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Alkali Swelling of Carboxylated Latices Having Glass Transitions at Ambient Temperatures

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SUMMARY: Carboxylated latices having glass transition temperatures, T_g's, close to ambient temperatures and different acid contents were prepared by a surfactant-free batch emulsion polymerization process at a pH of 4. The swelling properties of the latices at room temperature were investigated using a combination of photon correlation spectroscopy (PCS) and sedimentation field flow fractionation (SdFFF) at different pH's. The particle mass was obtained for the latices using SdFFF, and was found to be independent of the degree of swelling, as expected. When latices containing methacrylic acid (MAA) were studied using PCS, particle swelling was observed. The degree of swelling was dependent on both the amount of MAA copolymerized. By knowing the exact particle mass and particle size a model for heterogeneous particle swelling was developed. At low acid contents in the polymer, an unswollen core and a dense swollen shell appeared as the most likely swelling arrangement. On the other hand, with high acid content essentially homogeneous swelling of the particles was predicted.

Introduction

Latex particles are often modified by incorporating small amounts (0-10%) of vinyl acids. The acid groups derived from the carboxylic comonomer may concentrate at the particle surface due to their hydrophilic nature, [1, 2] and when exposed to a pH higher than the acid's pKa, the particles will swell. It has been shown that the polarity together with the T_g of the polymer are important factors affecting the degree of alkali swelling of a carboxylated latex[3-7]. The softer and the more polar the polymer, the more it will swell.

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In the present study, we have investigated the particle swelling in hydrophobic poly(styrene-*co*-butyl acrylate), PS/BuA, latices with different amounts of methacrylic acid, MAA, incorporated within the polymer. The main objective of this study was to determine the extent of particle swelling as a function of the acid content at various pH's for latices polymerized at a pH lower than the pKa of the MAA. Sedimentation Field Flow Fractionation (SedFFF), which is sensitive to the latex particle mass and also gave us the opportunity to collect fractions of the latices for further analysis with PCS, made it possible to observe small changes in the degree of swelling of the latices.

Methods

Latices were prepared by a surfactant free batch emulsion terpolymerization performed at 70 °C. Potassium persulfate (KPS) was used as initiator and sodium acetate/sodium chloride ($NaCH_3CO_2$/NaCl) buffer was used to keep the pH at 4.0 during the polymerizations, which is below the pKa of MAA (pKa=4.36)[8]. The polymer was a medium-soft terpolymer consisting of PBuA/PS with various MAA contents in the terpolymers. The polymer compositions and the latex characteristics are given in Table 1.

The latices were swelled for at least 24 hours using three different pH buffers (pH 4.0, 7.0 and pH 9.3) with 2.6 g SDS/L H_2O added prior to the analysis. The SdFFF instrument used was built in house (Center for Biopolymers at Interfaces, University of Utah)[9]. Sample fractions were taken during the SdFFF analysis for particle size measurement with PCS. The polymer densities were measured for unswollen latices at low pH's. The particle mass and the particle size together with the polymer densities were used to investigate the swelling properties of the latices at different pH's.

Sedimentation Field Flow Fractionation (SdFFF)

The SdFFF analysis of particle mass is based on the creation of an equilibrium distribution of the sample particles in a thin channel under influence of a sedimentation field. The theoretical machinery describing this distribution is identical to that used for equilibrium ultracentrifugation, with the simplifying feature that there is no radial variation in the centrifugal acceleration, due to the fact that the channel is of negligible thickness (254 μm) compared to the radius of rotation (155 mm). Under the applied field, then, particles of each sample mass distribute exponentially in the channel in the radial direction. For particles denser than the surrounding buffer, the highest concentration will be found right at the outer channel surface, with positions further in containing an exponentially decreasing particle load. Equilibration in the spinning channel does not in itself accomplish a separation. However, upon initiation of the laminar flow of buffer through the thin channel, the steep velocity gradient near the wall will cause distribution clouds of different thickness to travel downstream at different velocities. As a result, the effluent at the channel exit will produce a stream of particles sorted according to their buoyant, or effective, mass, with the smallest effective masses appearing ahead of larger ones[9].

SdFFF results

The particle masses for the different polymer latices obtained via SdFFF are given in Table I. The given values are the averages of at least two analyses and Table I shows that there was a high degree of precision between the measured particle masses of each sample at different pH's. Several of the analyses were performed using different analysis conditions, including different acceleration fields and sample concentrations, and different buffer densities and for the same latex, the same particle masses were obtained. Thus, the SdFFF technique appears to be a robust and reliable technique for determining the particle masses under a wide variety of experimental conditions.

Table 1. Latex characteristics.

Sample	Composition BuA/St/MAA	Terpolymer Density	T_g (DSC)	Particle Mass $x10^{14}$ g		
	wt %	g/ml	°C	pH 4.0	pH 7.0	pH 9.3
B1	43/57/0	1.063	27.4	4.296	4.146	4.382
B2	42/56/2	1.068	32.6	1.758	1.762	1.938
B3	41/54/5	1.071	36.3	2.159	2.078	2.213
B4	39/53/8	1.083	40.5	1.132	1.136	1.294

Table 2 lists the corresponding particle diameters calculated from the SdFFF particle masses and the polymer densities (Table 1). These results show that the masses retrieved from the SdFFF are for the unswollen polymer particles. Even for latices with a high degree of swelling at pH 9.3, there is no change in the measured particle masses between the unswollen and swollen states. The particle diameters obtained from the PCS measurements on samples collected at the sample peak in the SdFFF analysis are given in Table 2. The average ratio of the particle size obtained by SdFFF to that measured by PCS for an unswollen latex at pH 4.0 was found to be 0.957 for a large sample population. The observed particle size in PCS increases with increasing pH and represents the swelled particles.

