

Emulsifier-Free Emulsion Copolymerization of Styrene with Two Different Amino-Containing Monomers: II. Surface and Colloidal Characterization

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ABSTRACT: The colloidal and surface properties of copolymer latex particles prepared by batch emulsifier-free emulsion polymerization of styrene with two different amino-containing monomers (Amino Ethyl Methacrylate Hydrochloride (AEMH) and Vinyl Benzyl Amine Hydrochloride (VBAH)), and 2,2'-azobis(2-amidinopropane) dihydrochloride (V50) as initiator were investigated. The final particle size was found to decrease with increasing the functional monomer concentration. Different titration methods were used to quantify the surface amino (brought by the monomer) and amidino groups (originated from the initiator) on the latex particles. The same behavior was observed on both type of latexes: increasing the functional monomer concentration caused the surface amino groups density to increase from 0 to a plateau value at $8.2 \mu\text{C}/\text{cm}^2$, whereas the surface amidino groups density decreased from 18.5 to $2 \mu\text{C}/\text{cm}^2$. These results were confirmed by electrophoretic measurements and they corroborated those obtained in a previous kinetic study (Part 1) concerning the role of functional monomers as transfer agents. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2331–2342, 1997

Key words: polystyrene; cationic monomers; emulsion polymerization; functionalized particles; amino surface charges

INTRODUCTION

Functionalized polymer latexes are studied largely because of their numerous applications in various domains, especially in the biomedical field.^{1–4} Polystyrene-based particles, for instance, have long been used as solid-phase supports for diagnostic applications.

In such applications, the biomolecules (proteins, antibodies, enzymes, and nucleic acids) can be attached through physical adsorption; however, it has been found more advantageous to anchor the biomolecule via covalent coupling, a process ensuring irreversible fixation and avoiding

the possibility of desorption or displacement. In addition, better orientation of the biomolecule can be obtained in some cases. The immobilization of biomolecules containing carboxylic, amino, or thiol groups requires use of latexes bearing reactive groups incorporated into the particles via different routes.⁵

Soap-free emulsion copolymerization of styrene with a functional water-soluble monomer was found to be a convenient method for producing functionalized latexes. Many studies already reported the strong influence of the chemical structure of the functional monomer on the polymerization mechanism⁶ and on the final latex particle properties. In a first article,⁷ a detailed kinetic study has been presented comparing the effect of two amino-containing monomers, AEMH (Amino Ethyl Methacrylate Hydrochloride) and VBAH

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(Vinyl Benzyl Amino Hydrochloride) in batch emulsifier-free emulsion (co)polymerization of styrene. Results were explained and discussed referring to the physicochemical properties of both functional monomers (chemical structure, partition coefficient, and their ability to polymerize, through the determination of $k_p/\sqrt{k_t}$ values). Their influence on the kinetics of soap-free emulsion polymerization with styrene was examined and the determination of the molecular weight and distribution allowed one to prove the strong transfer activity of both functional monomers.

In the present work, the main objective was to examine the colloidal properties of these amino-containing latexes. First, we report on the effect of the nature of the functional monomer on the final particle size and distribution. Second, the electrophoretic mobility of the various latexes was determined upon varying pH and ionic strength. Then, the surface amino and amidino groups were quantified using both a colorimetric and a fluorescence method. Finally, the obtained results allowed us to corroborate the role of functional monomer as a transfer agent during batch emulsion copolymerization with styrene.

EXPERIMENTAL

Materials

Unless stated otherwise, reagents and solvents were used as received. Water was of milliQ grade (Millipore SA, France) and was boiled for 1 h under a nitrogen stream before using. Styrene (Janssen Chemica, France) was distilled under reduced pressure; 2,2'-azobis (2-amidinopropane) dihydrochloride (V50 from Wako Chemical GmbH, Germany), was recrystallized from a 50/50 water/acetone mixture. 2-Amino Ethyl Methacrylate Hydrochloride (AEMH from Kodak) was used as such. Vinyl Benzyl Amine Hydrochloride (VBAH) was synthesized according to a method described elsewhere.⁴ N-Succinimidyl 3-(2-pyridyldithio) propionate (SPDP from Pierce), Dithiothreitol (DDT from Aldrich, 99% pure), fluorescamine (from Roche), Triton X-405, t-Octylphenoxypolyethoxy-ethanol (from Sigma Chemical, St. Louis, MO) were used as received.

Preparation of Cationic Polystyrene Latexes

Polymerizations were performed batchwise in a thermostated glass reactor (250 mL) under a ni-

Table I Emulsion Copolymerization Recipes

Reagents	Quantities (g)
Water	200.00
Styrene	20.00
AEMH/VBAH	variable (between 0 and 0.32)
V50	0.32

trogen atmosphere during all the experiments. The reaction temperature was controlled at 70°C and the stirrer was adjusted at 300 rpm. The required amount of water and styrene were introduced and purged with nitrogen. Then, the functional monomer (AEMH or VBAH) and the initiator (V50) dissolved in water were added.

Sampling was carried out at given intervals to follow the polymerization kinetics.⁷ The reactions were run for about 20 h and the overall conversion, referring to the styrene, was determined thermogravimetrically. Polymerization recipes are given in Table I.

