ORIGINAL CONTRIBUTION

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# Functionalization of poly(*N*-ethylmethacryl-amide) thermosensitive particles by phenylboronic acid

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**Abstract** The synthesis of poly (*N*-ethylmethacrylamide) (NEMAM) thermosensitive particles functionalized with phenylboronic acid (PhBA) groups has been performed by emulsion/precipitation polymerization of NEMAM in water at 90 °C, using ethylene glycol dimethacrylate (EGDMA) as an hydrophobic crosslinker, phenylboronic acid methacrylamide (PhBA-MA) as a functional monomer, and potassium persulfate (KPS) as an initiator. The influences of the PhBAMA concentration and mode of monomer addition (batch or shot-growth processes) have been examined both on the polymerization kinetics and on the physicochemical and colloidal properties of the final particles. Results have been discussed according to the ionogenic and hydrophobic nature of the functional monomer. We have directly and clearly provided evidence that PBA was successfully incorporated at the particle surface by using ESCA analysis, especially when using a shot-growth process, a result that was indirectly confirmed by investigating the electrophoretic mobility behavior of the various latexes as a function of pH.

**Keywords** Poly(*N*-ethylmethacryl-amide) · Microgel particles · Phenyl-boronic acid · Polymerization kinetics · Thermal sensitivity

## Introduction

In the last two decades, functionalized latex particles have received increasing attention due to their application in many areas, especially as solid phase supports in numerous biological applications (immunoassay and DNA diagnostic, cell separation, drug delivery carrier, etc.) [1]. Such particles bearing appropriate reactive groups can indeed be used for the covalent immobilization of biomolecules including enzymes, antibodies, DNA fragments, and peptides, a process that may confer more stability to the formed conjugates than when simple adsorption is used. Many exhaustive reviews reported the different routes developed for manufacturing functionalized particles [1, 2, 3]. The copolymerization approach is more versatile and well adapted for the synthesis of polymer colloids by emulsion polymerization of a main monomer (mostly hydrophobic) in the presence of small amounts of a functional monomer. A large variety of monomers bearing reactive groups are indeed available either commercially or after relatively easy synthetic methods [3].

In this field, a great deal of effort has been dedicated to the preparation of latex particles with a hydrophilic character, since they were found to impart several advantages when dealing with immobilization of biomolecules: for example, higher colloidal stability against electrolytes than hydrophobic particles, a decrease in the physical adsorption of most proteins, and better biocompatibility. Various classes of hydrophilic dispersed materials in the colloidal range have been proposed; among these, submicronic alkyl(meth)acrylamide microgel particles have proved to be suitable and in addition they exhibit outstanding stimuli-responsive

properties. The development of such particles, especially those based on poly-(*N*-isopropylacrylamide) (NIPAM), has received much attention especially for application in the biological domain [4].

As part of a long-term research program on the design of reactive latexes keeping their hydrophilicity under physiological conditions (37 °C, high ionic strength, etc.), we have already reported the synthesis and properties of poly-(*N*-isopropylmethacrylamide) microgel particles [5, 6] with a volume phase transition temperature ($T_{VPT}$) around 44 °C, and very recently the preparation of poly-(*N*-ethylmethacrylamide) exhibiting a $T_{VPT}$ of 70 °C [7].

Based on this preliminary study, our strategy was to then incorporate a functional group to enable the oriented binding of appropriate biomolecules and also allowed the immobilization of the particles onto plane model surfaces (such as silica wafers). For this purpose, we selected the phenylboronate function which is well known to form stable complexes (cyclic ester) with carbohydrate molecules in basic media through interaction with the *cis*-diol group [8, 9, 10, 11, 12, 13] as schematically illustrated in Scheme 1.

Various workers took advantage of this specific and strong complexation reaction by designing several synthetic PBA-containing polymers, mainly for biomedical applications. Kataoka et al. [14] described the preparation of glucose-sensitive polymers systems based on *N*-alkylacrylamide-3-acrylamidophenylboronic acid (APhBA) copolymers with a broad range of $T_{VPT}$'s. The synthesis of 100–400 μm acrylamide-APhBA copolymer microgel particles has been described by the same group [15] who proposed their use as a novel controlled delivery system for insulin. The work of Tsukagoshi et al. [16] on the preparation of styrene-butyl acrylate copolymer latexes functionalized with PhBA, their characterization, and their suitability for the immobilization of glucose should be also mentioned.

This paper aims to report the synthesis of hydrophilic latex particles with a high $T_{VPT}$ and bearing phenylbo-ronic acid groups on the surface. Based on recent work devoted to the preparation of submicronic and monodisperse poly(NEMAM) microgel latexes, the main objective of this study was to investigate the influence of the presence of a PhBA monomer derivative, phenylboronic acid methacrylamide (PhBAMA), and the type of polymerization process on the polymerization kinetics of NEMAM, and physicochemical properties of the resulting dispersed polymer particles. The final latexes were characterized with respect to their conversion, particle size, size distribution, volume phase transition temperature, swelling behavior, PhBA surface incorporation, and electrophoretic mobility as a function of the nature of the polymerization process [batch versus shot-growth (PhBAMA monomer addition)].

## Experimental

### Materials

Water was of Milli-Q grade (Millipore SA, France) and was boiled for 2 hours under a stream of nitrogen before use. *N*-Ethylmeth-acrylamide (NEMAM) monomer (Polyscience, USA) was purified by filtration through an alumina column. Potassium persulfate initiator (KPS) from Sigma was used as received. Ethylene glycol dimethacrylate (EGDMA) from Merck, was used as received as a crosslinker.