Table 2. Particle size.

Sample	SdFFF particle diameter nm			PCS particle diameter nm		
	pH 4.0	pH 7.0	pH 9.3	pH 4.0	pH 7.0	pH 9.3
B1	426	421	429	407	405	406
B2	316	316	326	302	306	314
B3	337	333	340	329	337	357
B4	271	272	284	274	285	318

Swelling model

In the present work, we tried to distinguish between 1) homogeneous swelling of the whole polymer particle and 2) a compact unswollen polymer core surrounded by a polymer shell plasticized with water. To develop a model, the latex particles are assumed to have an unswollen core and a swollen shell. The radius of the swollen particle is R_P, with a core radius of R_C and a shell thickness, R_{SH}, equal to R_P-R_C. The core density is assumed to be the measured polymer density, ρ_P, the surrounding buffer solution density is ρ_{BU} and the shell density, ρ_{SH}, varies depending on the mass fraction, X, of polymer present in the shell.

The mass fraction of polymer in the shell, X_{PSH}, is given by the ratio between the mass of the polymer present in the shell and the sum of the buffer and the polymer masses present in the shell, as shown in the equation below:

$$X_{P_{SH}} = \frac{X \cdot m_p}{\left(V_{Sp} - V_{SH}\right) \cdot \rho_{Bu} + X \cdot m_p} \qquad (1)$$

where V_{Sp} is the volume of the swollen particle, V_{SH} is the volume of the swollen portion of the particle and m_p is the mass of the *unswollen* particle.

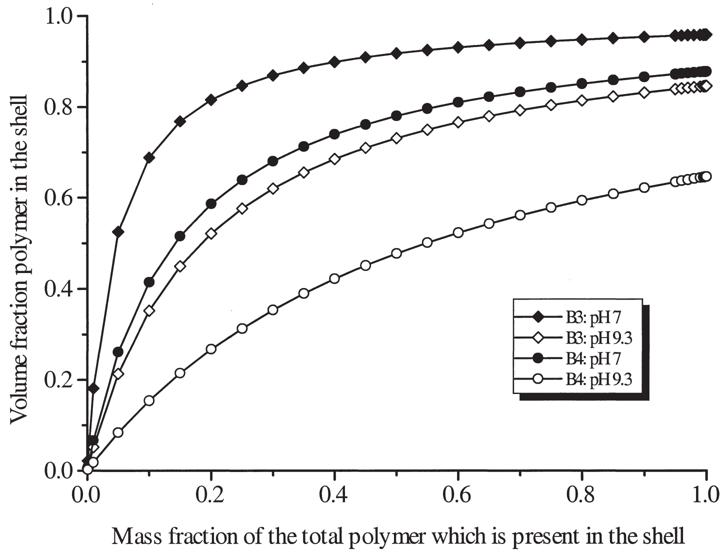

Fig. 1 The calculated volume fractions of polymer in the swollen particle shell as a function of the mass fraction of the total polymer in the shell at different pH's.

If the polymer in the particle is assumed to be homogeneously distributed within a given portion of the particle, the solutions to Equation (1) for the B3 and B4 latices are represented by the graphs in Fig. 1. These trends show the *volume fraction* of polymer in the shell as a function of the mass fraction of the total polymer that is present in the shell, X, at different pH's for alkali swollen latices. Latex B3 with 5 wt.% MAA at pH 7.0 is interesting because it is a polymer with an industrially realistic acid content and having a pH that can be found in many applications. As seen in Fig. 1, B3 is not highly swollen at pH 7.0 and the average swelling, if considered to be homogeneous, is only 5 % (i.e. X=1). However, when the core-shell model of swelling is applied it is evident that even with only 10 % (i.e. X=0.1) of the total polymer present in the shell, the volume fraction of polymer in the shell will be almost

70 %. Previous work with more hydrophilic polymers containing acrylic acid have suggested the presence of a diffuse hydrated layer surrounding the polymer particles but these results for the hydrophobic PS-*co*-BuA-*co*-MAA, suggests that the swollen shell is more densely populated by polymer.

Conclusions

SdFFF in combination with PCS is a very useful technique for studying alkali swelling of latices. The possibility to collect fractions during the SdFFF analysis and then to analyze them using another technique without any further treatment of the samples is a very attractive feature. The particle mass obtained for the latices using SdFFF was found to be independent of the degree of swelling and the observed particle masses are the polymer mass of each particle.

If a carboxylic acid is polymerized below its pKa, the efficiency of incorporation of the acid in the polymer particles is high. For latices prepared under such conditions the most probable swollen particle morphology is an unswollen core and a swollen shell. The swollen shell was found to be dense in polymer.

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