^\mathrm{w} \tag{30}$$

$$V_\mathrm{p} = V_\mathrm{pol} + V_\mathrm{S}^\mathrm{p} + V_\mathrm{A}^\mathrm{p} \tag{31}$$

Where K_wp^i is the particle/aqueous-phase partition coefficient for monomer i, V_i^j is the volume of monomer i in phase j, V_w and V_p are the volumes of aqueous phase and polymer particles, respectively, W is the volume of water, and V_pol is the volume of polymer.

3.7. Surface charge density

The mathematical model presented in this work assumed that the total surface charge density is given by the sum of the surface amidine groups provided by the cationic initiator and the amino groups provided by the cationic monomer.

$$\sigma_\mathrm{TOTAL} = \sigma_\mathrm{AMIDINE} + \sigma_\mathrm{AMINO} \tag{32}$$

$$\sigma_{\mathrm{AMIDINE}} = \sigma_0 + \frac{F\mathrm{mol}_{\mathrm{AMIDINE}}}{A_{\mathrm{p}}} \tag{33}$$

$$\sigma_{\mathrm{AMINO}} = \frac{F\mathrm{mol}_{\mathrm{AMINO}}}{A_{\mathrm{p}}} \tag{34}$$

where F is Faraday's constant; σ_0 is the surface charge density provided by the surface amidine groups on the seed particles; $\mathrm{mol}_{\mathrm{AMIDINE}}$ and $\mathrm{mol}_{\mathrm{AMINO}}$ are the amounts of amidine and amino groups on the surface of polymer particles, and A_{p} is the total surface area of the latex particles.

In Eqs. (33) and (34), the values of $\mathrm{mol}_{\mathrm{AMIDINE}}$ and $\mathrm{mol}_{\mathrm{AMINO}}$ were determined as follows:

$$\mathrm{mol}_{\mathrm{AMIDINE}} = \Phi^{\mathrm{SURFACE}}_{\mathrm{AMIDINE}}[2f(I_0 + F_I - I)] \tag{35}$$

where I_0 is the initial amount of initiator in the reactor, and $\Phi^{\mathrm{SURFACE}}_{\mathrm{AMIDINE}}$ is the ratio between the amidine surface groups and the total amidine groups in particles. The total amidine groups in the particles are not only located on the particle surface, they are also buried inside the polymer particles. In order to quantify the amidine groups on the surface, an experimental relationship between $\Phi^{\mathrm{SURFACE}}_{\mathrm{AMIDINE}}$ and the ratio AEMH/styrene feed was found. This relationship will be shown later.

$$\mathrm{mol}_{\mathrm{AMINO}} = \Phi^{\mathrm{SHELL}}_{\mathrm{AMINO}}[F_{\mathrm{A}} - A] \tag{36}$$

$$\Phi^{\mathrm{SHELL}}_{\mathrm{AMINO}} = \frac{A_{\mathrm{PARTICLES}}}{A_{\mathrm{PARTICLES}} + A_{\mathrm{WATER}}} \tag{37}$$

Where $\Phi^{\mathrm{PARTICLE}}_{\mathrm{AMINO}}$ is the fraction of cationic monomer polymerized in the outer shell, and $A_{\mathrm{PARTICLES}}$ and A_{WATER} are the quantities of cationic monomer reacted in the outer shell and in the aqueous phase, respectively. The mass balance for AEMH is given by the following equations:

$$\frac{\mathrm{d}A_{\mathrm{PARTICLES}}}{\mathrm{d}t} = -\left(k_{\mathrm{pSA}}P^{\mathrm{shell}}_{\mathrm{S}} + k_{\mathrm{pAA}}P^{\mathrm{shell}}_{\mathrm{A}}\right)[\bar{R}]_{\mathrm{shell}}V_{\mathrm{shell}}[A]_{\mathrm{p}}\frac{N_{\mathrm{p}}}{N_{\mathrm{A}}} \tag{38}$$

$$\frac{\mathrm{d}A_{\mathrm{WATER}}}{\mathrm{d}t} = -k_{\mathrm{pAA}}[R]_{\mathrm{w}}V_{\mathrm{w}}[A]_{\mathrm{w}} \tag{39}$$

