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Functionalization of Latex Particle Surface by Using Polymeric Insurfs

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SUMMARY: In this work the emulsion polymerisation of styrene was carried out in presence of the inisurfs (reactive surfactants). The reaction kinetics was followed by dilatometric and calorimetric measurements. The influence of the inisurf concentration in reaction mixture as well as the reaction temperature on the particle properties were studied. Resulting particles were characterised with FFFF–MALLS and PCS. Viscosity measurements indicate the formation of particle flocks in the solution at certain inisurf concentration in reaction mixture.
Keywords: inisurf, flocculation, hydrodynamic radius

1. Introduction

Surfactants play an important role in the production and application of dispersed polymers. To reduce the negative effects of the conventional surfactants (desorption from the surface, foaming etc.) a promising way is to use reactive surfactants.

Reactive surfactants in heterophase polymerisation can take part in the radical polymerisation process as polymerisable surfactants (surfmers [1-5]), as transfer agents (transurfs [6-11]) or as initiators (inisurfs [12-17]). Finally such a surfactant is bond covalently to the particle providing the stability of the dispersion and in some cases the functionalization of the particle surface. This offers benefits in different application fields.

However, the reactive surfactant concentration which influences the stability of the dispersion cannot be varied independently without changing the polymerization rate. Also, a cage effect was observed in such systems [13,14] which affects strongly the initiation efficiency.

In the present paper we describe the synthesis of polymeric nanoparticles in the presence of inisurfs which contain peroxy functions and have polyelectrolyte nature. The motivation for these investigations is the following. First, it is possible to prepare electrosterically stabilized polymer dispersions (it is believed that tailored polyelectrolytes are more effective in interphase stabilization than common low molar mass surfactants). Second, one can expect in films or in bulk materials made of these dispersions that the polar entities are homogeniously

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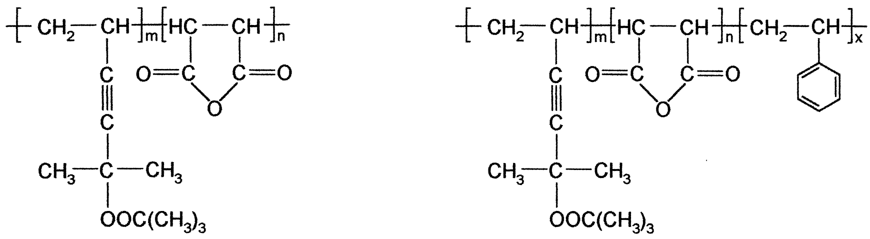
dispersed inside a continuous, nonpolar phase. Third, the surface of final particles is functionalized with peroxy groups which gives the possibility of further modification steps: - direct polymerisation of different monomers from the surface (creation of core-shell structures); - grafting of macromonomers (functionalization of the surface or increasing the stability of the particles for special applications).

2. Experimental

2.1. Materials

Styrene (St) (from Fluka) was purified by conventional methods and then vacuum distilled under nitrogen. Sodium dodecyl sulfate (SDS, Aldrich), sodium hydroxide (NaOH, Aldrich) and sodium azide (NaN_3, Merck) were used as commercially available. Distilled water was employed as polymerisation medium.

The synthesis of the reactive surfactants – binary copolymers of 5-*tert*-butylperoxy-5-methyl-1-hexen-3-yene (PM) with maleic anhydride (MA) or ternary copolymers of PM with MA and styrene (ST) (Fig. 1.) is described elsewhere [15] .



PM-MA **PM-MA-ST**

Fig. 1. Structures of the inisurfs

The inisurfs become soluble in water after reaction with NaOH and opening of the anhydride ring. Amount of added base in this case determines the neutralisation degree of the carboxylic acid groups in the macromolecules and therefore the charge of the polymer. In this study inisurfs with 50% and 90% neutralisation of carboxylic acid groups were used to compare the influence of the charge of polyions on the properties of latexes. The chemical composition of the inisurfs and their molecular weights are summarised in Tab. 1.

Tab. 1.

