# Preparation of Aminated Polystyrene Latexes by Dispersion Polymerization

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ABSTRACT: The preparation and characterization of aminated polystyrene-based latexes as attainable by dispersion polymerization technique are reported. Mixtures of Boc-*p*-aminostyrene and styrene monomers at various compositions were copolymerized under dispersion conditions in 2-propanol/water 3:1 by volume in the presence of α,α′-azobis(isobutyronitrile) as free radical initiator at 75 °C. Copolymer microspheres with uniform size distributions and average diameters comprised between 0.9 and 1.8 $\mu$m were obtained. Aminated microspheres were obtained by the simple removal of the Boc protective group under acidic conditions followed by neutralization, thus leading to *p*-aminostyrene/styrene copolymers. These chemical treatments when carried out under mild conditions (room temperature and dilute acid and basic solutions), demonstrated to be efficient without causing any major alteration of the microspheres morphology. XPS analysis of the prepared microspheres showed an increase of $NH_2$ groups with the increasing of the Boc-*p*-aminostyrene in the copolymer feed up to 10 mol %.

## Introduction

Polymer latexes are currently enjoying a fairly ample range of applications in many fields including among others biochemistry, colloid sciences, and medicine.[1−5] In particular, latexes containing functional groups, such as carboxyl, hydroxyl, and amino, exposed on the surfaces of the constituting particles can be used in immobilization by ionic or covalent bindings of biological molecules such as proteins, antibodies, and enzymes.[6−14]

Commonly the preparation of aminated latexes involves procedures requiring three reaction stages comprising styrene polymerization, nitration of polystyrene, and reduction of the nitro groups inserted on the aromatic rings in order to obtain aminated particles.[15] Other procedures usually are based on the grafting of appropriate functional polymers on the surface of the latexes previously prepared.[16] In all these cases the procedures involve a variety of reactions making them rather complex and time-consuming[17,18] and often susceptible of altering the inherent latex morphological properties.[19]

The present work is aimed at reporting on the preparation of aminated styrene-based latexes by copolymerization of Boc-*p*-aminostyrene[20] (Boc-AMST) and styrene (ST) under dispersion conditions[21,22] followed by selective removal of Boc group under morphology conservative conditions.[23] The P(ST-*co*-Boc-AMST) microspheres (protected form), considered as copolymers containing protected amino groups in its structure, were submitted to acid treatment (HCl in 2-propanol) followed by a basic treatment (NaOH(aq)). After the acid treatment it was possible to obtain the deprotected product by a removal of the Boc group from the aminated monomeric units of the copolymers. The particles in this case (unprotected form) presented the $NH_3^+Cl^-$ groups that by treatment under alkaline condition were quantitatively converted to the corresponding free amino groups. By a single pot reaction as represented in Figure 1 it was then possible to prepare amine-containing latexes at different contents of amino groups.

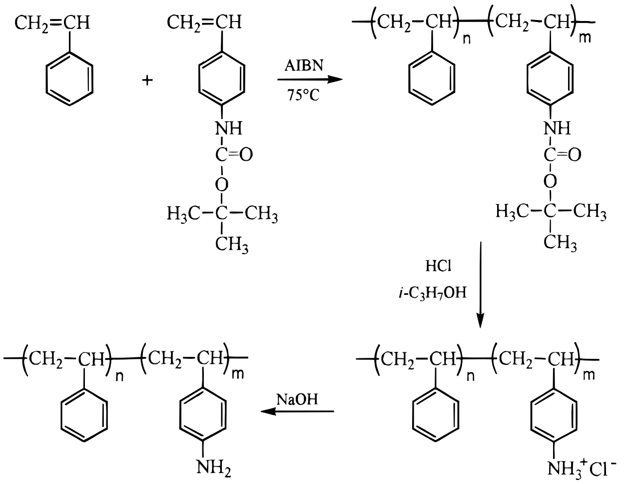

**Figure 1.** Preparation of aminated styrene-based copolymer latex by a single pot procedure: Boc-AMST/ST copolymerization scheme.

Both the protected and unprotected amino-containing latexes were characterized by FT-IR, $^1$H NMR, $^{13}$C NMR, and SEM analyses. The resulting aminated particles are currently under investigation for applications as supports in immunological reactions such as antigen−antibody conjugations.[24,25]

## Experimental Section

**Materials**. Styrene (ST) (Fluka) and *p*-aminostyrene (AMST) (Aldrich) monomers were distilled under vacuum before the polymerization. The initiator α,α′-azobis(isobutyronitrile) (AIBN) (Fluka Chimica) was recrystallized from ethanol prior the use. Di-*tert*-butyl dicarbonate $(Boc)_2$ (Aldrich) was used as received

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**Table 1. Copolymerization Experiments of Boc-AMST with ST**

| | feed | | polymer[a] | |
|---|---|---|---|---|
| sample | Boc-AMST/ST (mmol) | Boc-AMST/ST % (mol/mol) | Boc-AMST/ST % (mol/mol) | yield (wt %) |
| LB 1/99 | 0.45/41.3 | 1.1/98.9 | 1.2/98.8 | 98 |
| LB 5/95 | 1.74/34.6 | 4.8/95.2 | 5.8/94.2 | 93 |
| LB 10/90 | 2.60/23.3 | 10.1/89.9 | 12.1/87.9 | 91 |
| LB 20/80 | 4.80/18.7 | 20.4/79.6 | 20.5/79.5 | 88 |
| LB 30/70 | 6.66/15.38 | 30.2/69.8 | 31.0/69.0 | 87 |

[a] Calculated by $^1$H NMR.

in the preparation of the Boc-*p*-aminostyrene (Boc-AMST) monomer.[20] Poly(*N*-vinylpyrrolidone) (PVP) ($M_w$ 360 000, Fluka AG) was used as dispersant. Isopropyl alcohol and deionized water were used as reaction medium.

