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The properties of polyampholyte microgel particles prepared by microemulsion polymerization

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Polyampholyte microgels have been synthesized by copolymerizing the anionic monomer sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS), the cationic monomer (2-(methacryloyloxy)ethyl)trimethylammonium chloride (MADQUAT), and a crosslinking monomer *N,N'*-methylenebisacrylamide (BA), using an inverse microemulsion route. The swelling properties of so-called 'balanced' microgel particles (i.e. containing the same number of positive and negative monomers in the initial mixture), but containing variable amounts of the crosslinking monomer, have been investigated as a function of ionic strength using photon correlation spectroscopy. The microgel particles flocculate *below* a certain electrolyte concentration. Above this concentration they are stable and the particle size appears to be insensitive to both ionic strength and the crosslinker concentration in the monomer feed. The structure of the microgel particles in pure water has been investigated using transmission electron microscopy. The samples consist of both aggregates and isolated particles. The isolated particles are somewhat ellipsoidal in the collapsed state. In order to monitor the 'surface charge' of the particles, under various conditions, electrophoretic mobility measurements have been performed. The swelling behaviour of 'unbalanced' 20/80 [anionic/cationic] polyampholyte microgel particles has been examined. Unexpectedly, these microgel particles displayed only a very small decrease in size with increasing electrolyte concentration. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Polyampholytes are polymers containing both positive and negative charges along the same chain. Due to the presence of charges of opposite sign the dilute aqueous solution properties of these polymers is complex and is mainly governed by the intra-chain electrostatic interactions.

A 'balanced' polyampholyte (i.e. containing equal numbers of positive and negative charges) is usually insoluble in pure water because of the net electrostatic attraction between opposite charge groups along the chain. However, such chains become soluble upon the addition of electrolyte, as a result of the screening of these attractions. Hence, the viscosity increases with increasing electrolyte concentration. This is referred to as 'antipolyelectrolyte behaviour'. The conformation of a polyampholyte chain with a *net* charge (i.e. bearing different number of positive and negative charges) is the result of the competition between two antagonistic effects: (i) the *polyampholyte* effect, associated with the attraction between groups of opposite sign, which tends to lead to chain compression, and (ii) the *polyelectrolyte* effect, associated with the repulsion between like charges, which tends to stretch the chains.

Due to their interesting solution properties, polyampholytes have a number of potential applications[1–7], and recently much attention has been paid to both their theoretical and experimental aspects. Various models predicting the conformation of a single polyampholyte chain in aqueous solution have been developed[8–17].

Kashiwabara *et al.*[18] prepared monodisperse, reactive microgel particles which they converted into amphoteric ones. The particles were pH-sensitive and aggregated around the iso-electric pH. Kudaibergenov *et al.*[19] studied polyampholyte microgels prepared by the γ-irradiation initiated copolymerization of 4-(but-3-en-1-ynyl)-1-methylpiperidin-4-ol with acrylic acid, in a mole ratio 7/3. They reported an increase in the swelling degree of the polyampholyte gel, at the isoelectric pH, as the ionic strength increased. They explained this trend in terms of electrolyte screening of the electrostatic *attraction* between oppositely charged groups within the microgel particles. Tanaka *et al.*[20] have studied polyampholyte *macrogels*, prepared by the copolymerization of acrylamido methyl propyl sulfonic acid (AMPS-H) and methacryl-amido propyl trimethylammonium chloride (MAPTA-Cl) using N,N'-methylenebisacrylamide as a crosslinker (1.22 mol%). These authors have shown that the neutral network is collapsed at low ionic strength and begins to swell at about 10^{-2} M NaCl, due to the electrolyte screening.

Corpart *et al.*[21] have described the synthesis of polyampholytes in microemulsion systems. They examined the aqueous solution properties of a series of high-charge

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density, linear polyampholytes prepared by copolymerization of an anionic monomer with a cationic monomer[5]. Their results were found to be in good agreement with the theoretical predictions of Higgs and Joanny[8].

Microgels are colloidal dispersions of intramolecularly crosslinked polymer particles. Potential applications lie in areas such as drug delivery systems[22], water treatment[23], oil recovery[24], and paints[25]. However, very little attention has been paid to colloidal *polyampholyte* microgels, as compared to their macroscopic counterparts, namely polyampholyte *macro*gels or hydrogels[19,20,26–29].