Inisurf	MA (mol. %)	PM (mol. %)	ST (mol. %)	M_w
PM-MA	50	50	-	44 800
PM-MA-St 2	50	25	25	160 000
PM-MA-St 3	50	35	15	77 000

2.2. Polymerisation procedure

The solution of inisurfs was prepared by adding appropriate amount of sodium hydroxide and stirred overnight to ensure complete dissolving of the inisurf. Then monomer was added and the emulsion was stirred under nitrogen for min 1 hour with magnetic stirrer. The batch polymerisations were run at different temperatures (65, 70, 75, 80, 85 °C). The concentration of styrene was kept constant 1.00 mol/l, the amount of the inisurf was varied from 1,57 to 3,14 mmol/l. Latexes were prepared at ca.10 % solid content.

2.3. Kinetic investigations

Conversion was determined gravimetrically in the following manner. Samples were taken from the reactor with a long needle and placed into tared glass bottles which contain a few drops of 2% aqueous hydroquinone solution. After this procedure the bottles were cooled in ice and latter weighted. The water was evaporated to determine the solid content and therefrom the gravimetric conversion.

2.4. Polymer and latex characterization

Polymer dispersions prepared at different concentrations of the inisurfs were freed from monomer by dialysis. Latexes were dialysed against water using Millipore Amicon Miniplate membrane (MWCO – 10000).

Particle size measurements were done with Photon Correlation Spectroscopy (Zetasizer 3000, Malwern). Samples were diluted in 0.001 M KCl or in distilled water before measurement.

Additionally probes were characterised with Flow Field-Flow Fractionation coupled with Multi-Angle Laser Light Scattering (FFFF-MALLS). The fractionator F-100 (FFFractionation, Inc., Salt Lake City, USA) and DAWN-DSP light scattering photometer (Wyatt Technology Corp., Santa Barbara, USA) were used. Obtained data were interpreted by using ASTRA 4.50 software from Wyatt Technology Corp. Solvent for FFFF-MALLS measurements was deionized water containing 0.02% (w/w) SDS and 0.02% (w/w) NaN_3 as a bactericide. Samples were measured at constant cross flow rates.

Electron micrographs were taken with Gemini (Zeiss, Germany). Samples were prepared in the following manner. Dispersions were diluted with distilled water, dropped onto aluminium support and dried at room temperature. Pictures were taken at voltage of 4 V.

Polymeric dispersions were investigated with Bohlin CS Rheometer (Bohlin Instruments Inc.). The double gap measuring geometry was used. It consist of a hollow cylinder (outer diameter – 45,46 mm; inner diameter – 43,80 mm) which is lowered into a cylindrical groove in the outer cylinder (cylinder diameter – 50 mm; inner cylinder diameter – 39,82 mm). The sample is contained in the double annular gap between them.

2. Results and discussion

2.1. Synthesis of dispersions

The kinetics of emulsion polymerisation of styrene in presence of reactive surfactants was studied in the temperature interval 65-85 °C. The concentration of inisurfs was varied from 5 to 15 g/l. Conversion of monomer was determined by gravimetrical analysis. The selected conversion - time data of styrene polymerisation in presence of PM-MA are presented in Fig. 2.

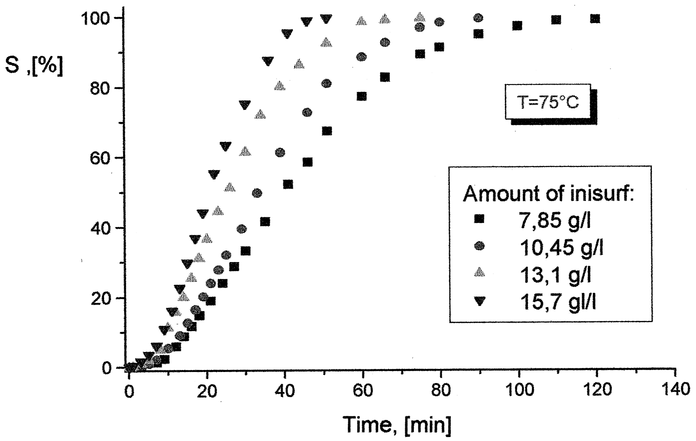


Fig. 2. Conversion-time curves of the emulsion polymerisation of styrene in presence of PM-MA (concentration of styrene 1,00 mol/l)