### *Synthesis of phenylboronic acid methacrylamide*

This synthesis is depicted in (Scheme 2). After dissolving methacryloyl chloride (0.34 g) in THF (20 ml), 3-aminophenylboronic acid (0.5 g) in anhydrous THF (15 ml) was added dropwise with temperature control (0 °C). After 25 min, triethylamine (1 ml) was rapidly added dropwise. The reaction time was about 2 hours. The crude product was purified by precipitation in ethyl ether (100 ml), then filtered and dried under vacuum. It was further purified on a chromatograph column using a pentane/acetone (65/35 v/v) mixture. The yield of the reaction was around 30%. The compound was characterized by $^1$H NMR [$\delta = 7.34$ (m, 4 H), 5.80 (s, 1 H), 5.50 (s, 1 H), 2.03 (s, 3 H)].

**Scheme 1** Equilibrium of the reaction between phenylboronic alkylamido acid and polyol compounds in aqueous solution
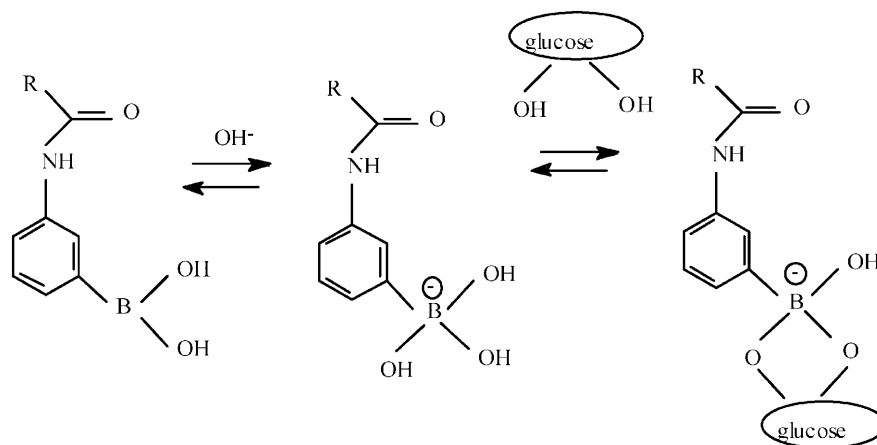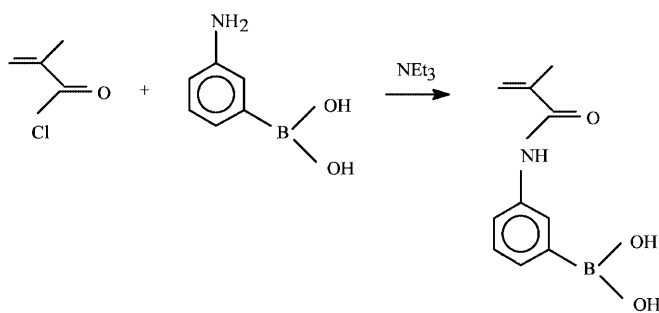
**Scheme 2** Synthesis of phenylboronic acid methacrylamide

*Preparation of latex particles*

The polymerization reactions were performed batchwise, using boiled oxygen-free deionized water, with a thermostatted reactor equipped with a mechanical stirring paddle and a nitrogen inlet. The stirring rate in all polymerizations was 280 rpm. The reaction temperature was controlled at 90 °C.

The required amounts of reactants are given in Table 1. The duration of the polymerization was 6 hours. Sampling was periodically carried out to follow the kinetics. Hydroquinone traces were added to quench the reaction, and the samples were stored at 4 °C.

To optimize the PhBAMA surface incorporation, three different polymerization processes were performed, namely batch, and two shot-growth processes. For the batch process, the reactor was charged with water, NEMAM, and EGDMA, and after stabilization of the system at the reaction temperature (90 °C), a basic solution of PhBAMA was added followed by the initiator (KPS) as a solution in a few ml of water. For the shot-growth process 1, the same batch protocol was started without PhBAMA. After 40 min reaction, a solution of the functional monomer was added portionwise (1 ml every 10 min). For shot-growth process 2, the same protocol was used but in addition, 10% of the initial reaction mixture was added together with the PhBAMA solution.

Characterization methods

Before any characterization, all latexes described here were cleaned by repetitive centrifugations and dispersions using Milli-Q water to remove free electrolytes and water-soluble polymers. The overall conversions were determined using $^1H$ NMR spectroscopy (500 MHz Varian Unity Plus spectrometer).

*Particle size and distribution*

Particles sizes were measured both by quasi-elastic light scattering (QELS) (Zetasizer 3000 HS Malvern Instrument) and by transmission electron microscopy (TEM) (Philips CM120, CMEABG, Claude Bernard University Lyon 1, France).

**Table 1** Recipe for the preparation of batch-functionalized P(NEMAM) particles

| Ingredients | Quantities (g) |
| --- | --- |
| NEMAM | 1 |
| KPS | 0.01 |
| EGDMA | 0.15 |
| PhBAMA | 0.01–0.08 |
| Water | 50 |

The hydrodynamic diameter ($D_h$) measured by QELS was used to investigate the effect of temperature (30–70 °C) on the particle size variation and evolution during the polymerization step.

*Volume phase transition temperature ($T_{VPT}$)*

The $T_{VPT}$ of latex particles was determined by recording the optical density ($OD$) of a highly diluted latex solution (pH 6 and $10^{-3}$ M NaCl) as a function of temperature (30–98 °C). The optical density was measured using a UV = $mc^2$ spectrophotometer (Safas, Monaco) at 500 nm wavelength. The $T_{VPT}$ was then calculated from the maximum of the d$OD$/dt variation as a function of temperature.

