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Carboxylated styrene–butyl acrylate and styrene–butadiene emulsion copolymers. Modelling the distribution of the acid monomer between serum, particle surface and the particle core

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The concept of the critical chain length for radical entry Z was used for modelling the rate of carboxylation between the particle surface and particle core. An average Z value was computed by a semi-empirical method from the individual Z values for homopolymers. Grafted, buried and water soluble polymerized acid could be computed as well as the molecular weight of the grafted and water soluble species. The model was tested on two different systems involving either styrene/butadiene or styrene/butyl acrylate as the main monomers and acrylic acid as the carboxylated monomer; it gave a good approximation of the actual rate of grafting and molecular weight. In butadiene containing recipes, gel permeation chromatography (g.p.c.) of the aqueous phase showed an unusual peak that might be assigned to the exit of butadiene radical followed by propagation and particle capture. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

Carboxylation of latex polymer particles is now commonly used in emulsion polymerization to improve overall properties of latex; it increases shear and freeze–thaw stability and brings desirable viscosity profiles vs. pH. It also has a positive effect on the polymer adhesion towards substrates like metals, clays, calcium carbonate or fibres. Given the industrial importance of the carboxylated latex, a large number of studies have been reported since the 1970s to characterize polymer emulsions obtained by copolymerization of a water insoluble monomer like styrene or butyl acrylate with a water soluble carboxylic monomer such as acrylic or methacrylic acid[1,9]. Most of these studies investigate the rates of incorporation of the acid in the serum, particle surface and polymer phase using dialysis, ion-exchange resin treatment, serum replacement technique or ultra centrifugation coupled with conductimetric titrations. Other water soluble functional monomers like N-methylol acrylamide[10], methyl acrylamidoglycolate methyl ether[11] and styrene sulfonate[12,13] were also examined in copolymerization with hydrophobic monomers. Recently some authors successfully described the individual rates of consumption of monomers using a kinetic scheme based on the monomer partition coefficient between water and polymer phase[10,11,14,15]. To our knowledge, however, no

quantitative treatment of the partitioning of the polymerized carboxylated monomers between the aqueous phase, the particle surface and particle core have been proposed so far. The present work deals with the modelling of the carboxylation of latex particles although the model is general and could be applied to any other functional water miscible monomer. This model is based mainly upon the critical oligomer size for particle entry Z, introduced, among others, by Hansen[16]. Very simple assumptions are made to relate the critical length for particle capture, Z, with the oligoradical composition. The weight average molecular weight of chains grafted on the polymer surface, $\bar{Z}$, and the weight average molecular weight of the chains terminated in the aqueous phase, $\bar{M}_{w_{aq}}$, are derived as well as the fraction of buried (particle core), grafted (particle surface) and water soluble acidic polymer fractions; it is exemplified with two different processes involving styrene/butyl acrylate and styrene/butadiene compositions. While the hypotheses we made were probably oversimplified, our main concern in this paper was to check the general trends encountered in emulsion polymerization in recipes with water soluble co-monomers.

EXPERIMENTAL

Materials

All monomers were supplied from Atochem (France) and used as received. Reagent grade ammonium persulfate (Prolabo, France) was used as initiator.

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Sodium dodecylsulfate (Sipon LCSV 95 Sidobre Sinnova, France) was used as surfactant. Deionized water was used in all experiments.

Emulsion polymerization

Synthesis were performed either on a 25 l high-pressure stainless-steel jacketed reactor (styrene–butadiene copolymer) or a 6 l glass vessel (styrene–butyl acrylate copolymer). Both reactors were temperature regulated, fitted with feed pumps and a sampling device. Emulsion polymerizations were performed on a semi-batch mode according to the recipes shown in *Table 1*. Once the set-up temperature was attained within the reactor, the initiator charge was introduced and the monomer feeding started at constant rate.

For each run aliquots of about 5 g were withdrawn from the reaction medium every 30 min or 60 min, quenched with hydroquinone and kept at low temperature. The sample was diluted in THF and analysed by h.p.l.c. for the residual monomers (conditions: Column C18 Spheri RP18; eluent, THF/water 65/35 in volume with addition of $4 g l^{-1}$ of concentrated sulfuric acid; detection, u.v. 254 and 280 nm).

Acid titration

The latexes were cleaned by the serum replacement technique: a 350 ml microfiltration cell (Amicon[®]) fitted with a membrane of 0.1 μm pore diameter (Nucleopore[®]) was filled with the latex diluted at 2% (w/w). The cell was then permeated by (a) deionized water, (b) diluted chlorhydric acid (10^{-2} mol l^{-1}), (c) deionized water. The deionized water was Super Q Millipore[®] grade. The rate of serum replacement was monitored by on-line measurement of the permeate conductivity; the serum replacement was deemed to be complete when permeate conductivity was lower than 0.2 μS cm^{-1}. An aliquot of the cleaned latex was titrated conductometrically using NaOH 2×10^{-2} mol l^{-1}. The weak acid portion of the titration curve was attributed to the carboxylic groups located at the particle surface. Another aliquot of the cleaned latex was then titrated using a non-aqueous potentiometric method (solvent: benzylic alcohol/ethanol, 70/30 in volume; titrant: tetrabutyl ammonium hydroxide 10^{-1} mol l^{-1}): this gave the sum of the surface COOH groups and the buried COOH groups; a mass balance gave the acid polymerized in the water phase.

In order to discriminate between physically adsorbed carboxylated oligomers and covalently anchored carboxylated chains, an additional 'washing' was performed with diluted ammonia (10^{-3} mol l^{-1}).