The kinetic data show strong dependency of the polymerisation rate on the concentration of the inisurf in the reaction mixture. The obtained kinetic data were used to calculate the polymerisation rate and the overall activation energy ($E_a = 61$ kJ/mol). Kinetic investigations were made also for polymerization of butylacrylate and methylmethacrylate in presence of inisurfs and details will be the subject of a separate paper.

If to compare with reaction systems where PM-MA-ST inisurfs were used the polymerisation rate is dependent on amount of peroxide groups in the macromolecule. Additionally as higher the molar mass of the inisurf the lower its concentration in reaction mixture was necessary to obtain stable latex. Generally the use of the inisurfs leads to high polymerisation yields and stable polymeric dispersions can be obtained.

2.2. Particle size analysis

PM-MA Inisurf

The changes of the hydrodynamic radius of the polymeric particles with the variation of inisurf PM-MA concentration and reaction temperature are presented in Fig. 3.

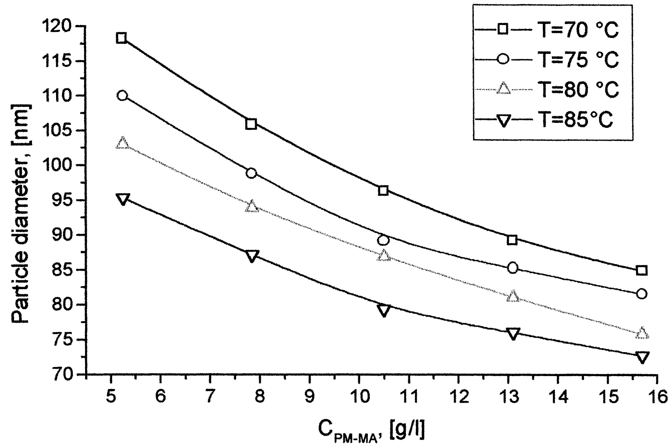


Fig. 3. Variation of the particle diameter with inisurf concentration and reaction temperature in the emulsion polymerisation of styrene in presence of PM-MA

Generally the size of polymer particles was founded to decrease with increasing the inisurf concentration and reaction temperature. This behaviour is typical for emulsion polymerisation. However the particle size does not vary strongly with changing the reaction parameters. It can be also seen from Fig. 3. that the final particle size becomes less influenced by the inisurf concentration at higher amounts of PM-MA in reaction medium.

PM-MA-ST Inisurfs

Totally different behaviour of the particle size was observed in the case of PM-MA-ST inisurfs. Fig. 4. presents the variation of the average hydrodynamic radius of dispersions prepared at T_{react} = 85 °C with the PM-MA-ST2 concentration in reaction mixture.

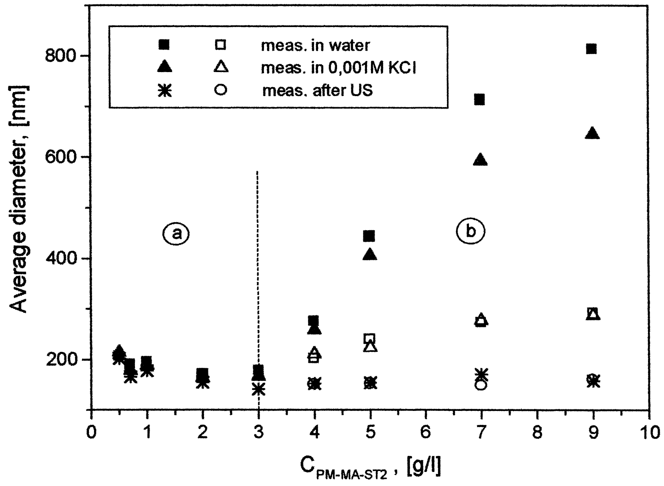


Fig. 4. Variation of the average diameter of polymer particles prepared at different PM-MA-ST2 concentrations (solid dots and hollow dots represent PM-MA-ST2 with 50% and 90% neutralisation of carboxylic groups respectively

