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Nanosized Polystyrene/Poly(Butyl Acrylate) Core-Shell Latex Particles Functionalized with Acrylamides

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The nanosized polystyrene-poly(butyl acrylate) latex particles with core-shell morphology were prepared through two-stage semi-continuous starved emulsion polymerization with polystyrene as a seed and butyl acrylate as a second stage monomer. For functionalization, N-methylol acrylamide (NMA) or N-(iso-butoxy-methyl) acrylamide (IBMA) were used. The effect of functional groups with different hydrophilicity and their locations in core-shell particles on the main colloid characteristic of latexes such as particle size, particle size distribution and viscosity were investigated. It was found that the size and viscosity of IBMA functionalized particles does not depend on the location of functional comonomer in the core or shell. In NMA functionalized particles the size, particle size distribution and viscosity strongly depend on the situation of the comonomer during polymerization. The morphologies of functionalized latex particles were examined by transmission electron microscopy.

Keywords core-shell, latex, functionalization, polystyrene, butyl acrylate, acrylamide

Introduction

Waterborne acrylic polymer dispersions as environmentally friendly materials attract the attention of researchers in various fields. They have found widespread use in modern coating technology because they have excellent durability, which makes them suitable for in and outdoor decorative paints and can be formulated into high resistance coatings for industrial uses (1).

Acrylic dispersions with core-shell morphology of particles are especially important in many different industrial applications (2–4). Compared to materials made by blending or copolymerization, particles of such well-defined morphology having unique physical properties as polymers with very different properties can be associated. For example, in polystyrene/poly (butyl acrylate) dispersions with core-shell particles a high T_g core (polystyrene) imparts improved mechanical stability, while the low T_g shell (poly(butyl acrylate))

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allows for good film-forming ability. In general, the ideal structures with complete phase separation within a particle cannot be obtained, but an interphase between the phases is formed (5). The structure and morphology of these particles depends on the choice of monomers, the synthesis parameters such as temperature, kind of initiator and surfactant, crosslinking density and many more variables (6).

Polystyrene/poly(butyl acrylate) dispersions with core-shell particles can be designed to provide the properties required of industrial coating by introducing functional groups that are capable of forming crosslinks after or during film formation under suitable reaction conditions. This can be self crosslinking or two component crosslinking with the addition of an external crosslinker (7). In both cases, the resistance properties of film against water and chemicals can upgrade significantly.

One of the best known series of compounds, by which cure is effected, are the reactive derivatives of acrylamide. N-methylol acrylamide (NMA), and N-(iso-butoxymethyl) acrylamide (IBMA) contain readily polymerizable vinyl groups, as well as a cross-linkable methylol or a iso-butoxymethyl group. Both monomers differ in their hydrophilicity. NMA is water soluble, meanwhile the iso-butoxymethyl group imparts organic solubility to IBMA. The organic solubility of IBMA enhances its compatibility with other vinyl monomers and that is why IBMA copolymerizes with most vinyl monomers such as acrylates and styrene.

The aim of this work is to investigate the effect of different functional groups of acrylamide derivatives and their locations in core-shell particles on the morphology and main colloid characteristics of polymer dispersions such as particle size, particle size distribution and viscosity.

Experimental

Materials and Methods

Styrene (Kaučuk, Kralupy) and butyl acrylate (Chemical Works, Sokolov) were distilled under argon reduced pressure, and then stored at 233K before use. N-methylol acrylamide (NMA) from (Merck) and N-iso-butoxymethyl acrylamide (IBMA) from (Cylink) were used as received.

Initiator Sodium dithionite dihydrate— $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Lachema, Brno) and activator Potassium peroxydisulfate— $\text{K}_2\text{S}_2\text{O}_8$ (Lachema, Brno), anal. grade were used as an aqueous solution. Slovasol, a nonionic emulsifier of the composition $\text{CH}_3(\text{CH}_2)_{23}\text{O}(\text{C}_2\text{H}_4\text{O})_{29}\text{C}_2\text{H}_4\text{OH}$ (Chemical Works, Novaky) and anionic emulsifier DDHS (Merck) were used as aqueous solution. All solvents and other chemicals used were analytical grade.