G.p.c. measurement of water soluble oligomers

Serum samples obtained during the cleaning procedure were analysed by g.p.c. (conditions: Columns TSK Gel G5000, G4000, $2 \times$ G3000; eluent, NaCl 3×10^{-1} mol l^{-1}; pH 7; flow rate, 1 ml min^{-1}; detection, RI). Molecular weight was expressed in POE equivalent.

Partition coefficients of acrylic acid

The determination of the partition coefficient of acrylic acid was carried out as follows: to 100 g of water was added the prescribed amount of acrylic acid. After complete dissolution a given weight of styrene/butyle acrylate (50/50 by weight) mixture was introduced and stirred overnight at room temperature. The aqueous and organic phases were decanted and the concentration of acrylic acid in each phase was measured by h.p.l.c.

MODEL DEVELOPMENT

Given the extraordinary number of possible events in emulsion polymerization, we have restricted our choice to the following assumptions:

(1) persulfate initiates polymerization in the aqueous phase giving rise to water soluble oligoradicals bearing a sulfate group at one end

The diffusion of the free radical to the particle surface is supposed to be so fast as not to be rate determining. The rate determining step for free radical capture by the seed latex particles is the aqueous phase propagation to a critical degree of polymerization Z. Of course the nature

Table 1 Details of recipe

	Ingredients	Styrene–butadiene recipe (parts per weight)	Styrene–acrylate recipe (parts per weight)
Initial charge	Styrene	6	2
	Butadiene	3.8	
	Butyl acrylate	–	2
	Acrylic acid	2	0.4
	SLS	0.5	0.2
	$K_2S_2O_8$	0.6	0.1
	NaHCO$_3$	0.3	–
	Water	100	85
Continuous feed	Styrene	54	47
	Butadiene	34.2	
	Butyl acrylate	–	47
	Acrylic acid	–	4.8
	$K_2S_2O_8$	–	0.3
	Water	–	15
Temperature (°C)		75	80
Feeding Time (h)		6	5

of the end group is essential in the model since it affects the hydrophilic/hydrophobic balance of the macro-radical. For the sake of simplicity it is assumed that the only possible end group derives from the initiating species SO_4^-. On this principle the chemical nature of the end group, whether it is a sulfate, an hydroxyl, etc., governs the critical length for entry. Each of these terminating entities generates a unique Z value depending on its hydrophilic character (ionicity, water solubility). Side-reactions in the aqueous thermolysis of persulfate give rise to hydroxyl radicals which were not considered in this kinetic scheme.

(2) The oligoradicals of critical length Z will be captured by particles and will continue to propagate within the monomer-swollen polymer particle

(3) The instantaneous composition is unique for the oligoradical population

This certainly is an oversimplifying assumption since in radical polymerization the bivariate distribution function leads to substantial broadening effects for chains of finite lengths. This will be discussed later in the model development.

(4) Oligoradicals can terminate in the aqueous phase by radical coupling

Polymerization in the aqueous phase

Let us first consider a binary monomer mixture of a sparingly water soluble monomer (e.g. styrene) and a totally water miscible monomer (e.g. acrylic acid). Using pseudo-kinetic coefficient of transfer, termination and propagation reaction $k_{tr,aq}$, $k_{t,aq}$, $k_{p,aq}$, instead of the individual kinetic coefficients makes it possible to treat a system with N monomers as a homopolymerization[17]; thus the rate of polymerization in the aqueous phase becomes

$$\frac{d[P_{aq}]}{dt} = k_{p,aq}[M_{aq}][R_{aq}^{\cdot}] \tag{1}$$

The rate of radical entry is given by

$$\rho = \frac{N_A}{N_c} k_{p,aq}[M_{aq}][R_{aq,z-1}^{\cdot}] \tag{2}$$

The estimation of Z will be addressed later. The total radical concentration in the aqueous phase is given by

$$2k_d[I] = k_{t,aq}[R_{aq}^{\cdot}]^2 + k_{p,aq}[M_{aq}][R_{aq,z-1}^{\cdot}] \tag{3}$$

$[R_{aq,z-1}^{\cdot}]$ is the concentration of oligoradicals of length $z-1$, obtained through the 'most probable distribution' function

$$2k_d[I] = k_{t,aq}[R_{aq}^{\cdot}]^2 + k_{p,aq}[M_{aq}][R_{aq}^{\cdot}](1-p)p^{z-2} \tag{4}$$

p is the probability for propagation of a macroradical

$$p = \frac{k_{p,aq}[M_{aq}]}{k_{p,aq}[M_{aq}] + k_{t,aq}[R_{aq}^{\cdot}]} \tag{5}$$

Equations (4) and (5) are solved numerically for $[R_{aq}^{\cdot}]$.

Computation of the serum, particle surface and particle core partitioning

It is assumed in the following that:

(a) the 'buried' acrylic acid corresponds to the acid copolymerized within the polymer particle;

(b) the 'surface' acid, or 'grafted acid', stems from the highly carboxylated oligoradical formed in the aqueous phase, captured by the particle;

(c) the entry event is irreversible;

(d) the 'water soluble' acid comes from the termination by coupling of the carboxylated oligoradical formed in the aqueous phase

In other words it implies that the grafted carboxylated oligoradicals stay at the water/polymer interface during reaction: no migration is taking place towards the aqueous phase (oligomer desorption) or towards the interior of the particle due to particle growth mechanism. It infers also that the chains terminated in water remain soluble and do not adsorb irreversibly onto the particle surface.