Table 1
Non-adjustable parameters values

$k_{\mathrm{pSS}} = 4.77\times10^5$ cm^3 mol^{-1} s^{-1}
$k_{\mathrm{tSS}} = 7.0\times10^{10}$ cm^3 mol^{-1} s^{-1}
$k_{\mathrm{fSS}} = 46$ cm^3 mol^{-1} s^{-1}
$k_{\mathrm{I}} = 6.67\times10^{-4}$ s^{-1}
$f = 0.65$
$K^{\mathrm{S}}_{\mathrm{wp}} = 1629$
$D_{\mathrm{p}} = 2\times10^{-6}$ cm^2 s^{-1}
$D_{\mathrm{h}} = 10^{-5}$ cm^2 s^{-1}
$D_{\mathrm{w}} = 2\times10^{-5}$ cm^2 s^{-1}
$m_{\mathrm{S}} = 70$
$k_{\mathrm{fAA}} = 11100$ cm^3 mol^{-1} s^{-1}
$K^{\mathrm{A}}_{\mathrm{wp}} = 0.91$

Table 2
Adjustable parameters values

B = 8.41
$k_{\mathrm{pAA}} = 2.78\times10^6$ cm^3 mol^{-1} s^{-1}
$r_{\mathrm{SA}} = 2.31$
$r_{\mathrm{AS}} = 6.84$
$k_{\mathrm{tAA}} = 1.45\times10^{11}$ cm^3 mol^{-1} s^{-1}
$m_{\mathrm{A}} = 29$
$b/a = 2.30$

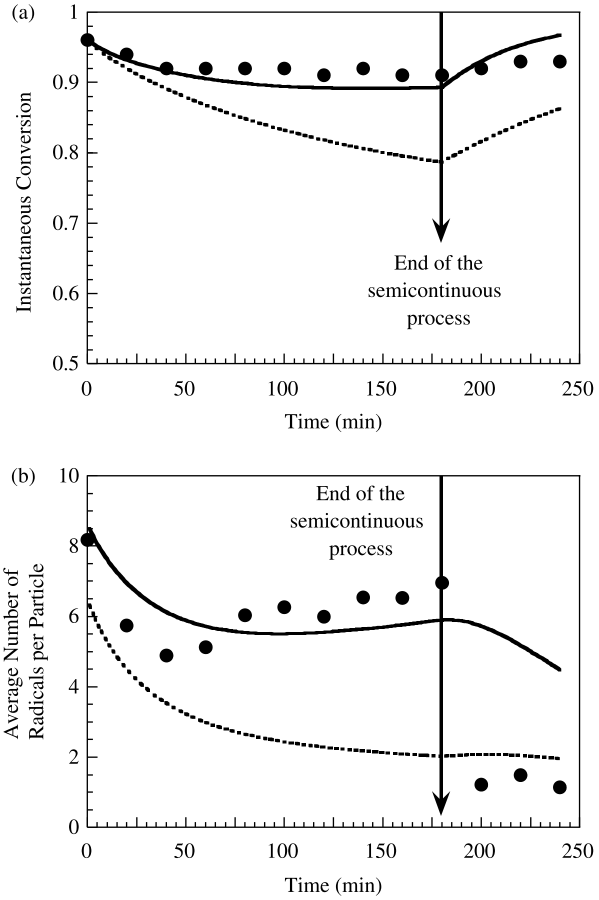

Fig. 1. Instantaneous conversions (a) and average number of radicals per particle (b) for the semicontinuous seeded cationic emulsion homopolymerization of styrene. (●) Experimental data in reaction AE0, (– – –) prediction using the expression for the gel effect proposed by Friis et al. [15] and (—) prediction using a new expression with the adjustable parameter $B = 8.41$.