*Electrophoretic mobility measurements*

Experiments were carried out with the Zetasizer 3000 HS (from Malvern Instruments, UK) at 20 °C. Latex electrophoretic mobilities were obtained in $10^{-3}$ M NaCl solution as a function of pH. Measurements quoted were the average of at least three individual determinations.

*Elemental analysis*

Contents of C,H,O,N, and B in freeze-dried samples were performed at the Service Central d'Analyse (CNRS, Solaize) using an atomic emission spectrometer equipped with a He Plasma and inductive coupling (ICPAES).

*ESCA*

Latexes were diluted (1/25 v/v) in water, and a drop was then deposited on an indium (or tantalum) support, and after drying, the sample was analyzed. Experiments were performed at the Institut de Recherche sur la Catalyse (CNRS, Villeurbanne) on an ESCALAB 200R spectrometer equipped with a hemispheric analyzer and a detection system with 5 channeltrons. The X-ray source was Mg (1253.6 eV), and the analysis energy was 50 eV. Detection was done perpendicular to the sample plan. Charge effects were corrected by fixing the C1s-ray energy at 284.5 eV.

## Results and discussion

For the preparation of the hydrophilic microgel poly(NEMAM) submicronic particles with PBA on the surface, the recipe previously used for the synthesis of poly(NEMAM) latex [7] was adapted to investigate the influence of PhBAMA and the protocol of polymerization on the polymerization kinetics. Then, the mode of polymerization was modified to optimize the surface incorporation of this functional monomer.

Influence of PhBAMA concentration
on polymerization kinetics

Figure 1 displays the conversion versus time curves for polymerization carried out without and with three different PhBAMA concentrations. It is clear that the

**Batch**
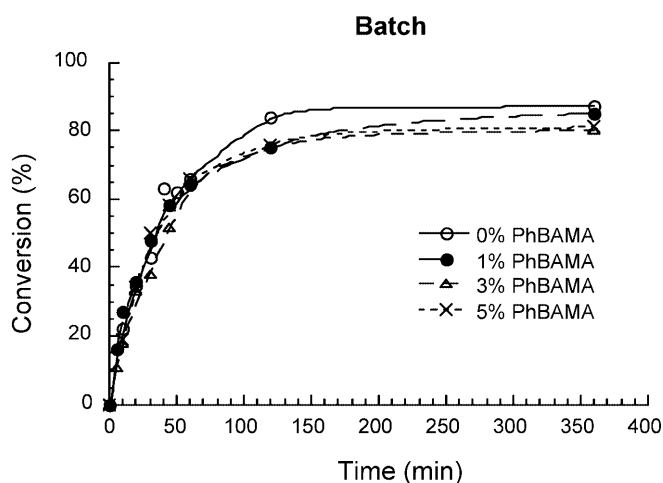


**Fig. 1** Influence of PhBAMA concentration (wt%) on NEMAM polymerization

functional monomer does not affect the initial polymerization rate with a conversion degree slightly lower than for NEMAM polymerization. The same was true for the other polymerization processes, i.e., the two shot-growth protocols 1 and 2. This behavior is quite surprising, particularly when running the batch process, since it has long been reported that the presence of a functional monomer, especially when it exhibits an ionic character, can dramatically affect the polymerization mechanism in heterogeneous media, by strongly increasing the polymerization rate [18].

Figure 2 reports the evolution of the hydrodynamic diameter versus time as measured by QELS. Changing the PhBAMA concentration does not significantly affect the particle size of latex, except perhaps when the PhBAMA concentration was 1 mole%, and provided a final particle size lower than for the other concentrations.
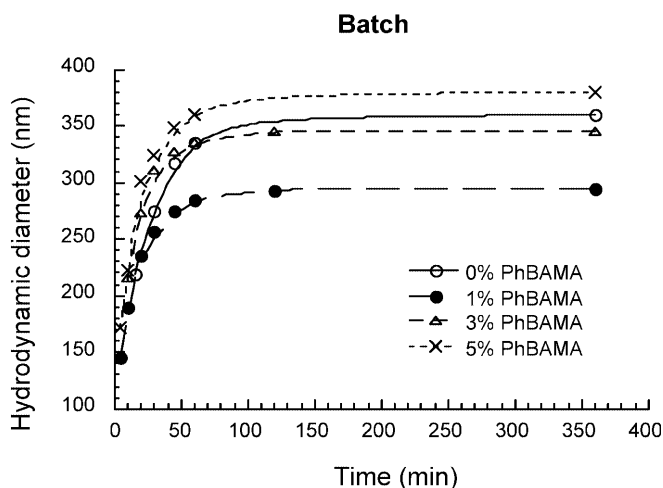
**Batch**



**Fig. 2** Influence of PhBAMA concentration (wt%) on the particle size variation versus time of batch polymerization of NEMAM

**Table 2** Influence of the PhBAMA concentration (wt%) on the particle diameter of final latexes at 20 °C for the various polymerization processes

|  | PhBAMA content in the recipe (wt%) | Particle diameter ($D_h$) of the final latex (nm) |
|---|---|---|
| batch | 0 | 360 |
|  | 1 | 295 |
|  | 3 | 345 |
|  | 5 | 380 |
| Shot-addition 1 | 1 | 345 |
|  | 3 | 355 |
|  | 5 | 323 |
|  | 8 | 380 |
| Shot-addition 2 | 1 | 367 |
|  | 3 | 362 |
|  | 5 | 375 |

As expected, for the polymerization carried out by shot-addition of the PhBAMA, the functional monomer does no affect the final particle size of the latexes (Table 2).