Polymerization Procedure. The functionalized polymer dispersions were prepared by two-stage emulsion polymerization (8–10). The polymerization system is inscribed in Table 1. In the first stage, styrene, or its mixture with NMA or IBMA, was added dropwise to the emulsion containing aqueous solutions of emulsifiers, initiator and activator. After the end of the first step, additional activator and initiator solutions were charged, and during the second step butyl acrylate, or its mixture with NMA or IBMA, was added continuously.

The Gel Content Determination. The polymer samples were put in the Soxhlet extractor at temperature 80°C for 6 h. Methyl ethyl ketone was used as the extraction solvent.

Table 1

The recipe of two-stage seeded emulsion polymerization of styrene and butyl acrylate. N-methylol acrylamide (NMA) and N-(iso-butoxymethyl) acrylamide (IBMA) were used for functionalization of latex particles

I. Step PS seed		II. Step BA shell	
Ingredients	Weight (g)	Ingredients	Weight (g)
Slovasol 2430	2.07		
DDHS	0.54		
K ₂ S ₂ O ₈	0.40	K ₂ S ₂ O ₈	0.40
Na ₂ S ₂ O ₄ · 2H ₂ O	0.13	Na ₂ S ₂ O ₄ · 2H ₂ O	0.13
S	19.13	BA	19.17
IBMA or NMA	1.16	IBMA or NMA	—
	—		1.16
	0.58		0.58
H ₂ O	32.23	H ₂ O	10.83

The insoluble parts were calculated from the weight difference of samples before and after the extraction.

Viscosity Measurement. The latex viscosity was measured with Rheotest RV rotational viscometer at 25°C at the shear rates up to 400 s⁻¹.

Particle Size Measurements. The latex products were characterized in terms of particle size and particle size distribution. Equipment Particle Sizer BI-90 with He-Ne laser was used for measurement. Dispersions were diluted by distilling water to 1–5 vol% of a dispersed phase.

Transmission Electron Microscopy (TEM). The morphology of latex particles was examined by transmission electron microscopy using a JEOL JEM-200 CX TEM. For sample preparation, the original latex was highly diluted until a barely visible turbidity was reached. To enhance the contrast strengthening phase regions in the colloidal particles, the treating with 2 wt% aqueous solution of uranyl acetate (UAc) and RuO₄ was used. The latexes were applied onto Formvar-coated grids.

Results and Discussion

The functionalized polystyrene/poly(butyl acrylate) PS-PBA latex particles with core-shell morphology were prepared through two-stage semi-continuous starved emulsion polymerization with polystyrene as a seed and butyl acrylate as a second stage monomer. We have applied a polymerization system whose composition was confirmed and applied in our previous works (8–10). The recipes are shown in Table 1.

For introduction of reactive groups in latex particles, two functional monomers N-methylol acrylamide (NMA) and N-(iso-butoxymethyl) acrylamide (IBMA) were used, because polymer dispersions with methylol or iso-butoxymethyl groups are interesting due to their potential application as coatings in various industrial fields. N-methylol

acrylamide and iso-butoxymethyl acrylamide were added in the first stage of polymerization together with styrene (core), or in the second stage together with butyl acrylate (shell), or the entire content of functional monomer was divided into the first and the second stages (core/shell).

Particle Size and Particle Size Distribution

In traditional emulsion polymerization, a functional monomer is used in small proportions (up to 10% based on the total monomer mixture). However, it should provide the base polymer with a sufficient amount of chemical groups, which are capable of modifying the physico-chemical properties of the resulting latex.

In this work, we used the functional monomers in the concentration range 1–3 wt%. First, we added the full amount of functional monomer together with butyl acrylate into the shell. We proceeded from the assumption that latex properties are more often than not influenced by the surface layer of a particle. We studied how the amount of added NMA can influence the particle size and the particle size distribution. The results are summarized in Table 2.

It is evident that NMA, in the shell up to the 2 wt% concentration, cannot bring about significant changes in these characteristics. There is a sharp increase in a particle diameter only at the concentration of 3 wt% of NMA by means of increasing the particle size distribution.

