

Monitoring the Stability of Nanosized Silica Dispersions in Presence of Polycations by a Novel Centrifugal Sedimentation Method

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ABSTRACT: The stability of Aerosil-silica dispersions is analyzed in dependence on the addition of polycations with different charge density and hydrophobic modification using the analytical centrifuge LUMiSizer. This novel centrifugal sedimentation method allows the direct calculation of the stability parameters like sedimentation velocity and prediction of the shelf life. The highly charged polycation poly (diallyl-dimethylammonium chloride) (PDADMAC) is compared with tailored cationic polyelectrolytes of equal degree of polymerization but lower and different charge density as well as various hydrophobic substitutions. The used technique allows to accelerate demixing and to quantify the stability of dispersions in a direct way. All polymers under study are able to stabilize aerosil dispersions, but the shelf life strongly depends on

the polymer concentration. Typically for polycations, the stability increases with the polymer concentration whereas at low-polymer content flocculation can be detected. In this context, the behavior of PDADMAC and three cationic PVB derivatives is similar, but, whereas the stability of PDADMAC containing dispersions decreases at higher polymer concentrations, PVB derivatives are effective stabilizers at higher concentrations too. The highest increase of the stability with increasing polymer concentration is obtained with the ampholytic terpolymer TP that has the lowest cationic charge. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 696–704, 2009

Key words: silica; stabilization; tailored polycations; centrifugation

INTRODUCTION

Silica (SiO₂) is a multi-functional material applied in various industries. Some application areas include, for instance, fillers, or processing aids in formulations like inks, paints, and coatings. The provided particles have a sufficient stability, which can be achieved by adding polymers or surface-active molecules.^{1–3} Stabilization is obtained by ensuring that there are strong repulsive forces between the particles to prevent their association. The chemical reagents used to control the stability of such formulations are usually active by adsorption at the particle surfaces. These mechanisms and their influencing factors were studied by different analytical methods such as electrokinetic investigations,^{4,5} photon correlation spectroscopy,⁴ viscometry, sedimentation tests,^{6,7} ¹³C NMR spectroscopy,⁸ or ellipsometry.⁵

The additives usually used for tailoring the stability of dispersions are surfactants or polyelectrolytes. The latter are high molecular weight compounds containing a multitude of electrical charges mostly in the side chains. Copolymers offer a wide variety of possibilities because they allow to modulate polymer/particle interactions and the number of available systems seems to be limited only by the chemistry of copolymerization.⁹

Stuart et al.¹⁰ developed dispersants with a new molecular architecture that enables a better control over the particle adlayer thickness. Because a steric barrier is necessary that counterbalances the attractive van der Waals forces, which are responsible for particle agglomeration, they were able to increase the solid content of dispersions by tailoring the chemistry and length of these dispersants.

Very often “stability” is discussed as the opposite of “flocculation” and both processes are investigated together. The influence of cationic polyelectrolytes on the flocculation (and stability) of dispersed particles was investigated by measuring zeta potentials, diffusion coefficients, and flocculation rates in dependence on the adsorbed amount of different charged copolymers at various salt concentrations and pH.

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TABLE I
Characterization of Polycations

	Polymer	P_n	Charge (meq/g)
PDADMAC	1	217	6.2
Poly(vinylbenzyl-trimethyl-ammoniumchlorid) (PVB-TMAC)	2	164	4.97
Poly(vinylbenzyl-dimethylbutylammoniumchlorid) (PVB-DMBAC)	3	164	3.9
Poly(vinylbenzyl-pyridiniumchlorid) (PVB-PYC)	4	164	4.46
Polyampholytic terpolymer (TP)	5		0.94

Stabilization is accomplished at low salt concentration at full coverage of the particle surface by electrostatic repulsion because of charge reversal. The influence of charge density and molecular mass of the polymers on different flocculation mechanisms (patching/bridging) is discussed as well as the influence of the hydrophobicity of the flocculants.^{11–13}

This type of investigations is very time dependent, and in most cases they are focused on the particle separation and not on the stability of such systems. But, for application, the characterization of the dispersed state of suspensions including declaration about the storage stability of formulations is very important.

We used a novel centrifugal sedimentation method (LUMiSizer) to characterize the stability of nanosized aerosil dispersions in dependence on polymer addition. The influence of the strong polycation PDADMAC was compared with new polycations with “medium charge”, differing in polymer structure and charge density, and an ampholytic terpolymer of low charge.

The aim of this work was to design and evaluate polymer molecules with cationic charge as dispersants for the stabilization of nanoparticles, to characterize quantitatively the effect of the added polymers and to study the stabilization mechanism.

METHODS AND MATERIALS

Particles

Fumed Silica (“Aerosil”) is an amorphous, high purity silica powder with great potential for application. It is provided by Degussa¹⁴ with different specific surface area and thus different primary particle size. In this investigation hydrophilic silica Aerosil OX 50 (primary particle size 40 nm; specific surface area—50 m²/g) was used as model to study the dispersion stability.