One can see two regions (a) and (b) on Fig. 4. separated by the dotted line. Up to 3 g/l of PM-MA-ST2 the average hydrodynamic diameter decreases slightly with increasing the inisurf concentration. This behaviour is typical for surfactants (inisurfs) in emulsion polymerisation. In this region the measured value of the hydrodynamic radius is practically not influenced by the measuring conditions (dilution medium, ultrasound) for samples with 50% and 90% neutralisation of the carboxylic groups of PM-MA-ST2. Starting from 3 g/l of PM-MA-ST2 in the reaction mixture one can see dramatic changes in the measured value of hydrodynamic diameter.

For the samples with 50% neutralisation of carboxylic groups the particle diameter is increasing rapidly and this is accompanied by fast broadening of the particle size distribution. By measuring the same samples in 0,001 M KCl water solution smaller values of the particle sizes were obtained probably due to the partial screening of the negative charges in PM-MA-ST2 macromolecules and contraction of the hydrodynamic shell. After ultrasonification of the samples diluted in 0,001 M KCl the detected hydrodynamic diameters and particle size distributions were comparable to the values obtained in interval (a). These data show that in the interval (b) particle agglomerates are formed in solution which can be destroyed by ultrasonification. It was founded that appr. 20 min after ultrasonification the particle size starts to increase again what means that the particle aggregates are build up again.

For the samples with 90% neutralisation of carboxylic groups of PM-MA-ST2 the average diameter increases up not so rapidly and reaches a plateau at 7 g/l of PM-MA-ST2. In this case nearly no difference was found in the values of hydrodynamic diameters for the samples measured in deionized water and in 0,001 M KCl water solution. However, after ultrasonification of the samples diluted in 0,001 M KCl the detected hydrodynamic diameters and particle size distributions were similar to the measured values for samples with a neutralisation degree of 50%.

It seems that the neutralization degree of carboxylic functions in the polymer chain plays the dominant role in the process of agglomerate formation in this particular system.

Fig. 5. shows the comparison of the experimental data measured with SEM and F-FFF (samples were prepared at 85°C and ultrasonificated before measurement). One can see that according to SEM data the average particle diameter (hard core diameter) decreases with increasing the PM-MA-ST2 concentration in the reaction mixture (see also Fig. 6.). On the other hand the behaviour of hydrodynamic radius is totally different. The hydrodynamic radius decreases with increasing the PM-MA-ST2 concentration up to 3 g/l (interval a), reaches a minimum and then increases with increasing PM-MA-ST2 concentration (interval b).

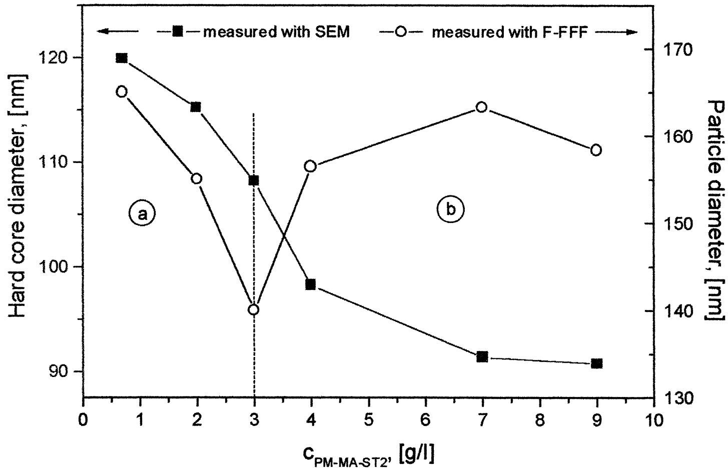
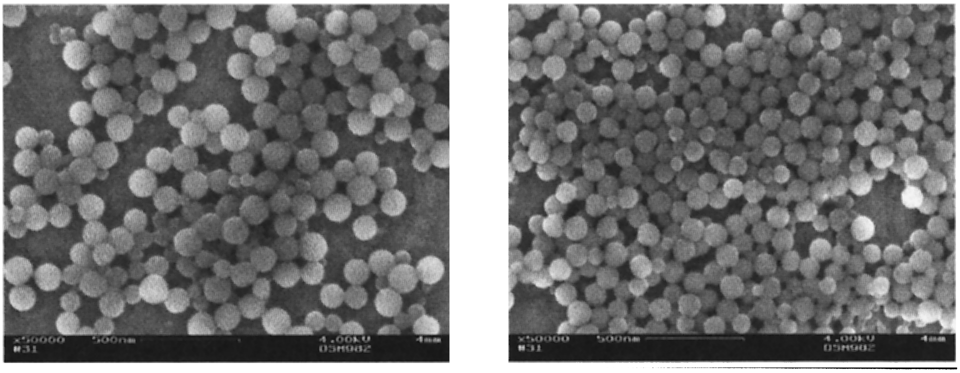