Further studies have been pursued to confirm whether the particle size of a final latex and their distribution depend only on the type of functional groups or on the location of functional groups in the particle. Three main types of functionalized latexes have been synthesized. First, the comonomer, together with styrene, was situated into a core P (S-NMA)/PBA, (PS-IBMA)/PBA. Second, the entire functional monomer was situated together with butyl acrylate into a shell PS/P (BA-NMA), PS/P (BA-IBMA). In the third case, the functional monomer was divided into a core and a shell so that the overall concentration should be kept P (S-NMA)/P(B-NMA), (PS-IBMA)/(PB-IBMA). The diameters of latex particles, after the first and second stages of synthesis, were measured and are given in Table 3.

The results have shown that final unfunctionalized and all IBMA functionalized latexes have a mean particle diameter under 100 nm. It was found that the size of IBMA functionalized particles does not depend on their location in the core or shell. The situation was completely different when NMA was used. While NMA is added in the core, the size of latex particles remains unchanged in comparison with unfunctionalized PS/PBA dispersions. When NMA was divided into core and shell, or only in the

Table 2

The particle size and particle size distribution of final PS/P (BA-NMA) dispersion prepared at various content of NMA in the shell

Content of NMA (wt%)	0	1	2	3
Particle size D [nm]	91	84	86	158
Coefficient of polydispersity	1.29	1.22	1.32	2.01

Table 3

The particle size of functionalized latex particles measured after the first and the second stages of synthesis. The total concentration of functional comonomer NMA or IBMA was 3 wt%

Dispersion	D (nm)		Dispersion	D (nm)	
	I.st./II.st.			I.st./II.st.	
PS/PBA	56/91		PS/PBA	56/91	
IBMA in core	62/90		NMA in core	58/92	
IBMA in core/shell	58/96		NMA in core/shell	61/102	
IBMA in shell	56/94		NMA in shell	56/158	

shell, the significant increase in diameter of particles was observed. The largest particles of 158 nm were created when all NMA was added in the shell.

The samples functionalized in both stages of synthesis were analyzed in more detail to find how the diameter of particles and their distribution changed during polymerization depending on the conversion. The curves of particle size distribution in Figures 1 and 2 show that the particle diameter during the first stage of synthesis (Figure 1a, Figure 2a) depends only slightly on the conversion and type of a functional monomer.

However, in the second stage of synthesis, the addition of NMA leads to a significant increase in particle size and their distribution mainly at the end of synthesis (Figure 1b). This is not observed in the latexes functionalized with IBMA (Figure 2b).

Gel Analysis

Acrylamide monomers with N-methylol or iso-(butoxy)methyl groups were introduced to the system during the synthesis of PS/PBA dispersions with the aim to utilize their reactivity in the crosslinking reactions. To verify this possibility, the gel analysis of functionalized PS-PBA dispersions were accomplished.

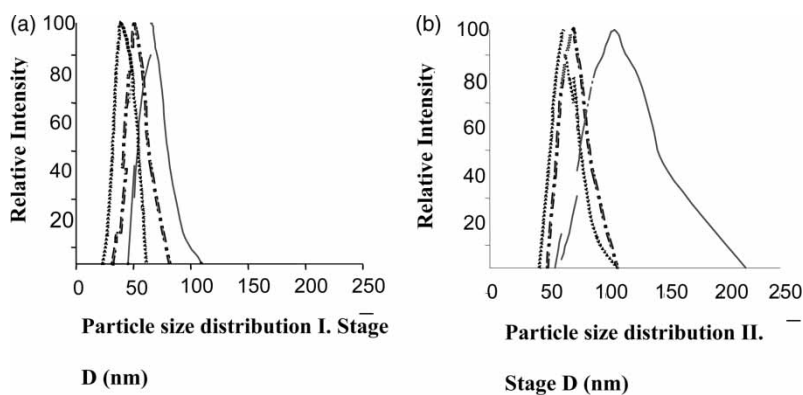


Figure 1. Variation of particle size distribution of P(S-NMA)/P(BA-NMA) samples functionalized in both stages of synthesis vs. time of polymerization. (a) NMA in concentration 1,5 wt%. was used in I. stage of polymerization. (⋯), 40 min; (---), 90 min; (—), 160 min; (b) NMA in concentration 1,5 wt%. was used in II. stage of polymerization. (⋯), 20 min; (---), 60 min; (—), 180 min.