Characterization and Colloidal Properties

All latexes were cleaned by repeated centrifugations and redispersed in deionized water in order to remove adsorbed species that could strongly influence the surface charge titration data and all physico-chemical properties of latexes as pointed out by Kamel et al.⁸

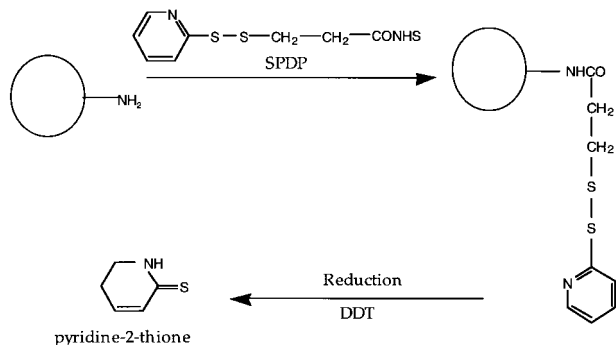
Particle size and Distribution

Particle size and distribution of latexes were measured both by Quasi Elastic Light Scattering (QELS) using N4DM apparatus from Coultronics-France, and by Transmission Electron Microscopy (TEM) equipment from Hitachi and Philips as described in Part 1.⁷

Surface Group Titration

Two different methods were used for the titration of the functional groups.

A chemical method, elsewhere detailed,⁴ uses SPDP to react with amino and amidino groups provided respectively by the functional monomers and the initiator (Scheme 1). A reduction reaction occurs in the presence of DTT leading to pyridine-2-thione, which was quantified by measuring the optical density at a wavelength of 343 nm. This titration method allows one to assess the direct amounts of available amino and amidino groups:



Scheme 1.

N_w (in mol of amino and amidino groups per gram of latex particles) or N_c (in Coulomb per cm² of latex particles) with:

$$N_c = \frac{N_w}{6} \times D_w \times \rho \times F \quad (1)$$

with D_w = particle diameter (cm) from TEM, ρ = density of polystyrene (1.045 g/cm³), F = Faraday constant (9.64×10^4 Coulomb).

The fluorescence titration method is based on the reaction of fluorescamine with primary amino groups (Scheme 2):

The titration was performed either on the various latex sera (obtained after centrifugation of latex particles) or directly on the latex particles. The measurements were carried out with a Perkin-Elmer LS50 on an Elisa-type 96-well plate.⁹

In the case of serum titration, the calibration curve was plotted from monomer solutions of given concentrations in a sodium borate buffer (0.1 mol/L; pH = 9.5), ranging from 0.01 to 0.1 g/L and from 0.05 to 1 g/L for VBAH and AEMH, respectively. With AEMH, solutions were incubated 12 h in the buffer before use, in order to make sure that amino groups were fully deprotected. In the other case, a latex with a known surface charge density was used to generate the calibration curve under the same conditions as previously described.⁹

Samples were prepared as follows: 100 μ L of monomer solution or latex serum containing the residual functional monomer or latex particles was added to 2.9 mL of borate buffer (0.2 mol/L, pH 9.5). Then, 1 mL of a fluorescamine in an acetone solution (0.3 g/L) was added and the reaction occurred in the dark. The fluorescence intensity was measured at 410 nm excitation wavelength and 470 nm emission wavelength.

This method allowed one to determine: (a) the

residual amount of functional monomer in the latex serum (C_s) from which the functional monomer amount, (C_i), is deduced by subtracting (C_s) from (C_i) the initial monomer concentration; and (b) the functional monomer amount (C_i) directly on the latex particles.

The quantification of the concentration of surface amino groups on the latex particles, N_w (in mol per gram of latex particles) can be expressed as follows:

$$N_w = \frac{C_i}{M_w \times SC_{\text{exp}}} \quad (2)$$

where: M_w is the molecular weight of the functional monomer, i.e., 166 g/mol and 170 g/mol for AEMH and VBAH, respectively, and SC_{exp} is the experimental solids content (Table II) of the washed latexes.

The incorporation yield is defined by the ratio of the incorporated amount of functional monomer to the initial functional monomer concentration:

$$MY = \frac{N_w \times M_w \times SC_i}{C_i} \quad (3)$$

where SC_i is the experimental final polymerization solids content (g per L).

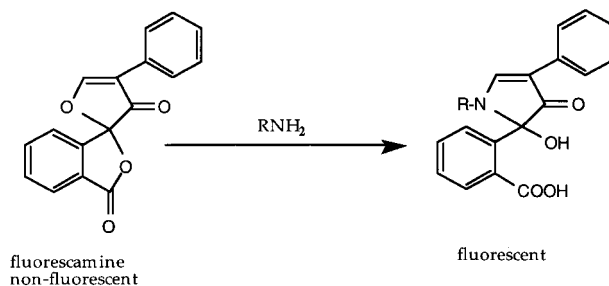
Electrophoretic Mobility Measurements

The electrophoretic mobility measurements were performed at 25°C with a Zetasizer III (from Malvern Inst. France) as a function of pH at a constant ionic strength (10^{-3} mol/L) or at a given pH and varying ionic strengths. Each value is the average of at least three measurements.

RESULTS AND DISCUSSION

Influence of the Functional Monomers on Final Conversion

As reported in Table II and Figure 1, the final conversion is significantly enhanced upon increas-



Scheme 2.