Again the trend observed with the batch process is unusual, since the presence of an ionic co-monomer generally leads to the formation of a large particle number due to the colloidal stability imparted by the ionic charges. This is in contrast to what was observed in the case of NIPAM polymerization performed, either in the presence of aminoethylmethacrylate hydrochloride [17, 18] or vinylbenzylisothiouronium hydrogen chloride [19].

This particle size analysis was completed by a transmission electron microscopy study of the various latexes. Figures 3a,b show the micrographs in the case of batch and shot-addition 1 processes, and the following observations can be made: i) all the polymerizations lead to monodisperse latexes regardless of the PhBAMA concentration and type of polymerization process. This suggests that particles are formed during a very short nucleation step, as has already been found in other alkylacrylamide precipitation polymerizations [5, 17, 18]; ii) all the particles exhibit a dark core surrounded by a more or less clear shell, which could be assigned to the development of a core-shell structure resulting from a concentration gradient of the crosslinker (EGDMA) originating in its rapid consumption rate. It was not possible to draw any conclusion from the measured TEM particle diameters, since as already mentioned, the hydrophilic particles were found to collapse on the TEM grid during the drying stage [20].

The final latexes were also characterized with respect to the contents of water-soluble polymer as recovered on centrifugation of the final latexes and subsequent analysis of the corresponding sera. This phenomenon is indeed typical of the heterogeneous polymerization of such systems; this rapid consumption of the crosslinker causes a loose entanglement of the poly(alkyl (meth)acrylamide) chains formed at later stages of the
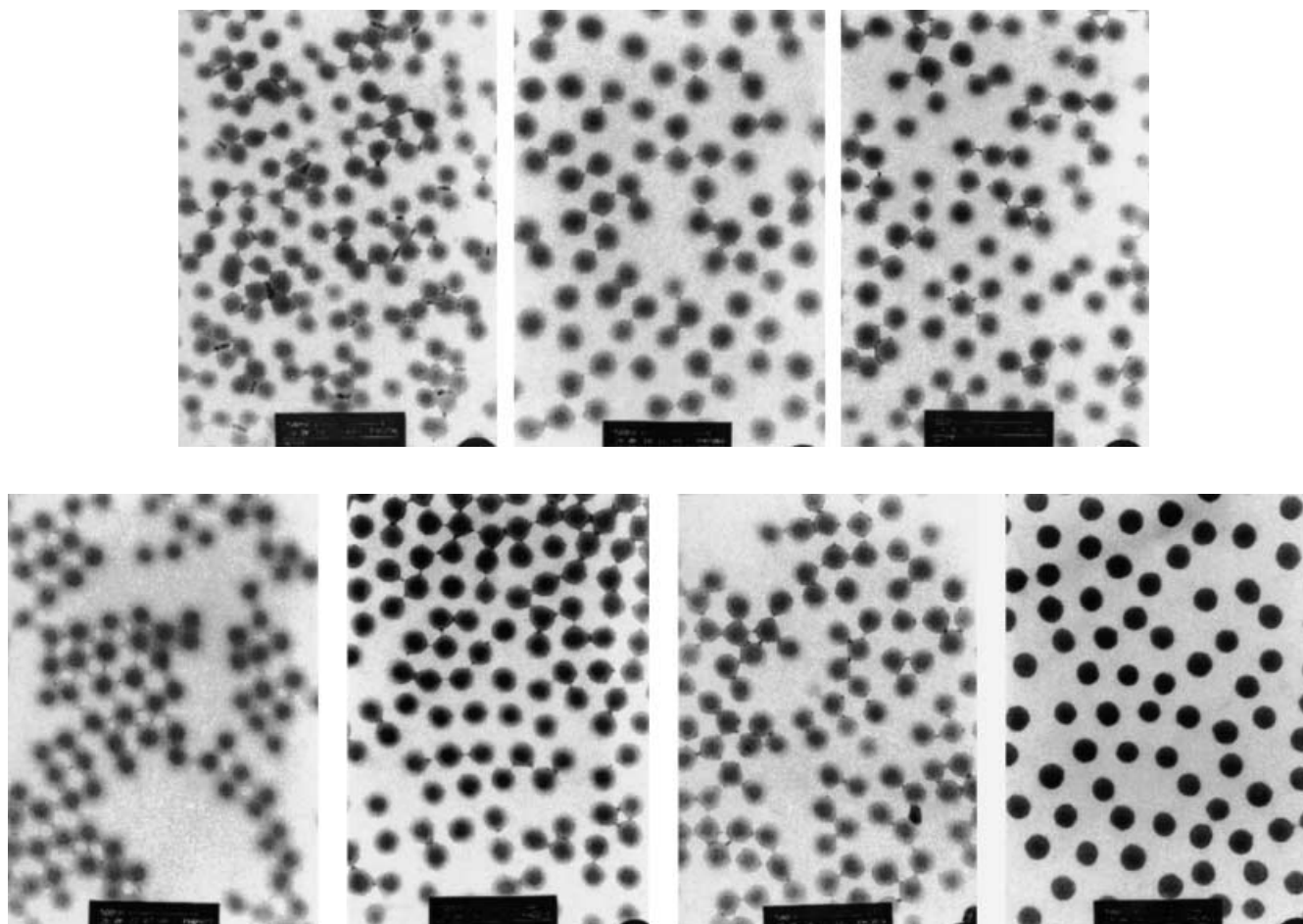
**Fig. 3a,b** TEM micrographs of functionalized P(NEMAM) latex particles prepared with various concentrations of PhBAMA: **a** batch process, **b** shot-addition process 1

reaction. As reported in Table 3, this water-soluble material is far from negligible, regardless of the PhBA-MA content, since 30–40% was obtained even though

**Table 3** Influence of the PhBAMA concentration (wt%) on the formation of the water-soluble polymer contents of latexes prepared by various processes

|  | PhBAMA content in the recipe (wt%) | Water-soluble material (wt%) |
| --- | --- | --- |
| batch | 0 | 31 |
|  | 1 | 41 |
|  | 3 | 43 |
|  | 5 | 43 |
| Shot-addition 1 | 1 | 39 |
|  | 3 | 32 |
|  | 5 | 34 |
|  | 8 | 35 |
| Shot-addition 2 | 1 | 42 |
|  | 3 | 39 |
|  | 5 | 39 |

the crosslinker nature and concentration had been previously optimized [7]. Using a batch process, it seems that the presence of PhBAMA leads to an increase of the water-soluble polymer content, but in other processes this tendency is not observed.