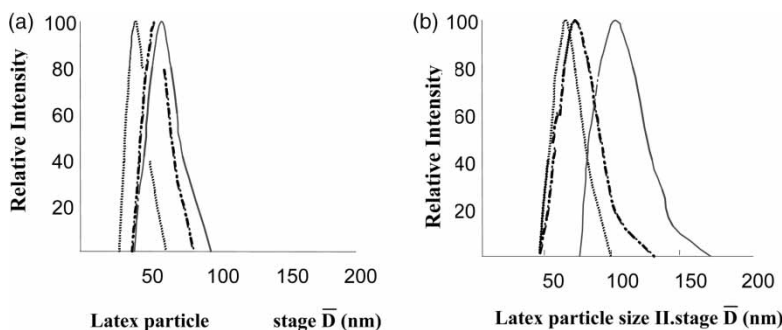


Figure 2. Variation of particle size distribution of P(S-IBMA)/P(BA-IBMA) samples functionalized in both stages of synthesis vs. time of polymerization. (a) IBMA in concentration 1,5 wt% was used in I. stage of polymerization. (. . .), 20 min; (- · -), 60 min; (—), 150 min. (b) IBMA in concentration 1,5 wt.% was used in II. stage of polymerization. (. . .), 20 min.; (- · -), 60 min; (—), 180 min.

As shown in Figures 3–4, the gel content as a function of the polymerization time, had, in both cases, a rising tendency. When NMA or IBMA were added only in the first stage of synthesis (Figure 3a), the growing gel content indicated that crosslinking reactions began in the first stage of synthesis and they proceed also in the second stage of synthesis even though no functional monomer was added in the system (Figure 3b). The crosslinking reactions during the synthesis of functionalized PS core did not affect the diameter of particles and the size of a final functionalized particle remained unchanged in comparison with unfunctionalized samples (Table 3).

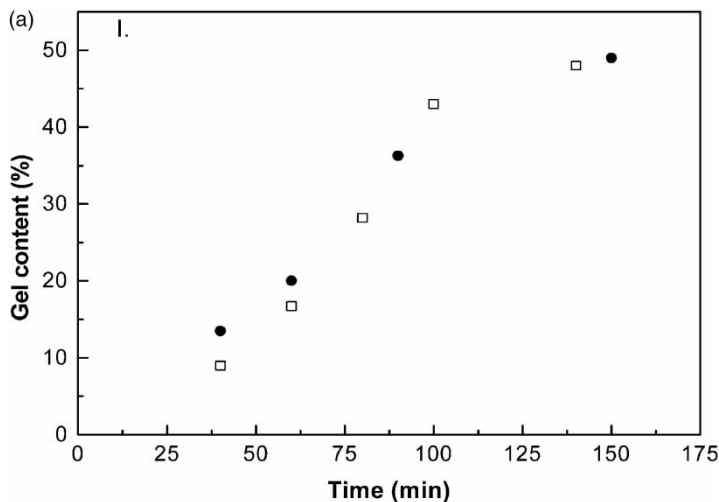


Figure 3. Gel content in P(S-NMA)/PBA or P(S-IBMA)/PBA polymer samples during polymerization. The entire volume of functional comonomer was added in the first stage in concentration 3 wt%. (a) I. stage of polymerization. (□) NMA, (●) IBMA (b) II. stage of polymerization. (□) NMA, (●) IBMA.

(continued)

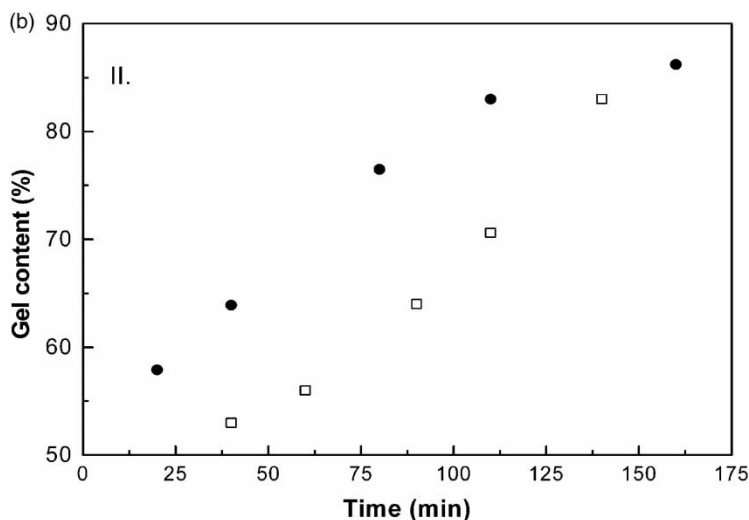


Figure 3. Continued.