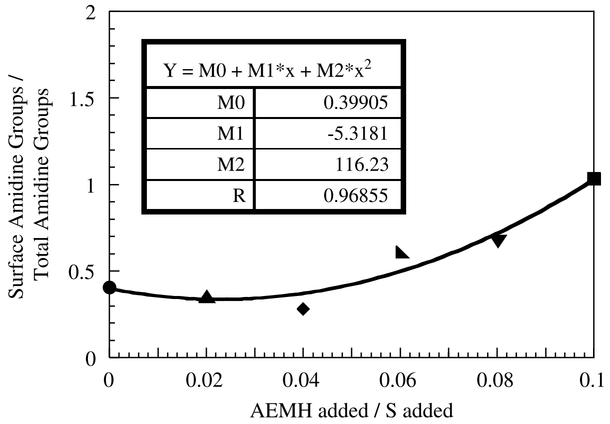

Fig. 2. (Surface/total) $_{\mathrm{amidinegroups}}$ ratio ($\Phi^{\mathrm{SURFACE}}_{\mathrm{AMIDINE}}$) versus (AEMH/S) fed ratio for reactions (●) AE0, (▲) AE2, (◆) AE4, (◣) AE6, (▼) AE8 and (■) AE10.

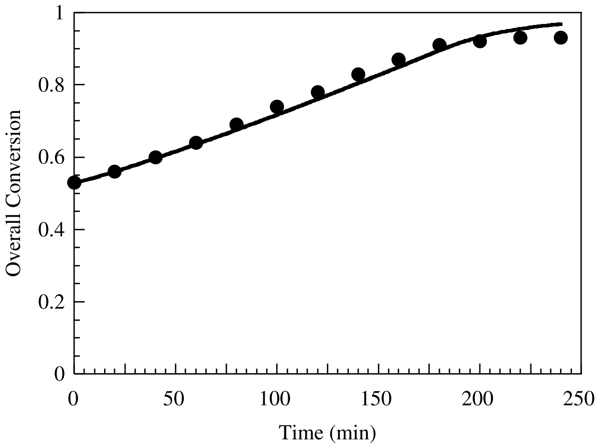

Fig. 3. Overall conversion for the semicontinuous seeded cationic emulsion homopolymerization of styrene in reaction AE0. (●) experimental data and (—) model prediction.

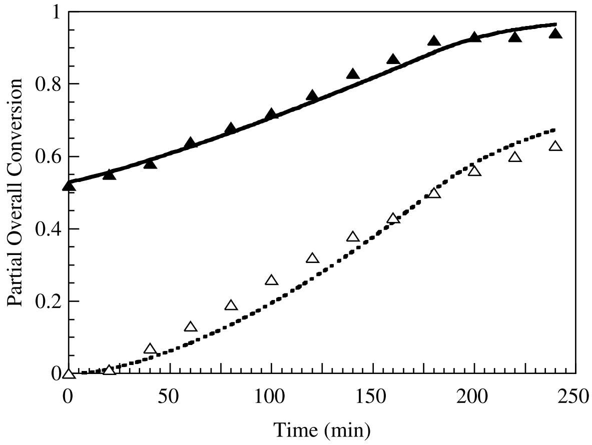

Fig. 4. Partial overall conversions for the semicontinuous seeded cationic emulsion copolymerization of S and AEMH in reaction AE2. Styrene data: (▲) experimental and (—) model prediction. AEMH data: (△) experimental and (– – – –) model prediction.

