Comparative thermodynamic study of functionalized homogeneous and multilayer latex particles

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ABSTRACT

In this work, two series of polymeric particles of poly(butyl acrylate-co-methyl methacrylate), P(BuA-MMA) functionalized with acrylic acid (AA) were synthesized by means of emulsion polymerization techniques. In both cases, the total carboxylic concentration was varied inside the particle between 0, 5, 10, 15 and 20 wt %. and number of particles was maintained constant in two systems. In the fist series, homogeneous latex particles were synthesized, whereas in second series, the latex particles were synthesized in three layers, where a gradient of carboxylic groups was generated inside the particle.

The behaviour of polymeric chains was determined by means of specific volume and adiabatic compressibility at infinite dilution, which were calculated from density and sound speed measurements at 30ºC.

Keywords: Emulsion polymerization, specific partial properties, functionalized polymers

1 INTRODUCTION

Functional groups are usually incorporated into polymeric latex by copolymerization with carboxylic acid comonomers[1]. These can impart colloidal stability, freeze-thaw stability, and improve film forming properties[2,3]. Another function of such monomers is as bonding agents in latex-based paper coatings. The carboxylic acid comonomer forms a major component of water soluble chains on the surface of the latex particle, proving both steric and electrostatic stabilization of the colloid (hence "electrosteric stabilization"). This surface coating of hydrophilic chains is often referred to as a "hairy layer"[4].

The applications of these kind of materials are in two main areas: (i) they can provide useful models for fundamental studies in colloidal science, physics and rheology[5], (ii) they can used in a broad range of applications, for example as binders in paints, adhesives, paper coatings, textiles, etc [6,7].

In recent years a new generation of carboxylic latex particles has been developed as supports in the biochemical and biomedical fields[8,9]. The carboxylic groups are able to form amine bonds with the amino groups of bioligands and they are frequently used to achieve protein binding[10,11]. The properties of these materials and their swelling process is affected by the synthesis process, quantity and location of functional groups inside the particle[12,13].

In this work two series of carboxylated latex particles synthesized by emulsion polymerization techniques were studied. Homogenous particles were synthesized in the first series while the second series, multilayer latex particles synthesized in four steps were prepared.

The analysis of behavior of polar and non polar groups of polymeric particle was made by means of specific partial properties, which indicated, the location of groups inside particle. In addition, a hydration process inside the particle was found.

1.1. Thermodynamics

The analysis of each latex was carried out, considering to latex as a three component system: water (component 1), non-polar groups (component 2) and polar groups (component 3). Now, two of these components (2 and 3) were group in an entity called fraction, which has internal composition. Therefore, the volume for a system composed by a component and a fraction is expressed as:

$$V = V(m_1, m_F, t_{f3}) \qquad (1)$$

where m_1, is the mass of the water and m_F the mass of polymeric particle:

$$m_F = m_2 + m_3 \qquad (2)$$

where m_2 and m_3 are the masses of non-polar and polar groups respectively. The variable t_{f3} is defined as:

$$t_{f3} = \frac{m_3}{m_F} \qquad (3)$$

and it is a measure of the composition of the fraction.
The limits at infinite dilution of component 2 (non polar groups) and component 3 (polar groups) are taken as follows:

$$\lim_{\substack{t_F \to 0 \\ t_{f3} = t_{f3}^c}} v_{2;1,3}(t_F, t_{f3}) = v_{2;1,3}(0, t_{f3}^c) \equiv v_{2;1,3}^{\Delta}(t_{f3}^c) \quad (4)$$

and

$$\lim_{\substack{t_{F} \to 0 \\ t_{f3} = t_{f3}^c}} v_{3;1,2}(t_f, t_{f3}) = v_{3;1,2}(0, t_{f3}^c) \equiv v_{3;1,2}^{\Delta}(t_{f3}^c) \quad (5)$$

In equations (4) and (5) the concentration of the fraction F tends to zero while its composition is kept constant.

Specific partial properties by non-polar and polar groups can be interpreted in terms of:

$$v^o_{2;13} = v^o_M + \Delta v^o_h \qquad (6)$$

where v_M^o is the intrinsic volume of the solute molecule, in which solvent molecules cannot penetrate, and is Δv^o_h and it is named as hydration term.