Let us first quantify G, the fraction of the instantaneous water soluble polymer formed at time t which will be captured by the polymer particles: G equals the rate of formation of Z-mers to the total rate of water phase polymerization, or, stated otherwise as

$$G = \frac{[\text{rate of radical entry}]Z}{R_{P_{aq}}}$$

$$G = \frac{k_{p,aq}[M_{aq}][R_{aq,z-1}^0]Z}{k_{p,aq}[M_{aq}][R_{aq}^0]} = N(z-1)Z \tag{6}$$

where $N(z-1)$ represents the oligomer molar fraction of chain length $Z-1$:

$$N(z-1) = \frac{p(1-p)^{Z-2}}{N_{tot}} \quad \text{with} \quad N_{tot} = \sum_{i=1}^{Z-1} p(1-p)^{i-1} \tag{7}$$

The partitioning between water, surface and particle core of the carboxylated monomer unit (indiced k) is obtained by integration as

$$P_{aq}(k) = \frac{\int_{t_0}^{t}(1-G)R_{P_{aq}}(k)\,dt}{\int_{t_0}^{t}[R_{P_{aq}}(k) + R_{P_{part}}(k)]\,dt} \tag{8}$$

$$P_{surf}(k) = \frac{\int_{t_0}^{t} GR_{P_{aq}}(k)\,dt}{\int_{t_0}^{t}[R_{P_{aq}}(k) + R_{P_{part}}(k)]\,dt} \tag{9}$$

$$P_{part}(k) = 1 - P_{aq}(k) - P_{surf}(k)$$

where $R_{P_{aq}}(k)$ and $R_{P_{part}}(k)$ are the rate of consumption of the acid monomer k in the aqueous and polymer particle phase respectively.

The weight average length of the surface graft is obtained by integration as

$$\bar{Z} = \frac{\int_{t_0}^{t} ZGR_{P_{aq}}(k)\,dt}{\int_{t_0}^{t} GR_{P_{aq}}(k)\,dt} \tag{10}$$

$DP_{w_{aq}}$, the instantaneous weight average degree of polymerization of the water soluble chains, is computed from the distribution functions of oligoradicals of chain length $N(i)$, accounting for termination by coupling or radical transfer. Some difficulty arises from the fact that

summation is usually carried out over the whole population of radicals whereas in the present case only the oligoradicals of length $< Z$ have to be considered.

$$DP_{w_{aq}} = \sum_{i=1}^{Z} \frac{i^2}{1-G} \tau N(i) + \frac{i^2}{1-G} \beta \sum_{i=1}^{2Z}$$
$$\times \sum_{\substack{j=1 \ j<Z \\ |j-i|<Z}} N(i-j)N(j) \qquad (11)$$

with

$$\tau = \frac{k_{tr,aq}[S_{aq}]}{k_{p,aq}[M_{aq}]}, \qquad \beta = \frac{k_{t,aq}[R_{aq}^0]}{k_{p,aq}[M_{aq}]}$$

$[S_{aq}]$ is the total concentration of chain transfer agent in the aqueous phase.

Substituting $N(i)$ by equation (7) leads to

$$DP_{w_{aq}} = \sum_{i=1}^{z} \frac{i^2}{1-G} \tau \frac{p(1-p)^{i-1}}{N_{tot}} + \sum_{i=1}^{Z-1} \frac{i^3}{1-G} \frac{\beta}{2} \frac{p^2(1-p)^{i-2}}{N_{tot}^2}$$
$$+ \frac{i^2}{1-G} \frac{\beta}{2} \sum_{i=Z}^{2(Z-1)} \frac{(2Z-i+1)p^{i-2}}{N_{tot}^2} \qquad (12)$$

The accumulated weight average molecular weight of the water soluble polymer, as measured by g.p.c. for example, is given by

$$\bar{M}_{w_{aq}} = \frac{\int_{t_0}^{t} \bar{M}(1-G)DP_{w_{aq}}dt}{\int_{t_0}^{t} (1-G)R_{P_{aq}}dt} \qquad (13)$$

where $\bar{M}$ is the average molar mass of the monomer unit at time t.

Estimation of Z the critical length for capture

As one can imagine, the estimation of Z for a system of N monomers of different polarity and water solubility is not straightforward. Maxwell et al.[18] proposed the following expression for monomers with a very low water solubility:

$$Z = 1 + \text{int}\left[\frac{-23 \text{ kJ mol}^{-1}}{RT \ln[M_{aq,sat}]}\right] \qquad (14)$$

(the integer function int( ) rounds off the quantity in brackets to the lower integer value). Z varies from 2 for styrene up to 7–8 for vinyl acetate. Obviously this expression is not applicable to water soluble monomers such as acrylic acid or styrene sulfonate. Thus for water soluble monomer (i.e. those whose water solubility is greater than 1 mol l^{-1}) we adopt the same concept as Maxwell et al. by substituting $[M_{aq,sat}]$ by a pseudo water solubility, defined as λ, which will be adjusted to fit the experimental data.

For copolymers an empirical expression is proposed for Z, built up from the critical length $Z(i)$ of the corresponding homopolymer i, and the weight fraction $w(i)$ of monomer i in the instantaneous copolymer

$$\frac{1}{Z} = \sum_{i=1}^{N} \frac{w(i)}{Z(i)} \qquad (15)$$

As we will see in this paper, although this law is totally arbitrary, it turned out to be close enough to our set of experimental data. Of course this computed value of Z will be critical in the estimation of the molecular weights of grafted and water soluble species as well as for the computation of the acid fraction in serum, surface and core particle.