Table II Solids Content (SC), Final Conversion (Conv), Particle Size (Determined Both by QELS [\overline{D}_z], and TEM, \overline{D}_n , \overline{D}_w), and Polydispersity (PDI) as a Function of the Amount of Monomer Introduced in the Polymerization Recipe

Code		Monomer Conc. ($\text{m} \cdot \text{mol} \cdot \text{L}^{-1}$)	SC g/L	Conv. %	\overline{D}_z nm	\overline{D}_n nm	\overline{D}_w nm	PDI
VBAH	0	0.00	71	82.5	620	473	473	1.001
	1	1.22	80	88.0	285	272	273	1.004
	2	1.90	82	90.0	230	212	215	1.013
	3	2.94	84	92.4	190	190	192	1.010
	4	4.12	82	90.0	169	152	157	1.030
	5	5.88	87	96.1	137	118	119	1.004
AEMH	6	8.24	87	95.6	126	115	117	1.021
	11	0.81	82	90.0	560	468	469	1.002
	12	1.51	85	91.8	360	319.7	320.4	1.002
	13	3.06	89	96.3	205	186	189	1.016
	14	6.15	91	97.1	150	144	145	1.014
	15	7.47	92	100.0	113	104	107	1.023
	16	9.72	91	99.0	100	85	93	1.090

ing the functional monomer concentration, with some difference according to the type of monomer: a maximum conversion of 96% was attained with VBAH instead of nearly 100% with AEMH. Because the functional monomers are both largely water soluble, they first start to react with solubilized styrene molecules through initiator decomposition. Surface-active oligomers are first formed, which later provide the precursors, and then mature particles according to the coagulative nucleation theory.¹⁰ However, AEMH is slightly more partitioned into the water phase than VBAH, as indicated by a higher partition coefficient value.⁷ Therefore, polymerization in the wa-

ter phase occurs more rapidly in the presence of AEMH than with VBAH, resulting in a more complete conversion of residual styrene. Unfortunately, this has not been proven by experiments⁷ because of the uncertainty in the analytical method (gravimetry). In addition, it might also be suggested that the increase in the polymerization rate caused by a copolymerization effect would be more important in the case of the copolymerization using methacrylate derivatives. Finally, from a given concentration of functional monomer (i.e., 3.0×10^{-3} mol/L), each curve reaches a plateau and exhibits a similar trend (Fig. 1).

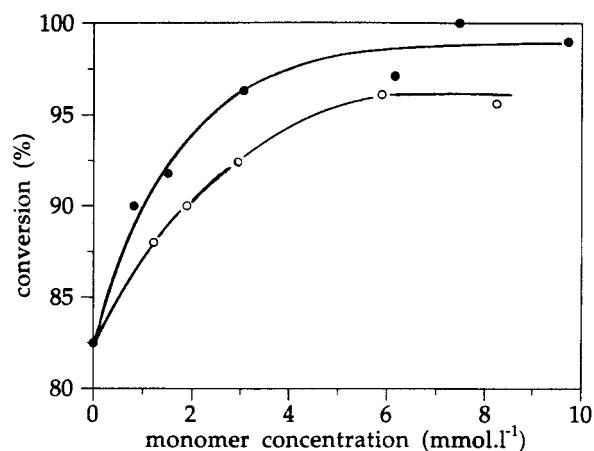


Figure 1 Final conversion vs. the functional monomer concentration (● AEMH; ○ VBAH).

Effect of the Functional Monomer on the Final Particle Size and Distribution

Particle size and distribution of final latexes, as obtained by Transmission Electron Microscopy (TEM) and Quasi-Elastic Light Scattering (QELS) are reported in Table II. Data values obtained from QELS are generally somewhat larger than those obtained by TEM; this might be caused by some shrinkage of the dried particles under the electron beam.

The final particle size variation vs. the functional monomer concentration is found to follow the same trend whether VBAH or AEMH is used; particle size significantly decreased with increases in the functional monomer concentration. This is a general trend that has been observed in emulsifier-free emulsion polymerization in the

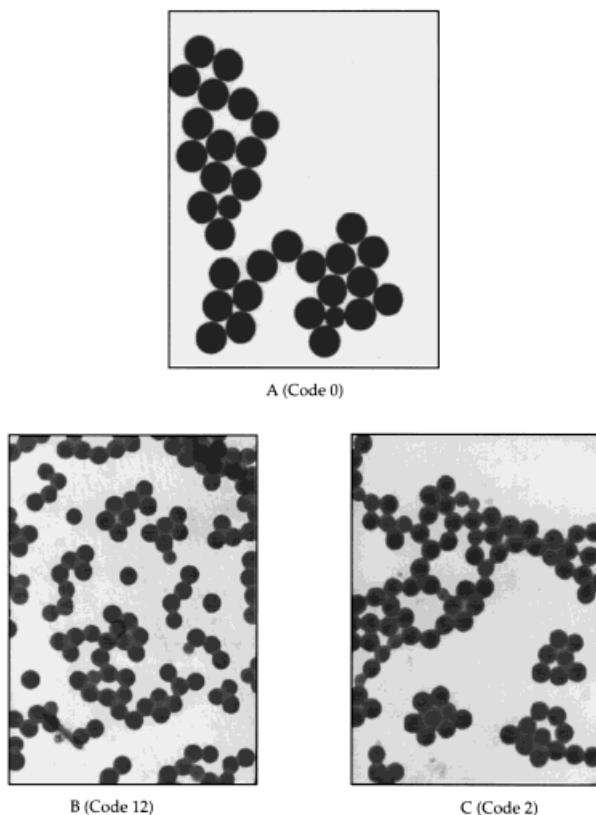


Figure 2 Transmission electron microscopy micrographs; (A) without functional monomer (Code 0); (B) with VBAH (Code 2); and (C) with AEMH (Code 12).

