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ORIGINAL CONTRIBUTION

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Chemical heterogeneity in poly [styrene-*co*-(butyl methacrylate)] copolymer latexes prepared using different monomer addition modes. A study by isopycnic centrifugation in density gradient

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Abstract Three different styrene-butyl methacrylate copolymer latexes were prepared by a uniform procedure but introducing styrene (S), butyl methacrylate (BMA), and minor amounts of acrylic acid (AA), in three different orders: i) simultaneous monomers addition, which yielded {P(SBMA)}; ii) addition of S (and half of the AA) followed by BMA (and the remaining AA), yielding {PS/PBMA} and iii) the inverse order, {PBMA/PS}. Product characterization was done by centrifugation in density gradients coupled to scattered light scanning photometry of the centrifugation tubes. IR and NMR spectra were obtained from bulk polymer as well as from isopycnic centrifugation fractions. In agreement with findings of other authors, the particles produced by simultaneous monomer addition {P(SBMA)} are made out of the statistical copolymer, whereas sequential monomer addition leads to the formation of latex with homopolymer domains. IR and NMR spectra of {PS/PBMA} and {PBMA/PS} are identical but isopycnic density band profiles of all three samples are distinct. Acrylic acid residues are not detected in the dialyzed latex, using both IR and NMR. Spectra of latex isopycnic fractions do also show significant differences arising from their monomer chemical compositions, but isopycnic centrifugation and spectral data do not reveal any correlation between particle density and monomer composition. Isopycnic centrifugation can thus solve two problems on latex characterization: first, it is a high-resolution preparative technique, unmatched by any other separation method. Second, it yields latex particle fingerprints, which are dependent on particle chemical characteristics, rather than on particle diameters.

Key words Polymer latex – emulsion polymerization – chemical heterogeneity – isopycnic centrifugation – density gradient

Introduction

The growing importance of emulsion polymerization and of its products is well documented in the literature [1]. This technique yields colloidal polymer particles dispersed in aqueous media, whose full product characterization usually requires a detailed evaluation of chain size distribution, together with an evaluation of particle size distribution.

Copolymerization is often used to produce latexes. In this case, further information about the monomer distribution among polymer chains and particles is necessary.

The question of monomer distribution among chains can now be addressed by many techniques, including chromatographic separation combined with spectroscopic measurements [2].

On the other hand, the problem of monomer distribution among particles has been generally neglected. It is assumed that this will derive from monomer partition among polymerization loci, as well as from reactivity ratios, but the experimental evaluation of the chemical heterogeneity of latex particles is seldom carried out. As with other cases of chemical heterogeneity determination among dispersed particles, there are only a few experimental ways to approach this problem. Isopycnic sedimentation in density gradients is perhaps the most effective and some authors have described its use in the literature [3–6].

These authors have used fast centrifuges or ultracentrifuges to minimize the required centrifugation times. However, this technique does not allow preparative-scale fractionation, and thus their conclusions are solely dependent on the sedimentation rates or on the isopycnic band profiles. The band profiles depend on particle sizes and/or densities, and thus they do not depend directly on the chemical composition of the particle.

This is a serious limitation because density measurements can be analytically useful, but the information obtained is often ambiguous due to the large range of density values presented by some polymers.

Therefore, we have preferred to use low-speed centrifugation in density gradients coupled to band fractionation, collection and further characterization by spectroscopic and other techniques. This has proven useful as an analytical tool for industrial product characterization and for latex particle aggregation studies [7–10].

In this work, we have prepared three latexes of styrene and butyl methacrylate, by using i) simultaneous addition of both monomers, ii) addition of styrene followed by butyl methacrylate and iii) addition of butyl methacrylate followed by the addition of styrene. The latexes were fractionated by centrifugation in density gradients, and the fractions were characterized by NMR and IR spectra in order to evaluate the differences of chemical composition among the particles of the three different latexes and among the fractions of each latex.

Experimental section

Materials

Water used in all experiments was doubly distilled from an all-Pyrex apparatus. Styrene (from Estireno do Brasil) and butyl methacrylate (from Polysciences) were employed with no previous treatment. The initiator, sodium persulfate (from Vetec), and the surfactants, sodium dodecylsulfate (from Merck) and nonylphenol ethylene glycol condensate with 30 ethylene glycol units (RENEX 300 from Ultraquímica) were used as received. Following a procedure used by some latex makers, a small amount of acrylic acid (from Riedel-de Haën) was employed as an ionogenic monomer to improve the stability of the latex dispersion. Sodium hydroxide (from Merck) was employed to control the medium acidity.

Synthesis of the latexes

The latexes were prepared by emulsion polymerization of styrene (S) and butyl methacrylate (BMA) following procedures similar to those described previously [10]. Three procedures with different orders of monomers addition were carried out: i) simultaneous addition of the three monomers, labeled {P(SBMA)}; ii) addition of S (together with 50% of the acrylic acid load) followed by BMA (and the remaining acrylic acid), {PS/PBMA} and iii) addition of BMA followed by the addition of S, {PBMA/PS}. The three latexes were prepared using the amounts given in Table 1. All emulsion polymerizations were carried out at 80 ± 2 °C in a 500 mL glass kettle reactor fitted with condenser, thermometer, glass paddle-type stirrer and N_2 gas inlet. The kettle was kept within a thermostated bath.