The location of functional comonomers in the second stage of synthesis, in samples functionalized in both stages of polymerization, leads to the rising of gel content with conversion as well. The different action of NMA and IBMA in the polymerization system has an impact on the size of the final latexes. In the NMA systems, enlargement of final particles was observed, while in IBMA latexes, the size of final particles remained unchanged.

Based on the gel analysis of PS/PBA dispersions, functionalized with NMA or IBMA, it can be assumed that cross-linking reactions already proceed in both systems

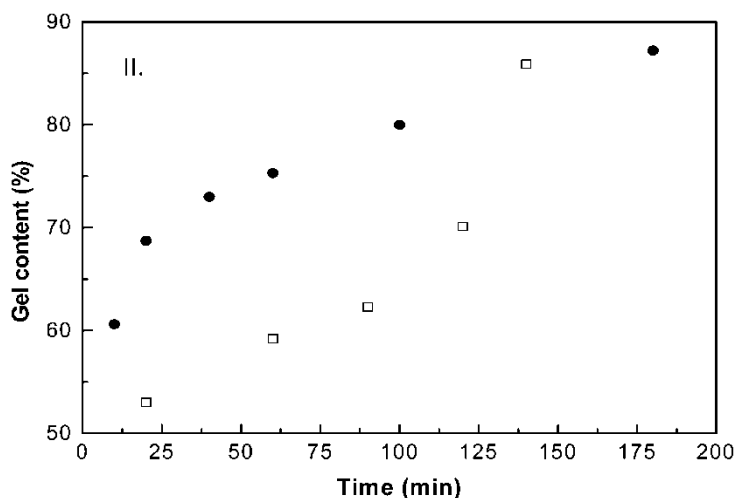


Figure 4. Gel content in P(S-NMA)/P(BA-NMA) or P(S-IBMA)/P(BA-IBMA) polymer samples during the second stage of polymerization. Functional comonomer was added both in the first and the second stages of polymerization in concentration 1.5 wt%. (□) NMA, (●) IBMA.

during synthesis. However, the character of gel rising is different. In NMA functionalized latexes, the significant rising of gel content has been observed at the end of the second stage of synthesis (Figure 4), which correlates well with the enlargement of latex particles. In IBMA functionalized latexes, the size of particles has been unchanged even though the gel content was rising constantly in both stages.

Viscosity

Functionalized PS/PBA dispersions are polymer colloids and their viscosity and rheological behavior depend on the polymer concentration, usually expressed as volume fraction, on the particle size, particle size distribution and the viscosity of water phase. Structural changes on the surface of particles are of great importance because the functional groups of various polarity and reactivity can significantly influence the stabilizing surface layer and hydrodynamic interactions among particles (11). In our case, the rheological behavior of unfunctionalized latexes and latexes with N-methylol or iso-butoxymethyl groups has been compared in Figures 5–6. The experimental viscosity-shear rate dependences clearly showed that NMA-functionalized latexes have higher viscosity in all ranges of shear rate. The viscosity of unfunctionalized latexes and the viscosity of latexes with iso-butoxymethyl group were almost the same. The obtained results have shown that functionalization of PS/PBA latexes with core-shell morphology by acrylamide derivates with different hydrophilicity influences their colloid characteristics like latex particle size, distribution of latex particles size and viscosity.