Preparation of the dispersions

The influence of the dispersing procedure (dispersion technology, time, intensity) of Aerosils in aqueous media (without salt) was intensively investigated previously. Ultrasound was shown to be more efficient than other techniques (rotor-stator principle).^{15–17} Therefore, in this work the particles

(solid content 10 g/L) were dispersed in polymer solutions of different concentration using ultrasound (5 minutes). The high intensity ultrasonic processor UP200s (Dr. Hielscher GmbH) operates at 4 kHz and up to 200 W. Sedimentation tests were performed with 1.8 mL of these dispersions using a LUMiSizer (refer Sedimentation tests section).

In addition, flocculation/stabilization was also characterized with “traditional methods” (sedimentation in 50 mL flasks; turbidity measurement; characterization of the supernatant with polyelectrolyte titration) in case of PDADMAC. The amount of added polymer solution (1.6 g/L) was varied between 0.1 mL and 0.2 mL per 50 mL of dispersion.

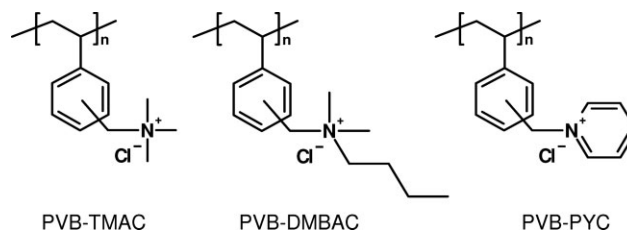
Polymers

Several different polymer samples (Table I), commercial as well as laboratory products, have been studied. Starting with the well-investigated highly charged polycation PDADMAC, we moved to three polycations with lower charge. They have similar structure, but differ in the type of hydrophobic units. Finally, we also examined the performance of a terpolymer containing hydrophobically modified cationic, hydrophilic nonionic, and anionic monomer units with an excess of cationic charges.

Polymer details

PDADMAC was supplied by Katpol (Bitterfeld, Germany) as Polyquat 40 S, (molecular weight 35,000 g/mol).

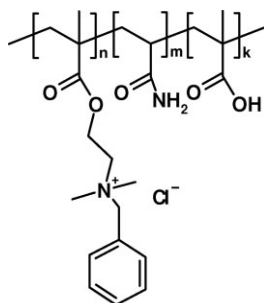
The synthesis of the cationic polyelectrolytes poly(*N*-vinylbenzyl-*N,N,N*-trimethylammonium chloride) (PVB-TMAC), poly(*N*-vinylbenzyl-*N,N*-dimethyl-*N*-butyl-ammonium chloride) (PVB-DMBAC), and poly(*N*-vinylbenzyl-pyridinium chloride) (PVB-PYC) was performed in two steps.



PVB-TMAC PVB-DMBAC PVB-PYC

First, the reactive precursor poly(vinylbenzyl chloride) with narrow molecular weight distribution was synthesized by nitroxyl mediated controlled free radical polymerization. The subsequent reaction with the corresponding amines results in the listed polyelectrolytes.¹⁸ The degree of functionalization was above 95% as revealed by ¹H-NMR-spectroscopy. As the molecular weight determination of the precursor polymer is well established,¹⁸ also precise data can be calculated for the polyelectrolytes. The charge density of these three polycations, determined with polyelectrolyte titration, is lower than that of PDADMAC.

The synthesis of the polyampholytic terpolymer TP of *N*-methacryloyloxyethyl-*N,N*-dimethyl-*N*-benzylammonium chloride (MADAMBQ), acrylamide (AAm) and methacrylic acid (MAS) again was carried out in two steps according to,¹⁹ namely by free radical copolymerization of MADAMBQ and AAm in aqueous solution followed by controlled hydrolysis of part of the ester groups. Due to the analyzed composition with 14 mol % cationic, 73 mol % non-ionic, and 13 mol % anionic units, low cationic charge (0.94 meq/g) was detected by polyelectrolyte titration at pH 6.0. The molecular weight of TP is 1.8 Mio g/mol.



Terpolymer TP

Sedimentation tests

LUMiSizer (L.U.M., GmbH Berlin), a novel centrifugal sedimentation method to characterize the (storage) stability of dispersions in dependence on the polymer addition used in this study allows to measure the intensity of transmitted light as a function of time and position over the entire sample length simultaneously. At the same time up to 12 different samples can be analyzed simultaneously at constant variable centrifugal force. Details are described in Ref. 20.

Our experiments had the following parameters: volume: 1.8 mL of dispersion; 3000 rpm, t_{Exp} : 3600 s, $\Delta t = 10$ s, $T = 20^\circ\text{C}$. All measurements were repeated at least twice.