The objective of the present work was to use a novel method to synthesize microgel particles based on the microemulsion polymerization technique developed in Candau's laboratory[5,30–33], but in this case copolymerizing an anionic monomer and a cationic monomer together with a crosslinking agent. To date, microgel particles have, in the main, been prepared by emulsion polymerization techniques. Antonietti *et al.* employed a microemulsion polymerization technique for the preparation of fine polystyrene latex particles[34,35].

This paper describes the morphology, the swelling behaviour and some electrophoretic mobility investigations of high charge-density microgel particles containing a balanced amount of anionic and cationic monomers, prepared by microemulsion polymerization. For comparison, the swelling behaviour of some *unbalanced* microgel particles is also reported.

EXPERIMENTAL

Materials

2-Acrylamido-2-methylpropanesulfonic acid (AMPS H), provided by Lubrizol, UK, was recrystallized from methanol and subsequently neutralized by slow addition to an aqueous sodium hydroxide solution of appropriate concentration, until pH 9 was reached. [2-(Methacryloyloxy) ethyl]trimethylammonium chloride (MADQUAT) was supplied by Aldrich as a 75% (wt/wt) aqueous solution from which the monomer was obtained as a white powder by precipitation in acetone. Both the crosslinking monomer N,N'-methylenebisacrylamide (BA) from Aldrich, UK, and the oil-soluble initiator azobisisobutyronitrile (AIBN), from BDH, were recrystallized from methanol prior to use. The oil *Isopar M* from Exxon Chemicals, UK, is a narrow-cut, isoparaffinic mixture (boiling range: 207–275°C). It was filtered before use. Distilled water was purified using a Millipore *Milli-Q* device. The mixture of nonionic surfactants required for the microemulsion consisted of sorbitan sesquioleate (*Arlacel 83*, which has an hydrophile–lipophile balance, HLB, value = 3.7) and poly(oxyethylene)sorbitol hexaoleate with 40 ethylene oxide residues (*Atlas G1086*, HLB = 10.2) supplied by ICI.

Preparation of the microemulsions

The required proportions of each monomer were dissolved in water to form the aqueous phase, which was subsequently adjusted to pH ~ 7. The organic phase consisted of the hydrophobic initiator AIBN (0.25 mol% with respect to the total monomer amount) and the blend of surfactants of the required HLB value which were dissolved in *Isopar M*.

The organic phase was added to the aqueous phase and stirred to form a thermodynamically stable and optically transparent monophasic microemulsion. The appropriate (optimum) HLB value was taken to be the minimum value in the plot of wt% of surfactants required to obtain a microemulsion vs. the HLB value of the surfactant mixture. This plot defines the limit between the emulsion domain and the monophasic domain. Moreover, the optimum HLB value is dependent on the composition of the monomer feed. In previous studies[5], concerning the preparation of linear polyampholytes by the microemulsion copolymerization of NaAMPS and MADQUAT, the optimum HLB value was found to occur at 9.7 for the balanced 50/50 ratio, and at 10.5 for the unbalanced 20/80 ratio : anionic to cationic monomer.

In the present work the optimum HLB value was found to be independent of the crosslinker concentration over the investigated range. The microemulsions used in the present studies were, therefore, all prepared with a surfactant blend characterized by the same HLB values established in the earlier work.

A typical recipe used for the microemulsion is the following (wt%): *Isopar M* 43.5%; water 21.75%; total monomer mixture 21.75%; surfactant blend 13%.

In this paper the composition of the microgel particles is designated as the relative ratio of anionic to cationic monomers followed by the molar percentage of crosslinker in the monomer feed.

Microemulsion polymerization and polymer recovery

The microemulsion polymerization was carried out at 20°C in a water-jacketed quartz reactor. Oxygen was first eliminated by bubbling nitrogen through the microemulsions.

Whilst stirring, the polymerization reaction was photo-initiated using a u.v. lamp. Total conversions (yields > 98%) were achieved within less than 1 h. The final products were clear and transparent, and appeared to be stable for at least a year.

In order to recover the polymer, the microemulsions were added, dropwise, to an excess of isopropanol and 'washed' several times with fresh isopropanol. The resulting white precipitates were dried for 48 h under vacuum, at 45°C.