**Instrumental Characterizations.** *Infrared Spectroscopy (FT-IR).* A Perkin-Elmer 1600 FT-IR instrument connected to a PC-DOC microcomputer was used for the characterization of the copolymer samples. The samples were prepared by casting from chloroform solution and in some cases by using KBr pellets. The spectra were recorded in the 4000−400 cm$^{-1}$ interval.

*Nuclear Magnetic Resonance Spectra.* The $^1$H NMR spectra were registered by using a Varian Gemini-200 (200 MHz) spectrophotometer. $CDCl_3$ sample solutions (5−10 wt %) were analyzed in tubes of 5 mm, using TMS as internal standard. The $^{13}$C NMR spectra were recorded by using a Varian Gemini-200 (22.63 MHz) spectrophotometer, and the samples were prepared as previously described for $^1$H NMR analysis.

*Gel Permeation Chromatography (GPC).* The analyses were carried out by using a Perkin-Elmer LC Series 10 chromatograph equipped with 2 columns Plgel 5 $\mu$ mixed C and an UV spectrophotometric detector (Perkin-Elmer LC-75). THF (HPLC grade) was used as eluent at 1 mL/min flow rate, and the samples were prepared at concentration of about 5−10 mg/mL in chloroform. A standard curve was built up by using monodisperse polystyrene samples of molecular weight comprised between 2100 and 233 000 using chloroform as solvent.

*Scanning Electron Microscopy (SEM).* The dried samples of latexes were fixed in suitable supports and then coated with a thin layer of gold. The photomicrographs of the copolymer particles were taken by a JEOL JSM-T300 scanning microscope at an accelerating voltage of 15 kV.

*X-ray Photoelectron Spectroscopy (XPS).* The nitrogen content on the copolymer microsphere surfaces was investigated by using an electronic spectrophotometer (AEI ES300). The spectra were recorded by a Du Pont 310 recorder. The sensibility factors of the instrument were fixed: pass energy at 93.900 eV, aperture 4 AI 300 W, angle 45°, and acquisition time 119.21 min.

*Size Distributions by Coulter Counter.* The average particle size and the particle size distribution of the prepared polymeric particles were carried out by using a Fritish Particle Sizer Analysette 22 that provided histogram type distributions.

**Copolymerization of Boc-AMST with ST under Dispersion Conditions.** The Boc-AMST monomer synthesized by reaction between di-*tert*-butyl dicarbonate and *p*-aminostyrene monomer according to a procedure reported elsewere[20] was copolymerized with styrene by free radical mechanism under dispersion polymerization conditions.

In a typical copolymerization experiment, namely LB 10/90, 2.6 mmol of Boc-AMST and 23.3 mmol of ST were dissolved into 24 mL of a mixture of isopropyl alcohol−water (3:1 v/v) with 0.83 w/v of PVP. AIBN was dissolved in the ST monomer, and then it was used as free radical initiator at a concentration of 2% (mol/mol) with respect to the overall comonomer mixture. The reaction was conducted at 75 °C for 24 h under reflux conditions, $N_2$ blanket, and magnetic stirring. In Table 1 are collected the copolymerization experiments carried out on different comonomer feeds according to the above-described procedure.

**Deprotection of Boc-Aminated Styrene Copolymers.** The deprotection reaction of Boc-AMST/ST copolymer samples was performed by acidic cleavage at either 50 °C or room

