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SHORT COMMUNICATION

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Influence of metal ions on the alkali-swelling behavior of carboxylated acrylic polymer latexes

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Abstract The alkalization of carboxylated acrylic polymer latexes by sodium hydroxide gives rise to swelling of the particles. For a poly(*n*-butyl acrylate) latex copolymerized with 15 wt % methacrylic acid (MAA) and 7 wt % acrylonitrile the particle volume increases by a factor of 30. The alkali-swelling does not depend on the type of monovalent cation used in the base (LiOH, NaOH, KOH, NH_4OH). In contrast, when bivalent cation bases such as $Ca(OH)_2$ are employed no latex swelling is observed during neutralization because of ionic crosslinking of the copolymer chains. Crosslinking also takes place when the bivalent cations (Ca^{2+}, Zn^{2+}, Mg^{2+}) are added as chlorides to dispersions with latexes previously swollen by sodium hydroxide. In these experiments the original size of the latexes is reached again at a molar ratio MAA: bivalent metal ion of 2:1, i.e. at charge compensation of the carboxyl groups. The shrinking behavior is almost independent of the type of bivalent metal ion used. On the other hand, it is more pronounced when trivalent cations such as Fe^{3+} are added. In general, the experiments demonstrate that the alkali swelling of acrylic latexes is dominated by electrostatic forces.

Key words Alkali swelling – Acrylic polymer dispersion – Ionic crosslinking – Ion exchange

Introduction

Many commercial acrylic polymer dispersions contain small amounts of copolymerized acrylic or methacrylic acid (MAA) in order to stabilize the latex particles. The stabilization occurs by neutralizing the carboxyl groups that are either incorporated into the latex polymer or the oligomeric species adsorbed on the latex surface. The neutralization or "charging" process of the incorporated carboxyl groups leads to a swelling of carboxyl-rich parts of the particle. This alkali-swelling behavior has been reported in a number of articles (see Refs [1–3]). It was shown that the swellability depends on the type, amount and loci of the incorporated carboxyl groups, the polymer composition and the flexibility of the polymer chains (i.e. the glass-transition temperature of the polymer). A high degree of swelling can be achieved by using copolymers with low glass-transition temperatures and by distributing the carboxyl groups evenly within the latexes.

Okubo and coworkers [4–6] recently used the alkali swellability of polymer latexes to produce multi-hollow structures within latexes. In their alkali/cooling method [6], for instance, polystyrene latexes containing about 10% MAA are first swollen by the addition of alkali-metal bases at temperatures above the glass transition of the copolymer. Then the swollen structure is cooled to room temperature producing particles with many hollows.

In contrast to the swelling of carboxylated latex particles in the presence of monovalent alkali-metal bases, bivalent cations such as Zn^{2+} give rise to ionic crosslinking of the polymer chains. Films cast from these dispersions yield coatings with excellent hardness [7]. Recently, Mächtle et al. [8] showed that the incorporation of bivalent metal ions, for example, Mg^{2+}, Ca^{2+}, Zn^{2+} and Pb^{2+}, into emulsion copolymers of 20% MAA, $78-x$% *n*-butyl acryate (BA), 2% methallyl methacrylate, x% methyl methacrylate ($x = 0, 10, \ldots, 60$) is a fast and complete process because of a high affinity of the bivalent cations toward the carboxyl groups. The latexes behave as submicron ion-exchange beads. Their potential for the removal of heavy metal ions from waste and natural waters has already been addressed by Morris et al. [9] in their work on thermosensitive anionic microgel dispersions of *N*-isopropylacrylamide modified by acrylic acid.

In the present work, we investigated the influence of the type and the valency of the cation present in the base on the alkali-swelling behavior of acrylic latexes copolymerized with MAA. The swelling was investigated by quasielastic light scattering (QELS) at high dilution of the latex dispersions.