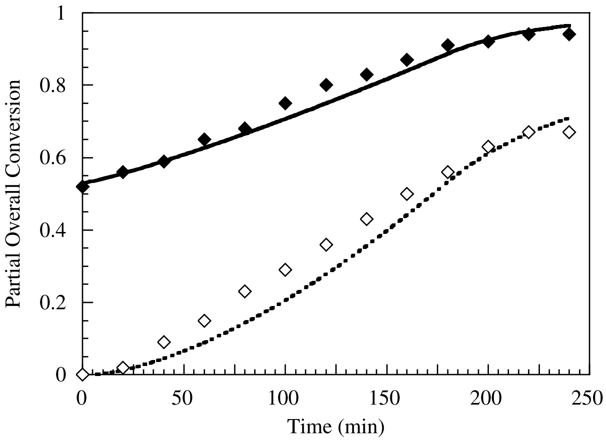

Fig. 5. Partial overall conversions for the semicontinuous seeded cationic emulsion copolymerization of S and AEMH in reaction AE4. Styrene data: (◆) experimental and (—) model prediction. AEMH data: (◇) experimental and (– – – –) model prediction.

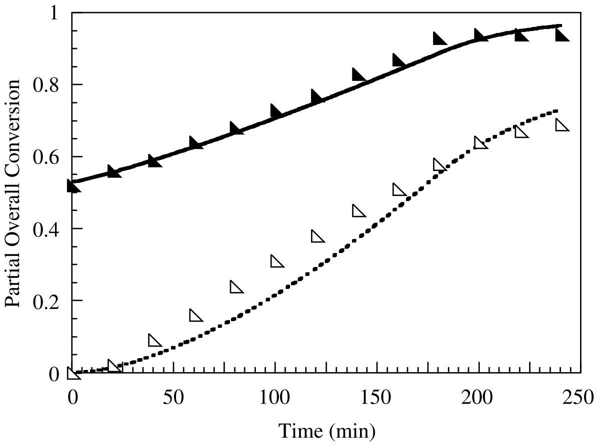

Fig. 6. Partial overall conversions for the semicontinuous seeded cationic emulsion copolymerization of S and AEMH in reaction AE6. Styrene data: (◣) experimental and (—) model prediction. AEMH data: (◺) experimental and (– – – –) model prediction.

All the parameters appearing in these two equations were described in Eq. (6).

3.8. Model parameters

In the mathematical model described above, the values of several parameters and physicochemical constants are required. The parameters considered as non-adjustable are shown in Table 1. These values were obtained from the literature or from experimental results. The propagation and termination constants (k_{pSS} and k_{tSS}) and the partition coefficient ($K_{\mathrm{wp}}^{\mathrm{S}}$) for styrene were taken from Mendoza et al. [12]. The chain transfer constants for styrene and AEMH (k_{fSS} and k_{fAA}) were taken from Ganachaud et al. [17]. The diffusion rate coefficient in the polymer particles, hairy layer, and aqueous phase (D_{p}, D_{h} and D_{w}) and the partition coefficient of styrene radical" in the shell (m_{S}) were taken from Asua [13]. The rate coefficient for initiator decomposition (k_{I}) was taken from Wako Chemical GmbH [18]. Finally, the efficiency factor

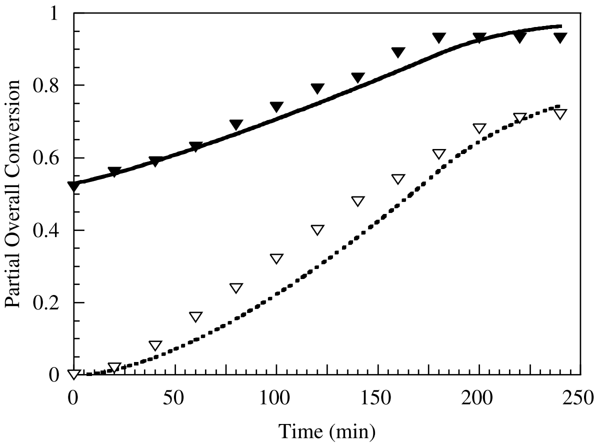

Fig. 7. Partial overall conversions for the semicontinuous seeded cationic emulsion copolymerization of S and AEMH in reaction AE8. Styrene data: (▼) experimental and (—) model prediction. AEMH data: (▽) experimental and (– – – –) model prediction.