Interestingly while this work was underway, Wang et al.[19] published a study on the characterization of water-soluble oligomers in acrylic acid–styrene emulsion copolymerization, which gave an unexpected credit to our assumption: they were able to measure Z values by short stopping aqueous phase polymerization with hydroquinone and analysing the molecular weight of the oligomers bearing a sulfate group at one end and a quinone group at the other. The largest peak was assigned to Z. In *Figure 1* we plotted the Z values obtained in ref. 19 vs. copolymer composition; it appeared that the empirical law (15) was unable to fit these experimental data with $\lambda = 0.7 \text{ mol l}^{-1}$.

The bivariate distribution effect

The polymer having a finite length and the monomer addition process being statistical, there is a chain length distribution as well as a composition distribution for macromolecules formed during an infinitesimal conversion interval (bivariate distribution). While this broadening effect of the composition distribution is normally negligible for high molecular weight, it becomes very large for oligomers. In our case it generates a distribution function of Z: oligomers highly loaded in styrene units will have a Z value close to 2; on the other hand macroradicals enriched in acrylic acid units will propagate to much larger Z values. How will this bivariate distribution affect the average critical length and the acrylic acid grafting efficiency?

Stockmayer[22] addressed the problem of the bivariate distribution for a 2-monomers system and arrived at the well-known bivariate distribution function, $W(y, L)$ giving the weight fraction of chain length L with composition comprised between $F_1 + y$ and $F_1 + y + dy$; F_1 is the average composition of the instantaneous copolymer (i.e. for an infinite molecular weight)

$$W(y, L) = K \exp\left[\frac{-Ly^2}{2F_1(1-F_1)K'}\right] \qquad (16)$$

with

$$K = \exp\left(\frac{-L}{DP_n}\right) \frac{L}{DP_n^2} \left[\frac{L}{2\pi F_1(1-F_1)K'}\right]^{1/2}$$

$$K' = [1 - 4F_1(1-F_1)(1-r_1r_2)]^{1/2}$$

r_1 and r_2 are the reactivity ratios and DP_n the number average degree of polymerization of the oligoradicals.

Let us consider now a copolymerization between styrene and acrylic acid whose individual Z values have been assigned to 2 and 1000, respectively. The soluble fraction will be computed by a double integration over the composition and chain length distributions (wherever the bivariate distribution is used the subscript '_b' is
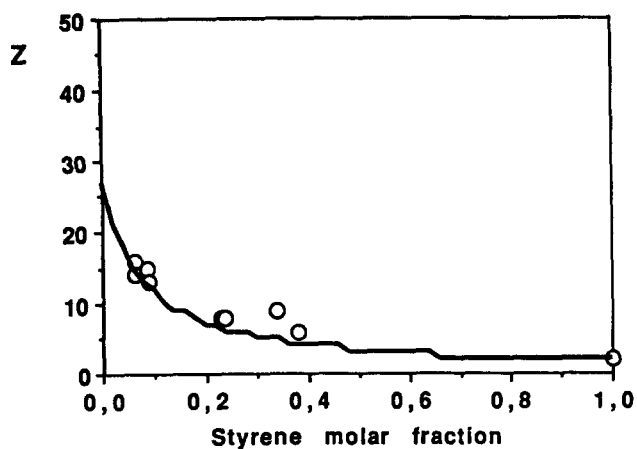
Figure 1 Critical chain length for radical entry Z (solid line: calculated, circles: experimental values reported by Wang *et al.*[19] vs. composition in a styrene/acrylic acid copolymer ($\lambda = 0.7\,\mathrm{mol\,l^{-1}}$)
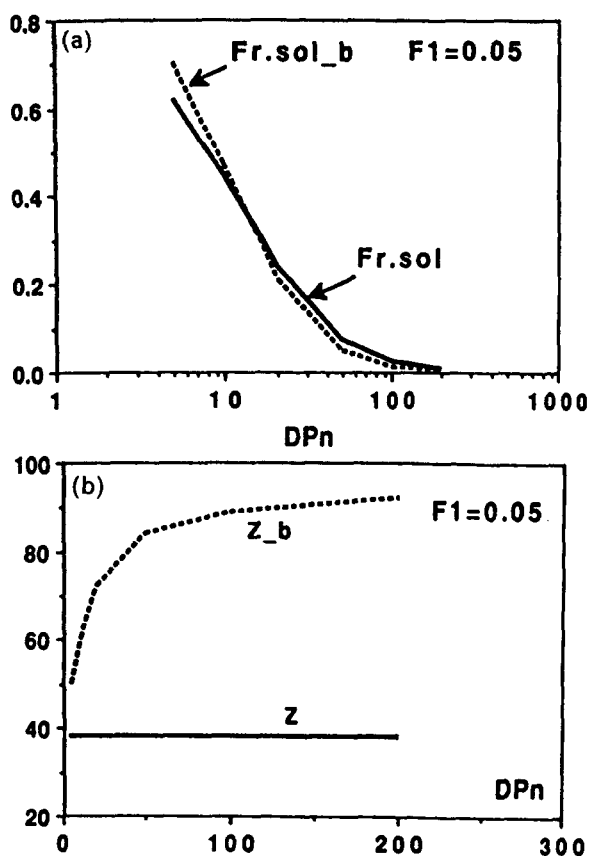

Figure 2 (a) Fraction of polymer terminated in the aqueous phase vs. the instantaneous number average chain length of the polymer formed in the aqueous phase. *Fr.sol*: assuming a unique composition for all the oligoradicals. *Fr.sol_b*: taking into account the bivariate distribution effect ($\lambda = 0.97\,\mathrm{mol\,l^{-1}}$). (b) Critical chain length for radical entry Z vs. the instantaneous number average chain length of the polymer formed in the aqueous phase. Z: assuming a unique composition for all the oligoradicals. Z_b: taking into account the bivariate distribution effect ($\lambda = 0.97\,\mathrm{mol\,l^{-1}}$)

added)

$$Fr.sol\_b = \int_{y=-F_1}^{y=1-F_1} \int_{L=1}^{Z=f(y)} W(y,L)\,\mathrm{d}y\,\mathrm{d}L \qquad (17)$$