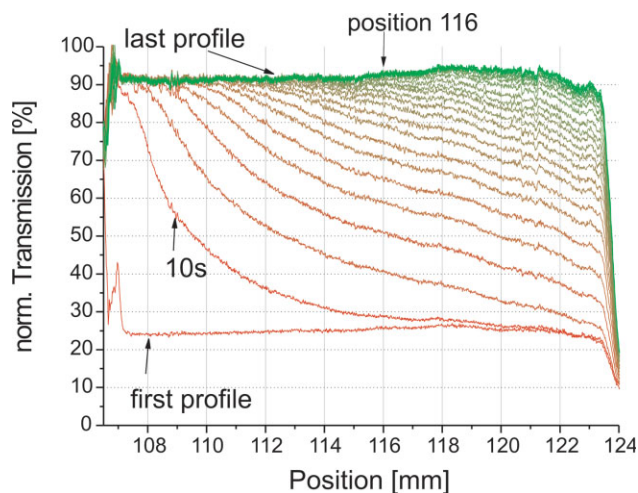


Figure 1 Recorded evolution (from left to right) of time dependent transmission profiles of an aqueous Aerosil dispersion. Profiles taken every 10 s at 3000 rpm during 3600 s. x-axis: position at the rotor. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS

Stabilization of Aerosil OX50 with PDADMAC

As previously investigated with turbidity measurement, well dispersed aqueous Aerosil dispersions were stable for some hours.¹⁷ In Figure 1, the transmission profiles of Aerosil OX 50 dispersions without polymer, recorded with a LUMiSizer, are shown. The intensity of transmitted light was detected as function of time and position over the entire sample length. The demixing process may be easily observed by measuring the transmission profiles. For instance, at position 116 (in the middle of the sample cell), the first profile is recorded at about 25%, the third at about 40%, and the last profile (after one hour of centrifugation) at about 90% transmission, whereas at position 108 (top of the cell) the transmission increases faster. The time difference between measurements, which can be varied, was 10 s in this experiment. After 20 s (after the second profile), we measured 75% transmission for the Aerosil dispersion without polymer.

The influence of the polymer concentration on the stability can be undoubtedly seen in Figure 2 for the addition of PDADMAC. In contrast to Fig. 1 (dispersion without polymer), the transmission profiles were completely different for low PDADMAC concentration, demonstrating a strong flocculation [Fig. 2(a)], whereas at higher polymer content the dispersion became stable again due to charge reversal (Fig. 2b–d) as described earlier.^{11,12} In Figure 2(a) the flocculation was represented by a fast increase of transmission (within 20 s). Flocculation occurred at PDADMAC concentration of about 0.0032 g/L