P(SBMA) latex synthesis

The reactor was loaded with water and surfactants, and 20% of the monomer mixture was added. The reactor was then heated to 50 °C and the initiator solution was added. After raising the temperature to 80 °C, the remaining monomer mixture was added using a peristaltic pump over a period of 3 h, with a steady rate of approximately 30 mL/h. After the end of the addition, the reaction mixture was kept at 80 °C for 1 h.

Table 1 Reagents used in latex preparations

Reagent	$mol \cdot dm^{-3}$
Styrene	1.25
Butyl Methacrylate	1.25
Acrylic Acid	0.22
SDS	10.84×10^{-3}
RENEX 300	4.81×10^{-3}
$Na_2S_2O_8$	5.91×10^{-3}
NaOH	31.25×10^{-3}

PS/PBMA latex synthesis

The reactor was loaded with water and surfactants, and 50% of the styrene and acrylic acid was added. The reactor was then heated to 50 °C and the initiator solution was added. After raising the temperature to 80 °C, the remaining styrene was continuously added using a peristaltic pump over a period of 1 h, with a steady rate of approximately 30 mL/h. One hour later, the methacrylate monomer and the remaining acrylic acid were added continuously over a period of 2 h, under a steady rate of approximately 30 mL/h. After the end of the addition, the reaction mixture was kept at 80 °C for 1 h.

PBMA/PS latex synthesis

The PBMA/PS latex was prepared similarly, except for the order of monomer addition. The reactor was loaded with water and surfactants, and 30% of the butyl methacrylate and 50% of the acrylic acid were added. The reactor was then heated to 50 °C and the initiator solution was added. After raising the temperature to 80 °C, the remaining methacrylate was continuously added using a peristaltic pump over a period of 1 h and 30 min, with a steady rate of approximately 30 mL/h. One hour later, the styrene monomer and the remaining acrylic acid were added continuously over a period of 1 h and 30 min, under a steady flow rate of 30 mL/h. After the end of monomer addition, the reaction mixture was kept at 80 °C for 1 h.

In the three cases, the initial viscous emulsions turned into milky dispersions, yielding conversions (as referred to the monomers weight) of 95.5% for P(SBMA), 91.1% for PS/PBMA and 91.3% for PBMA/PS, as determined gravimetrically right after the synthesis. The latexes were filtered and (in order to remove excess emulsifiers, unreacted monomer and unwanted electrolyte), subsequently dialyzed against water with daily changes over a 1-month period until the dialysate conductivity reached 4 μS/cm, and remained unchanged for 48 h. The dialysis tubing (a visking membrane from Sigma) was boiled in several quantities of distilled water, prior to use.

After purification by dialysis, part of each latex sample was lyophilized using a bench-top glass apparatus, to recover the solid polymer for spectral measurements. The remainder of the samples was dispersed in water, as required for reaching the desired concentrations.

TEM

The morphology of the latex particles was observed using a Carl Zeiss CEM 902 transmission electron microscope. Using a micropipette, one drop of each latex sample (1% solids content) was applied to carbon-coated parlodion films supported in 400 mesh copper grids. A micrograph of the PS/PBMA sample stained with RuO_4 was obtained following a procedure described by Trent [11]: the grid supporting the PS/PBMA sample was introduced for 15 min into a T-shaped glass tube, where RuO_4 vapour was generated from the oxidation of hydrated ruthenium dioxide ($RuO_2 \cdot 2H_2O$) by sodium periodate ($NaIO_4$) [12]. This sample was then immediately examined by TEM.

QELS

Latex particle size was measured by a quasi-elastic light-scattering (QELS) method in a Coulter N4MD instrument from Coultronics. Histograms of the size distribution were obtained from QELS data and using the instrument software, giving the number average diameter D_n, the weight average diameter D_w, and the weight-to-number ratio index of dispersity (D_w/D_n) such as:

$$D_n = \sum n_i D_i / \sum n_i \ . \tag{1}$$

$$D_w = \left(\sum n_i D_i^6 / \sum n_i D_i^3 \right)^{1/3} \ . \tag{2}$$

Infrared spectra

Infrared spectra were recorded in a Perkin Elmer FT-IR 1600 spectrophotometer. Two drops of a solution of 20 mg/mL of polymer in $CHCl_3$ were spread over a KBr plate and allowed to evaporate. Spectra were obtained in the range 4000–400 cm^{-1}.

Nuclear magnetic resonance spectra

NMR spectra were obtained at room temperature on a Varian Gemini 300 spectrometer operating at 300.08 MHz for ^1H. The samples were deuterated chloroform solutions of the polymers (20 mg/mL) using tetramethylsilane as the internal standard.

The recording conditions of the spectra were as follows: acquisition time, 2.73 s; relaxation delay, 2.0 s; pulse width, 24 degrees. T1 average was determined using a standard inversion-recovery pulse sequence so that under the conditions used, the absorption peak areas are proportional to the number of corresponding protons.

Centrifugation in density gradients

Linear density gradients ranging from 1.030 to 1.090 g·cm^{-3} were prepared from sucrose (Merck) aqueous solutions (8 and 22% w/w) using a two-chamber mixing cell [13], connected to a peristaltic pump. The gradient is poured with the Tygon tube pump outlet touching the wall of the centrifuge glass tube (outer diameter 13.0 mm, wall thickness 1.5 mm, height 100 mm) at the top.