If we do not take into account the bivariate distribution effect, the soluble fraction is obtained through a single

integration over the oligoradical chain length

$$Fr.sol = \int_{L=1}^{Z} W(L)\,\mathrm{d}L \qquad (18)$$

The weight average chain length of the captured radicals (or the surface grafted chains) is given by

$$Z\_b = \frac{1}{Fr.sol\_b} \int_{y=-F_1}^{y=1-F_1} \int_{L=1}^{Z=f(y)} W(y,L)Z\,\mathrm{d}y\,\mathrm{d}L \qquad (19)$$

We then evaluated the average Z value and the rate of water soluble polymer generated in the aqueous phase by using the bivariate distribution and compared it with our first model for a given monomer composition in the aqueous phase (styrene molar fraction, $F_1 = 0.05$ see *Figures 2a* and *b*): it shows that the partition between grafted/water soluble oligomers is very similar whether a unique Z value or a Z distribution function are used; however it concludes also that the critical length based upon the simple model is significantly lower than the averaged Z value computed from the bivariate distribution.

Unfortunately the bivariate distribution becomes untractable when we address more than two monomers. Therefore we kept to a simplified approach in the following discussion, bearing in mind that it does not change the rate of termination/radical entry but it does underestimate the molecular weight of both grafted chains and water soluble chains.

Initiator efficiency

The entry rate coefficient expressed in equation (2) reduces to

$$\rho = \frac{N_A}{N_C} R_i \left(\frac{L}{L+1}\right)^{Z-1} \qquad (20)$$

Therefore, we can deduce easily the capture efficiency f as

$$f = \left(\frac{L}{L+1}\right)^{Z-1} \qquad (21)$$

For hydrophobic monomers (i.e. Z close to 2) f is very close to 1 and aqueous phase termination is marginal. As the monomer becomes more and more hydrophilic (larger Z) the probability of termination in water increases especially when the kinetic length is low, corresponding to low monomer concentration, low propagation coefficient and high rate of initiation.

Partitioning of monomers between polymer phase and water

The distribution of monomers between the two phases is a first-order parameter to account for the individual rate of consumption of monomers. This model is based on the partition coefficients defined as $K_m = [M_{aq}]/[M_{part}]$. For water immiscible monomers K_m were measured from monomer–latex synthetic mixtures and found to be insensitive to polymer/water ratio[21]. For water-miscible monomers K_m were obtained experimentally from ternary mixtures styrene/butyl acrylate/acrylic acid assuming that the organic phase composed of the monomer mixture behaves the same as the copolymer with the same composition. K_m values are listed in *Table 2*; it can be seen that K_m varies not only

Table 2 Partition coefficients of acrylic acid between the aqueous and monomer (St/BuA 50/50 by weight) phases at room temperature

Water/monomer (v/v)[a]	K_m	AA[b] (%)	K_m
4.00	∞	1.0	5.4
2.33	12.3	2.5	4.8
1.50	3.5	5.0	4.4
1.00	2.8	7.0	3.8

[a] Ratio AA/(St + BuA) = 5 (wt%)
[b] Ratio AA/(St + BuA); water/monomer = 1.66 (v/v)

Table 3 Comparison of simulated data and experimental data on the distribution of carboxylic groups between particle surface and serum phase, and molecular weight of water soluble polymers

| Recipe	λ (mol l^{-1})	Surface (%)	Serum (%)	$\bar{M}_{w_{aq}}$ (g mol^{-1})
S/BuA/AA	0.6	33	12	500
	0.7	26	19	2700
	0.8	18	27	3200
	–	43[a]	17[a]	2500[a]
S/B/AA	0.99	22	40	2120
	0.90	27	34	1760
	0.80	34	28	443
	0.70	40	21	< 200
	–	38[a]	22[a]	4000[a]
	..	24[b]	36[b]	n.d.

[a] Experimentally found
[b] Idem (a) after extensive latex cleaning with NaOH 10^{-3} mol l^{-1}
S/BuA/AA: 47.75/47.75/4.5   S/B/AA: 6/38/2 (wt%)

with the acrylic acid concentration but increases dramatically with the water/organic phase ratio. These dependencies of K_m were implemented in the model. As it is known that carboxylated monomer reactivities changed with pH because of the different reactivity ratios, partition coefficient and propagation coefficient of the basic and acidic form, the pH in all experiments was kept in the range 2.5–3.

RESULTS AND DISCUSSION

In a semi-continuous process the recording of the instantaneous monomer concentration is much more sensitive than cumulative conversion to assess the reliability of a kinetic model. Monomer concentrations were plotted as functions of the total conversion in *Figure 3*: it indicates that styrene and butyl acrylate have reached a pseudo-stationary state after approx. 20% conversion. Free acrylic acid tends to accumulate up to 30% conversion whereafter it decreases slowly; this phenomenon is a result of the water to polymer ratio dependence of the partition ratio K_m of acrylic acid (see *Table 2*). As reaction proceeds, particle volume fraction increases together with K_m; since the polymerization rate is 3 to 4 orders of magnitude higher in the polymer particle the residual acrylic acid is consumed faster.