In order to calculate the specific partial adiabatic compressibility at infinite dilution is

$$k^o_{3;1,2} = \left(\frac{\partial v^o_{3;1,2}}{\partial P}\right)_S = k^o_M + \Delta k^o_h \quad (7)$$

It is important to point out that v^o_M and k^o_M are positive and Δv^o_h and Δk^o_h are negative. The swelling process involves the repulsion of charges and a process of hydration inside the particle. In this way the repulsion between charges will increase the terms v^o_M and k^o_M while the process of hydration will decrease the terms Δv^o_h and Δk^o_h.

2 EXPERIMENTAL

2.1 Materials

The monomers butyl acrylate (BuA), methyl methacrylate (MMA), and acrylic acid (AA) (National Starch & Chemical) were commercial grade and were used as received. Sodium dodecylbenzene sulfonate (SDBS) and potassium persulfate (from Aldrich) were reactive grade and were employed as surfactant and initiator, respectively; both were used without purification. The dispersion medium was distilled water.

2.2 Latex preparation

The carboxylated poly(BuA-MMA) samples were prepared via emulsion polymerization. All reactions were carried out in a semicontinuous reactor consisting of a jacketed rector and a feeding tank. A continuous flow of pre-emulsion material was ensured by a dosing pump. The reactor consisted of a 1-L stirred glass reactor under a dynamic flow of N_2 and at a temperature of 70 °C, controlled by a thermal bath. The stirring rate was adjusted to 250 rpm. In all cases, a seed of poly(BuA) was synthesized as a first stage and the number of particles was maintained constant. The AA total content in the latex was varied from 0 to 20 wt.%. The pH during reactions was kept at a value lower than 4 to ensure the incorporation of acrylic acid. The homogenous particles were carried out in two steps, including the seed, while the multilayer latex particles were prepared by four consecutive polymerization sequences. The formulation used to prepare both latex is presented in table 1 and 2.

Component	Content (g)	
	Stage 1	Stage 2
BuA	6.0	-
MMA		51.0
AA		3.0
Potassium sulfate	0.14	0.7
Tensoactive	0.02	2.52
Water	193.0	293.0

Table 1. Polymerization recipe for homogenous latex particle

Component	Content (g)			
	Stage 1	Stage 2	Stage 3	Stage 4
BuA	6.0	-	-	-
MMA	-	15.0	18.0	18.0
AA	-	2.0	1.0	-
Potassium sulafate	0.14	0.23	0.23	0.24
Tensoactive	0.02	0.76	0.76	1.0
Water	193.0	97.0	97.0	99.0

Table 2. Polymerization recipe for multilayer latex particles

2.3 Densimetry and utrasound speed

A DSA 5000 Anton Paar density and speed of sound analyzer was used. The samples were prepared as follows: A solution stock of 1.74 wt.% of polymer was made, and it was diluted to concentrations of 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 wt.% of polymer. This procedure was made for each latex synthesized. The samples were degassed before to use. The measurements were made at 30 °C.

3 RESULTS AND DISCUSSION

The specific partial volume and adiabatic compressibility of non-polar groups ($v^{\Delta}_{2;1.3}$) and polar groups ($v^{\Delta}_{3;1.2}$) were calculated with following equations:

$$v^{\Delta}_{2:1,3}(t_{f3}) = v^o_{F;1}(t_{f3}) - \left(\frac{dv^o_{F;1}}{dt_{f3}}\right) \times t_{f3} \qquad (6)$$

$$v^{\Delta}_{3:1,2}(t_{f3}) = v^o_{F;1}(t_{f3}) + \left(\frac{dv^o_{F;1}(t_{f3})}{dt_{f3}}\right) \times (1 - t_{f3}) \qquad (7)$$

$$k^{\Delta}_{2:1,3}(t_{f3}) = k^o_{F;1}(t_{f3}) - \left(\frac{dk^o_{F;1}}{dt_{f3}}\right) \times t_{f3} \qquad (8)$$