Experimental

The swelling measurements were performed on a poly (BA) latex copolymerized with 15 wt % MAA and 7 wt % acrylonitrile. The latex was prepared by semicontinuous emulsion polymerization (85 °C, feeding time 2 h) using 0.8 wt % initiator (sodium persulfate) and 0.45 wt % emulsifier (K30, Bayer, sodium C_{13-17}-alkyl sulfonate). The final solids content of the dispersion was 45 wt%. No cleaning procedure was performed before the swelling experiments.

According to capillary hydrodynamic fractionation (CHDF) the dispersion was unimodal (Fig. 1). The mean CHDF diameter was in good agreement with the hydrodynamic diameter, 152 nm, as measured by QELS (first cumulant, scattering angle 90°, wavelength 633 nm).

The swelling studies were performed with automated apparatus. The metal hydroxide or metal chloride solution was added stepwise to the diluted dispersion (100 ml, solids content 0.25 wt %) which was then pumped into the flow cell of a light-scattering goniometer where the particle size was measured by QELS. All dilutions were performed with Millipore water having a specific resistance of 18 MΩ cm.

The light-scattering apparatus consisted of the following components: HeNe laser (wavelength 632.8 nm, 5 mW, NEC model GLG 535/S 5302), goniometer (Malvern, scattering angle 90°), photomultiplier tube (Knott NL-2020-02-04), amplifier/discriminator unit (Thorn EMI C604) and digital correlator BI-2030AT (128 data channels, Brookhaven Instruments). The autocorrelation functions were analyzed by the cumulant method. The particle diameters reported are averages of three measurements (duration 1 min each). No systematic changes in the diameters or the pH values were observed during these repetitions. All measurements were performed at room temperature (≈22 °C).

Results and Discussion

The swelling behavior of the latex particles on addition of 0.5 M sodium hydroxide and 0.0156 M calcium hydroxide (solubility maximum) is shown in Fig. 2. For the experiment with sodium hydroxide the back-titration with 0.5 M hydrochloric acid is also shown.

The figure reveals that the addition of sodium hydroxide gives rise to swelling of the latex particles, which starts at pH values greater than 8. The maximum expansion is reached when the neutralization of the carboxyl groups is stoichiometric (approximately at pH 10.2). On further addition of sodium hydroxide the particles shrink again because of the increasing ionic strength of the dispersion medium. The maximum degree of swelling corresponds to a volume increase of the particles of a factor of about 30.

When the latex is back-titrated with hydrochloric acid pronounced hysteresis of the particle size as a function of pH is observed. At pH 5, however, the latexes shrink to their original size again. In contrast, the scattering intensity of the dispersion after the back-titration reaches only two-thirds of the value before the

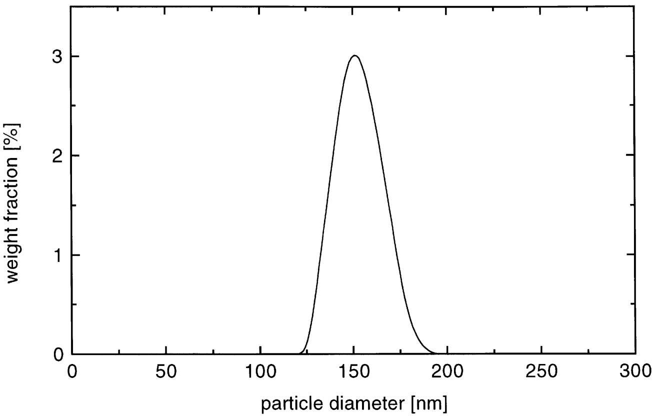


Fig. 1 Particle size distribution of the investigated latex dispersion as measured by capillary hydrodynamic fractionation

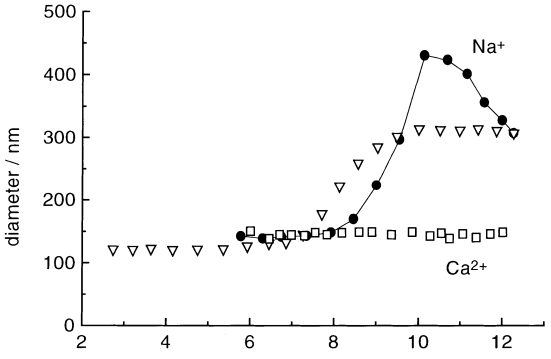
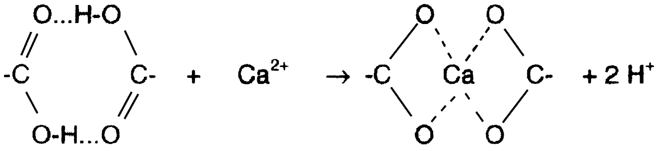