Microgel particles

In the case of the balanced microgels, the aqueous microgel dispersions were prepared by the addition of the required volume of salt solution to the required amount of dry polymer. The samples were rotated gently overnight. They were then sonicated (ultrasonic bath) for 5 min. Diluted samples were prepared, over a range of ionic strengths, by the appropriate additions of water and a concentrated salt solution (filtered through a Millipore GS 0.22 μm filter). The resulting samples were stirred overnight to allow swelling equilibrium to be reached, and then sonicated for about 10 min. The same procedure was applied for the unbalanced microgel samples, except that the sonication step was unnecessary, since the particles dispersed readily in this case.

Transmission electron microscopy

TEM experiments were performed with a JEOL *100X* electron microscope. The samples in this case were prepared by adding water (rather than salt solution) to the white powder. This mixture was stirred on a rotating wheel for 48 h and then sonicated (in an ultrasonic bath) for 10 min. A droplet was placed on a carbon-coated copper grid, and the water allowed to evaporate.

Photon correlation spectroscopy

These experiments were carried out at 25°C using a *Zeta Plus Analyser* (Brookhaven Instruments Corporation, New York), operating at a wavelength of 632.8 nm and at a fixed scattering angle of 90°.

Electrophoretic mobility measurements

The electrophoretic mobilities were determined using a Phase Analysis Light Scattering[36] instruments (constructed in this laboratory) which enables very small electrophoretic mobilities to be determined in both polar and non-polar colloidal dispersions.

RESULTS AND DISCUSSION

Transmission electron microscopy

Figures 1a and *b* show electron micrographs, taken from two different regions of the supporting copper grid, of balanced microgel particles, which contained 2 mol% BA (crosslinking monomer) and had been redispersed in *pure water*. Aggregate structures, consisting of a large number of individual particles, can be clearly observed in *Figure 1a*. *Figure 1b*, however, shows that there are isolated particles present, as well as aggregates. Nevertheless, it was not possible to redisperse the polymer in water to give only single particles. Corpart *et al.*[5], who prepared a series of linear polyampholytes involving the copolymerization of NaAMPS and MADQUAT, in fact showed that the linear, neutral polymer chain is insoluble in pure water, in line with the theoretical model of Higgs and Joanny[8]. It is also possible that the process of heating the white powder at 45°C (see earlier) is responsible for some limited particle 'fusion', thus preventing complete redispersion of the particles. However, a similar heating process had been used previously for the preparation of *linear* polyampholytes[5] and for the preparation of very fine polystyrene particles[34], both using microemulsion polymerization.

Figure 1c shows the singlet particles at a higher magnification. The particles appear to be elongated (ellipsoidal) and somewhat 'soft'. It may be that the vacuum drying process in the electron microscope results in some 'flattening' of the particles, leading to the apparent ellipsoidal shape. The mean diameter of these particular particles was determined from the electron micrographs using software which takes into account the shape of the objects analysed. The value for the mean diameter of the (dry) particles is 50 ± 29 nm. Even if the standard deviation is high, the reproducibility of the mean value is ±7%. Although better redispersion of the powder, to yield distinct (if swollen) particles occurs in *salt solution*, rather than in water, unfortunately salt crystals precipitate, on evaporating the water, and these obscure the particles in the micrographs.

Photon correlation spectroscopy (PCS)

The diameters of the various (inverted) microemulsions are shown in *Table 1*. It would seem that there is no real dependence of the size on the percentage of the cross-linking monomer used. For the balanced (50/50) microgels, the average droplet size is ~110 nm, whereas for the unbalanced [20/80] ones the diameter is ~91 nm.