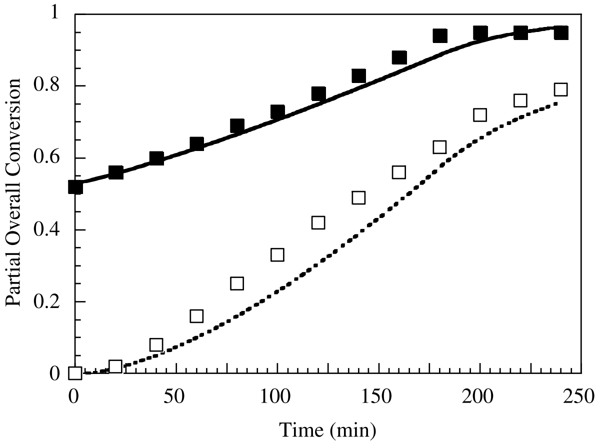

Fig. 8. Partial overall conversions for the semicontinuous seeded cationic emulsion copolymerization of S and AEMH in reaction AE10. Styrene data: (■) experimental and (—) model prediction. AEMH data: (□) experimental and (– – – –) model prediction.

of the cationic initiator (f) and the particle/aqueous-phase partition coefficient for the cationic monomer AEMH (K_{wp}^{A}) were calculated as in a previous article [3].

The adjustable parameters used in this model are shown in Table 2. The estimation of these parameters was carried out using the method proposed by Nelder and Mead [19] by minimizing the residual sum of squares between the experimental data and model predictions for the partial overall conversions.

4. Results and discussions

The reactions used in this work were carried out by means of a semicontinuous seeded cationic emulsion polymerization under starved conditions for styrene, the main monomer used [3]. Monomer-starved conditions are generally defined as the conditions under which the instantaneous conversion is greater than 90% [20]. This means that the concentration of polymer in latex particles is much higher than the monomer concentration, causing a diffusion-controlled termination process. In Fig. 1, the solids dots show the experimental instantaneous conversion (a) and the average number of radicals per particle (b) for the semicontinuous seeded cationic emulsion polymerization of styrene in reaction AE0 (this reaction is a homopolymerization of styrene). The first approach in our model was the introduction of the general expression for the gel effect proposed by Friis et al. [15] at 70 °C. As can be seen, this expression (discontinuous line) did not fit the experimental data obtained in reaction AE0 well. The experimental conversions and the average number of radicals per particle ($\bar{n}$) were higher than the values predicted by the simulation curves, indicating that the termination constant (k_t) calculated from their values was greater than the k_t observed under our experimental conditions. In order to improve the model predictions, the experimental relationship between the gel effect and instantaneous conversion shown in Eq. (27) was used. In this equation, the adjustable parameter B is 8.41, and the predictions for instantaneous conversion and $\tilde{n}$ are shown in Fig. 1 by the solid line.

Table 3
Predicted values for the thickness of the outer shell (δ) in the different polymerizations

Reaction	Ratio (AEMH/S)(%)	δ (nm)
AE0	0	0
AE2	2	1.7
AE4	4	1.9
AE6	6	2.2
AE8	8	2.5
AE10	10	2.8

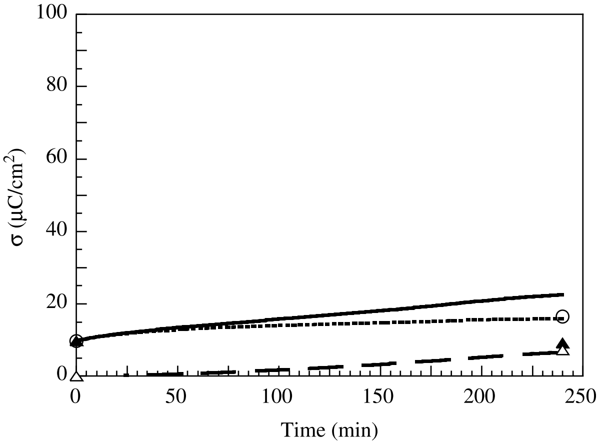

Fig. 9. Surface charge densities for reaction AE2: σ_{TOTAL} (○) experimental and (—) model prediction, $\sigma_{\mathrm{AMIDINE}}$ (▲) experimental and (– – – –) model prediction, and σ_{AMINO} (△) experimental and (– –) model prediction.