presence of an ionic comonomer: the number of particles increases, and as a consequence, the particle size decreases.¹¹ With several highly reactive and water-soluble functional monomers, some authors^{11,12} reported a particle size increase together with a broadening of the size distribution at relatively high functional monomer concentrations. This was explained by the formation of a high level of polyelectrolytes, which might cause bridging flocculation of the growing particles, and also favored secondary nucleation.^{2,4,10,13,14} Such a tendency was not observed in the concentration range investigated with VBAH and AEMH monomers except maybe for the highest concentrations (AEMH; Code 16) for which the uniformity ratio slightly increases (see also TEM micrographs in Fig. 2).

As already found in the literature,^{15–18} the log-log plots of D_w vs. functional monomer concentration clearly exhibit two straight lines (Fig. 3) with a slope slightly different for both amino-containing monomers. VBAH and AEMH monomers strongly affect the final particle size with a power

variation of 0.64 and 0.53, respectively, indicating that the latter does more significantly influence the particle nucleation compared to the former monomer. AEMH has a more pronounced effect on the particle size, especially at low concentration.

Electrokinetic Studies

A preliminary study was performed in order to determine the pK_a of the two amino-containing monomers; then, the electrophoretic mobility of the different latexes was examined.

Determination of the pK_a

As the pK_a of the NH_2 functional group depends on the chemical monomer structure,¹⁹ we attempted to estimate the acid dissociation constant, pK_a , of both cationic monomers. These constants were measured by potentiometric titration using equimolar monomer solution and using NaOH as a strong base. Titration curves are reported in Figure 4, from which several remarks may be raised:

1. The initial pH value for the weak acid depends on the acid dissociation constant, pK_a , of the monomers, i.e.:

$$pH = \frac{1}{2}(pK_a - \log c) \quad (4)$$

where c is the initial monomer concentration. The pH value of VBAH at the origin of the titration curve is higher than AEMH,

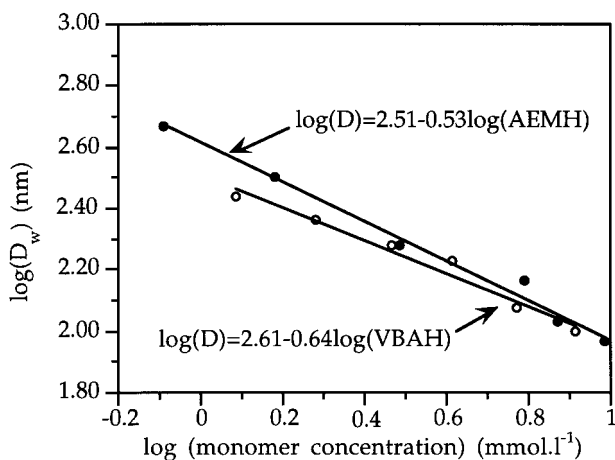


Figure 3 Log-log scale of diameter variation vs. the functional monomer concentration (● AEMH; ○ VBAH).

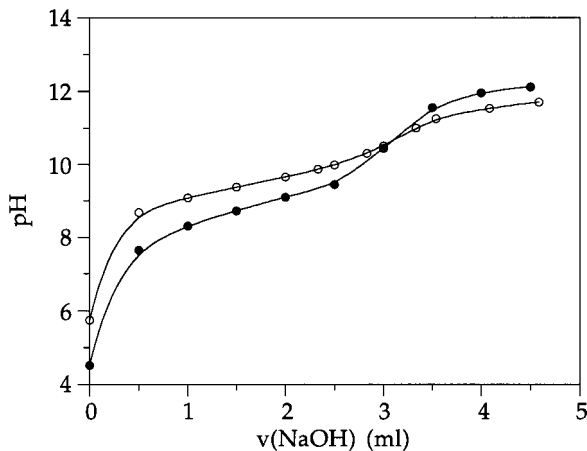


Figure 4 Potentiometric titration curves of both functional monomers by NaOH (● AEMH; ○ VBAH).

reflecting that AEMH is more acid than VBAH.

- The pH at semiequivalence is the best method so as to assess the pK_a of the two monomers, such as:

$$pK_{a_{MAE}} = 8.7$$

$$pK_{a_{VBAH}} = 9.4 \quad pK_a(\text{Benzylamine})^{19} = 9.34$$

This is another evidence of the acidity difference between the two monomers. The equivalent point was determined by the tangent method, i.e. at pH = 10.5.

- Finally, the curve profile is another way to compare the acidic strength of the monomers. The pH difference before and after the equivalent point is larger in the case of AEMH ($\Delta\text{pH} = 2$), which definitely can be considered as a stronger acidic monomer than VBAH ($\Delta\text{pH} = 1$).