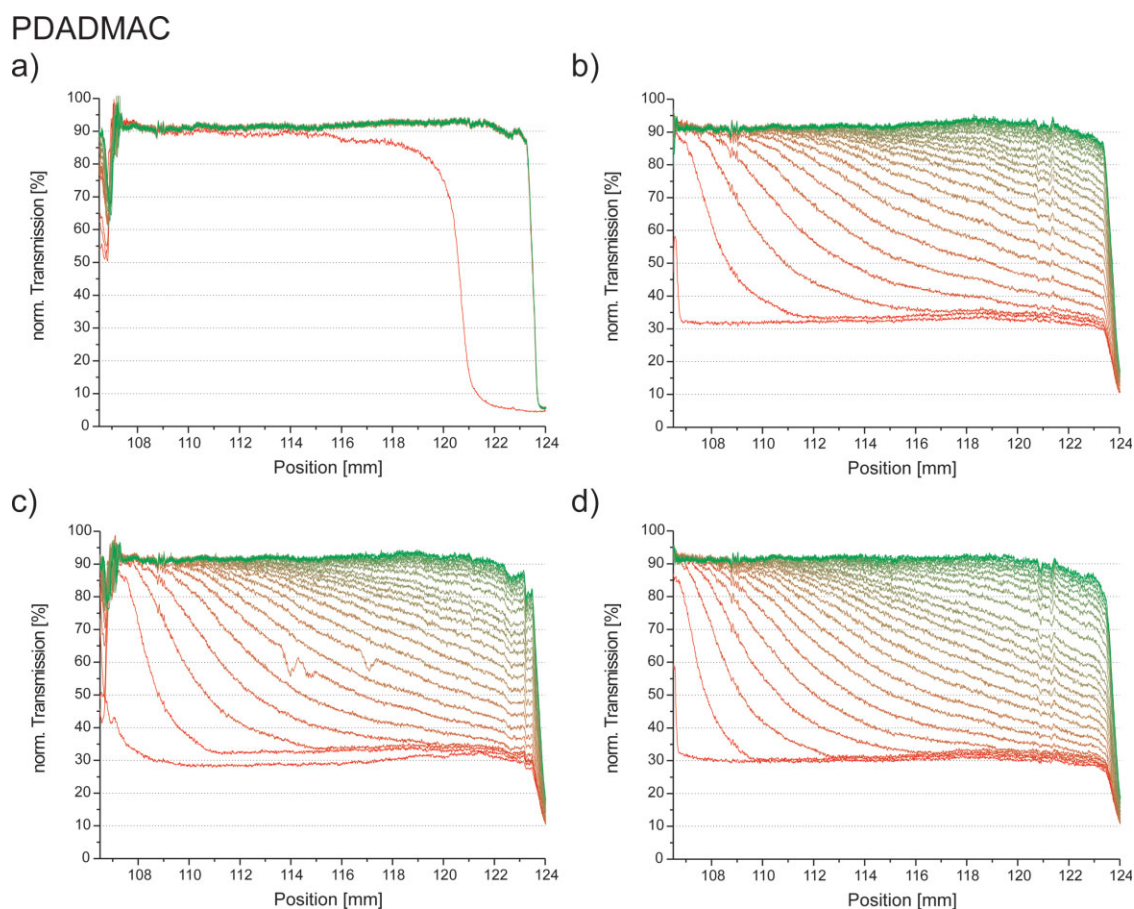


Figure 2 a-d: Transmission profiles of Aerosil OX 50 dispersions (10g/L), in dependence on PDADMAC – concentration: a) 0.0032, b) 0.032, c) 0.32, and d) 1.6 g/L. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(20 μmol PDADMAC). Compared with the results of aqueous dispersions without added polymer in Figure 1, higher PDADMAC concentrations stabilized the dispersion by charge reversal (Fig. 2 b–d and further transmission profiles which are not shown here).

For a better comparison between different systems, the dispersion stability can be quantitatively described by integration of the transmission profiles (kinetics of the evolution of zones of clarification) displayed against the measuring time (Fig. 3). The “slope” of such curves is directly related to the stability, as shown later. High values of the slope represent instability. Flocculation is noticed with 0.0032 g/L of PDADMAC. At higher concentrations the polycation acts as stabilizer. The stability of such polymer-stabilized systems is higher than for aqueous dispersions.

To assess the results of flocculation/stabilization experiments with Lumisizer in comparison with conventional investigations, some traditional flocculation tests in the same concentration range as shown

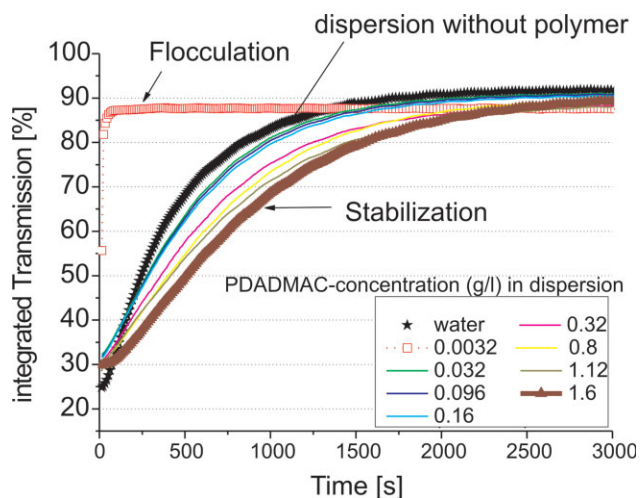


Figure 3 Influence of PDADMAC concentration on the stability of Aerosil OX 50 dispersions; Integrated transmission curves; the most effective concentration is accentuated with triangles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

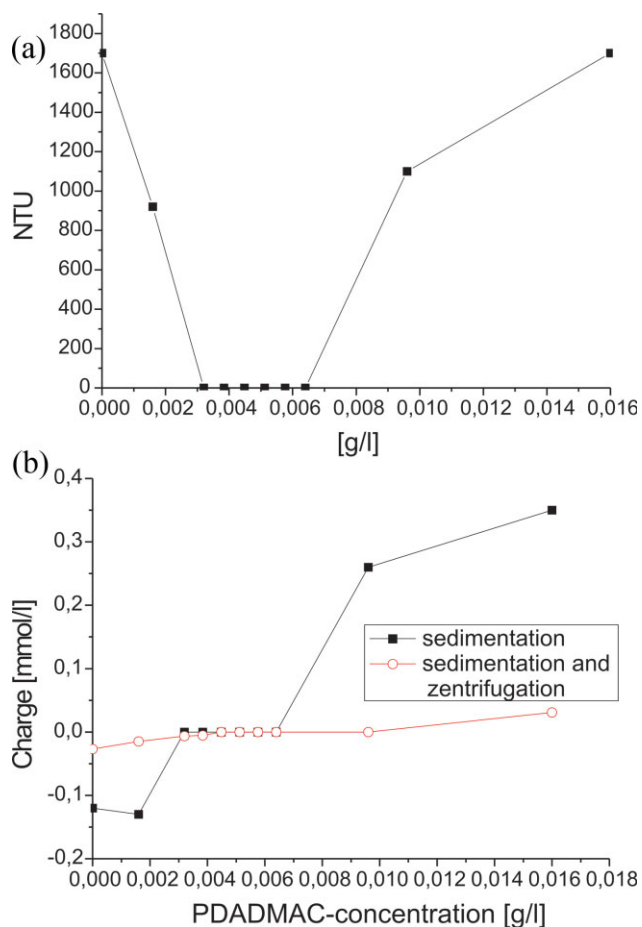


Figure 4 “Traditional” investigation (without LUMiSizer) of Aerosil OX 50 dispersions in presence of PDADMAC; Turbidity (a) and charge of the supernatant (b) in dependence on polymer concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in Figure 3. were carried out. The dispersions with concentrations between 0.0032 and 0.0064 g/L PDADMAC were observed by the naked eyes for 20 h (without centrifugation).