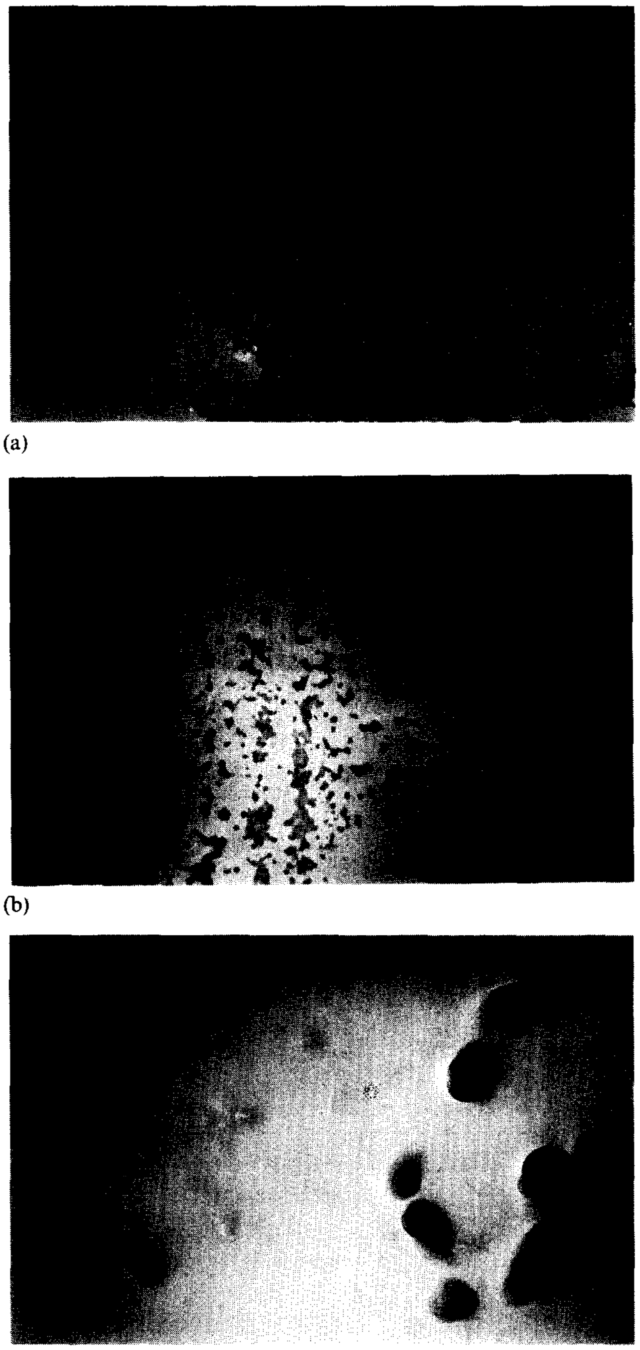
(a)
(b)
(c)

Figure 1 Transmission electron micrographs of microgel 50/50-2BA in the collapsed state: (a) magnification 33 000; (b) magnification 20 000; (c) magnification 50 000

Table 1 Hydrodynamic diameters of the microemulsion droplets

Monomer feed composition (ratio anionic/cationic charges—mol% crosslinker)	Hydrodynamic diameter (nm)
50/50-0BA	94.4 ± 2.3
50/50-1.41 BA	116 ± 11
50/50-2BA	106.8 ± 2.2
50/50-5BA	121.5 ± 4
20/80-0BA	84.2 ± 2.7
20/80-2BA	91.3 ± 2.9

With regard to redispersion of the dried polymer into aqueous media, it was found that electrolyte needed to be present to obtain reasonably monodisperse particles, as indicated by the PCS results. To this end $MgCl_2$ was

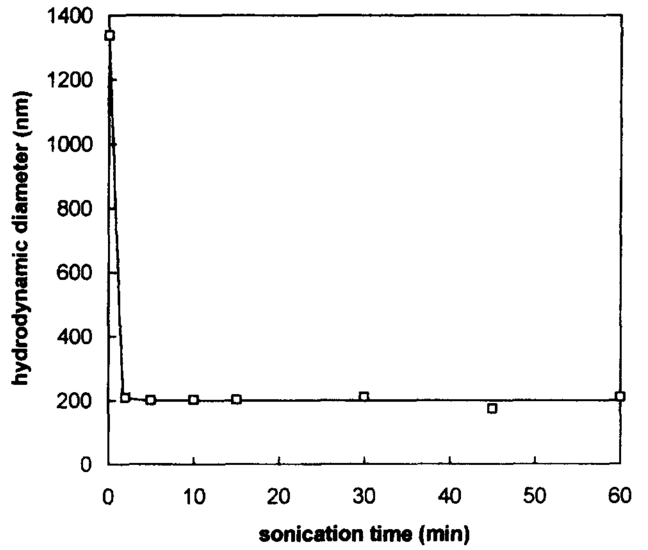

Figure 2 Effect of the sonication time on the hydrodynamic diameter in the case of 50/50-2BA microgel particles redispersed in 1 M $MgCl_2$