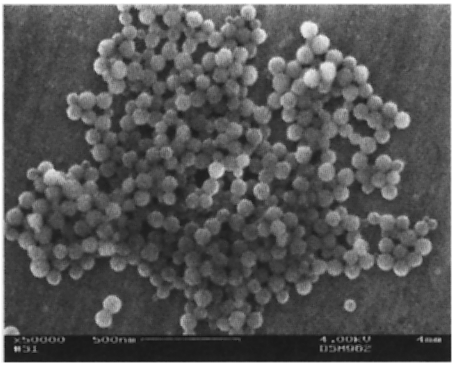
Fig. 5. Changes of the particles diameter with PM-MA-ST2 content (PM-MA-ST2 with 50% neutralisation of carboxylic groups)

Fig. 6. shows the changes of the particle size of the obtained dispersions with varying the inisurf concentration.



a) $c_{PM\text{-}MA\text{-}ST2}$=0,7 g/l

b) $c_{PM\text{-}MA\text{-}ST2}$=2 g/l

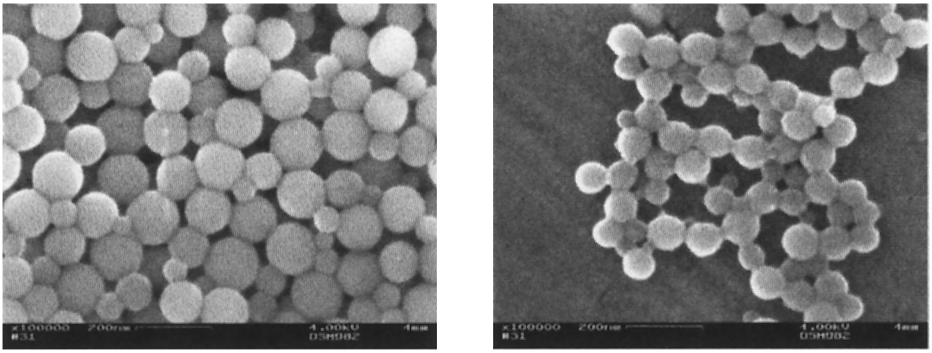


c) $c_{PM\text{-}MA\text{-}ST2}$=9 g/l

Fig. 6. SEM pictures of polymeric particles prepared with inisurf PM-MA-ST2 (T_{react} = 85 °C, 50% neutralisation degree of -COOH groups of PM-MA-ST2)

One can recognise significant differences in values of the hard core diameter and hydrodynamic diameter of the particles (ca. 40 nm in interval (a)). In interval (b) when the amount of PM-MA-ST2 is higher then 3 g/l this difference increases rapidly up to 70 nm. If to suppose that after ultrasonification all aggregates are destroyed then this increase of the shell thickness is an evidence of some conformational changes of PM-MA-ST2 chains on the particle surface. This conformation change can be induced by more close packing of charged chains and increasing of repulsion forces. To minimize these forces polymer chains will be orientated away from the particle surface and form more or less "hairy" structure. This can be the reason for multiplete adsorption of PM-MA-ST2 chains and cluster formation. It seems that these particle flocks cannot be fully redispersed with ultrasound.