As shown in Figure 4(a), the aqueous dispersion was stable during this time whereas at the lowest polymer concentration (0.0032 g/L) flocculation occurred in accordance with LUMiSizer. The “flocculation window” was found between 0.0032 and 0.0064 g/L. The clear supernatant is uncharged (over the whole concentration range), whereas higher polymer concentration leads to turbid supernatants with a positive charge, demonstrating restabilization due to an excess of polymer. When the particles in the turbid supernatant are separated by centrifugation, their charge increases with increasing PDADMAC concentration, but only very slowly. The supernatants are almost neutral, demonstrating that the polymer is adsorbed on the particles. The particle dispersion in water is negatively charged. In

presence of polycation this negative charge of particle dispersion becomes smaller, but not positive. With polyelectrolyte titration, we were able to show that separated particles are negatively charged too (not shown here).

Figure 5 shows that small differences in the polymer concentration can significantly alter the sedimentation velocity and, as a result, the amount of supernatant denoted as their height in millimeter. So, the dispersion with 0.016 g/L of PDADMAC was very stable for many hours whereas a supernatant, which was clear or had very low turbidity, was noticed very soon for dispersions with lower polymer concentrations.

Stabilization of Aerosil OX50 with the cationic derivatives of PVB

According to the transmission profiles these three polymers with medium charge density exhibit similar behavior as PDADMAC. For better comparison of different polymers, the change of the position of the interface between the particle free solution and the dispersion as a function of time is shown in Figure 6 a–c. Improved and similar stabilization behavior (compared with Aerosil OX in water) is obtained with each of the polymers at concentrations >0.1 g/L. It was surprising that the structural differences in hydrophobicity did not have a significant influence on stabilization. Usually, the stability increases with increasing polymer concentration. Most stable dispersions were obtained with 7.5 g/L of PVB-TMAC and PVB-PYC, whereas the maximum stability of PVB-DMBAC containing dispersions was found

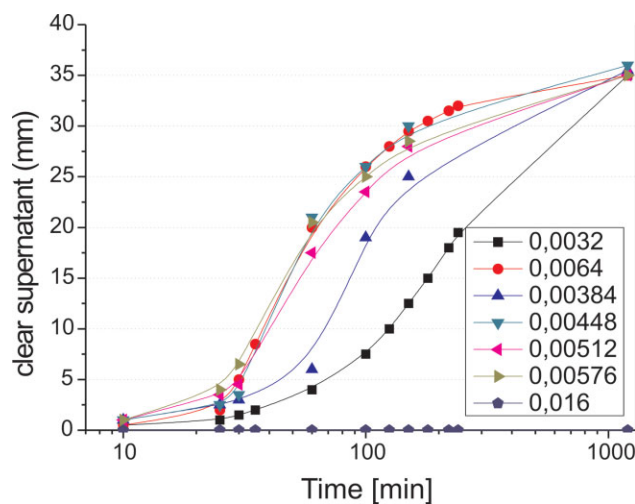


Figure 5 “Traditional” investigation (without LUMiSizer) of Aerosil OX 50 dispersions in presence of PDADMAC; Height of clear supernatant versus time in dependence on polymer concentration (g/L). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