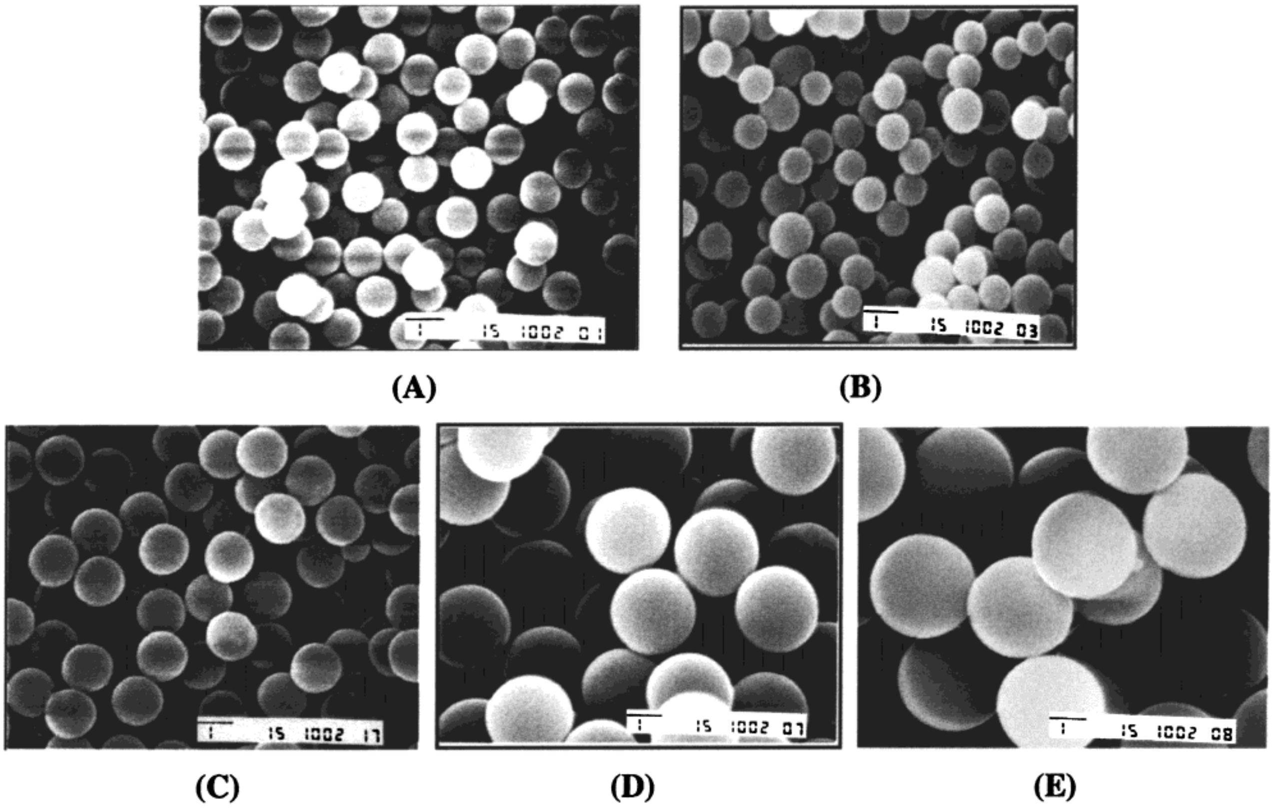


**Figure 2.** SEM photomicrographs of the Boc-AMST/ST copolymer latexes: (A) LB 1/99; (B) LB 5/95; (C) LB 10/90; (D) LB 20/80; (E) LB30/70.

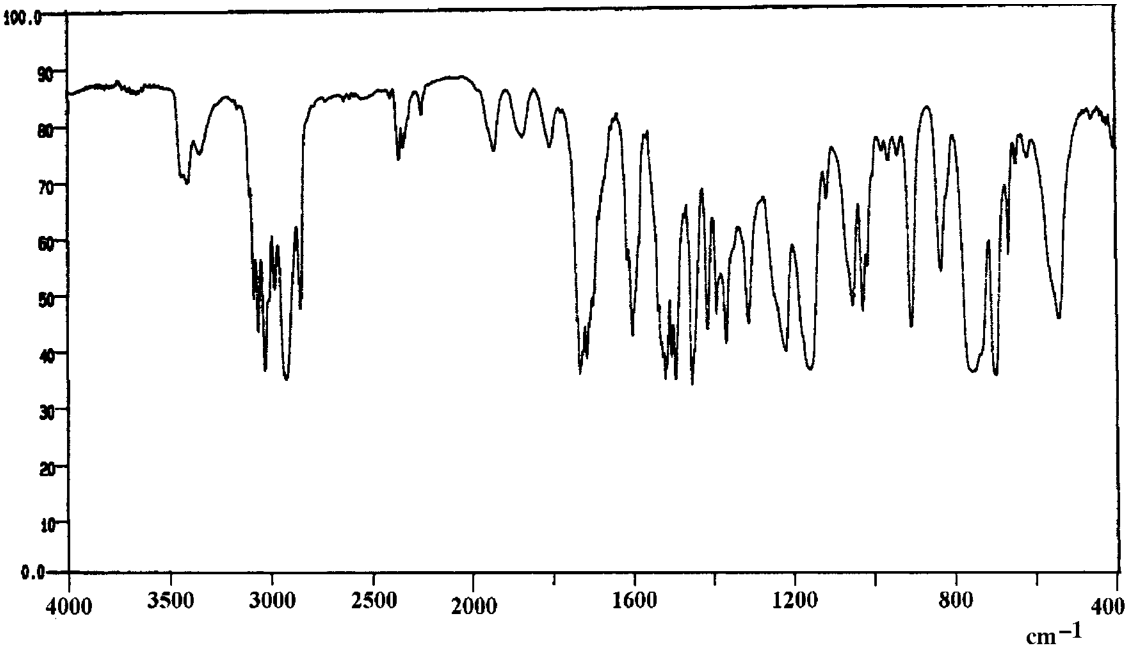


**Figure 3.** FT-IR spectrum of the Boc-AMST/ST copolymer sample LB 10/90.

temperature followed by basic treatment carried out at either 3 or 0.01 M concentrations.

In a typical experiment, about 500 mg of copolymer sample LB 10/90 after purification by washing with deionized water, centrifugation, and vacuum filtration was treated at either HCl 2 M in isopropyl alcohol at 50 °C or HCl 2 M in isopropyl alcohol−water 3:1 v/v at room temperature and then washed with deionized water until neutral pH, filtered, and dried under vacuum. The treated and dried product was suspended in deionized water without any dispersant and 20 mL of a NaOH at either 3 or 0.01 M aqueous solution were added, and the reaction was maintained under magnetic stirring at room temperature and agitation for 4 h. Afterward, the microspheres were repeatedly rinsed with deionized water until neutral pH and dried under vacuum.

## Results and Discussion

A series of five copolymer latex samples based on Boc-AMST and ST were prepared under dispersion polymerization conditions with molar ratios of Boc-AMST/ST comprised between 1/99 and 30/70. The yields obtained and the experimental conditions are reported in Table 1.

The copolymerization products isolated as microspheres characterized by a nicely uniform size distribution and morphological integrity (Figure 2) were submitted to SEM and Coulter-Counter instrumental analyses.