Fig. 2 Alkali swelling behavior of the acrylic latex using 0.5 M NaOH (●) and 0.0156 M $Ca(OH)_2$ (□) as neutralizing agents. For the experiment with NaOH the back-titration curve with 0.5 M HCl is also shown (▽)

beginning of the experiment. Partial dissolution of the particles at high pH can therefore not be excluded and is a possible explanation for the observed hysteresis. Another source of irreversibility might be the hydrolysis of some of the BA ester groups in the alkaline medium.

In contrast to sodium hydroxide the addition of calcium hydroxide (0.0156 M) does not give rise to any swelling (see Fig. 2). A comparable observation was made by Bassett and Hoy [2] in swelling studies on acrylic latexes containing 2 wt % acrylic acid: with sodium hydroxide swelling occurred at pH values greater than 7, and with barium hydroxide swelling was inhibited. From the work of Mächtle et al. [8] we know that bivalent ions are quickly and completely incorporated into carboxylated latexes. The lack of any swelling of the particles upon addition of calcium hydroxide, as shown in Fig. 2, must therefore mean that the Ca^{2+} ions are able to ionically crosslink the charged polymer chains within the particles. Obviously, no water is imbibed by the incorporation of the Ca^{2+} ions as is the case for Na^+ ions. We surmise that dimeric structures of hydrogen-bonded carboxylic acid groups facilitate the incorporation of Ca^{2+} ions



This type of dimer is typical for carboxylic acids in nonpolar environments. The dimers are also found in polymer latex films and recognized in FTIR by a shift of the carboxylic acid carbonyl stretching vibration to lower wave numbers [10, 11]. The complexation of the Ca^{2+} ions in these structures might be additionally supported by oxygen atoms of other acrylic ester groups existing in the surroundings.

The alkali-swelling behavior of the latex particles is shown for different monovalent bases (LiOH, NaOH, KOH and NH_4OH) in Fig. 3. Identical swelling curves result for all four bases. The type of monovalent cation therefore has no influence on the water and salt uptake during the neutralization process.

In order to study the effect of different multivalent cations on the swelling behavior (Zn^{2+}, Mg^{2+} and Fe^{3+} in comparison to Ca^{2+}), a different approach had to be used because of the very low solubilities of the corresponding hydroxides. In this case the pH of the dispersion was first adjusted to pH 11 by the addition of sodium hydroxide and then the water soluble chlorides of the above-mentioned cations were added stepwise. The results of these experiments are shown in Figs. 4 and 5.

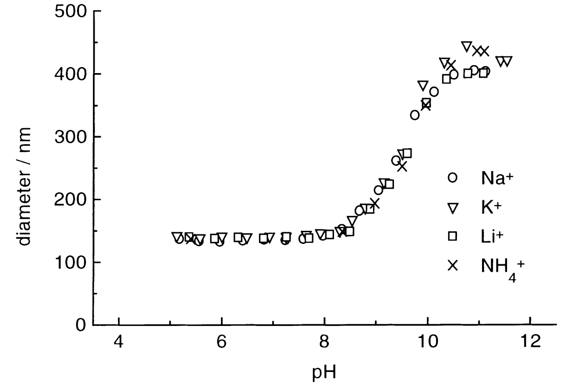


Fig. 3 Influence of monovalent cations on alkali swelling. Alkalizations by 0.1 M NaOH (○), 0.1 M KOH (▽), 0.1 M LiOH (□) and 4.7 M NH_4OH (×)