Different values of λ defined in equation (14) were tested in order to get a best fitting. Results are listed in *Table 3*: the best value for λ would lie somewhere around 0.6 which is coherent with what we found in *Figure 1* ($\lambda = 0.7$ mol l^{-1}). Experimentally the molecular weight of the water soluble fraction is found to be much larger than predicted. This finding, however, is in good agreement with our expectations: as stated in the previous section the averaged critical chain length for
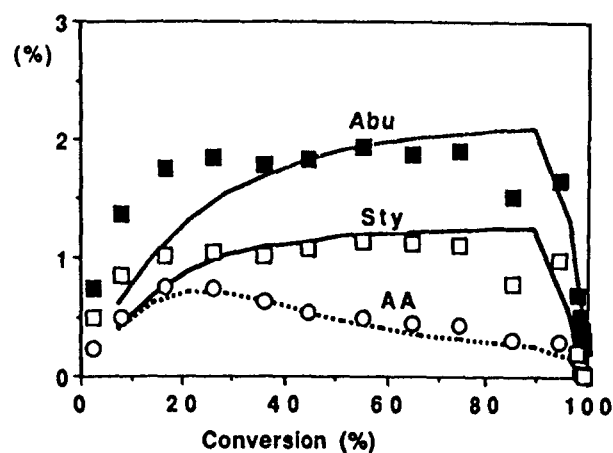
Figure 3 Residual monomer (weight percent of monomer referred to the latex) vs. conversion for the styrene/butyl acrylate/acrylic acid recipe. Comparison between experimental points and model (Sty: styrene. ABu: butyl acrylate. AA: acrylic acid)
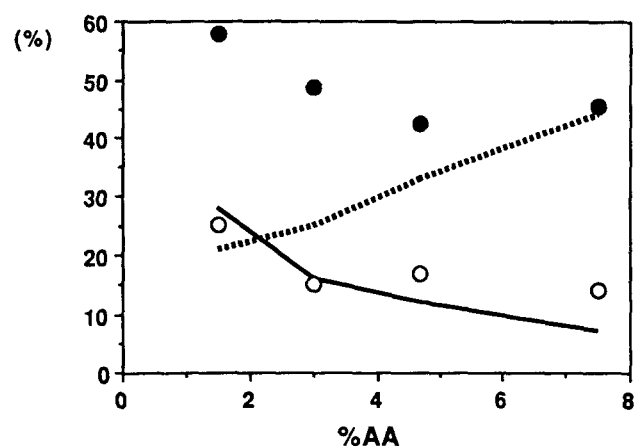
Figure 4 Distribution of the polymerized acrylic acid between the aqueous phase (open symbol: experimental, solid line: model) and the particle surface (filled symbol: experimental, dotted line: model)

radical energy is underestimated if we do not include the bivariate distribution effect in the model.

The effect of the acrylic acid charge in the recipe was studied and all other parameters kept equal; the program was run keeping the same set of adjustable parameters (k_t/k_p, $k_{t,aq}$, λ). *Figure 4* shows the fractions of carboxylated materials found at the particle surface and in the serum phase. While the soluble fraction is correctly predicted by the model, the grafted fraction found experimentally lie well above the model predictions. Consequently the 'buried' fraction measured experimentally dropped abruptly when the acrylic acid charge was lower than 3%. The ratio buried/(aq.sol.+ grafted) should only be affected by the K_m of acrylic acid during the reaction, which according to *Table 2* does not change that much with the acrylic acid level.

It is true that the K_m values obtained from organic monomer–water mixture partitioning experiments should not be extrapolated to the actual K_m associated with the copolymer particles. An accurate measurement of the partitioning of acid monomer between water and swollen copolymer particles would be necessary to conclude on this matter, but it would deserve a thorough investigation that goes beyond the scope of this work.
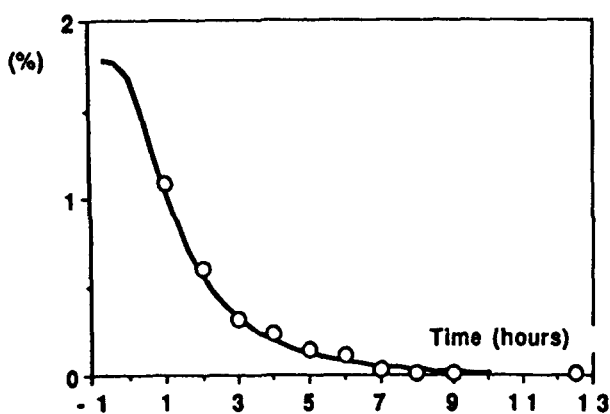
Figure 5 Residual acrylic acid (wt% of monomer referred to the latex) as a function of time for the styrene/butadiene/acryl acid recipe. Comparison between experimental points (open circles) and model
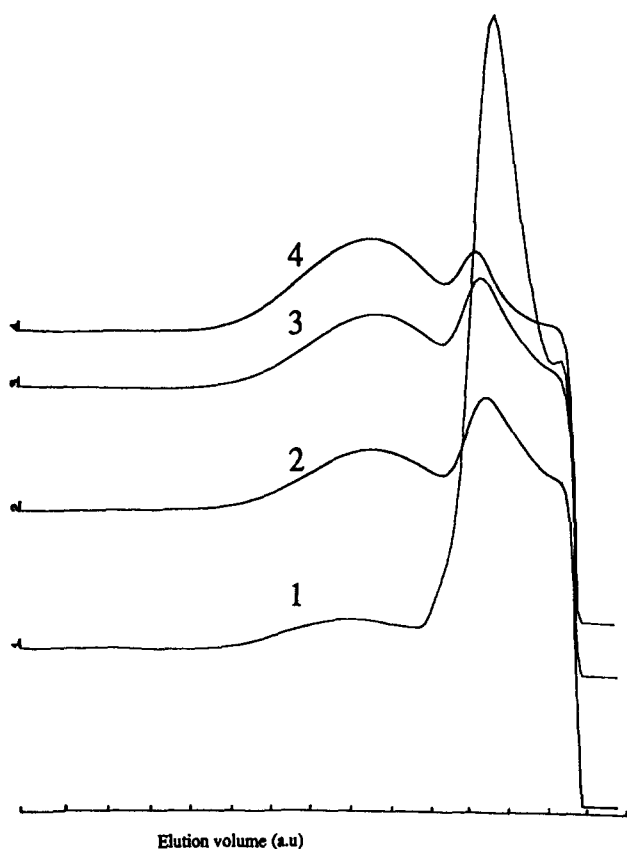