In Figures 3 and 4 are reported as typical examples the FT-IR spectrum and the $^{1}$H NMR (Figure 4A) and $^{13}$C NMR (Figure 4B) spectra of the sample LB 10/90.

The FT-IR spectrum displayed a spectral profile characterized by the presence of specific bands related to the polystyrene, at 3024 cm$^{-1}$ ($-$C$-$H aromatic), 2921 and 2847 cm$^{-1}$ ($-CH_2$), 1600 cm$^{-1}$ ($-$C=C aromatic), 1492−1451 cm$^{-1}$ ($-C_6H_5$, in plane), 1200−1100 cm$^{-1}$ ($-$CH= aromatic, out-of-plane), 900−600 cm$^{-1}$ ($-$CH= aromatic, in-plane). Bands associated with the amino group could be evidenced at 3500−3300 cm$^{-1}$ ($-$N$-$H), 1620 cm$^{-1}$ ($-$N$-$H partially overlapping 1600 cm$^{-1}$ band of the $-C_6H_5$), 1400 and 1340−1250 cm$^{-1}$ ($-$C$-$N), and 800−666 cm$^{-1}$ ($-$N$-$H angular and symmetric).

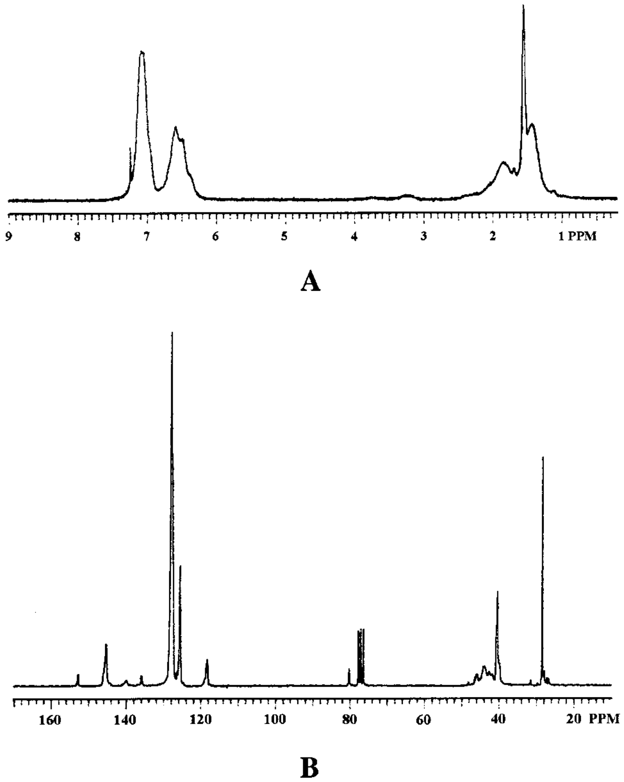


**Figure 4.** $^{1}$H NMR spectrum (A) and $^{13}$C NMR spectrum (B) of the Boc-AMST/ST copolymer LB10/90 sample.

The $^{1}$H NMR and $^{13}$C NMR spectra are characterized by signals attributable at both Boc-AMST and ST monomeric units. The $^{13}$C NMR spectrum shows very clearly the signals of the Boc group at 28 ppm (methyl), 82 ppm (quaternary C), and 152 ppm (C=O) and the signals related to the aromatic carbons between 110 and 145 ppm. In the $^{1}$H NMR spectrum from the relative ratio of the intensities of the signal attributable to the *tert*-butyl group (1.5 ppm, 9H) with respect to the aromatic protons (7.3 ppm, 4H), it was possible to determine the copolymer composition. The reported data (Table 1) are in keeping with a comparable reactivity

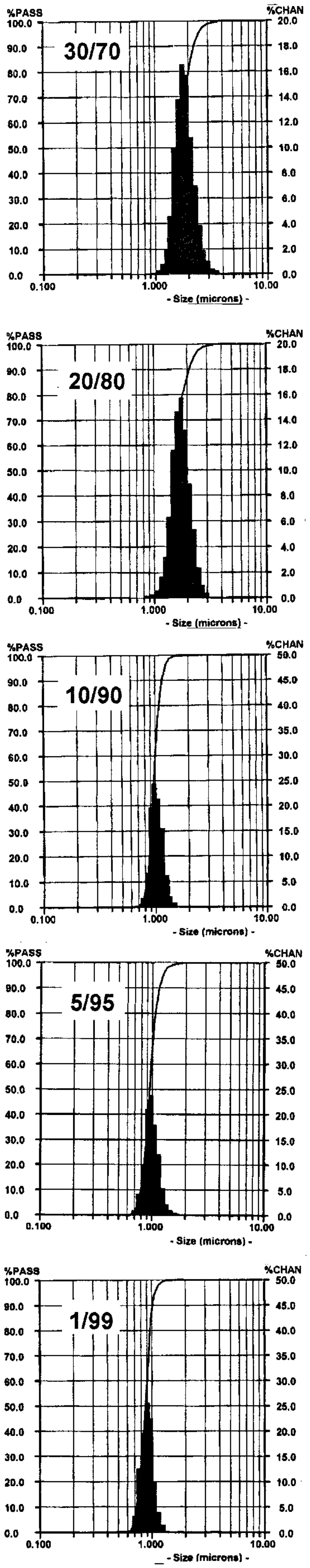


**Figure 5.** Monomodal particle size distributions graphics of the Boc-AMST/ST copolymer latexes series.

**Table 2. Characterization of the Boc-AMST/ST Copolymer Microspheres with Monomodal Size Distribution**

| | microspheres characteristics | | |
|---|---|---|---|
| run | diameter ($\mu$m) | $\overline{M}_{W}$ | DI[a] |
| LB 1/99 | 0.87 ± 0.11 | 10 200 | 1.9 |
| LB 5/95 | 0.96 ± 0.13 | 46 100 | 1.9 |
| LB 10/90 | 0.98 ± 0.13 | 51 000 | 2.0 |
| LB 20/80 | 1.70 ± 0.12 | 67 600 | 1.9 |
| LB 30/70 | 1.78 ± 0.12 | 45 000 | 2.0 |

[a] Polydispersity index: $\overline{M}_{W}$.