Physicochemical characterization of the functionalized latexes

A complete analysis of the physicochemical and colloidal properties of the functionalized latexes was investigated with a view to provide suitable direct and indirect information on the surface incorporation of PhBAMA, which will be useful for monitoring further applications of these particles. The following analyses will be successively discussed: quantification of PhBAMA in the latexes, volume phase transition temperature, swelling capacity, and electrophoretic mobility.

*PhBAMA incorporation into the latexes*

The various cleaned latexes (i.e., free of water-soluble polymers) were analyzed firstly by elemental analysis,

which gives the overall amount of PhBA copolymerized in the whole particles, and secondly by ESCA to quantify the surface incorporation of this functional group.

Elemental analysis allowed quantification of the amount of boron in the sample and Fig. 4 summarizes the data obtained for the latexes prepared according to different processes. We found that the amount of boron increases with increasing concentration of PhBAMA in the recipe, but with a tendency varying with the type of process. The largest overall quantities were observed with batch latexes, which is not surprising, since when dealing with the shot-addition process, the recovered water-soluble polymers are probably PhBAMA-rich due to the lack of crosslinker at the conversion (around 80%) when the addition of PhBAMA was performed.

ESCA analysis was more appropriate to detect the presence of PhBA at the particle surface and Fig. 5 provides a general spectrum recorded on a dried functional sample. It is worth mentioning the presence of boron (B 1s) and sulfur (S 2p) which suggests both the incorporation of PhBA and sulfate (from initiator decomposition), however in a very small proportion compared to the other atoms; this required scan accumulation to get precise data (but still within a 20% uncertainty).

The final results are collected in Fig. 6, showing the variation of the atomic proportion of boron at the particle surface as a function of the PhBAMA added in the latex recipe. As previously noticed, the boron incorporation increases with increasing amounts of PhBAMA in the recipe, and it is clear that shot-addition 1 process allows the best surface immobilization of PhBA. This result would suggest that the two other processes favor the incorporation of the functional monomer more deeply inside the particle.
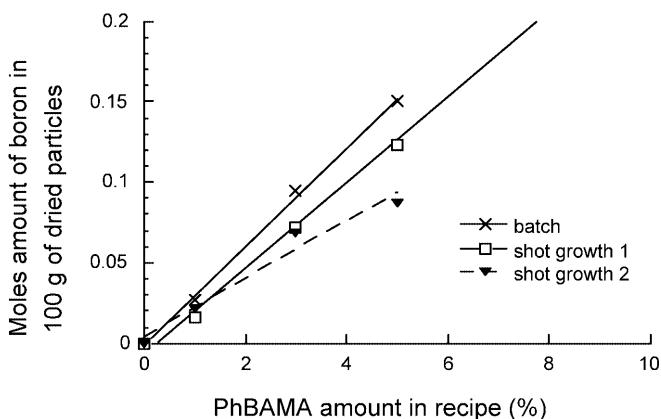
## Volume phase transition temperature ($T_{VPT}$) of particles

The volume phase transition temperature ($T_{VPT}$) of the various latexes has been examined by turbidity measurements as a function of temperature, and results are reported in Fig. 7. It first appears that the transition occurs in a broad temperature range, a feature typical of such crosslinked particles and second, a displacement of $T_{VPT}$ toward low temperature with functionalized particles is clearly evident, regardless of the type of production process used for the latexes (results are only shown for batch latexes). This behavior corroborates the observations already quoted by Kataoka et al. [14] and more recently by Yi et al. [21] in the case of poly(NIPAM)-co-(PhBA-acrylamide) and poly(NIPAM)-co-(NTBA) (N-tert-butylacrylamide) linear polymers, respectively. Such a decrease can be explained by the relative hydrophobicity of the PhBA functions below pH 8 (only 6 mole% of the functions are ionized at pH 7.6), causing some collapse of the PhBA-rich P(NEMAM) chains located at the particle surface. Moreover, the crosslinking density profile could be slightly more modified in those particles than in the case of unfunctionalized ones.

The thermal-sensitivity of the latex particles was confirmed by studying the hydrodynamic diameter of the P(NEMAM) particles as a function of temperature, and results are given in Fig. 8. In comparison with the behavior of the unfunctionalized particles (1 % KPS, 15% EGDMA, 0 % PhBAMA), a different trend is indeed observed for the functionalized ones, since the particle size slightly and continuously decreases at low temperature (at 20 °C for the richest PhBAMA particles (3 % and 5 % PhBAMA, respectively) instead of 40–50 °C for the others (0 % and 1 % PhBAMA, respectively).