Dialyzed latex sample aliquots (250 μL, 10% solid content) were applied on top of the preformed sucrose gradients and spun in a Sorvall RC3B centrifuge (swinging-basket H-6000 A rotor, 3500 rpm, 25 °C) until equilibrium sedimentation was reached, which took less than 96 h. In order to record the band profile, the centrifugation tubes were mounted on a holder vertically displaced in front of a He–Ne laser beam. The light scattered was detected at an angle of 34°, and the detector signal was fed to the interface of a personal microcomputer (Fig. 1).

Two fractions of each latex band at equilibrium were collected, one of lower density, in the upper region of the gradient, and another of higher density, in the lower region of the gradient. The fractions were collected with the aid of a syringe fitted with a long needle, which was carefully introduced into the centrifuge tube so that the gradient was not disturbed. The latex contained in each fraction was transferred to other centrifuge tubes and then coagulated upon the addition of 2 mL of a 2M NaCl aqueous solution. The coaguli were sedimented by centrifugation, and the liquid supernatant was discharged. The coaguli were resuspended in water by intense stirring, and centrifuged again. The coaguli were thus washed several times with water to remove the remaining sucrose and other water-soluble substances. After repeated washing, each polymeric coagulus was transferred to a spot-test plate and dried for 72 h in the atmosphere. The polymer (ca. 10 mg) was then dissolved in $CDCl_3$ and analyzed by NMR and IR spectroscopy as described above. Following this procedure, even the water-soluble polyelectrolytic fractions should be removed from the latex.

Results

TEM and QELS

The latexes micrographs are shown in Fig. 2. They show that individual particles are spherical, however deforming while in aggregates. This is an indication that they have a low glass transition temperature, *Tg*, or that one of their domains has a low *Tg*. DSC thermograms (not shown) reveal that P(SBMA) has only one *Tg* at 49.8 °C, but PS/PBMA has two *Tg*s, at 19.0° and 99.6 °C, corresponding to those of the homopolymers.

The average diameter and the dispersity of the latex samples, as determined by QELS are shown in Table 2.

The average diameter of the latex particles of the three samples is equal to or lower than ca. 100 nm. This is close to the lower threshold of the normal range of latex particles size [14].

The latexes are polidisperse [15] and the dispersity of the latexes produced in two stages, PS/PBMA and PBMA/PS, is much lower than that found for the latex produced in a single stage, P(SBMA). This fact may be related to the existence of different polymerization sites [16, 17], in the two cases: i) the pre-formed latex particles (seed polymerization) in the two-stage latexes, PS/PBMA and PBMA/PS, and ii) mixed (micellar and solution), in P(SBMA).

^{1}H Nuclear magnetic resonance

The ^{1}H NMR spectra of the polymer samples are shown in Fig. 3. The NMR spectra of the PS/PBMA and PBMA/PS

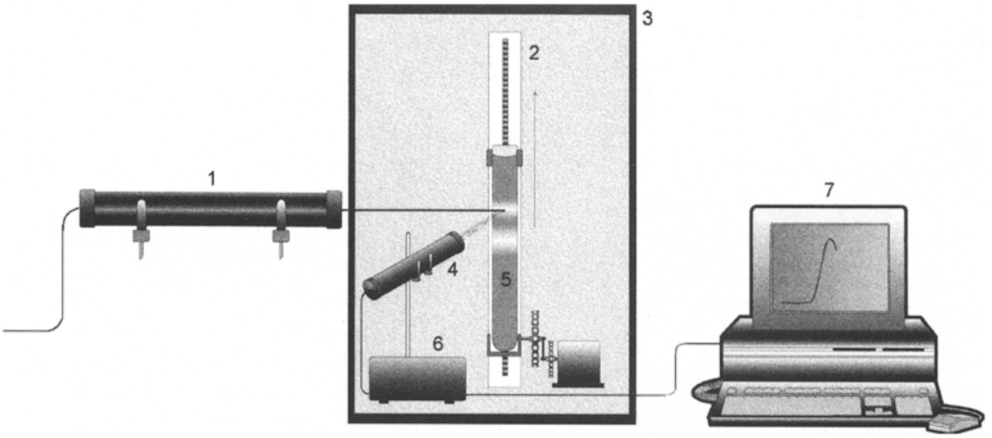


Fig. 1 Scattered light scanning photometer: 1) laser He–Ne; 2) elevator with sample holder; 3) light proof chamber; 4) photodiode detector; 5) test tube containing the sample within the density gradient; 6) current amplifier signal; 7) personal interfaced computer

