

Effect of Charge Density, Molecular Weight, and Hydrophobicity on Polycations Adsorption and Flocculation of Polystyrene Latices and Silica

S. Schwarz,¹ S. Bratskaya,² W. Jaeger,³ B.-R. Paulke³

¹Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany

²Institute of Chemistry, Far East Department of Russian Academy of Sciences, 159, Prosp. 100-letiya Vladivostoka, Vladivostok 690022, Russia

³Fraunhofer-Institut für Angewandte Polymerforschung, Geiselbergstr. 69, 14476 Golm, Germany

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ABSTRACT: Adsorption and flocculation behavior of two series of synthetic polycations was investigated in dispersions of silica and polystyrene latices with various particle size and surface charge densities. Polycations of the first series (polydiallyldimethyl ammonium chloride-PDADMAC) varied in molecular weight only, while polycations of the second series (derivatives of polymethacrylic acid) varied in both molecular weight and hydrophobicity. We have found that maximum adsorbed amount of high molecular weight PDADMAC on latex particles was nearly independent of the surface charge density when the particle size was comparable to the polymer coil dimensions in solution. Both low and high molecular weight PDADMACs were efficient flocculants, although significantly lower amounts of high molecular weight polyelectrolyte were required for the

phase separation in the dispersions due to particles aggregation through “charge patch” mechanism. The increase of polymer hydrophobicity leads to higher adsorbed amounts and broadening of flocculation window by polycations of the second series on both substrates. However, no strong enhancement of segment–surface interactions on hydrophobic substrates was observed. Since formation of multilayers upon adsorption was also excluded, the difference in adsorption and flocculation behavior was related to the more compact conformation of hydrophobically associating derivatives in solution and at the interface. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3422–3429, 2006

Key words: adsorption; flocculation; latices; polyelectrolytes; hydrophobically modified polymers

INTRODUCTION

The adsorption of synthetic and natural polyelectrolytes at solid/liquid interfaces was extensively studied in last decades, first of all, due to the great importance of this phenomenon in numerous processes in nature and technology. Several comprehensive reviews^{1,2} were focused on correlation of theories with experimental data and prediction of polyelectrolyte behavior near charged surfaces. However, fundamentals of polyelectrolyte adsorption are still less developed relative to that of nonionic polymers and are far from being completely understood.^{3,4} One of the complications in data analysis originates from using not well-defined substrates and polymers in adsorption investigations. This problem can be eliminated if monosized latex particles with controlled surface chemistry are used. Apart from being a good model system, latices are of rapidly growing interest for formation of functional coatings on planar surfaces, protein separation,

biochemical analysis, and many other applications, for which detailed information on polyelectrolyte adsorption behavior at the latex surface is important.

Progress in polymerization techniques now allows obtaining latices varying in type of surface functional groups, charge density (CD), and hydrophobicity. The latter parameter is crucially important to link polyelectrolyte adsorption and flocculation behavior in model latex dispersions with industrially relevant emulsions or suspensions of pronounced surface hydrophobicity. This makes latex dispersions particularly interesting for efficiency evaluation of polyelectrolytes with hydrophobic functionalities, which have been shown to exhibit superior properties in oil-recovery⁵ and oil and grease removal.⁶

In this article, we have investigated adsorption and flocculation behavior of two series of synthetic polycations in dispersions of polystyrene (PS) latex particles and silica varied in particle size and surface CD. In the first series, polycations (polydiallyldimethyl ammonium chloride) had constant CD and varied in molecular weight, polycations of the second series (derivatives of polymethacrylic acid) varied in both

Correspondence to: S. Schwarz (simsch@ipfdd.de).

TABLE I
Substrate Characteristics

	Particle diameter (nm)	Surface area (m ² g ⁻¹)	Charge density (mC m ⁻²)	Charge separation (nm) ^a
PS latices				
Latex A-60	54 ± 4	105.4	-37	2
Latex B-60	60 ± 4	94.9	-82	1.4
Latex A-200	221 ± 7	25.9	-48	1.8
Latex B-200	233 ± 7	25.9	-73	1.5
Silica				
Silica-200	200	14	-28	2.5
Silica-1000	1000	3	-49	1.8

^a Charge separation was calculated assuming homogeneous distribution of sulfate groups on the surface of latex particle.

molecular weight and hydrophobicity, which was controlled by introduction of pending hydrophobic functionalities into the polyelectrolyte backbone.