## Swelling capacity of the particles

The swelling capacity of the various prepared latexes were determined by measuring the hydrodynamic diameter ($D_h$) at 20 °C and $D_n$ (from TEM data), and calculating the ratio $(D_h/D_n)^3$, as illustrated in Table 4. The main effect was that the introduction of PhBAMA in the recipe makes the swelling ratio decrease by a factor of about 2, with a value of around 11 for the unfunctionalized particles, instead of 5–7 for the functionalized latexes irrespective of the polymerization process. Due to the uncertainty of the TEM diameters (because of the partial collapse of the dried particles on the grids), no clear trend can be highlighted regarding the influence of PhBAMA and the mode of polymerization. Nevertheless, this behavior would corroborate that the surface incorporation of PhBAMA below pH 8 imparts some hydrophobicity to the particle shell, causing a reduction in the swelling capacity. A change in



**Fig. 4** Variation between the amount of boron (atom g$^{-1}$ per 100 g of dried material) detected in the dried particles and the quantity of PhBAMA (wt%) introduced in the recipe

the crosslinker distribution within the shell particle might also contribute to that effect.

### Electrophoretic mobility

The various latexes were examined with respect to their electrophoretic behavior as a function of pH, and the results are illustrated in Fig. 9a–c for the batch, shot-growth 1 and 2 latexes, respectively. The observations can be summarized:

1. The unfunctionalized P(NEMAM) latex exhibit the lowest electrophoretic mobility ($\mu e$ order of $0.5 \times 10^{-8}$ m cm $V^{-1}$ $s^{-1}$) due to the hairy structure of the particle below the $T_{VPT}$. The negative value obtained is due to the presence of sulfate groups (as also identified by ESCA) which originated from the KPS



**Fig. 5** **a** General ESCA spectrum of 8 wt% PhBAMA (introduced by batch process) dried latex sample. **b** Enlargement of the spectrum corresponding to boron and sulfur atoms
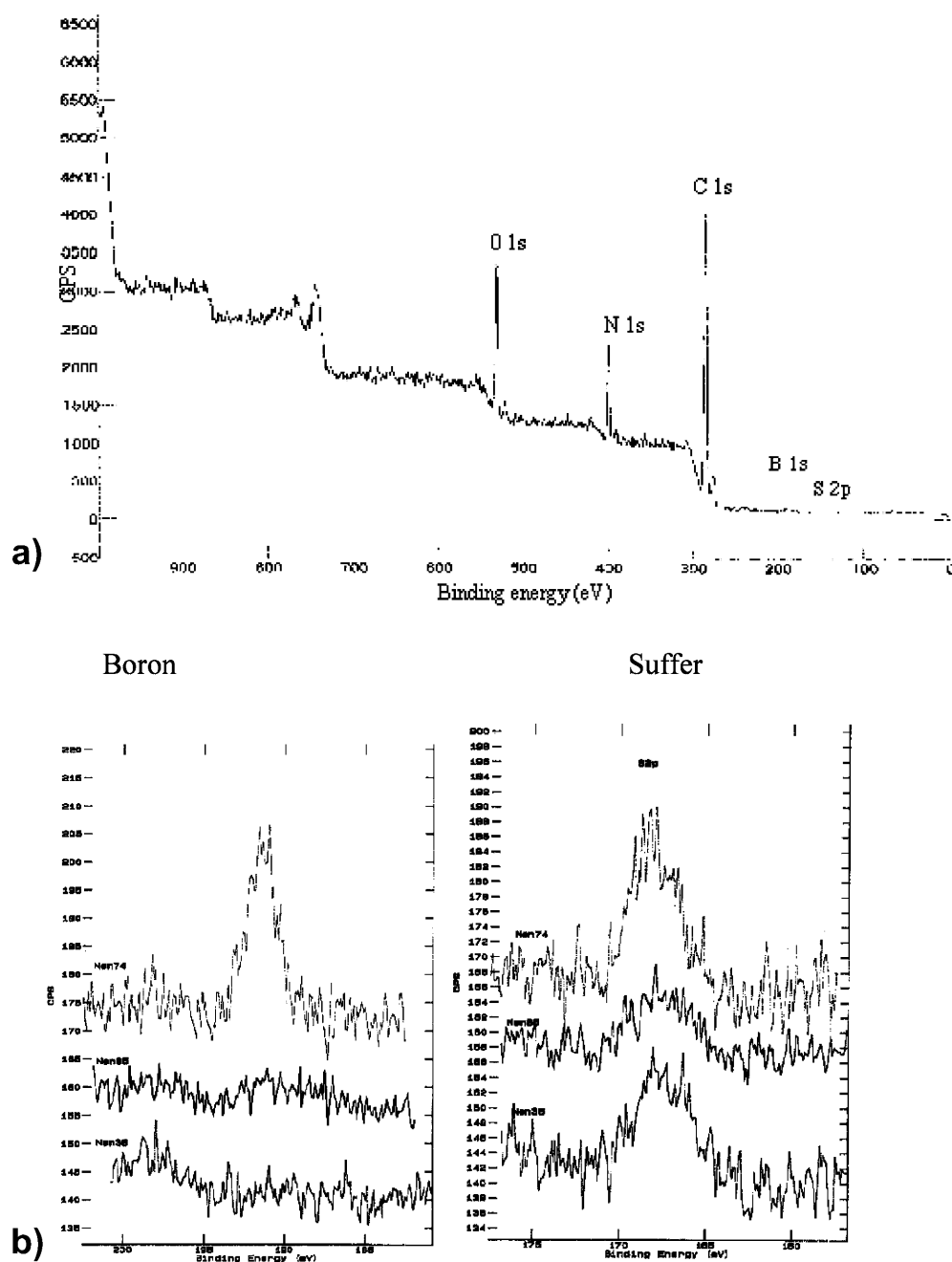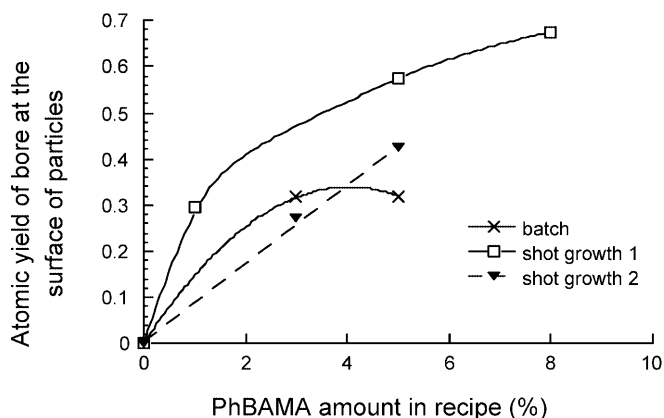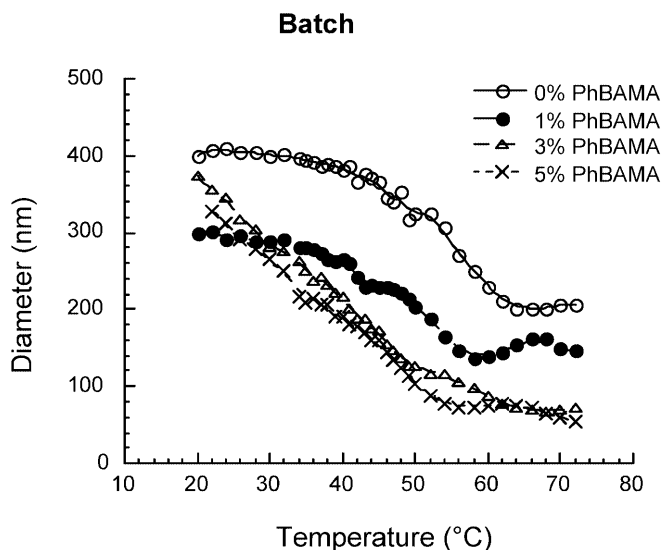
**Fig. 6** Boron atomic percentage at the particle surface as a function of the concentration of PhBAMA (wt%) introduced in the various latex recipes (batch, shot-addition 1 and 2)
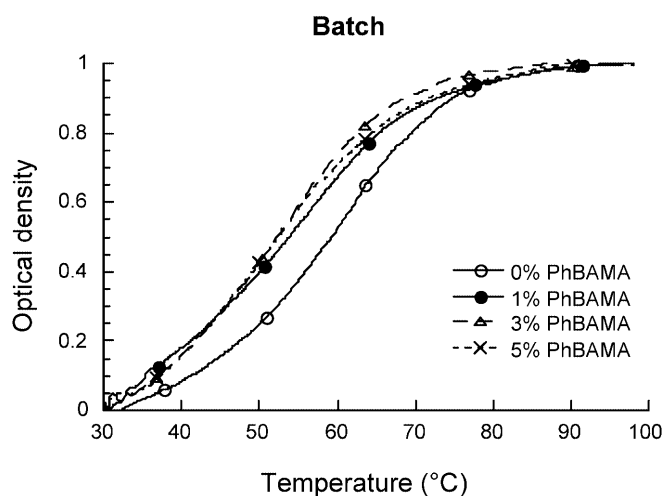