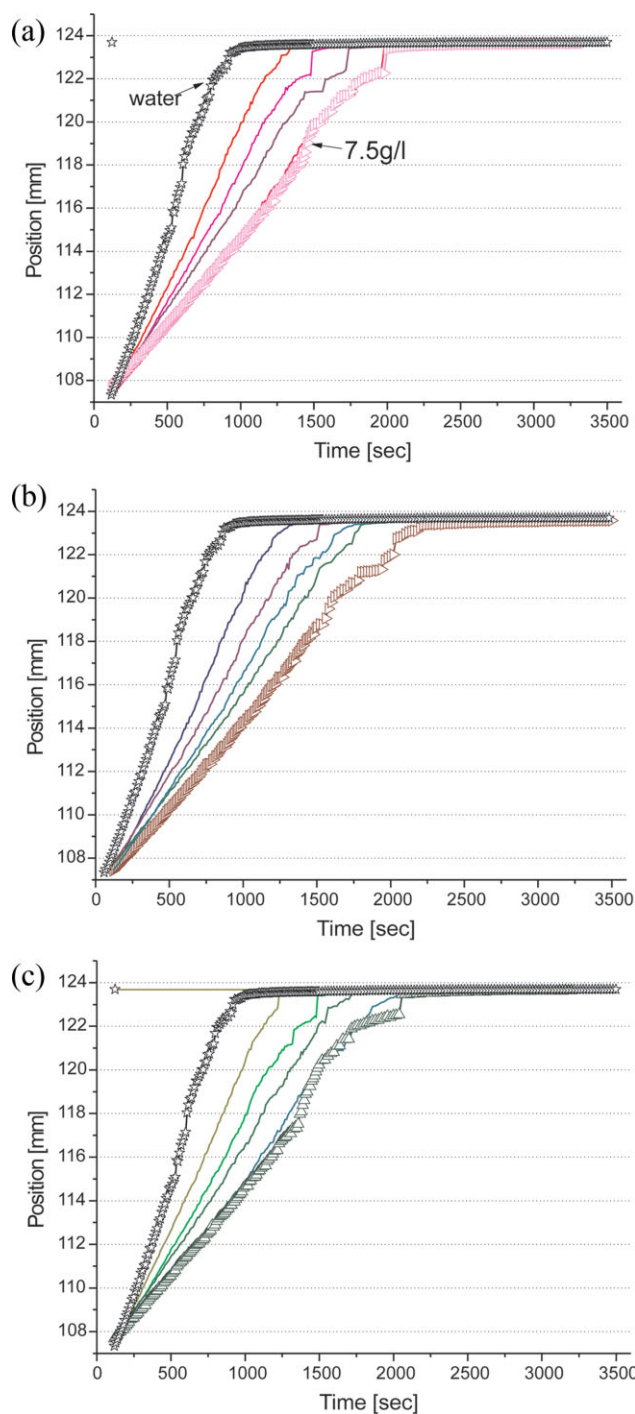


Figure 6 a-c: Stabilization with cationic derivatives of PVP ($c = 0.1, 1, 2.5, 5, \text{ and } 7.5 \text{ g/L}$); Graphic interface position against time; Comparison between different concentrations of (a) PVB-TMAC, (b) PVB-DMBAC, (c) PVB-PYC. The most effective concentration of each polymer is accentuated with triangles. (Lower concentrations, which cause flocculation, are not shown here.) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with somewhat lower concentrations. Up to now, we do not have any explanation for this difference between PVP derivatives.

But as shown in Figure 7 for PVB-DMBAC, all the PVB derivatives (like PDADMAC) can flocculate as well as stabilize the Aerosil dispersions. Fast separation was noticed with low polymer concentrations (at 0.01 and 0.02 g/L), whereas the dispersion is stable at very low (0.001–0.005 g/L) and higher polymer content. The so called “flocculation window” is very small because the influence of the polymer concentration on the sedimentation velocity is significant.

Stabilization of Aerosil OX50 with the terpolymer TP

Aerosil dispersions can be stabilized with terpolymers with low cationic charge too. The results were similar to the PVP-polymers of medium charge, but with higher flocculation concentration (0.02–0.06 g/L) (Figure 8). Most stable dispersions were obtained with the highest concentration of the terpolymer.

Comparison between different polymer types/discussion

We found that the polymer concentration of all investigated polymers had large influence on the stability of Aerosil dispersions. But, because the charge interaction between positively charged polymers and negatively charged Aerosil particles should be responsible for the stabilization, we tried to compare the flocculation/stabilization behavior in dependence on the “added effective polymer charge” which was calculated by the charge of the polymer solution according to polyelectrolyte titration and the polymer concentration in dispersion (Fig. 9). The “stabilizing quality” of the dispersion was represented by the slope which was about $20 \mu\text{m/s}$ for aqueous dispersions without polymer and lower in case of stabilization. But, because the separation process was very fast at low polymer concentrations, and in some cases the flocculation was finished within 10 s, it was difficult to get realistic values for the slope in such cases. Therefore, the points in the flocculation range in Figure 9 are shown only for comparison.

The charge of the investigated polymers was different and reached from highly cationic (PDADMAC) to very low cationic (terpolymer). The PVB-derivatives have medium charge density (Table I). From Figure 9, we see that the slope decreases with increasing polymer charge. Therefore, electrostatic stabilization should be the main mechanism for all of the polycations. But, because the slope is different for different dispersions (with the same amount of charges), and the terpolymer and the PVB derivatives are more effective as stabilizer than PDADMAC, we suppose that the stabilization of such systems is caused not only by electrostatic but also