Although the amount of cationic initiator added was the same in all reactions, it was observed and reported [3] that the amount of amidine groups on the particle surface was higher when the amount of cationic monomer (AEMH) fed increased. This implies that the functional monomer (AEMH) has some effect on the number of amidine groups provided by the cationic initiator. In Fig. 2, the ratio between the amidine

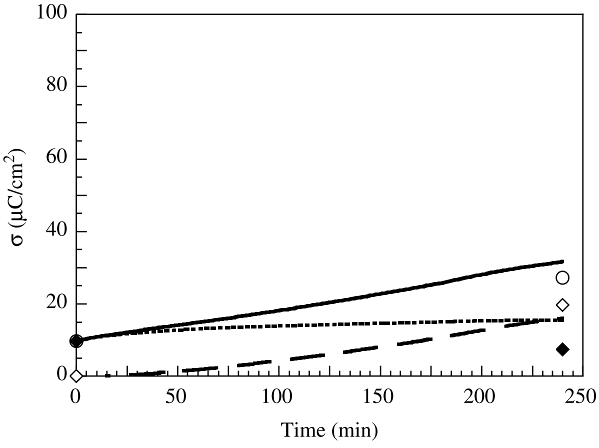

Fig. 10. Surface charge densities for reaction AE4: σ_{TOTAL} (○) experimental and (—) model prediction, $\sigma_{\mathrm{AMIDINE}}$ (◆) experimental and (– – – –) model prediction, and σ_{AMINO} (◇) experimental and (– –) model prediction.

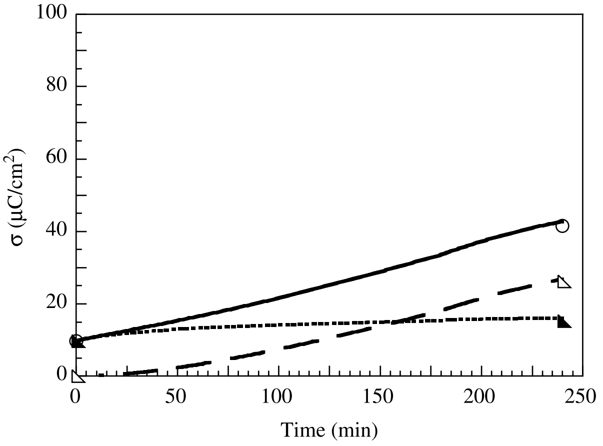

Fig. 11. Surface charge densities for reaction AE6: σ_{TOTAL} (○) experimental and (—) model prediction, σ_{AMIDINE} (◣) experimental and (– – – –) model prediction, and σ_{AMINO} (◇) experimental and (– –) model prediction.

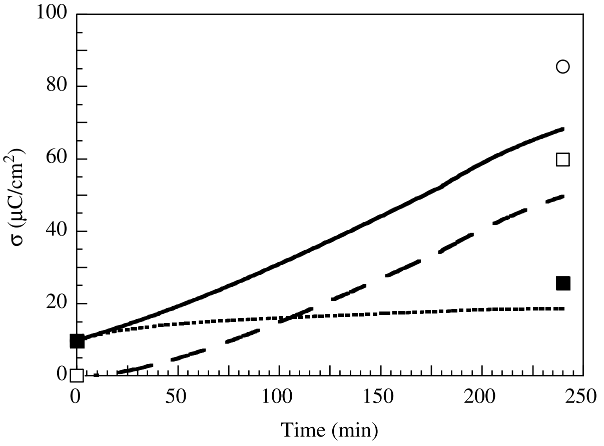

Fig. 13. Surface charge densities for reaction AE10: σ_{TOTAL} (○) experimental and (—) model prediction, σ_{AMIDINE} (■) experimental and (– – – –) model prediction, and σ_{AMINO} (□) experimental and (– –) model prediction.