EXPERIMENTAL

Materials

Substrates

Polystyrene latices with surface sulfate groups were obtained by classical emulsion and emulsion copolymerization as described in Ref. 7. Monosized silica was purchased from Geltech (USA). Characteristics of latices and silica particles used as substrates for polyelectrolyte adsorption are summarized in Table I.

Polyelectrolytes

Polydiallyldimethyl ammonium chloride (PDADMAC) with molecular weights of 5000 and 400,000 g mol⁻¹, further referred as PDADMAC 5 and PDADMAC 400, respectively, were synthesized by free radical polymerization of corresponding monomers in aqueous solution.

Polymethacryloyloxyethyltrimethylammonium chloride (PM) and methacryloyloxyethyl-dimethylbenzylammonium chloride (PM BQ) differing in *N*-substitutes, methyl and benzyl groups (Fig. 1), were synthesized by free radical polymerization of the corresponding monomers in aqueous solution as described elsewhere.⁸ Isolation, purification, and characterization of the polyelectrolytes synthesized were carried out as previously described.⁹ ¹³C NMR (400 MHz) spectroscopy (inverse gated decoupling, without NOE decoupling) of the synthesized polycations were carried out with a Unity 400 (Varian, Germany), Table II.

Characteristics of the polycations used for investigation of adsorption and flocculation are summarized in Table III.

Methods

Photon correlation spectroscopy (PCS)

PCS measurements were performed at a scattering angle of 90° with Zetasizer 3000 (Malvern Instru-

ments, UK) equipped with 10 mW He-Ne laser as a light source. The operating wavelength was 633 nm. Analysis of autocorrelation function $g^2(\tau)$ was done automatically to yield diffusion coefficients that allowed to calculate apparent mean hydrodynamic diameters of particles from Stokes-Einstein equation.

Polyelectrolyte titration

Charge densities of polyelectrolytes and latex particles were determined by colloid titration in a particle charge detector (PCD-03, Mütek, Germany) combined with 702 SM Titrino (Metrohm, Switzerland). Solutions of low molecular weight sodium polyethylene sulfonate (PES-Na) or PDADMAC were used as ti-

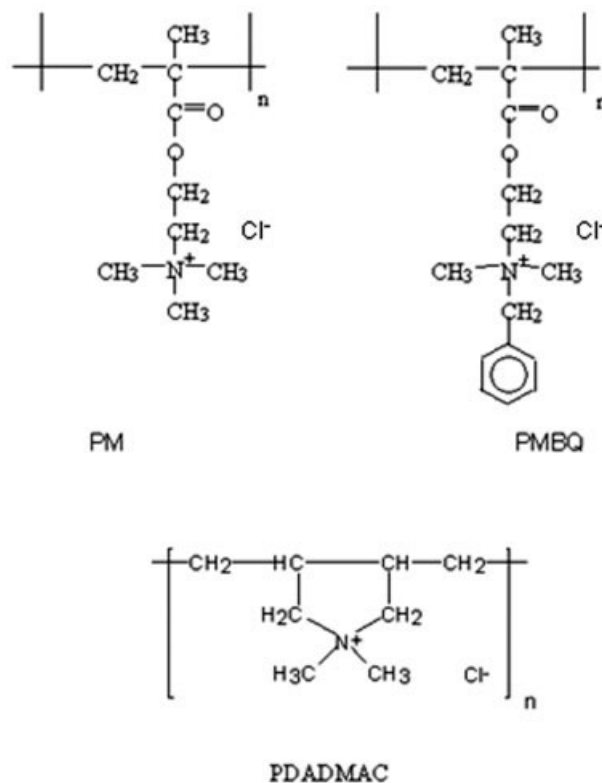


Figure 1 Chemical structure of polycations.