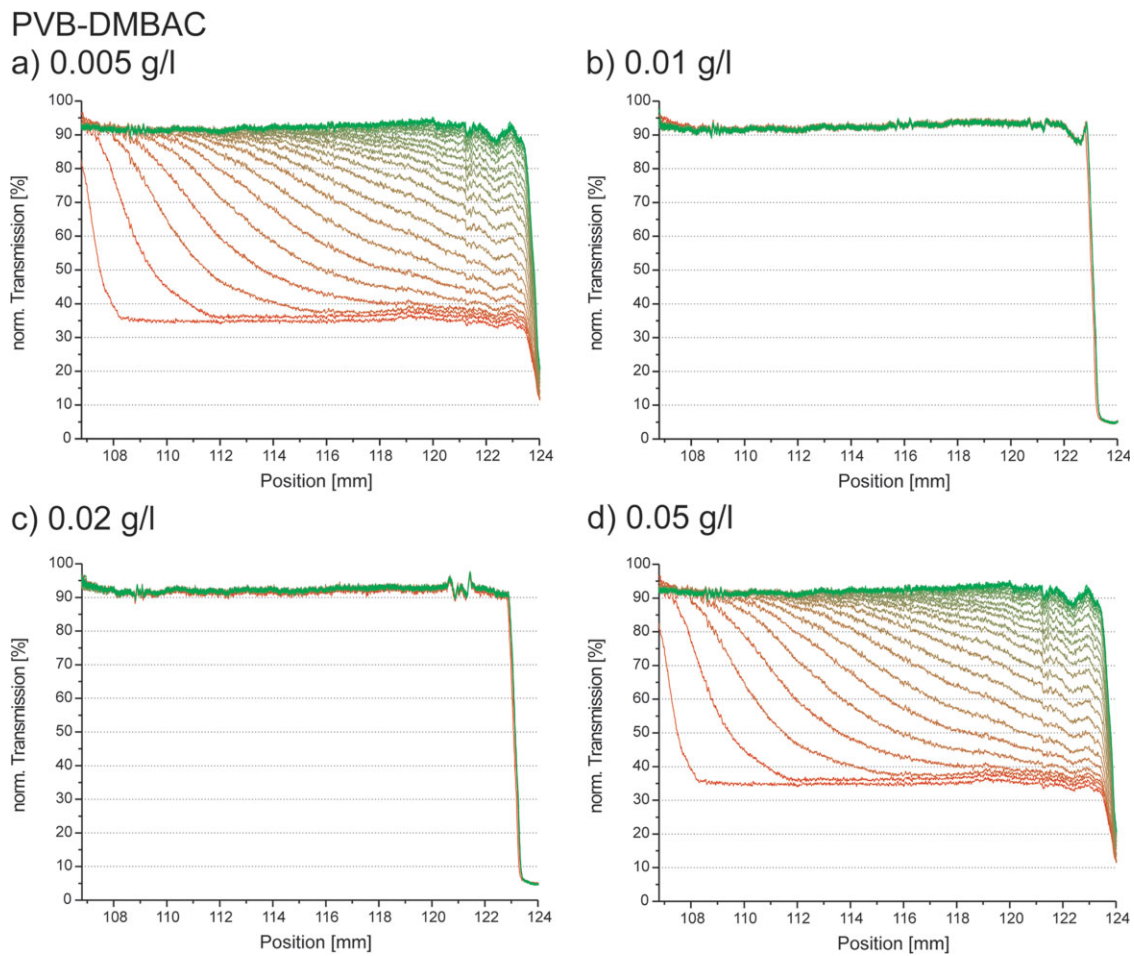


Figure 7 a-d: Transmission profiles of Aerosil OX 50 dispersions (10 g/L), in dependence on certain PVB-DMBAC—concentrations: a) 0.005 g/L (stabilization), b) 0.01 (flocculation), c) 0.02 (flocculation), and d) 0.05 g/L (stabilization). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

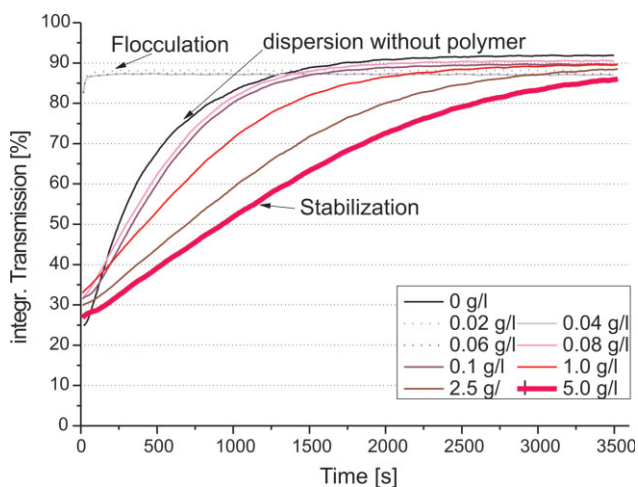


Figure 8 Influence of terpolymer—concentrations on the stability of Aerosil OX 50 dispersions; Integrated transmission curves. Flocculation is accentuated with a dashed line and the most effective stabilization concentration is accentuated with a bold line. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

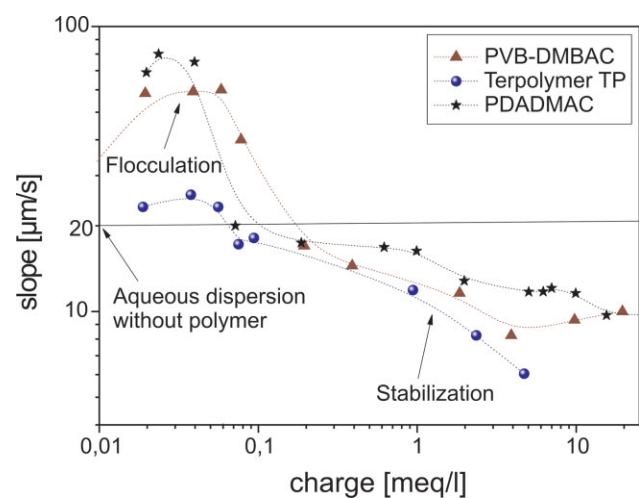


Figure 9 Influence of the polymer charge on the stability of Aerosil OX 50 dispersions; Slope in dependence on total charge; the lines in the flocculation area are only to guide the eye. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Slope (Increase of Integral Transmission Per Time) of Dispersions, Stabilized with Different Polymers; Influence of Concentration (Without Flocculation Range); Integration From 108 to 124 mm; 3000 rpm, 3600 s