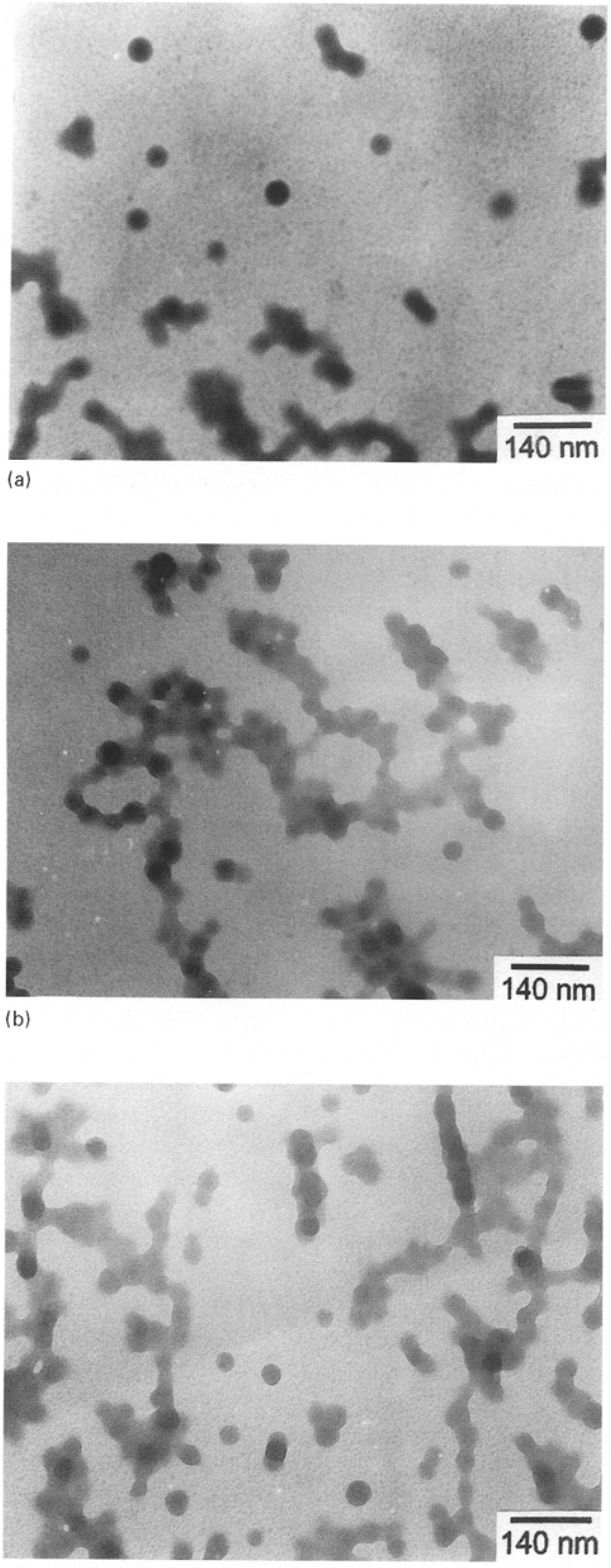


Fig. 2 Transmission electron micrographs of the latexes: a) P(SBMA), b) PS/PBMA, c) PBMA/PS

Table 2 Particle size determination. Number average diameter, D_n, weight average diameter, D_w, and dispersity, P, of latex samples

Sample	D_n (nm)	D_w (nm)	P
P(SBMA)	81	129	1.59
PS/PBMA	71	90	1.27
PBMA/PS	60	69	1.17

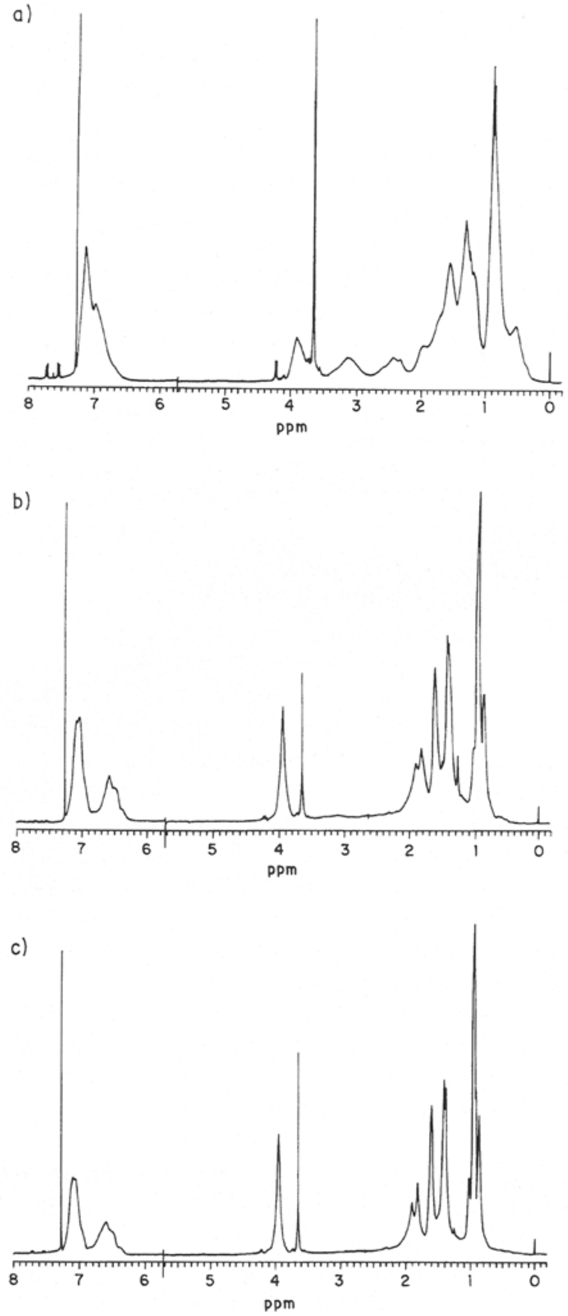
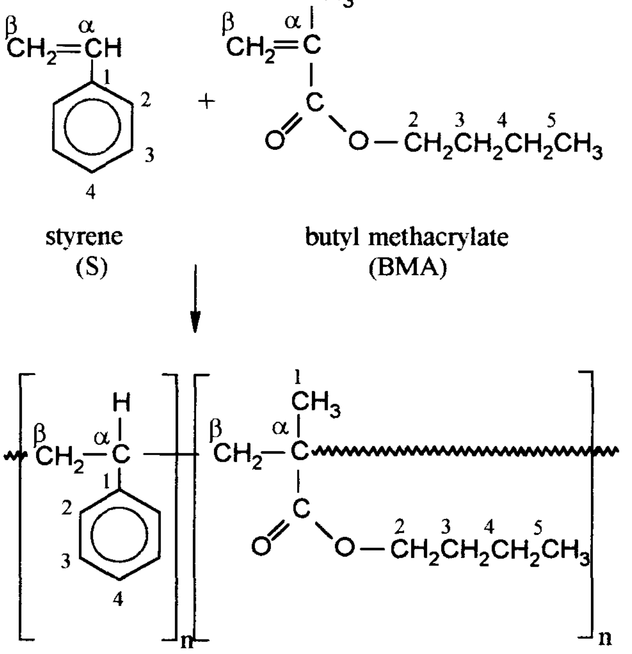