groups on the particle surface to the total amidine groups in particles ($\Phi^{\text{SURFACE}}_{\text{AMIDINE}}$), versus the ratio (AEMH/S) fed for the different polymerizations carried out is shown. The data for the different reactions can be fitted by a quadratic equation with $M_0 = 0.39905$, $M_1 = -5.3181$ and $M_3 = 116.23$. This equation was employed in the mathematic model in order to predict the surface charge density due to the amidine groups.

In order to validate the mathematical model, experimental data from reactions carried out by means of a semicontinuous seeded cationic polymerization varying the amount of cationic monomer (AEMH) fed were used. In Figs. 3–8, the experimental and theoretical evolutions of the partial overall conversions for the different polymerizations carried out are shown. As can be seen, the model predicts the experimental data for both monomers quite well in all reactions. In the case of styrene, the evolutions of its partial overall conversion predicted by the model are insensitive to the increasing amount of AEMH fed. These results agree with previously reported experimental data [3]. However, in the case of AEMH, the evolutions of its partial overall conversion are affected by the amount of cationic monomer added. The model predicts an increase in the overall conversion for the cationic monomer when the amount of AEMH fed increased in the reaction. Furthermore, our model predicts a limiting conversion for AEMH in all reactions due to chain transfer reactions [3]. Pichot et al. [17] found a strong chain transferring activity of the non-protected AEMH form (AEM), even if there is a small amount of AEM in the system (pH 3). As can be seen in Table 1, the transfer rate constant to AEMH monomer is 250 times higher than that of styrene. The radical chain transfer to AEM occurs in the aqueous phase and on the particle surface (outer shell), because the cationic monomer is hydrophilic.

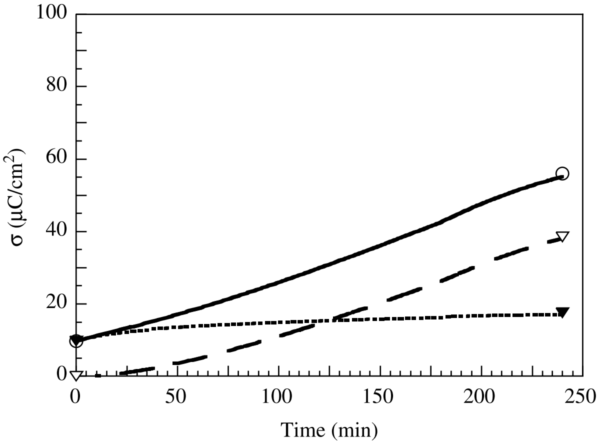

Fig. 12. Surface charge densities for reaction AE8: σ_{TOTAL} (○) experimental and (—) model prediction, σ_{AMIDINE} (▼) experimental and (– – – –) model prediction, and σ_{AMINO} (▽) experimental and (– –) model prediction.

In Table 3, the predictions for the thickness of the outer shell (δ) for the different polymerization reactions carried out are shown. This δ value increased when the amount of AEMH fed increased, which means that on increasing the cationic monomer concentration, the copolymerization extent in the outer shell is higher. However, the thickness of the outer shell is much smaller than the diameter of the particles. This implies that most of the styrene homopolymerizes in the core and only a small amount copolymerizes in the outer shell. Therefore, in our model, the styrene conversion is not affected by the transfer reactions to AEMH, but the polymerization in the water phase and on the particle surface (outer shell) are.