**Fig. 7** Normalized curves of the optical density (OD) (in $10^{-3}$ M NaCl) variations as a function of temperature for different PhBAMA concentrations added in the batch latex recipe



**Fig. 8** Hydrodynamic diameter (from QELS data) of various PhBA-functionalized batch latexes as a function of temperature

**Table 4** Particle size (hydrodynamic ($D_h$) and TEM ($D_{TEM}$) diameters) and swelling ratio of P(NEMAM) particles versus PhBAMA concentration and polymerization process

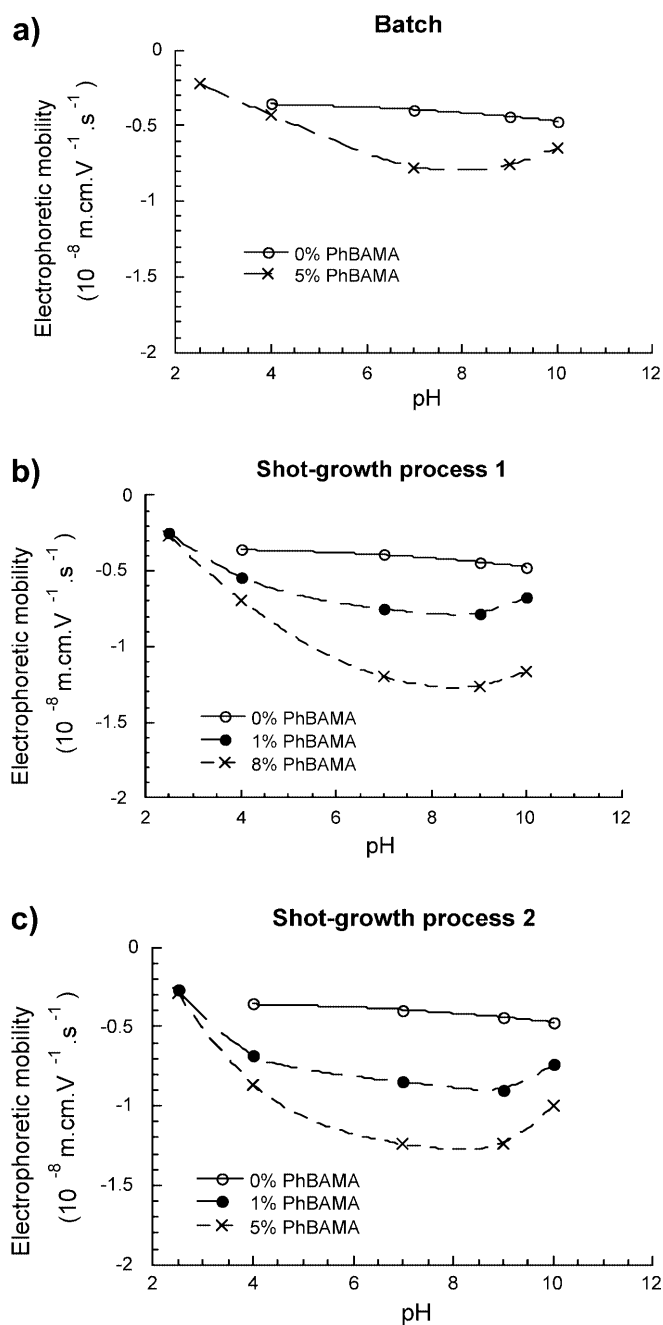| Polymerization process | PhBAMA content in recipe (wt%) | $D_h$ (20 °C, nm) | $D_{TEM}$ (nm) | SR = $2(D_h/D_{TEM})^3$ |
|---|---|---|---|---|
| Batch | 0 | 360 | 160 | 11.4 |
| | 1 | 294 | 165 | 5.6 |
| | 3 | 378 | 197 | 7 |
| | 5 | 342 | 185 | 6.3 |
| Shot-growth 1 | 0 | 360 | 160 | 11.4 |
| | 1 | 345 | 204 | 4.83 |
| | 3 | 355 | 186 | 7 |
| | 5 | 316 | 182 | 5.2 |
| Shot-growth 2 | 0 | 360 | 160 | 11.4 |
| | 1 | 373 | 208 | 5.4 |
| | 3 | 362 | 208 | 5.3 |
| | 5 | 375 | 240 | 3.8 |

decomposition, and consequently no significant change of $\mu e$ occurs with this strong acid upon varying the pH.

2. The functionalized P(NEMAM) particles display a more negative $\mu e$, especially when lowering the pH. A general trend is that $\mu e$ decreases from pH 2.5 to 7, and then a plateau value is reached in the pH range 7–10. This behavior would be a confirmation of the presence of the functional monomer at the particle interface, with a progressive ionization of PhBA between pH 2.5–7. In addition, the value of pKa for surface immobilized PhBA (about 7) seems lower than the value reported in the literature (8.7) [22] for linear copolymers. A recent paper by Tsukagoshi et al. [16] reported the same difference for PBA-functionalized poly(butylacrylate)-polystyrene latex particles.

3. This behavior in the $\mu e$ variation versus pH of functionalized latexes is reinforced when PhBAMA was introduced through shot-addition; this confirmed that relative to the batch process, more boronate functions are incorporated in the interfacial layer of the particle leading to an increase in the surface charge density. The larger the PhBAMA added in the recipe, the higher the absolute value of the $\mu e$ of the particles.

## Conclusions

Monodisperse and submicronic P(NEMAM) latexes functionalized with phenylboronic acid groups can be

**Fig. 9a–c** Electrophoretic mobility variation versus pH for latexes prepared with different PhBAMA concentrations (wt%): **a** batch process, **b** shot-addition 1, **c** shot-addition 2

produced by emulsion/precipitation polymerization of NEMAM in water using an hydrophobic crosslinker (EGDMA) and in the presence of phenylboronic acid methacrylamide (PhBAMA). The influence of both the PhBAMA concentration and polymerization process has been examined on both the polymerization kinetics and physicochemical and colloidal properties of the final

latexes. It is worth highlighting the following main results:

1. PhBAMA was found to only very slightly modify the batch and shot-growth polymerization kinetics of NEMAM regardless of the initial added concentration. The particle size number did not significantly change either, which is indicative that this functional monomer would not play an important role in the formation or the stabilization of the particles. Such a behavior is quite unusual considering the ionogenic character of PhBA, since it is well known that the introduction of an ionic or ionogenic comonomer (added in a very small proportion) can dramatically affect the kinetics of heterogeneous polymerizations, especially precipitation polymerization of alkyl-acrylamide [18]. It might be suggested that PhBAMA would behave more as a hydrophobic comonomer for two reasons: (i) the presence of the phenyl group might reduce the global polarity of the monomer and, (ii) the undissociated form would predominate as a consequence of the KPS decomposition in the reaction medium, which generally leads to a pH decrease of 1 or 2 units. This would indeed displace the equilibrium $B(OH)_2/B(OH)_3^-$ towards the undissociated form. This assumption could be indirectly evidenced by two experimental observations: (i) the functionalized particles should show a lower $T_{VPT}$ compared to that of the P(NEMAM) ones and, (ii) a significant reduction in the swelling capacity of the particles.

2. As directly detected by elemental and ESCA analyses, PhBA groups have been successfully incorporated into the particles, and the larger the amount of PhBAMA initially added in the latex recipe, the higher the detected PhBA on the particle surface, especially when dealing with shot-addition processes. This surface immobilization of PBA was clearly confirmed by comparing the electrophoretic behavior of the functionalized latexes with the unfunctionalized one as a function of pH. The high PhBAMA concentrations associated with the shot-addition processes (1 or 2), definitely afford an efficient interfacial incorporation of the phenylboronic functions.

In conclusion, these well-characterized phenylboronic acid surface functionalized P(NEMAM) latexes particles provide useful colloidal reactive supports for various applications, and their performances have initially been explored for the modification of silica wafers by covalent immobilization. This study will be described in a future paper.

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