The latexes were prepared by a two-stage emulsion polymerization which enabled the location of N-methoxy or iso-butoxymethyl groups in the core, the shell, and/or the core and shell at the same synthesis. Although the syntheses were carried out under unchanged conditions, we assume that the location of functional groups in the final latex particles were different due to different hydrophilicity of functional monomers. The results indicated

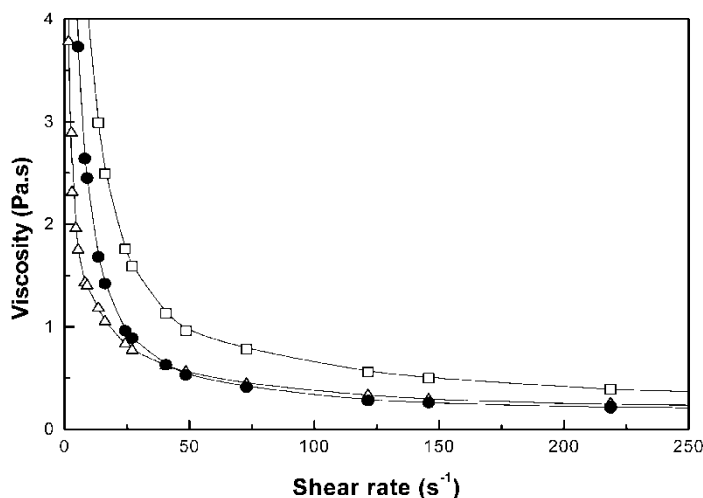


Figure 5. Viscosity vs. shear rate for PS/P(BA) and P(S-NMA)/P(BA-NMA) or P(S-IBMA)/P(BA-IBMA) latexes functionalized in both stages of synthesis in concentration 1,5 wt%. (∇) unfunctionalized PS/PBA, (□) NMA, (●) IBMA.

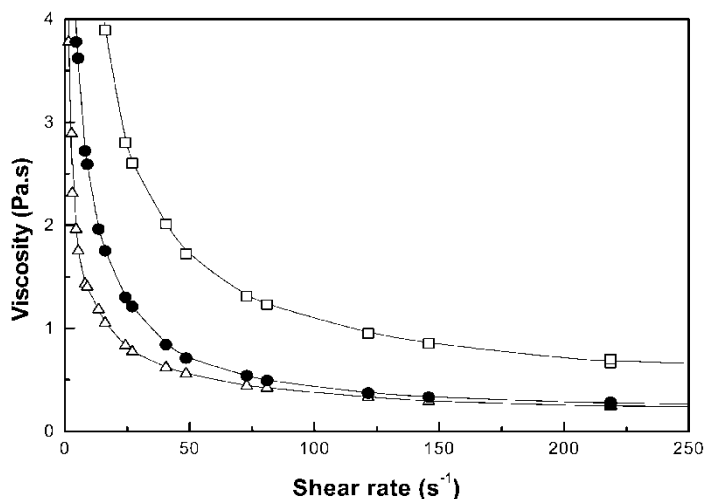


Figure 6. Viscosity vs. shear rate for PS/P(BA) and PS/P(BA-NMA) or PS/P(BA-IBMA) latexes. All functional comonomer was added only in the second stage of synthesis in (▽) unfunctionalized PS/P(BA), (□) NMA, (●) IBMA.

that the properties of PS/P(BA) latexes depend strongly, in particular, on the location of monomers with reactive groups. It is assumed that N-methylol groups from NMA, due to their polarity, are located to a great extent on the surface of the latex particle, mainly when all NMA was added in the second stage of synthesis. Some authors review (12), that NMA does not copolymerize with butyl acrylate, and as far as styrene is concerned, it is in a limited manner. Moreover, the homogeneous nucleation of NMA in the water phase must be taken into account as well. The created oligomer radicals of PNMA can lose their mobility due to absorption on the surface of particles (13), or by nucleation of PNMA particles in the water phase. N-methylol groups on the particle surface can form a crosslinked layer at the butylacrylate shell or can take part in interparticle cross-linking between two or more particles at the origin of hydrogen or covalent bondings.

These assumptions correlate well with the statements of Hidalgo (14, 15), who studied PS/P(BA) latexes functionalized in the second stage of synthesis by acrylamides in detail. They affirm that hydrogen bonds may be formed both between two functional units and between one functional unit and butylacrylate functional group, while covalent bonds may only appear between two N-methylol groups. On the other hand, at temperatures above 100°C, the reaction between methylol group and butylester group from butyl acrylate cannot stand aside (16). When the entire NMA content was added in the core, it is assumed that functionalization of a core leads to its crosslinking, or disreacted functional groups take part in crosslinking a core with its shell. This is confirmed by an increasing gel content in the second stage of synthesis, even though no functional monomer was added in the second stage.