Fig. 3 300.08 MHz proton NMR spectra of the polymer latexes: a) P(SBMA), b) PS/PBMA, c) PBMA/PS. Solvent $CDCl_3$ at room temperature

polymers are indistinguishable and can be interpreted as the addition of the spectra of the homopolymers. However, the P(SBMA) polymer spectrum has different characteristics compared with the added spectra of the homopolymers.

The S and BMA copolymers are represented by the following structural units:



The assignments were made by comparing the spectra of the latexes with those of the corresponding homopolymers [18, 19]. The multiplet between 0.80 and 1.10 ppm is due to the methyl protons (C1 and C5) of the BMA units in PS/PBMA and PBMA/PS. The same resonances in P(SBMA) occur as a broad peak centered at 0.55 ppm for C1 and as a multiplet between 0.80 and 1.00 for C5. The methylene protons (C4) of the BMA give an absorption superimposed on the methylene protons (β-C) of the S units shaped as a multiplet between 1.30 and 1.50 ppm for PS/PBMA and PBMA/PS and between 1.05 and 1.30 for P(SBMA). The methylene protons (C3) of the BMA show a broad peak centered at 1.61 ppm in all three samples. The methylene protons (β-C) of the BMA give a broad peak centered at 1.81 ppm, which is partially superimposed on the absorption of the methine proton (α-C) of the S units. This is also a broad peak, centered at 1.91 ppm in the PS/PBMA and PBMA/PS samples. In the P(SBMA) the main-chain protons signal is broadened and less intense, within the 1.60–2.30 ppm range. This is caused by a large number of closely spaced, unresolved chemical shifts, reflecting the large number of comonomer and stereosequences in this copolymer.

The methoxy protons (C2) absorption peak is broad, centered at 3.94 ppm in the PS/PBMA and PBMA/PS. In the P(SBMA) sample, the absorption due to these protons is split into three different broad peaks centered at 3.90, 3.12 and 2.43 ppm. This splitting is assigned to the cotacticity of the styrene-methacrylate-styrene triads (S-BMA-S), which are expected in statistical copolymers. The splitting of the methoxy protons absorption in three peaks confirms that this is a statistical copolymer and that it has all three possible stereosequences related to the S-BMA-S triad, namely, co-syndio, co-hetero and co-iso. These assignments were made based on reports on analogous systems, e.g., styrene-methyl methacrylate [20] and styrene-ethyl methacrylate [21]. This splitting is caused by the vicinity of the methoxy protons next to the aromatic rings from the styrene units. When these protons are located between two phenyl rings on the same side of the chain, ring current shielding effect occurs, shifting the absorption to higher field. When the two rings are on the opposite side of the chain, the shielding effect vanishes and the absorption occurs at a lower field. The intermediate absorption corresponds to the rings placed on opposite sides of the chain. The areas under each one of the three peaks are approximately identical, which is an indication that there is not a predominant stereosequence in this copolymer. The aromatic protons belonging to the S units are responsible for two well resolved peaks in the PS/PBMA and PBMA/PS. The ratio between the areas of these peaks is approximately equal to 3:2. The peak at 7.09 ppm is due to the *meta* and *para* protons while the one at 6.59 ppm is due to the *ortho* protons. Both absorptions are shifted to higher field in relation to alkyl benzene aromatic protons and styrene, whose chemical shifts are greater than 7.00 ppm. Such peculiar shielding of the aromatic protons, especially of the *ortho* protons, is observed in the polystyrene homopolymer, and in copolymers where there are large sequences of styrene units. In the later case, the splitting of the aromatic proton resonances in two different peaks is used as an estimate of the size of the styrene blocks [22]. The origin of the aromatic protons shielding is also related to the aromatic ring current effect of the styrene units. In P(SBMA) the *para* and *meta* protons absorption centered at 7.14 ppm and the *ortho* protons absorption centered at 6.99 ppm mostly overlap. In this case, the decrease in the resolution in the aromatic protons absorption is due to the nature of this copoloymer, which determines that many S units are kept apart by the BMA units. Two narrow and intense peaks which cannot be assigned to any of the monomer units are also observed in the NMR spectra of the three samples. The one at 7.27 ppm is assigned to a small amount of non-deuterated chloroform. The other at 3.65 ppm is due to the methoxy protons of the ethoxylated surfactant used in the synthesis, in which there are 120 such protons per molecule. This is an evidence that dialysis did not remove all of the surfactant used in the synthesis.