All these results can easily be explained by the influence of the various monomer components on the acidic group as reported in Part 1.⁷

Electrophoretic Mobility Measurements of Latexes

The electrokinetic behavior of the various latexes was investigated as a method to characterize the surface of polymer particles.^{20,21}

First, measurements were carried out at constant ionic strength with varying pH; the results

are reported in Figure 5. The following remarks may be pointed out:

- The electrophoretic mobility (e.m.) of both series of latexes exhibit, as expected, a positive value in the acidic region and progressively decreases above pH 7 because of the neutralization of the ionogenic groups. At a given ionic strength, an isoelectric point (i.e.p) is defined in between 9 and 10.5, according to the type of latex. The negative values of electrophoretic mobilities above pH 10 can be explained by the presence of anionic surface charges that might originate from the hydrolysis of the amidino surface functional groups under basic conditions²² and providing some carboxylic surface charges.
- Some differences were evidenced according to the nature and surface charge of the latexes. In the absence of cationic monomers, the latex bearing only amidino groups (Code 0) exhibits an i.e.p around pH 9.6, corresponding to that of amidino groups. However, as the concentration of AEMH or VBAH is increased, there is a slight increase of the i.e.p, reaching a plateau value around pH 10.7, as illustrated in Figure 6. The shift of i.e.p. toward higher pH could indicate that the contribution of surface amino groups increases with the functional monomer concentration. As shown in Figure 5, the two monomers do not exhibit exactly the same isoelectric point because they have a different pK_a as previously dis-

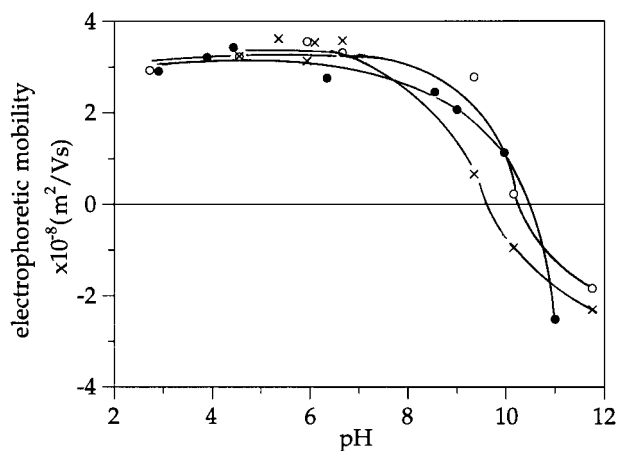


Figure 5 Variation in electrophoretic mobility as a function of pH at a constant ionic strength $10^{-3} M$ (● AEMH, Code 12; ○ VBAH, Code 3; × Code 0).

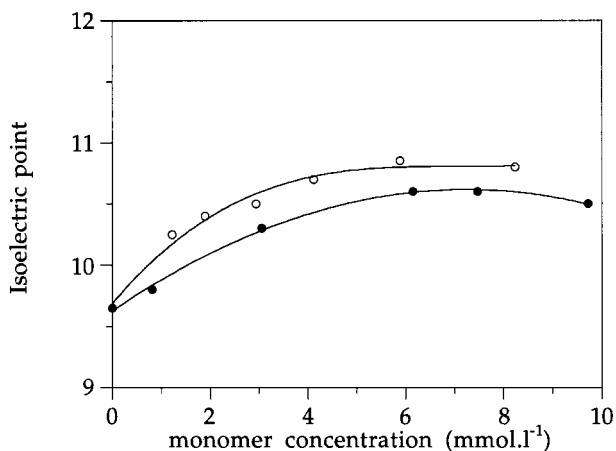


Figure 6 Isoelectric point as a function of functional monomer concentration (● AEMH; ○ VBAH).

cussed; then, i.e.p. depends not only on the nature of the surface charges, but also on the type of functional monomer used.

Second, measurements were conducted at given pH with varying ionic strength; these results are plotted in Figure 7. Three different latexes were studied, one prepared without functional monomer (Code 0), and the two others with AEMH (Code 12) and with VBAH (Code 3), respectively. The curve obtained in the case of the amidino-containing latex (Code 0) is similar to that recently reported in the literature for the same kind of latex²³: a “bell”-type curve with a maximal electrophoretic mobility appearing around $5.0 \times 10^{-3} M$ NaCl. It is claimed that this maximum is the consequence of a hairy layer at the particle surface; however, this explanation is still controversial. On the contrary, the profile of the curve obtained with the amino-containing latexes is different: the maximum is shifted towards higher ionic strengths (about 0.01), and at lower ionic strengths, the curve is flat. This behavior has only been observed by de Las Nieves et al.²¹ on polystyrene latexes functionalized with sodium styrene sulfonate. It seems that the curve profile is modified according to the type of latex (with or without functional monomer), which could reflect a difference in the interfacial structure of the particles due to the presence of surface groups different from those induced by the initiator.

Surface Functional Group Characterization

As described in the Experimental part, two different methods were used to perform the titration of

the amino and amidino surface groups. The assay is slightly different for the two monomers, even if they do not exhibit the same ability of being titrated. The potentiometric measurement showed that the amino function of AEMH is less basic than VBAH, and we could suppose that AEMH is less reactive towards SPDP or fluorescamine than VBAH. Table III reports the total surface charge densities of the polystyrene latexes prepared in the presence of VBAH and AEMH, as well as the functional monomer incorporation yield (MY). The following remarks may be raised: (a) the overall surface charge density originated from both amidino and amino groups and increases slightly upon increasing the functional monomer concentration, (b) the two methods provide $N_w B$ and $N_w C$ values for the surface charge density expressed in $\mu\text{Eq/g}$, which are in good agreement and similar to those reported by Van Streun et al.⁶ It is worth noting that the surface amino group density is higher for latexes prepared with AEMH than with VBAH. However, we have to keep in mind that a small particle size difference can influence these results expressed in μEq per gram of latexes; (c) the incorporation yield of the functional monomer is relatively large, with no significant difference according to the type of monomer; it ranges between 48 and 63% (with an average of 50% for both AEMH and VBAH).