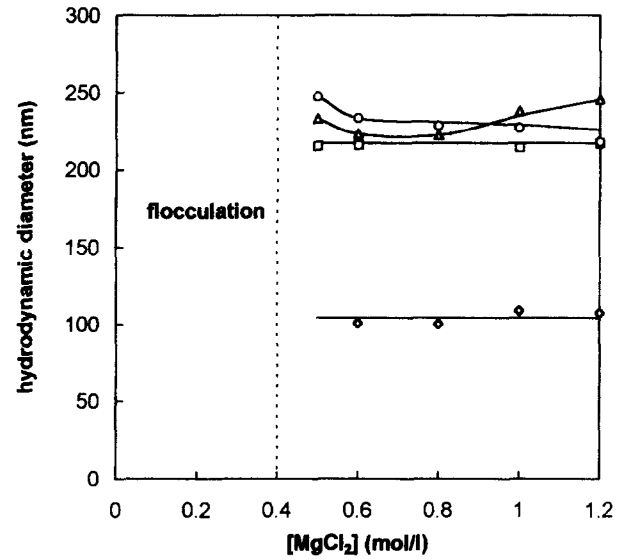

Figure 3 Hydrodynamic diameter of the 50/50-*y*BA microgel particles, redispersed in $MgCl_2$ as a function of the ionic strength, $y = 0$ (◇), 1.41 (□), 2 (△), 5 (○)

found to be more effective than NaCl. The diameters of the balanced polyampholyte microgel particles [50/50—2BA], redispersed in 1 M $MgCl_2$, at a polymer concentration 2×10^{-4} g cm^{-3}, as a function of the sonication time (using an ultrasonic bath), is shown in *Figure 2*. It would seem that sonication results in a limiting value (after about 2 min) of about 220 nm. Longer sonication times (or the use of a *Soniprobe*—with its greater power input) did not lead to any further decrease in the mean size. The value of 220 nm is significantly higher than the electron microscope (collapsed state) value of ~50 nm, reported above, suggesting that the particles are indeed swollen at that concentration of electrolyte solution. Although redispersion could be effected by simply *stirring* a dispersion of the powder in 1 M $MgCl_2$ solution, this was not as effective as sonication.

When the microgel dispersion in 1 M $MgCl_2$ solution was repeatedly dialysed against pure water (until the conductivity of the dialysate equals that of pure water), then the diameter of the particles was reduced to 180 ± 10 nm. This indicates *deswelling* in pure water, as expected.

Figure 3 shows the hydrodynamic diameters of various *balanced* microgel particles, containing variable cross-linker amounts, redispersed in $MgCl_2$ solution, as a function of $MgCl_2$ concentration. The microgel particles were flocculated below a value of 0.4 M $MgCl_2$, irrespective of the amount of crosslinker used. At higher $MgCl_2$ concentrations the particles were stable, and the average particle size does not appear to increase with increasing ionic strength. Corpart *et al.*[5], who observed that the corresponding balanced *linear* polyampholyte molecules are insoluble in pure water, also found that a minimum electrolyte concentration was required to solubilize the polymer. This minimum concentration was again 0.4 M in the case of $MgCl_2$.

Another feature, shown in *Figure 3*, is that the size of the microgel particles (i.e. those containing cross-linker) is, as expected, significantly (about a factor of two) larger than the corresponding uncrosslinked polyampholyte chains. However, the diameter of the particles in (>0.4 M) $MgCl_2$ solution is, more or less, independent of the concentration of crosslinker used in the preparation. One might have expected those particles