Fig. 7. shows the micrographs of dispersions prepared at different inisurf content. Note the smooth surface of PS particles prepared at $c_{PM\text{-}MA\text{-}ST2}$=2 g/l (picture a). When the dispersion was prepared at $c_{PM\text{-}MA\text{-}ST2}$ = 9 g/l. one can see the „melting" of the rich surface layer consisting out of PM-MA-ST2 macromolecules under the electron beam at higher magnification and this caused deformation of the particles and no sharp image is obtained.



a) $c_{PM\text{-}MA\text{-}ST2}$=2 g/l

b) $c_{PM\text{-}MA\text{-}ST2}$=9 g/l

Fig. 7. SEM pictures of polymeric particles prepared with inisurf PM-MA-ST2 (T_{react} = 85 °C, 50 % neutralisation degree of -COOH groups of PM-MA-ST2)

The same effects were detected by analysing the dispersions prepared with PM-MA-ST3. However, in this case the flocculation point was shifted to higher inisurf concentrations (ca. 4,5 g/l) For both inisurfs the reaction temperature has no influence on cluster formation and similar behaviour of the particle sizes were found.

2.3. Viscosity measurements

Zero-shear viscosity of the dispersions prepared with several inisurfs and at different experimental conditions was measured and the experimental data are presented in Fig.8.

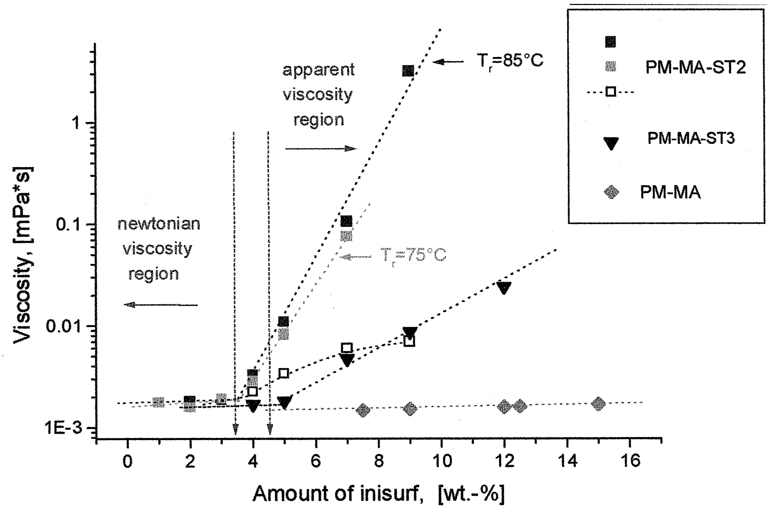


Fig. 8. Variation of zero-shear viscosity of polymer dispersions with the amount of the inisurf in the reaction system (solid and open symbols correspond to the inisurf at 50% and 90% neutralisation of carboxylic groups, respectively)

In case when PM-MA-ST2 was used as inisurf in emulsion polymerisation the experimental curves have clear break point at ca. 3,5 g/l PPM-MA-ST2. Samples prepared with higher amounts of PM-MA-ST2 show rapid increase of the viscosity. At the same concentration of PM-MA-ST2 a rapid increase of the average particle diameter was detected (see Fig. 4.). As can be seen from Fig. 8. the viscosity behaviour of dispersions prepared with PM-MA-ST2 at different neutralisation degree is similar to the particle diameter behaviour – when the PM-MA-ST2 with 90% neutralisation degree was used the dispersions show lower viscosity if compared with latexes prepared with PM-MA-ST2 where neutralisation degree of carboxylic groups was 50%. Also it is shown that the reaction temperature has no influence on the effect of increasing viscosity of the dispersions.

In case when PM-MA-ST3 was used like inisurf the point of zero-shear viscosity increase is shifted to the concentration 5 g/l and this increase is not as significant as in the previous case.