The surface charge density determined by fluorescence and SPDP titrations expressed in $\mu\text{mC/cm}^2$ is independent of the particle size, as illustrated in Figure 8. It seems clear that the two monomers exhibit the same influence on the latex particle stability as well as on the final surface

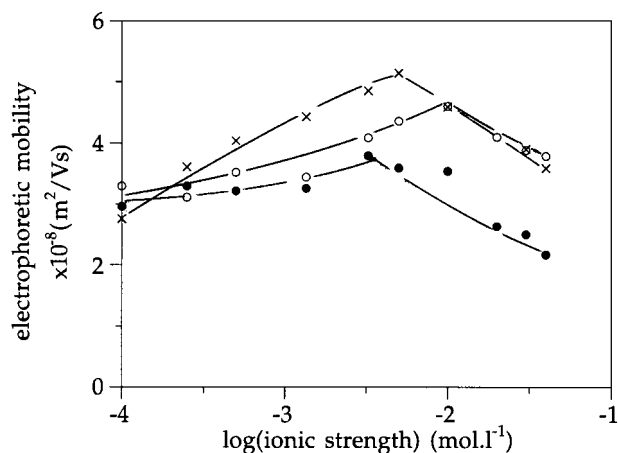


Figure 7 Variation in electrophoretic mobility as a function of ionic strength at pH 4 (× Code 0, ● AEMH, Code 12; and ○ VBAH, Code 3).

Table III Comparison between Fluorescence Titration Results of the Particles and the Serum, Expressed in $\mu\text{Eq/g}$

Code	Monomer Concentration ($\text{mmol} \cdot \text{L}^{-1}$)	Method A	Method B		Method C
		$N_w\text{A}$ $\mu\text{Eq/g}$	$N_w\text{B}$ $\mu\text{Eq/g}$	MY %	$N_w\text{C}$ $\mu\text{Eq/g}$
	0	23.5	0	0	0
VBAH	1	35	8.3	54	8.70
	2	32	14.7	63	16.50
	3	35	19	54	21.00
	4	37	25	50	25.50
	5	45	40	60	43.00
	6	*	49	52	*
AEMH	11	25	*	*	*
	12	22	*	*	17
	13	31	15	54	22
	14	33	32.6	48	32
	15	41	*	*	38
	16	*	52.3	49	*

Method A: SPDP titration, Method B: fluorescence titration of the serum, and Method C: fluorescence titration on the particles. Functional monomer incorporation yield (MY) calculated from Method B.

* Not determined.

charge density. This is of paramount importance because it means that the maximal extent of amino functionalization in a batch process reaches an average value of $8.2 \mu\text{C}/\text{cm}^2$.

This follows the tendencies reported in the literature such as, for instance, the case of a batch soap-free emulsion polymerization of styrene with 3-(methacrylamidinopropyl) trimethylammonium

for which the surface charge density is in the range $9.2\text{--}20.5 \mu\text{C}/\text{cm}^2$ according to the cationic monomer concentration.⁶ The monomer incorporation is indeed limited for at least two reasons: (1) the increase in electrostatic repulsions between surface charges and charged oligomers as polymerization proceeds, which makes their capture efficiency decrease; and (2) a part of the oligoradicals, as a result of termination reactions, can terminate either at the water phase interface or in the aqueous phase (this has been pointed out in ref. 7, and it will be discussed later on in this article).

In any case, as already reported in many recent works, batch process cannot be used to produce highly charged latex particles, whereas seeded-batch or shot-growth methods were indeed found more suitable in this purpose.^{9,14}

All the surface characterization data tend to prove that if even both monomers present a different chemical structure, the two series of latexes exhibit an almost identical surface charge density. Based on that similar trend, the following results will only refer to the case of VBAH-functionalized latexes, knowing that the same behavior is observed in the case of AEMH.

It can be instructive to estimate the proportion of charges brought either by the initiator fragments or by the functional monomer. The SPDP

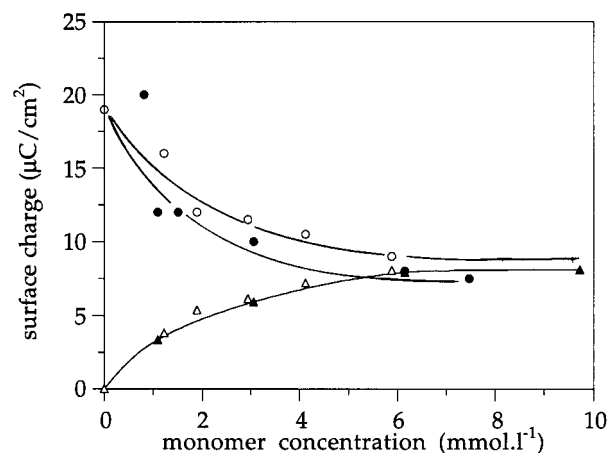


Figure 8 Surface charge titration results obtained both by SPDP titration (Method A) and fluorescence on the serum (Method B) as a function of monomer concentration expressed in $\mu\text{C}/\text{cm}^2$ (● AEMH-Method A; ○ VBAH-Method A; ▲ AEMH-Method B; and △ VBAH-Method B).

method (Method A) provides the amount of amino and amidino groups, whereas the fluorescence method (Methods B1 or B2) only gives primary amino groups. Hence, the difference between these methods would permit estimation of the surface charges brought about only by the initiator fragments.