In contrast to NMA, IBMA copolymerizes well with both main monomers due to good compatibility with styrene and butyl acrylate. We can assume that depending on the IBMA addition, the latex particles will have the core or the shell formed by a particular copolymer PS-P(IBMA), P(BA)-P(IBMA), respectively. N-iso-(butoxy)methyl groups will probably be orientated into the latex particles and they will not participate in connecting particles together. Also, however in this case, an increasing gel content confirms that

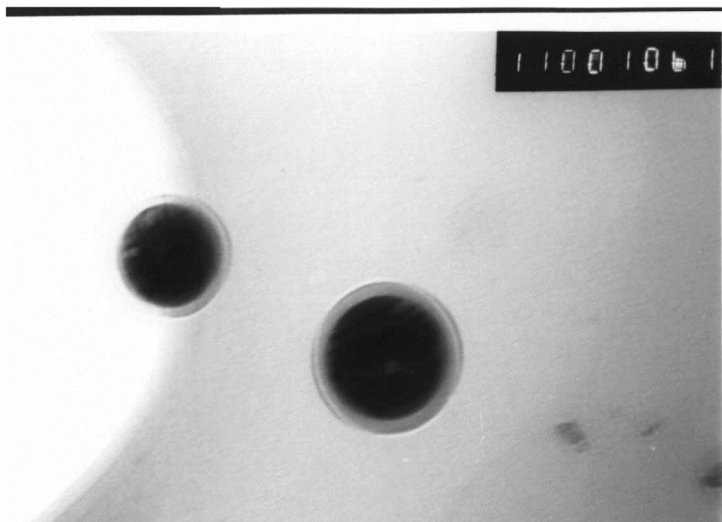


Figure 7. SEM photographs of unfunctionalized PS/PBA latex particles. Magnification 110 000.

intraparticle crosslinking proceeds and the crosslinked core, shell, and/or the core and shell may form.

For verification, this hypothesis, the particle morphology was investigated by transmission microscopy. The TEM pictures for the unfunctionalized PS/PBA particles is shown in Figure 7, from which it is possible to clearly distinguish between two phases, polystyrene core and butylacrylate shell. In Figures 9–10 there are photos of PS/P(BA-NMA) particles functionalized in the second stage of synthesis. It is evident that the particles have kept the core shell morphology and still they have the tendency to accumulate together and form aggregates. A lack of sharp interface between the shell

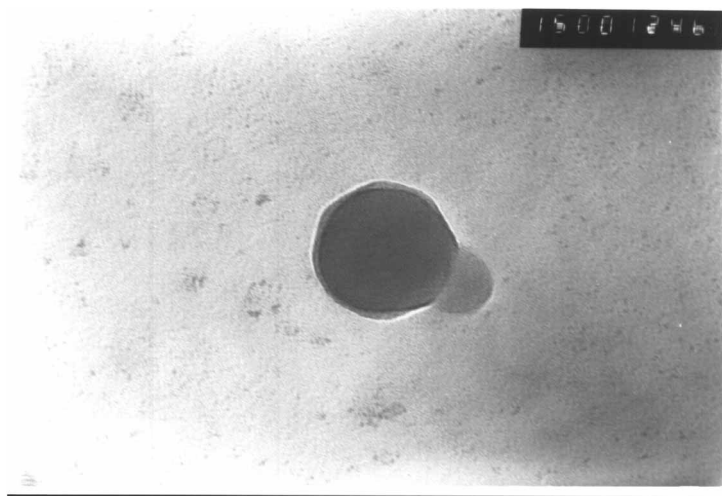


Figure 8. SEM photographs of PS/P(BA-IBMA) latex particles functionalized with IBMA in the shell. Magnification 150 000.