The ^{1}H NMR spectra show that the P(SBMA) latex particle is formed by statistical copolymer chains, while there is strong evidence that PS/PBMA and PBMA/PS latex particles are formed by large homopolymer domains. No evidence was found for acrylic acid residues, in this spectra. Considering the absence of a peak which could be assigned to –COOH groups and the spectral S/N ratio, we estimated that acrylic acid/styrene content in the polymers is less than 3%. This means, most of the acrylic acid used in the preparations is converted to water-soluble forms.

The TEM micrograph of the PS/PBMA latex stained with RuO_4, shown in Fig. 4, gives a morphological proof that its particles are formed by large homopolymer domains. Various morphologies can be observed in the TEM, namely core and shell, sandwich-like, half moon like [27–29], where the darker domains are selectively generated by RuO_4 reacting with polystyrene, but not with methacrylate [11].

IR spectra

Absorption bands in the IR spectra of the polymer latexes have been assigned by comparison with the corresponding homopolymers, i.e., poly(butyl methacrylate) [26] (PBMA) and polystyrene [27] (PS). They are similar to the superimposed spectra of the two homopolymers. The three latex samples show very similar spectra and there is no shift in the position of absorption bands, in any case. IR spectra do not offer any evidence for the presence of acrylic acid groups in the polymers, but this technique is less sensitive than NMR, for this purpose.

The most important aspect of the IR spectra is observed in the region between 1300 and 1100 cm^{-1} (Fig. 5), which corresponds to the C–O–C stretching, and to the C–C and C–C–O skeletal stretching absorptions, mainly due to the methacrylate units. In this region, the spectra of the latexes PS/PBMA and PBMA/PS show two doublets at 1260 and 1150 cm^{-1} with a resolution similar to that exhibited by the corresponding block copolymer (from Polymer Standard Science [28]) and by the butyl methacrylate homopolymer. This is not the case with the P(SBMA) latex, which shows a significant broadening of the bands in this region. The broadening of these bands can be explained if it is assumed that this is a statistical copolymer. In this case, the absorption in this region shifts and broadens because the copolymer possesses a high C–C site diversity, in its backbone. No IR peak from the latex fraction spectra can be unequivocally assigned to acrylic acid residues.

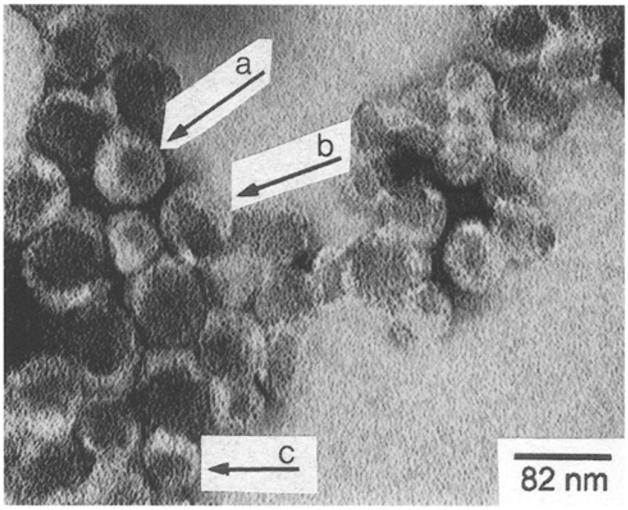


Fig. 4 Transmission electron micrograph of PS/PBMA latex stained with RuO_4 vapor. PS is the darker phase. Arrows a, b and c indicate particles of different domain morphologies

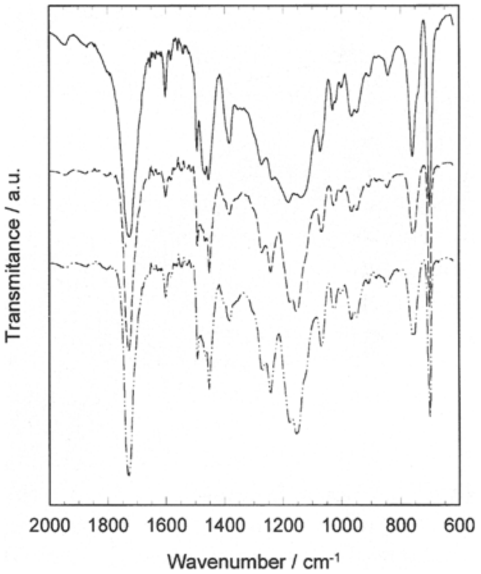


Fig. 5 Infrared spectra of the polymer latexes: —— P(SBMA), – – – PS/PBMA, —-- PBMA/PS

Polystyrene units in copolymers are hardly affected by the environment, therefore the spectral differences are due only to the absorption of methacrylate units. It is probable that the structure of the bands in this region is associated to the specific conformation of the polymethacrylate chains [29]. According to the synthetic method, the methacrylate sequences are shortened in the copolymerization with other monomers. This shortening keeps the copolymer methacrylate sequences from assuming conformations similar to those of the methacrylate homopolymers.