1. The theoretical initiator incorporation yield can be determined through the amount of the initiator molecules that have been decomposed, N_{dec} (mol/L), and the amount of amidino surface charges. N_{dec} can be calculated according to the relationship:

$$N_{\text{dec}} = N_{\text{initial}}(1 - e^{-k_d t}) \quad (5)$$

where $k_d = 1.15 \times 10^{-4}$ mol/s is the decomposition rate constant of the initiator at 70°C;^{2,24} N_{initial} is the initial concentration of initiator, which was kept constant in all experiments, i.e., 5.36 mmol/L; t is the time at which conversion stops to increase corresponding to the completion of styrene consumption; it is calculated with the experimental values of the polymerization rate (R_p) (mol/L/s):

$$t = N_{\text{sty}}/R_p, \quad (6)$$

N_{sty} (mol/L) is the amount of styrene monomer consumed during the polymerization reaction.

2. The initiator incorporation yield is defined by:

$$IY = \frac{(N_w A - N_w B)}{N_{\text{dec}}} \times SC \quad (7)$$

where: SC is the polymer solids content (g/L), $N_w A$ is the total surface charge density determined by Method A ($\mu\text{Eq/g}$), $N_w B$ is the amino surface charge density determined by Method B ($\mu\text{Eq/g}$).

The incorporation yield of the initiator is calculated from the experimental values of the polymerization rate, R_p , and the surface charge

(Method A and B) as a function of monomer concentration; the results are reported in Table IV.

It is surprising to note that the total surface charge (Fig. 9) decreases upon increasing the monomer concentration and reaches a limit at high VBAH concentration; moreover, the contribution of the surface charges brought about by the initiator becomes progressively less important. The evolution of the initiator incorporation yield as a function of VBAH (Fig. 10), seems to exhibit a maximum value at 2.0×10^{-3} mol/L in VBAH. This can be explained by the various radical reactions that occur in the aqueous phase at the beginning of the polymerization, which involve radicals originating from initiator decomposition:

1. $R^\bullet + R^\bullet \xrightarrow{k_{\text{ter}}} 2R$ bimolecular termination
2. $R^\bullet + M \xrightarrow{k_{p1}} RM^\bullet$ reaction with styrene
3. $R^\bullet + A \xrightarrow{k_{p2}} RA^\bullet$
reaction with the functional monomer
4. $R^\bullet + M \xrightarrow{k_{tr}} R_H + M^\bullet$
transfer reaction to styrene
5. $R^\bullet + A \xrightarrow{k_{tr}} R_H + A^\bullet$
transfer reaction to functional monomer

where R^\bullet corresponds to the initiator radicals, M the main monomer, styrene, and A the functional monomer.

1) In the case where no functionalized monomer A was added, the initiator incorporation is limited to 32%: contribution of reaction 4 is not important because of the low styrene concentration in the aqueous phase, and 1 and 2 are in competition so that a portion of the primary radicals originating from the decomposition of initiator is left in the aqueous phase as water-soluble oligomers.

2) At low functional monomer concentration, the initiator incorporation yield is increased to 45%. In that case, radicals could react both with styrene and VBAH or AEMH (reactions 2 and 3) so that less termination reactions 1 could occur than in the absence of functional monomer. It may be suggested that the presence of the functional monomer results in an enhanced efficient of the primary radicals.

3) At larger functional monomer concentra-

Table IV Initiator Incorporation Yield (IY) Calculated from the Following Experimental Values: Polymerization Rate (V_p), Total Amount of Decomposed Initiator (N_{dec}), Surface Amidino Groups (ΔN), Which Correspond to the Difference between Methods A and B

Code		Monomer Concentration (mmol · L ⁻¹)	V_p (10 ⁵ mol · L ⁻¹ · s ⁻¹)	N_{dec} (10 ³ mol · L ⁻¹)	ΔN μEq/g	IY %
	0	0	1.64	5.33	23.5	31
VBAH	1	1.22	3.75	4.86	26.7	44
	2	1.90	10.20	3.15	23.8	45
	3	2.94	9.58	3.33	16	40
	4	4.12	13.60	2.60	12	38
	5	5.88	18.10	2.22	5	20
AEMH	11	0.81	2.46	5.23	*	*
	12	1.51	3.08	5.10	13	22
	13	3.06	8.90	2.87	12.5	31
	14	6.15	15.30	2.54	1	4
	15	7.47	22.00	1.97	0.4	4

* Not determined.

tion, a large decrease of the initiator incorporation yield was observed. Under such conditions due to the chain transfer activity of the functional monomer as was evidenced in the first part of this study,⁷ a lower number of primary radicals are able to react with monomers to provide propagating species. Indeed, the transfer rate constant to functional monomer during emulsion polymerization with styrene was found to be quite large (10 L · mol⁻¹ · s⁻¹) and it may be assumed that this value remains important in the aqueous phase: as the functional monomer concentration increases, reaction 5 is the dominant event compared with reactions 1, 2, and 3. Chain transfer of the amid-

ino-terminated oligoradicals to VBAH or AEMH at the interface produces dead chains forming water-soluble oligomers containing VBAH or AEMH. As a result, the initiator incorporation yield and surface amidino group concentration decrease drastically whereas the surface charge tends to be saturated by amino groups.