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$$k^{\Delta}_{3:1,2}(t_{f3}) = k^{o}_{F;1}(t_{f3}) + \left(\frac{dk^{o}_{F;1}(t_{f3})}{dt_{f3}}\right) \times (1 - t_{f3}) \quad (9)$$

where $v^{o}_{F;1}$ and $k^{o}_{F;1}$ were specific volume and the specific adiabatic compressibility of fraction (polymeric particle) of system, which were calculated as:

$$v = v^{o}_{F;1} + (v_1 - v^{o}_{F;1})t_1 \quad (10)$$

where v is the specific partial volume, v_1 is the specific partial volume of water in its pure state and t_1 is the fraction mass of component 1. In the same way, $k^{o}_{F;1}$ was calculated from specific adiabatic compressibility, k using the equation:

$$k = k^{o}_{F;1} + (k_1 - k^{o}_{F;1})t_1 \quad (11)$$

The specific partial volume (v) of latex samples was calculated from the density data, measurement at 30 ºC by the following equation:

$$v = \frac{1}{\rho} \quad (12)$$

and the specific adiabatic compressibility (k) was calculated from the experimental density and sound speed data, measurement at 30 ºC using the following equation:

$$k = \left(\frac{1}{\rho u}\right)^2 \quad (13)$$

The specific partial volume and specific adiabatic compressibility of non-polar and polar groups are shown in Figure 1.

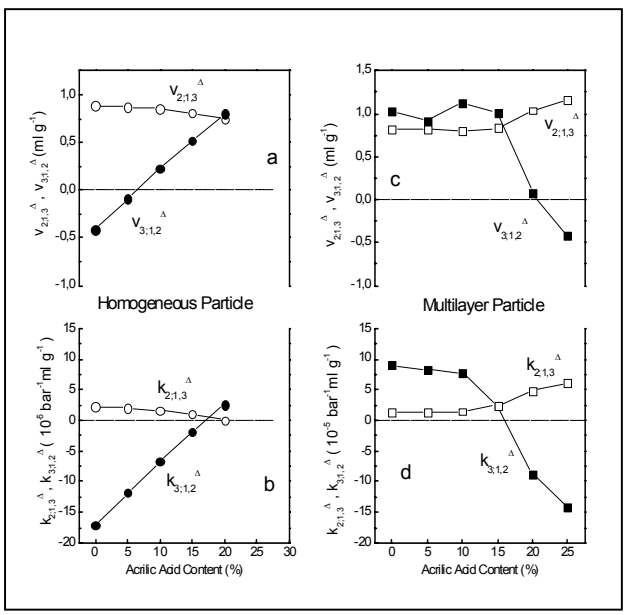

Figure 1. Specific partial thermodynamics properties of non-polar and polar groups of homogenous (panel a and b) and multilayer latex particles (panel c and d).

In the case of homogenous latex particles, both, the volume and adiabatic compressibility of polar groups have negative values when the acrylic acid concentration is low. This means that polar groups have a great hydration and this behavior is only possible if the carboxylic groups are on the surface of particle. When the acrylic acid concentration is increased, the value of thermodynamic properties is more positive. This is explained, when the carboxylic groups are located in the interior of particle, that is, that polar groups in the surface are more hydrated that polar groups in the interior of particle. While the non-polar groups are hydrated when the polar groups concentration is increased. For this reason, the thermodynamic properties decreased when the acrylic groups are raised.

The values of the specific partial thermodynamic properties of polar groups in the multilayer latex particles, suggest that a low concentration of polar groups, the hydration of these groups is not important. However, when the acrylic acid concentration is increased, the hydration of polar groups is higher. The results of thermodynamic properties of non-polar groups indicate that they suffer a dehydration when 15 wt.% of the acrylic acid concentration is reached. This behavior is interpreted in terms of the hydration of multilayer latex particle is located in the bound of each layer.

4 CONCLUSIONS

A simple methodology was developed by means of measurements of density and sound speed for the calculation of specific partial thermodynamic properties. The methodology employed to indicate the behavior of polar and non-polar groups in the polymeric chain.

The polar groups in the homogenous latex particle are located from the surface to the interior of the particle, while in the multilayer latex particle are located in the bound of each layer. In the same way, the hydration in the multilayer particle is not homogenous, because is located in the bound of each layer.

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