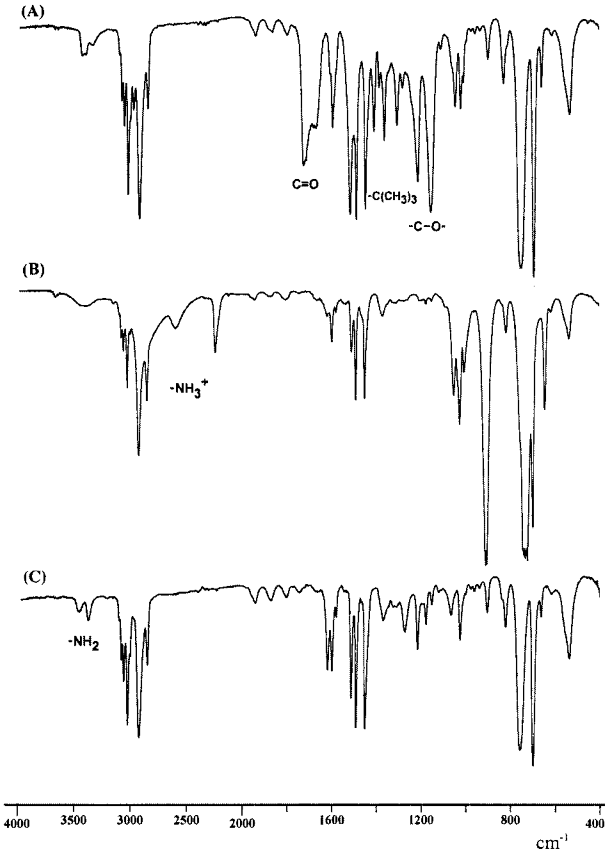


**Figure 6.** FT-IR spectra of the LB 10/90 copolymer sample in different forms: Boc-protected (A), after the acidic treatment (B), and basic treatment (C).

of ST and Boc-AMST and hence with a quasi-statistic distribution of monomeric units.[20]

All the copolymerization products were isolated as microspheres that when analyzed by Coulter-Counter analyses were characterized by monomodal size distributions (Figure 5). The average diameter size was in the range 0.9−1.0 $\mu$m for the first three copolymer samples, whereas in the case of the samples richer in Boc-AMST (LB 20/80 and LB 30/70) a microsphere diameter nearly double was observed.

The molecular weights of the polymer samples were between $1 \times 10^4$ and $6.8 \times 10^4$ and increased by increasing the content of Boc-AMST in the feed mixture (Table 2) with the exception of the sample LB 30/70. The distribution of molecular weights was monomodal for all the copolymer compositions, indicating that no renucleation process occurred, and rather narrow polydispersity (DI $\approx$ 2) was detected independent of the copolymer composition.

The overall comonomer conversion ranging between 87 and 98% was found to decrease with the increase of

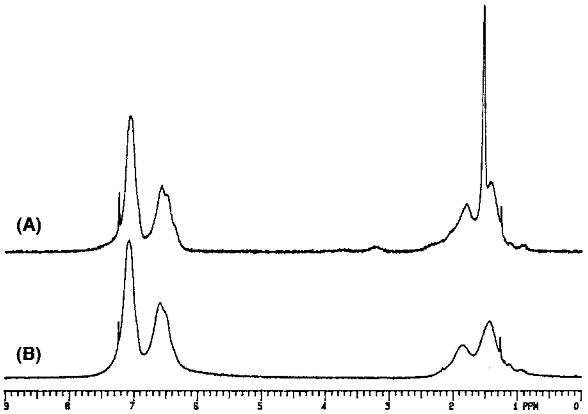


**Figure 7.** $^1$H NMR spectra of the LB 20/80 copolymer sample in different forms: the starting Boc-AMST/ST copolymer (A) and after acidic treatment (B).

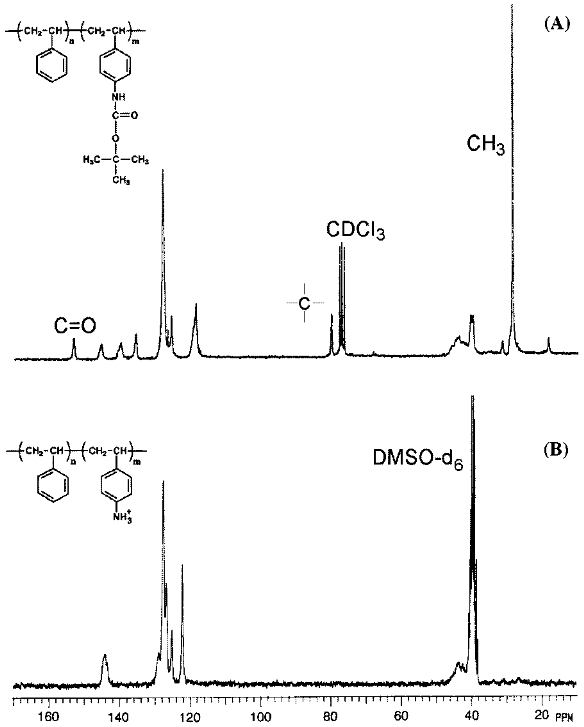


**Figure 8.** $^{13}$C NMR spectra of the Boc aminated styrene copolymer sample LB 20/80 in the protected (A) and deprotected (B) status.