Figure 6 Serum analysis of the styrene/butadiene/acrylic acid latexes. G.p.c. traces (refractometric signal) recorded at different times: 1: 1 h, 2: 6 h, 3: 8 h, 4: 12 h

Styrene–butadiene–acrylic acid copolymers

The reaction process used in this instance is somewhat different from the styrene–butyl acrylate system: all the acrylic acid and a part of the styrene–butadiene mixture are fed in the initial charge. Unexpectedly the g.p.c. curves of the water soluble polymer exhibit a bimodal distribution shown in *Figure 6*, while in the case of styrene–butyl acrylate only unimodal elution curves were observed; let us first consider the peak centered at about 4000 g mol^{-1}; an interpretation of the second polymer population at $M_w = 1000$ g mol^{-1} will be given later in this section.

The rate of disappearance of residual acrylic acid, as can be seen in *Figure 5*, is well predicted by the model. *Table 3* shows some of the simulations run with different values of λ.

Apparently the model could not reconcile the acid distribution data with the molecular weight of the water soluble polymer. When λ was set to 0.7 mol l^{-1} to fit the experimental acid distribution, the computed $\bar{M}_{w_{aq}}$ corresponded to no more than a couple of monomer units, very far from the actual value (4000 g mol^{-1}). It was thought that the acid fraction found on the particle surface according to our titration procedure was probably overestimated; the latex was then washed extensively with diluted ammonia and titrated again. It turned out that more than one third of the 'grafted' acid oligomers were removed by this treatment; unfortunately g.p.c. could not be performed on those desorbed species because of their very low concentration in the washing serum. The new figures of the acid distribution were then much closer to the predicted value, even if the computed $\bar{M}_{w_{aq}}$ was lower than the actual value for the same reason developed earlier (bivariate distribution effect). This simple experiment shows how important is the choice of the separation and titration conditions to get reliable data on the partition of carboxylated polymer between serum, surface and particle phase.

Some authors had noticed this problem before and proposed alternative procedures[13] such as repeated ultra centrifugation/redispersion operation to remove any material not chemically bound to the particle surface.

The question arises on the definition of the pseudo-water soluble polymer strongly adsorbed on the particle surface and the grafted polymer. According to our first assumptions they are fundamentally different in their structure: the former is *a priori* a statistical polymer mainly composed of hydrophilic units and some hydrophobic monomer units. The latter is *a priori* a diblock or a triblock copolymer in which the hydrophilic part is very similar to its water soluble counterpart, the hydrophobic sequence being composed most exclusively of butadiene and styrene. The average molecular weight of the hydrophobic part of these grafted copolymers is quite large and should preclude any desorption or micellization in the aqueous phase.

On the other hand the origin of the low molecular weight species appearing at $M_w = 1000$ g mol^{-1} is still questionable. In fact this peak shows some unusual features:

(a) very intense at short reaction time then decreasing quite fast;
(b) exhibits a higher extinction coefficient in u.v. compared with the rest of the sample;
(c) specific to the styrene–butadiene system.

Our interpretation of this phenomenon is that butadiene monomer is prone to transfer reaction from propagating radical producing butadienyl radicals which then desorb from the polymer particles[20]. Most of these butadienyl radicals will start adding water soluble monomers and grow to a critical chain length whereby they are captured by the existing particles. The corresponding Z value should be lower than for the persulfate-initiated chain due to the absence of sulfate group at one end. This proposed mechanism is

consistent with the experimental facts if we further assume that:

(a) the lower Z value will shift the terminated chains distribution towards smaller M_w;
(b) the terminated chains bearing a diene terminal group will copolymerize with growing macroradical to end up in the polymer phase, so disappearing from the aqueous phase.

CONCLUSIONS

A kinetic model is proposed to predict the rates of carboxylation on the particle surface, in the latex serum and within the polymer phase. The critical length for radical entry is generalized to highly polar macroradicals using an apparent water solubility, even for a water miscible monomer. Weight average molecular weight of the polymer in the serum phase was computed as well as for the polymer chain grafted at the particle surface. Taking into account the effect of the bivariate distribution of macroradicals makes the problem more complicated than it looked initially. Bivariate distribution did not seem to affect the rate of surface capture to water phase termination, but generated a distribution of the Z values which led to larger mean Z values. Model confrontation with two different set experimental data, styrene–butyl acrylate on one hand, and styrene–butadiene on the other, generally gave satisfactory results. Nevertheless two important limitations deserve to be mentioned: first of all, this model was shown to be very sensitive to the partition coefficient K_m of the acrylic acid between the water and the polymer phase. K_m values need to be accurate over a large range of experimental conditions such as particle composition, acrylic acid level and water/particle ratio. The other difficulty comes from the experimental determination of the acid distribution; separation of strongly adsorbed amphiphilic oligomer at the particle surface need to be calculated properly to discriminate between chemically anchored oligomers stemming from macroradical capture and adsorbed species.