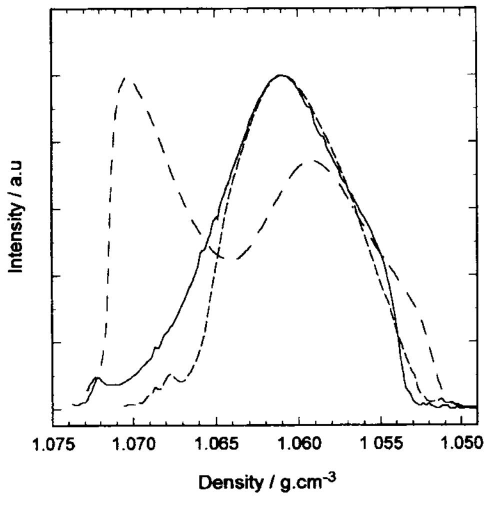
Isopycnic band profiles and analysis of isopycnic fractions

Light scattering profiles of latex zones at isopycnic equilibrium are given in Fig. 6. The profiles of two latexes, one obtained by simultaneous addition of monomers P(SBMA), and the other prepared by addition of S followed by BMA (PS/PBMA) both have a single maximum, at $\rho = 1.058$ g·cm^{-3}. On the other hand, the band profile of the latex prepared by addition of BMA followed by S (PBMA/PS) displays two maxima, at $\rho = 1.060$ and 1.070 g·cm^{-3}. The densities of all three samples cover broad ranges, 1.055–1.065 (P(SBMA) and PS/PBMA) and 1.051–1.072 g·cm^{-3} (PBMA/PS). This indicates that there are detectable chemical heterogeneities among the samples, which required the analysis of ^{1}H NMR and infrared spectra from both upper and lower fractions of isopycnic bands of the three latexes. These spectra are displayed in Fig. 7.

The ^{1}H NMR spectra displayed in Fig. 7 can provide a wealth of information. First, they can be used to evaluate S and BMA contents in each fraction, by using the integrated intensities of the phenyl resonance of the S residues in the range 7–8 ppm and the CH_3, CH_2 and CH groups of both S and BMA residues in the range 0–4 ppm. Assigning x to the mole fraction of S in the polymer, the ratio R of the areas of the phenyl and non-phenyl regions can be expressed by:

$$R = \frac{5x}{(1-x)14 + 3x}, \quad \text{and therefore} \quad x = \frac{14R}{(5 + 11R)}. \quad (3)$$

Fig. 6 Scattered light profiles obtained at isopycnic equilibrium of 250 μL of each latex (10% solid content), in aqueous sucrose density gradient: —— P(SBMA), – – – PS/PBMA, —-- PBMA/PS



The results for the determination of x are shown in Table 3. In every case, BMA contents in the latex are higher than in the overall polymerization reactor monomer feed. Furthermore, there is always a difference in the monomer contents of the upper and lower fractions of the three latexes. This difference is smaller in P(SBMA), in which the lower fraction is richer in styrene than the upper fraction. Larger differences are observed in the latexes prepared by sequential addition of monomers, but while the upper PS/PBMA fraction is richer in BMA than the lower one, the opposite happens in PBMA/PS.

The results discussed in the previous paragraph show that there is not a simple correlation between particle density and the chemical composition of the particles in these latexes.

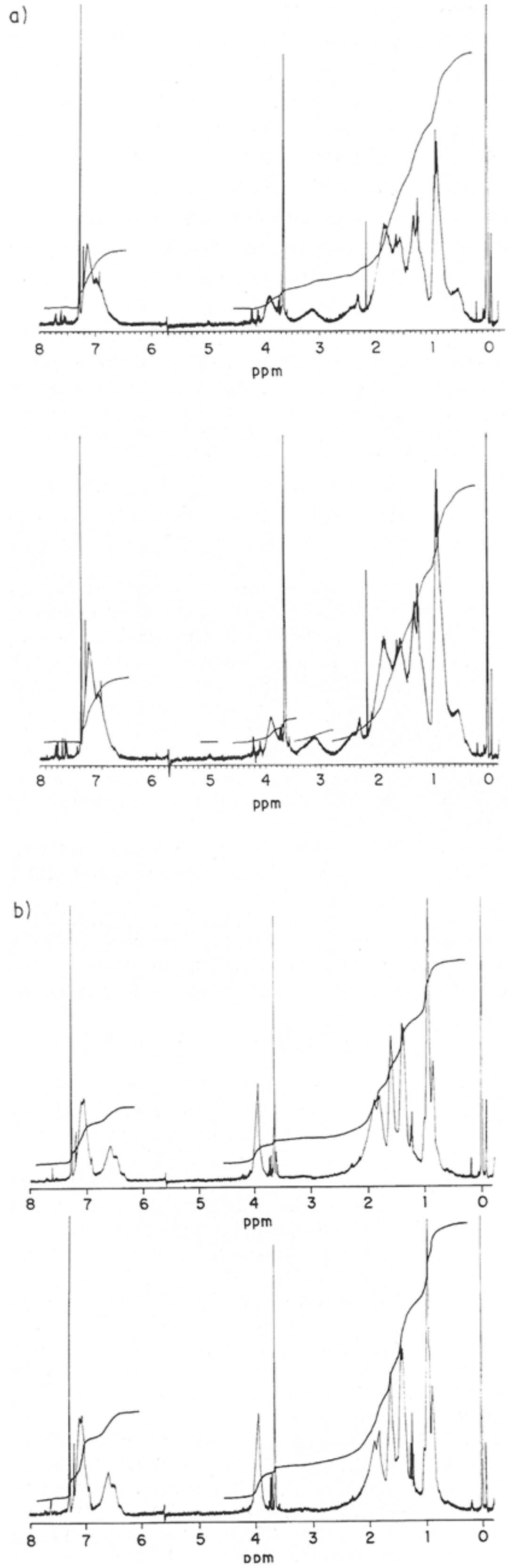
Significant qualitative differences between the spectra of upper and lower fractions of P(SBMA) and PS/PBMA latexes are not observed. However, the fractions of PBMA/PS latex display significant differences at 1.3 and 1.8 ppm, dominated by peaks assigned to protons from the main chain CH_2 and CH groups, from both styrene and butyl methacrylate. Infrared spectra can also be used to verify the heterogeneity of the chemical composition among latex fractions, since the ratios of the absorbances determined at 1728 and 700 cm^{-1} are proportional to BMA/S molar ratio, in the latex fractions. The values presented in Table 2 confirm the results from the NMR data in Table 1. The IR spectra of the latex fractions show only a few differences in the relative band intensities, as discussed below.