This limit is reached when 6 mmol · L⁻¹ of functional monomer was used (Fig. 9), leading to a final latex with an amino surface charge of 8.2 μC/cm². It is interesting to observe that the overall surface charge (as deduced from the SPDP method) is 18 μC/cm² in the absence of VBAH and decreases to 10 μC/cm² for the highest VBAH

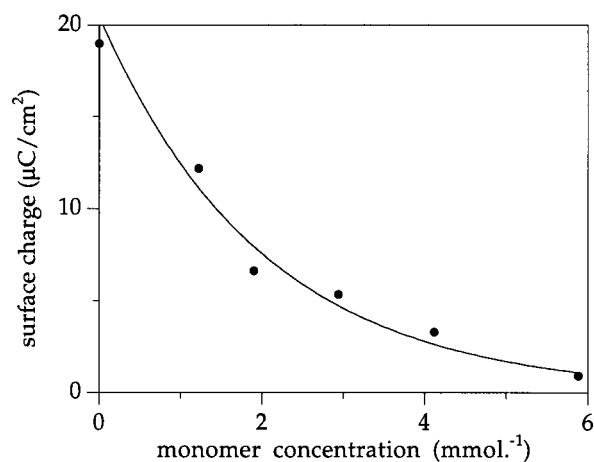


Figure 9 Variation of amidino groups as a function of VBAH concentration.

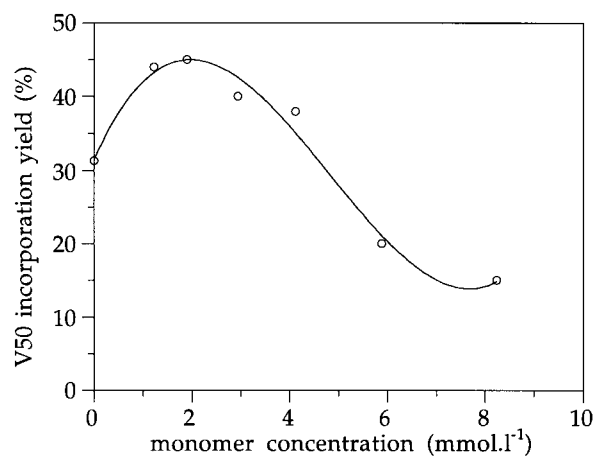


Figure 10 Initiator (V50) incorporation as a function of VBAH concentration.

concentration. Differences between data obtained from the SPDP method and from fluorescence allow one to estimate the contribution of amidino surface charges, dropping from $18 \mu\text{C}/\text{cm}^2$ to $2 \mu\text{C}/\text{cm}^2$. These results are quite instructive concerning the ability of controlling the surface charge density with either the initiator or the cationic monomer. In addition, the results show that the shift in the isoelectric point (Fig. 6) of the latex particles originated from the increasing contribution of the surface amino groups. It seems that in the absence of a functional monomer, the cationic initiator fragments can achieve a higher surface charge density than in the presence of the cationic comonomer. This can be discussed with respect to the surface activity of the water-phase oligomers: in the absence of cationic monomers, these oligomers would be more hydrophobic and more easily captured by the particles; on the contrary, in the presence of cationic monomers, they are more hydrophilic, then decreasing the capture efficiency and favoring the formation of polyelectrolytes; however, due to the presence of more ionic charges, they would be able to confer more stability to the particles.

At high functional monomer concentration, it appears that most of the surface charges are provided by the amino-containing charges. However, in that case, a compromise should be found between the size dispersity of the particles and the control of the type of surface charge.

CONCLUSIONS

The comparison of the colloidal and surface properties of two series of functionalized latexes synthesized by soap-free emulsion copolymerization of styrene with two different amino-containing monomers (amino ethyl methacrylate hydrochloride, AEMH, and vinyl benzyl amine hydrochloride, VBAH) leads to the following conclusions:

1. At a given concentration of functional monomer, both types of latexes exhibited the same kind of colloidal properties. Increasing the functional monomer concentration increases the final conversion up to 96 and 100%, and the number average particle diameter to decrease to 115 and 85 nm, for VBAH and AEMH, respectively.
2. A slight difference in the isoelectric point of the two series of latexes was pointed out

by electrophoretic mobility measurement, which confirmed a slight difference in the acid dissociation constants of the amino groups covalently bound on the surface whether the latex were prepared with AEMH and VBAH.

3. The characterization of the latex surface charge was a very important point; it clearly showed that the final surface charge was independent of the chemical structure (Part 1)⁷ of the functional monomer as well as the pK_a . An optimal surface charge value of $8.2 \mu\text{C}/\text{cm}^2$ was attained, i.e., an average of 50% of the initial monomer amount was incorporated on the latex surfaces either with AEMH or VBAH.

Both kinetic (Part 1)⁷ and colloidal studies on these latexes prove the strong transfer activity of the two functional monomers during the emulsion polymerization with styrene where transfer reactions can take place in the particle and in the aqueous phase. Such a reaction leads to a drastic decrease of the initiator fragment (amidine) at the particle surface upon increasing the functional monomer concentration.

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