Boc-AMST concentration in the comonomer feed (Table 1). This fact can be associated with the higher solubility of Boc-AMST in the dispersion media containing isopropyl alcohol and hence of the relevant monomeric units in the reaction medium. The growing polymeric chains of Boc-AMST/ST copolymer in the final of reaction can still remain in solution, and during the purification process of the samples they may be discarded, resulting in an apparent lower conversion rate.

By considering that for all copolymer experiments the overall comonomer concentration was constant (12.5% w/v), a monotonic increase of the particle size was detected with the relative increase of Boc-AMST concentrations. When the polystyrene particles were prepared under the same experimental conditions, smaller particle size diameters were detected.[23]

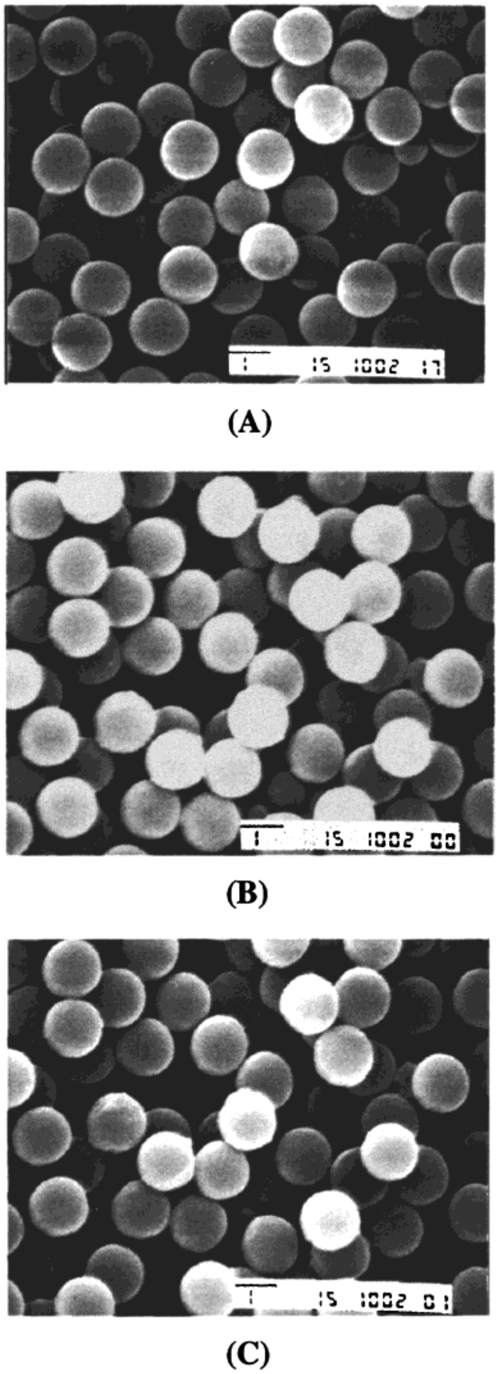
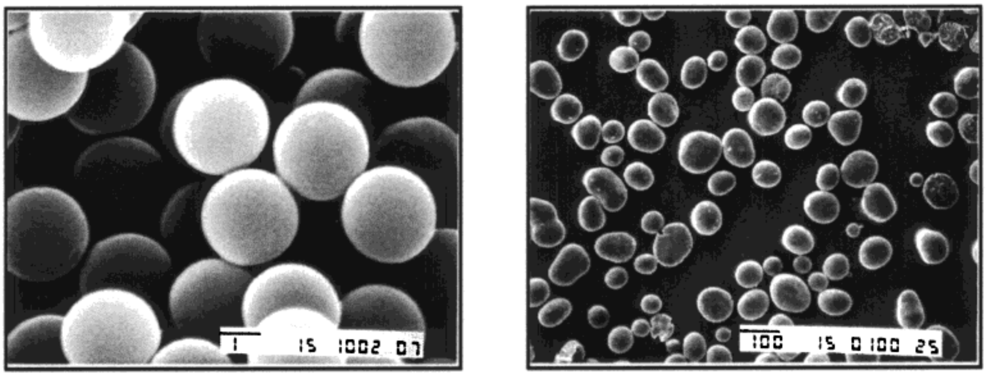


**Figure 9.** SEM photomicrographs of the Boc-AMST/ST copolymer sample LB 10/90 before and after mild acidic and basic treatments: the original Boc protected form (A); the corresponding acidic (B) and basic (C) forms.

At relative concentrations of Boc-AMST in the comonomer feed ranging from 5 to 30% fairly high molecular weights were observed ($M_w = 45-67$ kDa), contrary to what happens for the copolymer samples obtained from a feed containing 1% of Boc-AMST ($M_w = 10$ kDa).