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NOMENCLATURE

$DP_{w_{aq}}$	instantaneous weight average degree of polymerization of the dead polymer in the water phase
f	capture efficiency
G	instantaneous grafted fraction
k_d	decomposition rate constant of persulfate $(l^{-1} s^{-1})$
$k_{p,aq}$	average propagation constant in the water phase $(l\,mol^{-1}\,s^{-1})$
$k_{t,aq}$	average termination constant in the water phase $(l\,mol^{-1}\,s^{-1})$
$k_{tr,aq}$	average transfer constant in the water phase $(l\,mol^{-1}\,s^{-1})$
K_m	partition coefficient of monomer between water and polymer phase
L	kinetic length in the aqueous phase
$N(i)$	molar fraction of water phase free radical of chain length i
N_A	Avogadro number (mol^{-1})
N_C	particle concentration (l^{-1})
$\bar{M}$	weight average molar mass of the monomer unit $(g\,mol^{-1})$
$\bar{M}_{w_{aq}}$	weight average molecular weight of the water soluble polymer $(g\,mol^{-1})$
$P_{aq}(k)$	fraction of acid, indiced k, polymerized in the water phase
$P_{part}(k)$	fraction of the acid, indiced k, buried within the particle
$P_{surf}(k)$	fraction of the acid, indiced k, grafted on the particle surface
$R_{P_{aq}}(k)$	rate of polymerization of monomer k within the particle $(mol\,s^{-1})$
$R_{P_{part}}(k)$	rate of polymerization of monomer k in the water phase $(mol\,s^{-1})$
R	gas constant $(J\,K^{-1}\,mol^{-1})$
R_i	rate of initiation within the aqueous phase $(mol\,l^{-1}\,s^{-1})$
T	temperature (K)
$w(i)$	weight fraction of monomer i in the oligoradical
$Z(i)$	critical chain length of the homopolymer i
Z	critical chain length of the instantaneous copolymer
$\bar{Z}$	weight average length of the grafted chains on the particle surface
$[M_{aq,sat}]$	aqueous solubility of the monomer $(mol\,l^{-1})$
$[M_{aq}]$	total monomer concentration in the aqueous phase $(mol\,l^{-1})$
$[M_{part}]$	monomer concentration in the polymer phase $(mol\,l^{-1})$
$[R_{aq}^{\cdot}]$	total radical concentration $(mol\,l^{-1})$
$[R_{aq,z-1}^{\cdot}]$	concentration of radicals with chain length $z-1$ $(mol\,l^{-1})$

Greek symbols

τ	transfer termination rate to propagation rate ratio
β	coupling termination rate to propagation rate ratio
λ	apparent water solubility for water miscible monomer $(mol\,l^{-1})$
ρ	rate of radical entry (s^{-1})

REFERENCES

1 Greene, J. and Sheetz, M. *J. Coll. Interf. Sci.* 1970, **32**, 91
2 Greene, J. *J. Coll. Interf. Sci.* 1973, **43**, 449
3 Hen, J. *J. Coll. Interf. Sci.* 1974, **49**, 425
4 Chatterjee, R. *Rubber Chem. Technol.* 1984, **56**, 994
5 Vijayendran, N. *J. Appl. Polym. Sci.* 1979, **23**, 893
6 Okubo, M., Kanaida, K. and Matsumoto, T. *J. Appl. Polym. Sci.* 1987, **33**, 1511
7 Zosel, A., Heckmann, W. and Machtle, W. *Coll. Polym. Sci.* 1987, **265**, 113
8 Emelie, B., Pichot, D. and Guillot, J. *Makromol. Chem.* 1988, **189**, 1879
9 Dobler, F. PhD. Thesis, University L. Pasteur, Strasbourg, 1991
10 Bonardi, C., Christou, P., Llaurro-Darricades, S., Guillot, J., Guyot, A. and Pichot, C. *New Polym. Mater.* 1991, **2**, 295

11   Magnet, S. and Guillot, J. *Makromol. Chem., Macromol. Symp.* 1990, **35/36**, 367
12   Turner, S. R., Weiss, R. A. and Lundberg, R. D. *J. Polym. Sci., Polym. Chem. Ed.* 1985, **37**, 535
13   Kim, J. H., Chainey, M., El Aasser, M. S. and VanderHoff, J. W. *J. Polym. Sci., Polym. Chem. Ed.* 1992, **30**, 171
14   Shoaf, G. L. and Poehlein, G. W. *J. Appl. Polym. Sci.* 1991, **42**, 1213
15   Lange, D. M. and Poehlein, G. W. *Polymer Reaction Eng.* 1992, **93**, 1
16   Ugelstad, J. and Hansen, F. K. 'Emulsion Polymerization' (Ed. I. Pürma), Academic Press, New York, 1982

17   Hamielec, A. E. and MacGregor, J. F. in 'Polymer Reaction Engineering' (Eds K. H. Reichert and W. Gersler), Hanser, 1983
18   Maxwell, I., Morrison, B., Napper, D. and Gilbert, R. G. *Macromolecules* 1991, **24**, 1629
19   Wang, S. T. and Poehlein, G. W. *J. Appl. Polym. Sci.* 1993, **50**, 2173
20   Weerts, P. A. PhD. Thesis, 'Emulsion Polymerization of Butadiene a Kinetic Study', Eindhoven University of Technology, Eindhoven, The Netherlands, 1990
21   Rhône Poulenc Recherches, internal report, 1994
22   Stockmayer, W. H. *J. Chem. Phys.* 1945, **13**, 199