Table 3 Styrene (S) contents of the upper and lower isopycnic fractions of the latexes

Sample	S (mol%)	
	upper	lower
P(SBMA)	37.8	38.3
PS/PBMA	41.7	45.4
PBMA/PS	44.2	40.7

Table 4 Infrared absorption ratios for the upper and lower isopycnic fractions of the latexes, calculated using the integrated bands at 1730 and 700 cm^{-1}

Sample	Ratio A_{1730}/A_{700}	
	upper	lower
P(SBMA)	5.80	5.76
PS/PBMA	4.58	4.03
PBMA/PS	4.31	4.83



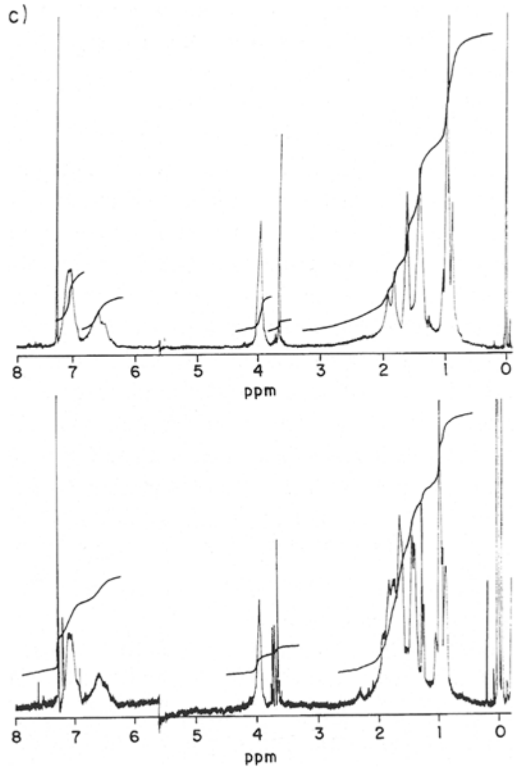


Fig. 7 300.08 MHz proton NMR spectra of the upper and lower fractions of the latexes, collected in the isopycnic equilibrium: a) P(SBMA); above: upper fraction; below: lower fraction, b) PS/PBMA, c) PBMA/PS

Discussion

The system investigated in this work is perhaps the most difficult copolymer latex system to be studied by isopycnic sedimentation, because the two corresponding homopolymers have nearly identical densities. However, the high resolution that can be achieved by using this technique reveals many of the intricacies of the distribution of chemical composition of particles. Nevertheless, its analysis was made easier by the absence of significant amounts of acrylic acid in the dialyzed particles.

A definite result is the absence of correlation between particle density and chemical composition, in this system. This correlation has been quite useful in the interpretation of sedimentation data [5], but it should apply only to those cases in which the respective homopolymers have widely different densities. Even in these cases, the present results show that this correlation may be perturbed by other factors, which can only be elucidated by further work. In this laboratory, we have recently demonstrated a significant effect of particle surface solvation and aging, on particle density measurements [30].

The case of the latexes prepared by sequential addition of the two monomers is very interesting. Their spectra are identical, irrespective of the order of monomer addition. Moreover, they are nearly indistinguishable from the convoluted IR and NMR spectra of the two homopolymers. However, a difference among them is easily revealed by their band patterns in isopycnic sedimentation experiments. Other differences were found by the spectroscopic examination of latex fractions, which will be further examined in future work. Such differences are not surprising, because the loci of polymerization in the two cases are different. Particles of both latexes contain separate homopolymer domains, out of which the innermost domains are styrene rich [31]. However, in the case of PS/PBMA latex the shell is formed in the later stages of latex preparation, whereas in the case of PBMA/PS the shell is formed in the earlier part of the reaction, and the final morphology is reached by interfacial tension-driven migration of the styrene and acrylic domains to the inner and outer parts of the particles respectively, so that the most wettable polymer ends up at the shell [26–28].

To the best of the author's knowledge, the sedimentation technique described in this work is the only available latex particle fingerprinting technique which is sensitive to particle chemical composition and capable of supplying fractions suitable for further characterization work.

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