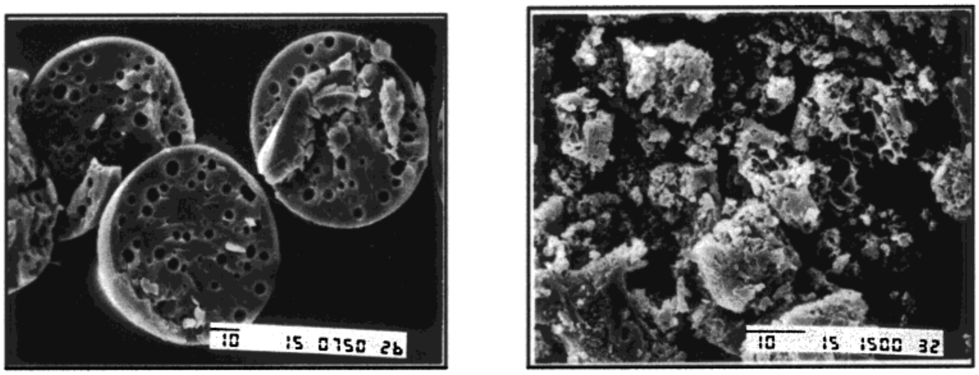
**Deprotection of Boc-AMST/ST Copolymer Samples.** Various procedures have been reported in the literature for the deprotection of amino group in macromolecular structure protected with the Boc moiety.[26] Among them the treatment of the Boc-AMST/ST copolymer samples with HCl 2 M in 2-propanol/water 3/1 v/v at room temperature followed by neutralization with diluted sodium hydroxide solution (0.01 M) was found as the best suited one.[23]

The removal of the Boc group from the copolymer structure with formation of $NH_3^+$ group was monitored



A) untreated LB 20/80 sample

B) acidic form



C) section of the acidic form

D) basic form

**Figure 10.** SEM photomicrographs of the Boc-AMST/ST copolymer sample LB 20/80 when severe deprotection and neutralization conditions were experienced: (A) Boc aminated; (B) and (C) after acid treatment at 50 °C; (D) after neutralization with NaOH 3 M aqueous solution.

by FT-IR. In Figure 6 the FT-IR spectra of the Boc-protected copolymer LB 10/90 (A) after the acidic treatment (B) and basic treatment (C) are reported.

The disappearance of the *tert*-butyl group band between 1401 and 1366 $cm^{-1}$, the C=O group band at around 1704 $cm^{-1}$, and the C−O−C band between 1300 and 1200 $cm^{-1}$ coupled with the appearance of two bands in the range 2800−2000 $cm^{-1}$ assignable to the $NH_3^+$ stretching vibrations, typical of primary amines chlorhydrate salts, is indicative of a complete removal of the Boc group under the adopted reaction conditions.

The deprotected aminated styrene copolymers in the acidic form could be converted into the corresponding free amine counterparts by treatment with dilute aqueous sodium hydroxide. In Figure 6C the FT-IR spectrum of the aminated styrene copolymers in basic form is reported. The complete disappearance of the band associated with the $NH_3^+$ group is accompanied by the appearance of the absorption bands correlated to the N−H asymmetric and symmetric stretching of the free amino group between 3500 and 3300 $cm^{-1}$ and with the NH bending at 1620 $cm^{-1}$.

Analogous evidence on the efficacy of the deprotection reaction can be gained by $^1$H NMR and $^{13}$C NMR spectra related to the LB 20/80 sample.

The original Boc-AMST/ST copolymer (Figure 7A) after acidic treatment displays in the $^1$H NMR spectrum the complete disappearance of the *tert*-butyl protons signal at 1.5 ppm (Figure 7B), whereas in the $^{13}$C NMR spectra (Figure 8) the disappearance of the Boc carbon signals at 28, 82, and 152 ppm was also clearly detected (Figure 8B). A substantial modification was noted in the shape and position of the aromatic carbons between 110 and 145 ppm due to the effect of the positive charge of the $NH_3^+$ group in the para position.

It is worth mentioning that the chemical and physical treatments to which the microspheres of Boc aminated styrene copolymers were submitted for their conversion to the corresponding *p*-aminostyrene/styrene copolymers did not alter appreciably the morphology and integrity of the original polymer microspheres at least when these treatments are carried out under mild conditions. In Figure 9 a relative comparison of SEM photomicrographs recorded on a typical sample of the original Boc aminated styrene copolymer (A) and the corresponding deprotected counterparts in the acidic (B) and basic (C) form is reported.

On the contrary, when more severe deprotection conditions (HCl 2 M in 2-propanol, $T = 50$ °C, and NaOH 3 M) were used, the copolymer samples LB 20/80 and LB30/70 with higher content in Boc-AMST monomeric units experienced dramatic changes in the morphology and integrity of the microspheres, as can be appreciated by the sequence of photomicrographs recorded on the original Boc aminated styrene copolymer sample (A) and the corresponding deprotected in the acidic (B, C) and basic (D) forms (Figure 10).

The copolymer samples richer in Boc-AMST can generate more *tert*-butyl alcohol and $CO_2$ as resulting products of deprotection reaction by action of 2 M HCl solution at 50 °C (Figure 11), in comparison with the other sample at lower content in Boc-AMST. The *tert*-butyl alcohol under the reported conditions can be converted to the *tert*-butyl chloride which under alkaline conditions can gave rise to isobutene. The swelling of the particles richer in polar groups ($NH_3^+Cl^-$) combined

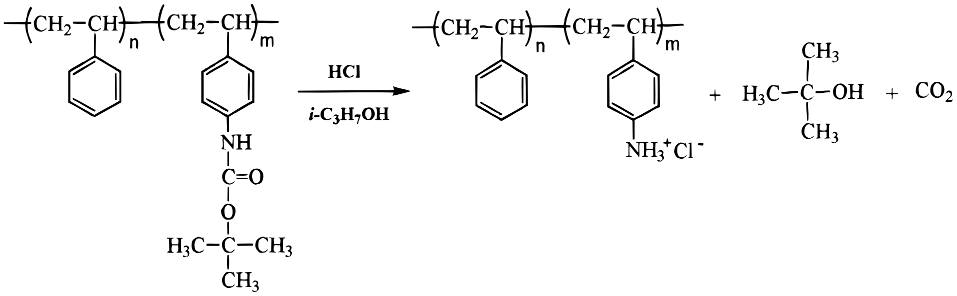


**Figure 11.** General scheme for the Boc-AMST/ST copolymers deprotection reaction with the resulting *tert*-butyl alcohol and CO$_2$ products.