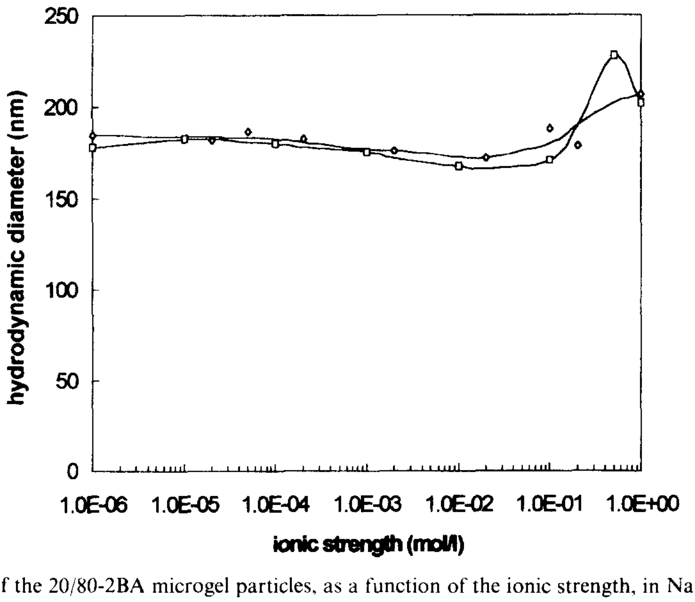

Figure 4 Hydrodynamic diameter of the 20/80-2BA microgel particles, as a function of the ionic strength, in NaCl (◇) or $MgCl_2$ (□)

containing the higher concentrations of cross-linker to be less swollen, but maybe not all of the crosslinker takes part in the polymerization reaction and, above some minimum concentration, similar amounts of cross-linker are incorporated.

With regard to the *unbalanced* (20/80 ratio anionic/cationic monomer, 2% BA) microgel particles, these redispersed readily in pure water, as discussed earlier. In *Figure 4* the diameter of these particles is plotted, as a function of log (ionic strength), for both NaCl and $MgCl_2$. For both electrolytes, the variation is similar. This is not surprising, since, because of the excess *cationic* monomer present in these particles, the 'active' counter ion (Cl^-) is the same. The hydrodynamic diameter decreases only slightly, if at all, with increasing ionic strength up to 0.1 M. Above 0.1 M the apparent particle size increases, presumably due to flocculation. The, albeit slight, decrease in size up to 0.1 M ionic strength is analogous to the normal 'polyelectrolyte effect'. However, the variation here is very much less than that observed by Corpart *et al.*[5] in the case of the corresponding *uncross-linked* chains of similar anionic/cationic composition. The smaller variation in the case of the cross-linked microgel particles may be attributed to the rigidity of the particles. Removal of the added electrolyte by dialysis results in the particles having the same size as in the original dispersions in water. The average size of the swollen particles is ~ 180 ± 10 nm, over the ionic strength range 0–0.1 M. This is smaller than the size of the *balanced* microgel particles (~220 nm) in $MgCl_2$ solution. One might have anticipated the opposite trend, because of the net internal electrostatic repulsions in the former microgel particles, but these are reduced by the presence of the electrolyte. It is of interest that the sizes of the original, 'parent' inverted microemulsion droplets, obtained from TEM (*Table 1*), are ~91 nm and ~110 nm, respectively, for the unbalanced and the balanced microgel particles, i.e. about a factor of two smaller in both cases.

Electrophoretic mobility

The variation of the electrophoretic mobility of the *balanced* (50/50) microgel particles (containing 5% cross-linker) with NaCl concentration is shown in *Figure 5*. The dispersions of NaCl solution were obtained by either stirring the dried polymer directly into the salt solution, or by sonication. The reduction in mobility resulting from sonication presumably reflects the smaller particle size obtained. Although the absolute values of the mobility are significantly less (by about one order of magnitude) compared, say, to a typical polystyrene latex in similar electrolyte solutions[38], one might intuitively have expected these 50/50 particles to be neutral. A net negative charge implies that there is an excess of the anionic monomer in the outer region of the particles. This could be a result of unequal conversion of the two monomers and/or two non-similar reactivity ratios. Corpart *et al.*[5] have in fact determined the reactivity ratios for the anionic and cationic monomers used here, within the microemulsion system, and showed that co-polymerization of these two monomers (albeit, in the absence of the third monomer; the cross-linker), should lead to an almost *random* distribution of the two monomers within the chains. It may be, that the presence of the cross-linker upsets this distribution.

The influence of the pH on the electrophoretic mobility has been investigated for the 50/50-2BA microgel particles, dispersed in 0.5 M NaCl, over the pH range 2–11.5. No real dependence was found. This is as expected, since the cationic species are quaternary ammonium groups and the anionic species are sulfonate groups, i.e. strong base/acid groups, respectively.