It should be noted that samples prepared with PM-MA-ST2 and PM-MA-ST3 before the break point behave like a Newtonian liquid and then like "pseudo elastic" substances.

Conclusions

The inisurfs were successfully used in the heterophase polymerisation of styrene. The negative charge generated by the carboxylate groups along the polymer chains of the inisurfs grafted onto the particle surface provide efficient electrosteric stabilization of the dispersions. Additionally, the DSC measurements indicate the presence of undecomposed peroxide groups on the particle surface, which can be used in a subsequent reaction step (shell formation) for direct polymerisation of secondary monomer from the particle surface [18].

The limited aggregation of the latex particles which was detected by light scattering and viscosity measurements can be speculatively explained in the following way. At low ionic strength of the aqueous phase and at low polyelectrolyte load (PM-MA-ST2), the repulsion between the charged segments as well as between the latex particles is high. Since the ionic groups in PM-MA-ST2 are distributed statistically, it is very likely that polystyrene and peroxide units form some hydrophobic segments. In this case the polymer chain is expected to be not only attached to the particle surface after partial decomposition of peroxide groups but also adsorbed with this hydrophobic segments. This leads to multiple adsorption points per molecule on the particle surface and charged loops into the water phase (Fig. 9a).

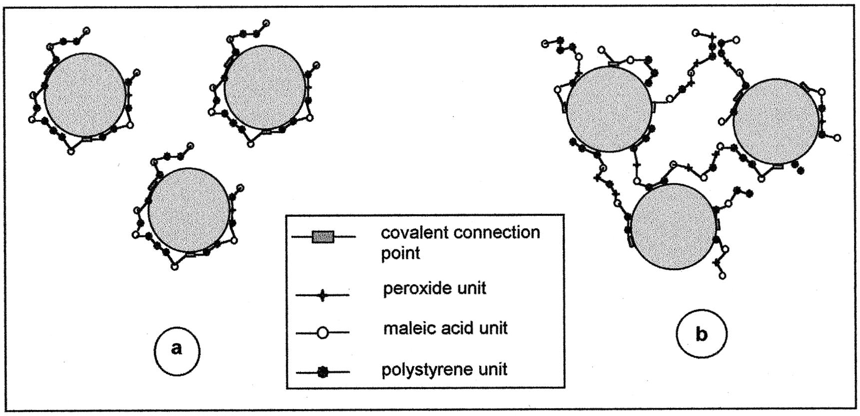


Fig. 9. Illustration of the behaviour of the inisurf on the particle surface

a) concentration of PM-MA-ST2 up to 3 g/l;

b) concentration of PM-MA-ST2 above 3 g/l

Increasing the polyelectrolyte (PM-MA-ST2) concentration on the interface results in the screening of the Coulomb interaction until the electrostatic interaction is less extended than the distance between the different hydrophobic domains of the polymer chain. Exceeding this critical value, each chain can adsorb onto several latex particles leading to aggregation through interparticle bridging which depends on the inisurf as well as on the latex concentration. The formation of flocks at higher inisurf concentrations is also enhanced by hydrophobic interaction of those hydrophobic domains of different chains which are not adsorbed onto the particle surface (Fig. 9b).

Following this model increasing of the neutralisation degree of PM-MA-ST2 macromolecules leads to increasing the charge of the polyelectrolyte and therefore polymer chains became more stretched. The interactions of hydrophobic domains in this case are minimised due to the electrostatic repulsion. In this case PM-MA-ST2 should be less afflicted with the problem of partial bridging. The experimental data confirm this idea (see Fig. 4, 6)

The same model can be applied to the inisurf PM-MA-ST3 but experimental data indicate that in this case all effects described above are not so strong and the point of the limited aggregation is shifted to higher concentrations of PM-MA-ST3 (Fig. 5, 6). The experimental data for the inisurf PM-MA show nearly no particle aggregation in the system (Fig. 6). The molecular masses of the inisurfs decrease in the row PM-MA-ST2>PM-MA-ST3>PM-MA what means that molecular weight has a strong influence on the thickness of the hydrodynamic shell around the particle and therefore influences the particle bridging effect in this system.

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