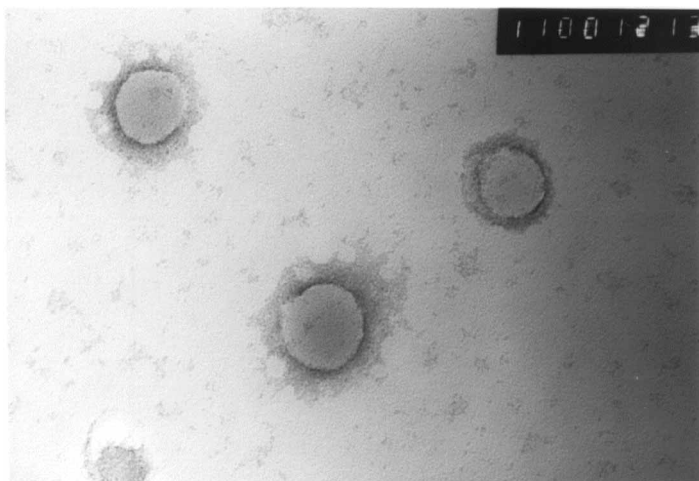


Figure 9. SEM photographs of PS/P(BA-NMA) latex particles functionalized in the shell. Magnification 110 000.

of particles and its surroundings indicates the location of polymeric PNMA fragments on the shell of latex particles. The presence of a set of greater particles in systems with NMA, which have not been observed in the classical synthesis of PS/PBA dispersions, has led to the hypothesis that interparticle crosslinking reactions arise already in the course of synthesis. TEM photos of IBMA functionalized particles (Figure 8) are completely different than NMA functionalized particles and indicated the absence of reactive groups at the surface of the IBMA particles.

The different morphology of IBMA and NMA functionalized particles leads to the explanation of highest values of viscosity in NMA functionalized samples. The presence of hydrophylic fragments of PNMA at the particles surface causes their

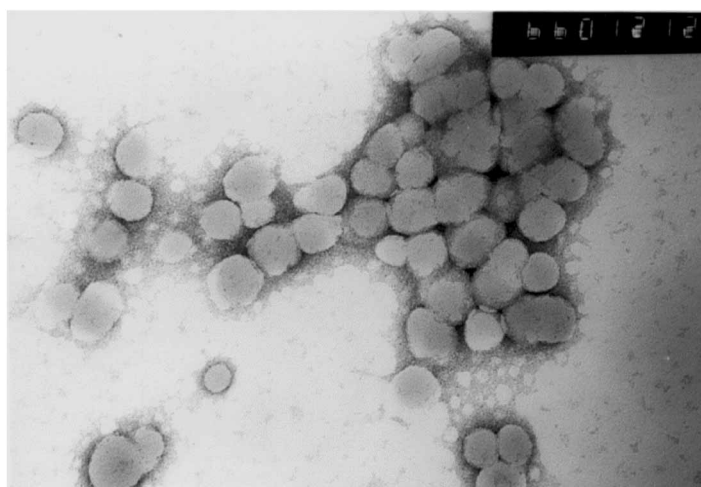


Figure 10. SEM photographs of PS/P(BA-NMA) latex particles functionalized in the shell. Magnification 66 000.

swelling of water and an increase of the hydrodynamic volume and the volume occupied by the disperse phase, respectively. It is well known that the effective hydrodynamic volume of the dispersion particles is proportional to the intrinsic viscosity. In some cases, the accumulation of particles and interparticle crosslinking can form non-spherical macroparticles, which gives higher viscosity (17) as well. In the particles functionalized with N-(iso-butoxymethyl) groups, the particle diameter and viscosity were almost the same as in unfunctionalized particles.

Conclusion

Polystyrene/poly(butyl acrylate) core-shell latex particles containing N-methylol or N-(iso-butoxymethyl) group in the core, shell and/or core and shell were prepared by a two stage emulsion polymerization. The influence of reactive functional groups and their location in the particles on the latex particle size, particle size distribution and viscosity were studied. The morphology of functionalized and unfunctionalized dispersion was also studied.

It was found that different hydrophilicity of introduced monomers strongly influence all studied properties. The IBMA functionalized latex particles tends to show behavior close to that of the unfunctionalized PS/PBA particles. Latex particle size, polydispersity and viscosity of PS/PBA latexes and latexes with iso(butoxy)methyl groups were almost the same. In contrast, introduction of more hydrophilic N-methylol groups leads to formation of latexes with a higher diameter of particles, polydispersity and viscosity than in unfunctionalized samples. In both cases the introduced reactive groups take part in crosslinking reactions already during synthesis.

Acknowledgment

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