**Table 3. Characteristics of AMST/ST Copolymer Microspheres Surfaces by XPS**

| run | AMST [mol %] | elements on the surface | | ratio N 1s/C 1s | |
|---|---|---|---|---|---|
| | | (%) C 1s | (%) N 1s | exp | theor |
| LB 1/99 | 1.2 | 88.8 | 2.9 | 0.033 | 0.0015 |
| LB 5/95 | 5.8 | 88.3 | 3.7 | 0.042 | 0.0072 |
| LB 10/90 | 12.1 | 86.3 | 4.4 | 0.051 | 0.0151 |
| LB 20/80 | 20.5 | 88.7 | 3.5 | 0.039 | 0.0256 |

with the onset of appreciable electrostatic repulsion can be further enhanced by the development of the gaseous components (CO$_2$ and isobutene), thus causing a marked breakage of the swollen particles (Figure 10D).

When the deprotection reactions were carried out under milder conditions (2 M HCl in 2-propanol/water 3/1, at room temperature under stirring for 1 h), the morphology of the particles was maintained.

**Distribution of the Amino Groups on the Microsphere Surfaces.** After deprotection and neutralization reactions of the Boc-AMST/ST copolymer samples resulting in free amino groups on the particle surfaces, the nitrogen content was determined by X-ray photoelectron spectroscopy (XPS). The deprotection treatment coupled with the following neutralization and repeated washing of the microparticles ensured for the complete removal of PVP as also confirmed by FT-IR spectra. Therefore, the nitrogen content as determined by XPS can be nearly exclusively attributable to the amino groups of the aminate styrene units. The results obtained, expressed in terms of nitrogen/carbon atomic ratio and relative concentrations, are reported in Table 3.

The experimental values of the atomic N 1s/C 1s ratios are 1 order of magnitude higher than theoretical values. In Figure 12 the plots of the experimental data and the theoretical values of the N 1s/C 1s ratios against the content of *p*-AMST in the copolymer are reported. The atomic N 1s/C 1s ratios for both data increase by increasing of the content of the aminated monomer. The lower is the content of *p*-AMST in the copolymer samples, the higher is the tendency of the amino group to distribute on the microsphere surface.

This behavior appears to be in agreement with the occurrence of substantial interactions of free amino group within the core of the microspheres that increase with increasing of the *p*-AMST content.

It is worthwhile remembering that the XPS analysis regarding the LB 20/80 sample was performed as the fragmented microspheres, and then the nitrogen content could be affected by increase of relative surface area.

## Conclusions

The copolymerization of Boc-AMST with styrene under dispersion polymerization conditions demonstrated to be very efficient for the preparation of microspheres containing *p*-aminostyrene units. The utilization of the new functional monomer Boc-AMST appeared to offer good advantages in the preparation of the aminated latexes. The *p*-AMST/ST copolymer latexes could be obtained under one pot reaction conditions. The adopted procedure results are by far more convenient with respect to other more cumbersome and time-consuming systems based on nitration of polystyrene followed by reduction of nitro groups.

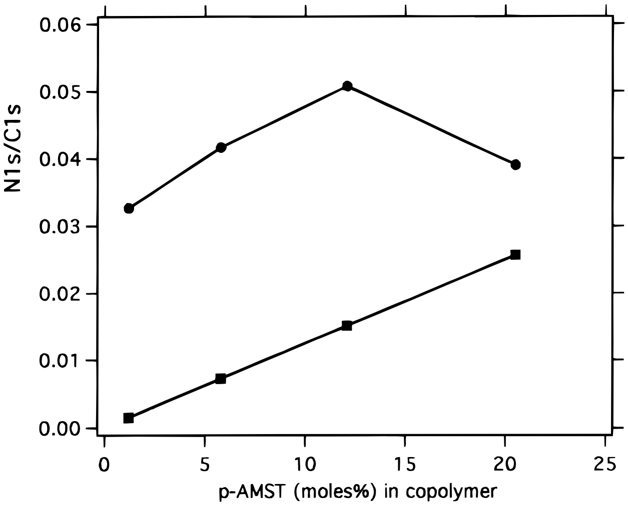


**Figure 12.** Experimental (circles) and theoretical (squares) trend of ratio N 1s/C 1s in the AMST/ST copolymer vs the content of AMST.

In addition, the procedure described in the present paper appeared to be very versatile and amenable to the preparation of a fairly wide range of aminated latexes with predetermined content of amino groups in the overall microspheres relevant surfaces. The microspheres were characterized by uniform size distributions comprised in the 0.9–1.8 $\mu$m range, with higher values being recorded increasing the Boc-AMST content in the monomer mixture feed. This fact connected also to the maintenance of the integrity of the microsphere morphology turned out to be very promising for the future development of the research activity aimed at the utilization of the prepared aminated microspheres in immunoassay applications.

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