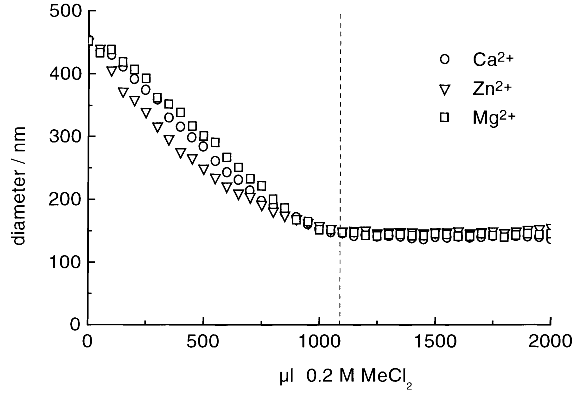


Fig. 4 Influence of bivalent metal ions (Me^{2+}) on the size of the swollen latex particles at pH 11 (adjusted with NaOH). Concentrations and pH values of the added electrolytes: 0.1 M $CaCl_2$ (pH 9.7), 0.2 M $ZnCl_2$ (pH 6.3) and 0.2 M $MgCl_2$ (pH 7). The *vertical broken line* corresponds to a molar ratio MAA:Me^{2+} of 2:1

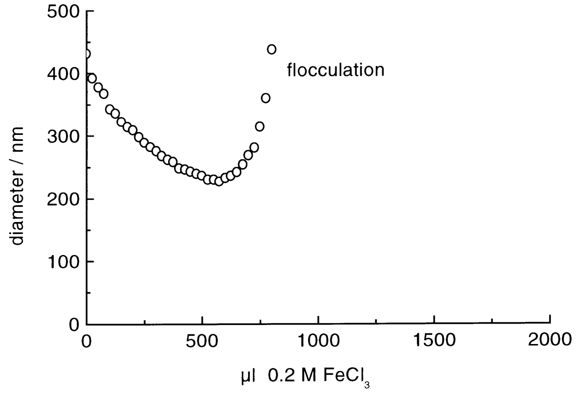


Fig. 5 Influence of 0.2 M $FeCl_3$ (pH 2) on the size of the swollen latex particles at pH 11 (adjusted with NaOH)

Figure 4 shows that the latex particles swollen at pH 11 shrink upon addition of the bivalent metal cations. The original particle size (as measured in acid medium after polymerization) is reached again at a molar ratio MAA: bivalent metal ion of 2:1, i.e. at complete charge compensation of the carboxylate groups by the cations. Only a small influence of the type of cation is revealed in the figure. The somewhat stronger shrinking in the presence of Zn^{2+} ions is probably due to the substantial pH decrease (from 11 to 7) which was observed during the addition of zinc chloride solution. In contrast, for magnesium and calcium chloride solutions the pH of the dispersion changed only slightly during the shrinking process. The pH drop observed for Zn^{2+} ions is probably due to the precipitation of zinc hydroxide, which has a very low solubility in water compared to the other two chlorides.

The bivalent cations studied differ in size and belong to the groups of transition and non-transition elements. If specific interactions between the different cations and the carboxylate groups (i.e. metal ion/ligand complex formations) are of major importance for the shrinking/swelling behavior of the acrylic latex particles stronger differences should be visible in Fig. 4. We therefore conclude that the particle swelling is dominated by electrostatic forces.

In accordance with this conclusion the addition of ferric chloride leads to a greater shrinking of the latex particles when compared on a molar basis to the bivalent cation chlorides (Fig. 5). Unfortunately, because of the high charge of the Fe^{3+} ion flocculation takes place during the shrinking process.

Conclusions

In summary, the investigations show that the alkali swelling of the acrylic latex dispersion studied is mainly affected by electrostatic forces. Specific interactions between the metal ions and the carboxylate groups such as those observed in metal ion/ligand solution complexes do not seem to be of major importance for the state of the particle swelling. When monovalent metal ion hydroxides are used for the alkalization, swelling is observed: the swelling is independent of the type of monovalent cation used. Bivalent and trivalent cations give rise to ionic crosslinking of the charged polymer chains within the particles, and this is also dominated by the charge and not by the type of metal ion.

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