Furthermore, the model presented can predict some colloidal features of the semicontinuous seeded cationic emulsion copolymerization of styrene and AEMH. From Figs. 9–13, the total surface charge density (σ_{TOTAL}) and the partial ones provided by the cationic initiator (σ_{AMIDINE}) and the cationic monomer (σ_{AMINO}) are shown for the different reactions carried out. The model predictions fit the experimental data for all reactions very well, especially in the case of σ_{AMINO} provided by surface amino groups. Moreover, the model is sensitive to the amount of surface amidine groups with the increasing feed ratio of cationic monomer through the experimental relationship shown in Fig. 2. When the amount of AEMH fed increases, the surface amidine groups estimated by the model increase. Therefore, this model can predict the best conditions to obtain well-defined latexes with specific amounts of surface amino and amidine groups.

5. Conclusions

A mathematical model for a semicontionuous seeded cationic emulsion polymerization was developed. The model includes the most distinctive features of the copolymerization of a cationic hydrophilic monomer (AEMH) with a hydrophobic one (styrene), including polymerization of AEMH in the outer shell of polymer particles and in the aqueous phase, and the possibility of having radical concentration profiles in the polymer particles.

The model predicts the evolution of the fractional overall conversions, the thickness of the outer shell, the total surface charge density and the partial ones. Furthermore, the model can distinguish between the surface charge density provided by the cationic monomer from that given by the cationic initiator.

Acknowledgements

This work has been supported by the Spanish Programa Nacional de Materiales (MAT 2003-08356-CO4-02) and the Gobierno Vasco ETORTEK 2002-2004, under the project MAAB. J. Ramos acknowledges a grant from the Ministerio de Educación, Cultura y Deportes. The authors thank Dr P.D. Armitage for reviewing the manuscript.

References

[1] Ramos J, Martín-Molina A, Sanz-Izquierdo MP, Rus A, Borque L, Hidalgo-Álvarez R, et al. J Polym Sci, Polym Chem 2003;41:2404–11.
[2] Sanz-Izquierdo MP, Martín-Molina A, Ramos J, Rus A, Borque L, Forcada J, et al. J Immunol Methods 2004;287:159–67.
[3] Ramos J, Forcada J. J Polym Sci, Polym Chem 2005;43:3878–86.
[4] de la Cal JC, Asua JM. J Polym Sci, Polym Chem 2001;39:585–95.
[5] Chern CS, Poehlein GW. J Polym Sci, Polym Chem Ed 1987;25:617–35.
[6] de la Cal JC, Urzay R, Zamora A, Forcada J, Asua JM. J Polym Sci, Polym Chem Ed 1990;28:1011–31.
[7] Forcada J, Asua JM. J Polym Sci, Polym Chem Ed 1985;23:1955–62.
[8] Li BG, Brooks BW. J Polym Sci, Polym Chem 1993;31:2397–402.
[9] Asua JM, de la Cal JC. J Appl Polym Sci 1991;42:1869–77.
[10] Lopez de Arbina L, Barandiaran MJ, Gugliotta LM, Asua JM. Polymer 1996;37:5907–16.
[11] Ugelstad J, Hansen FK. Rubber Chem Technol 1976;49:536–609.
[12] Mendoza J, de la Cal JC, Asua JM. J Polym Sci, Polym Chem 2000;38:4490–505.
[13] Asua JM. Macromolecules 2003;36:6245–51.
[14] Marten FL, Hamielec AE. ACS Symp Ser 1979;104:43–90.
[15] Friis N, Hamielec AE. J Polym Sci, Polym Chem Ed 1973;11:3321–5.
[16] Gilbert RB. Emulsion polymerization. A mechanistic approach. London, UK: Academic Press; 1995.
[17] Ganachaud F, Sauzedde F, Elaissari A, Pichot C. J Appl Polym Sci 1997;65:2315–30.
[18] Azo Polymerization Initiators, Wako Chemical GmbH, Germany.
[19] Nelder JA, Mead R. Comput J 1964;7:308–13.
[20] Lovell PA. In: Lovell PA, El-Aasser MS, editors. Emulsion polymerization and emulsion polymers. New York: Wiley; 1997.