Polymer g/l	PDADMAC $\mu\text{m/s}$	(PVB-TMAC) $\mu\text{m/s}$	(PVB-DMBAC) $\mu\text{m/s}$	(PVB-PYC) $\mu\text{m/s}$	TP $\mu\text{m/s}$
0.1	16.9	12.5	14.4	11.83	18.1
1	11.7	11.7	11.6	14.6	11.9
2.5	9.7	9.9	8.25	9.9	8.3
5	9.8	8.8	9.3	9.0	6.0
7.5	11.2	7.9	10.0	7.8	

The slope, as measured for aqueous dispersions under the same conditions is 20.7 $\mu\text{m/s}$.

by steric interactions. In case of the terpolymer TP, which has the lowest charge, the slope was significantly reduced by polymer addition, demonstrating that the mechanism changed from charge neutralization to a mixed mechanism as described, for instance in Ref. 9. The higher the amount of added charge (and also of polymer), the higher the stability.

As shown in Figure 9, we had three groups of polymers with similar, but also with different stabilizing behavior. For the direct comparison of all polymers the slopes (increase of integral transmission per time) are summarized in Table II. The higher the slope, the more unstable is the dispersion. The highest stability was obtained with terpolymer TP.

Finally, we tried to predict the shelf life of different dispersions, which is important for the industrial application. Because in our case for a given dispersion the demixing velocity is proportional to Relative Centrifugal Force (RCF), sedimentation behavior can be recalculated to gravity conditions (velocity at RCF divided by RCF) and shelf life predicted in a direct

way.²⁰ The shelf life without any detectable demixing by naked eye (less than 0.25 mm clear supernatant in the cuvette) was calculated for different polymers and concentrations. As shown in Figure 10, all investigated polymers are able to stabilize Aerosil dispersions. Typically, the stability increases with polymer concentration. The behavior of polycations 1–4 is similar, but, whereas the stability of PDADMAC-dispersions decreases, the PVP-derivatives and the terpolymers are much more effective at higher polymer concentrations. This result confirms our thesis that not only electrostatic, but also steric interactions are responsible for stabilization. The highest increase of stability with polymer concentration is obtained with the ampholytic terpolymer TP.

The time to receive 0.25 mm of sediment (at 1 g) increases from 1 h (without polymer) to about 10 h for 5 g/L of PDADMAC or cationic derivatives of PVB up to 15 h for 5 g/L of TP.

CONCLUSIONS

The investigated polycations strongly modify the interactions between particle surfaces, inducing either flocculation or enhanced stabilization. Up to now, the interaction between inorganic particles and PDADMAC and the occurrence of a "flocculation window" due to charge compensation, was described for different particles with particle size in the micrometer range such as silica or clay.^{11–13} Now, this result can be confirmed also for the application of relevant Aerosil dispersions containing nano-particles. For strong polycations flocculation is obtained at low polymer concentration because of a partial electrostatic interaction (patching). Outside of this flocculation range, where the particles are positively charged due to polymer adsorption, the influence of the polyelectrolyte concentration on the stabilization is minor. The adsorbed amount of polymers depends on different parameters such as solid content, specific surface area, and charge of dispersion which is influenced by the pretreatment. Due to the adsorption of the polycation the negative charge of the particle dispersion is reduced.

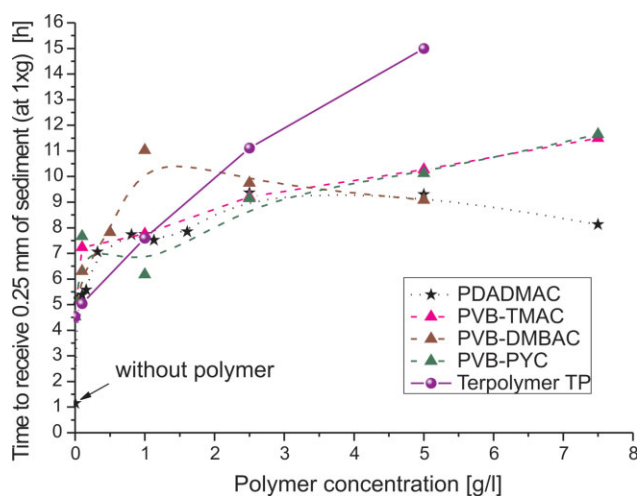


Figure 10 Predicted shelf life data in dependence on polymer concentration [according to Ref. 20]; most stable dispersions are obtained with TP which has the highest values for the time to receive 0.25 mm of sediment (at 1 g). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

All investigated polymers are able to stabilize Aerosil dispersions via electrostatic interactions, but by using polymers with reduced charge density, the interaction mechanism moves to steric stabilization. The ampholytic terpolymer TP, which has the lowest cationic charge but offers the possibility of intra- and intermolecular association, has the best stabilizing performance.

The novel centrifugal sedimentation method allows the direct calculation of the stability parameters like sedimentation velocity and prediction of the shelf life.

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