Since the PCS measurements were made in $MgCl_2$ solution (which, as described earlier, seemed to be a more effective dispersing medium than NaCl), electrophoretic mobilities of the 50/50-2BA microgel particles were also determined as a function of $MgCl_2$ concentration. Interestingly, in this case the values recorded were actually close to zero (within experimental error) in this case. This could be due, perhaps, to Mg^{2+} ions (unlike Na^+ ions) specifically adsorbing onto some of the 'exposed' sulfonate groups at the periphery of the microgel particles, the net 'surface charge'. If this is the case, then this underpins the fact that microgel particles are stable (to aggregation) in $MgCl_2$ solution, not because of interparticle, electrostatic repulsive forces,

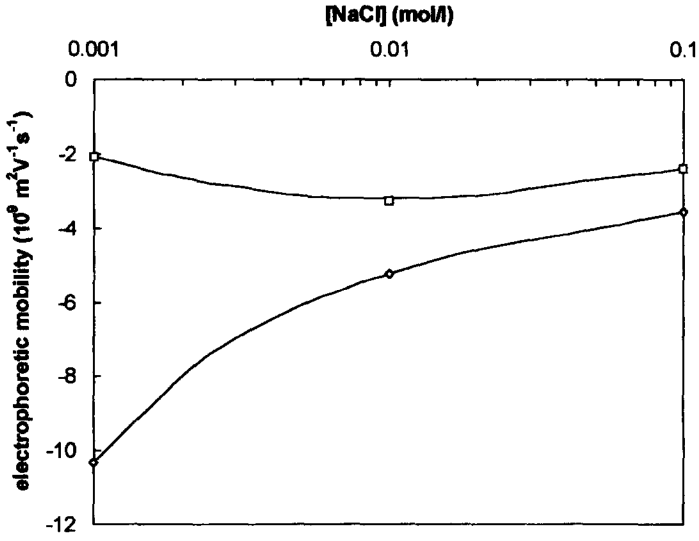

Figure 5 Electrophoretic mobility, as a function of ionic strength, in the case of 50/50-5BA microgel particles in NaCl solution, before sonication (◇) and after sonication (□)

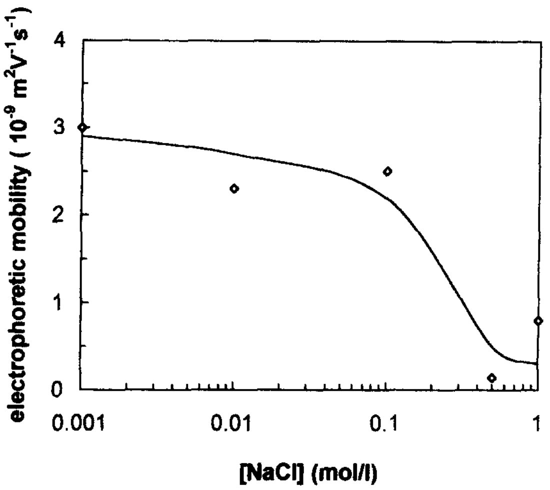

Figure 6 Electrophoretic mobility, as a function of ionic strength, in the case of 20/80-2BA microgel particles redispersed in NaCl solution

but because the particles are indeed swollen with water. The net Hamaker constant of the particles is then close to that of the medium; this reduces significantly the van der Waals attractive forces which drive aggregation.

Figure 6 shows the variation of the electrophoretic mobility for the *unbalanced* (20/80-2BA) microgel particles, as a function of NaCl concentration. The values are now positive, as expected, reflecting the fact that these particles contain an excess of cationic units. However, the rather low magnitudes obtained suggest that, as with the 50/50 microgel particles, there is either less conversion of the cationic monomer, or the reactivity ratios lead to a tendency for the anionic monomer to accumulate more on the periphery of the particles. The mobility decreases slightly, as the ionic strength increases up to 0.1 M, and then decreases more strongly up to 1 M NaCl.

CONCLUSIONS

This investigation has shown that it is possible to produce polyampholyte microgel particles using a microemulsion polymerization technique. The high-charge density microgel particles containing a balanced amount of positive and cationic units are collapsed in pure water. Even though they swell upon addition of electrolyte, due to the screening of opposite charges within the particles, they flocculate below a minimum electrolyte concentration. They are, however, stable above this minimum value, making them suitable for applications where high ionic strengths are required, e.g. in absorbent cloths. In contrast, high-charge density polyampholyte microgel particles, with a large excess of cationic monomer, are swollen at *all* ionic strengths, although they do flocculate at very high ionic strengths.

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