TABLE II
Chemical Shifts in NMR Spectra of Polycations Relative to TMS Signal (in descending order)

Polymer	Group	Chemical shift (ppm)	
		¹³ C	¹ H
PDADMAC	—N—CH ₂ —	71.1	3.8, 3.3
	—N—CH ₃	54.8, 53.1	3.2, 3.1
	—CH—	39.4, 39.0	2.7
	—CH ₂ —	27.2	1.5, 1.3
	—C=O	178.7	
	—N—CH ₂ —	64.8	
	—O—CH ₂	60.0	
	—N—CH ₃	54.6	
	—CH ₂ —	53.9	
	—C _q —	45.8	
PM	—CH ₃	19.7	
	—C=O	178.0	
	—C=(arom.		
	C2, C1, C3, C4)	133.8, 131.7, 130.1, 127.6	
	—N—CH ₂ —ar.	69.1	
	—N—CH ₂ —	63.2	
	—O—CH ₂	60.0	
	—CH ₂ —	54.5	
	—N—CH ₃	50.9	
	—C _q —	45.7	
PMBQ	—CH ₃	20.2	

trants for cationic and anionic systems, respectively. CD (mequiv g⁻¹) was calculated according to the following formula:

$$CD = C_{\text{titrant}} V_{\text{titrant}} Vm,$$

where C_{titrant} is the concentration of titrant (mequiv L⁻¹), V the volume of titrated solution, V_{titrant} the equivalent titrant volume, and m is the content of polyelectrolyte or latex in titrated solution (g L⁻¹).

Adsorption isotherms

The adsorption of cationic polyelectrolytes on silica and latex was investigated at pH = 5.7 and $T = 22^{\circ}\text{C}$. Silica and latex dispersions with solid content of 1 g

L⁻¹ and initial polyelectrolyte concentrations from 10 to 70 mg L⁻¹ were gently agitated during 15 min. Residual concentration of polyelectrolyte in the supernatant was determined by colloid titration after centrifugation at 22,000 rpm over 30 min. Preliminary tests have proven that free polyelectrolyte did not precipitate from solution under these conditions. Charge stoichiometry ($n^+_{\text{polymer}}/n^-_{\text{substrate}}$) was calculated according to the following formula:

$$n^+ / n^- = CD_{\text{pol}} A_{\text{pol}} F / CD_{\text{substrate}}$$

CD_{pol} is the charge density of polyelectrolyte (equiv g⁻¹), A_{pol} the polyelectrolyte adsorption (g m⁻²), $CD_{\text{substrate}}$ the surface charge density of substrate (C m⁻²), and F is the Faraday number (96,485 C mol⁻¹).

Flocculation

Flocculation was investigated as batch test in a series of beakers, each containing 20 mL of silica or latex dispersion with solid content of 1 g L⁻¹. To complete phase separation, after addition of aliquots of polyelectrolyte solution, mixtures were stirred for 15 min and allowed to sediment for 20 min for silica and 1 h for latex dispersions. Then 5 mL of the supernatant was taken from the beaker surface and its optical density (D^{500}) was measured at 500 nm using Lambda 800 UV-vis Spectrometer (Perkin-Elmer).

RESULTS AND DISCUSSION

Effect of surface CD and particle size

It is well known that the conformation of adsorbed polyelectrolyte molecules is a key factor determining its efficiency as flocculant or stabilizer in colloidal dispersions. Numerous experimental^{10,11} and theoretical works^{12,13} dealt with investigations of polyelectrolyte adsorption on planar surfaces and spherical particles that allowed to conclude that highly charged polyelectrolytes tend to adsorb at oppositely charged surface in a flat conformation, while decrease of poly-

TABLE III
Characteristics of Polycations

	Molecular weight ^a (Mw, g mol ⁻¹)	Charge density ^b (CD, mequiv g ⁻¹)	Polydispersity index
PDADMAC 5	5,000	6.2	2.1
PDADMAC 400	400,000	6.2	1.5
PM-I	340,000	4.8	1.6
PM-II	3,100,000	4.8	1.5
PM BQ-I	880,000	3.5	1.7
PM BQ-II	8,000,000	3.5	1.6

^a Determined by GPC.

^b Determined by polyelectrolyte titration in 10⁻³N KCl.

TABLE IV
Adsorption of PDADMAC on Latex Particles

Polyelectrolyte	Substrate	Adsorption (mg m ⁻²)	Charge stoichiometry (n ⁺ _{polymer} /n ⁻ _{substrate})	Area per monomer (nm ²)	Coverage degree (%)
PDADMAC 5	LatexA-60	0.11	1.77	2.43	12.39
	LatexB-60	0.20	1.45	1.33	22.72
	LatexA-200	0.16	1.98	1.67	18.04
	LatexB-200	0.22	1.79	1.21	24.87
PDADMAC 400	LatexA-60	0.1	1.61	2.67	11.30
	LatexB-60	0.14	1.02	1.90	15.86
	LatexA-200	0.11	1.36	2.43	12.43
	LatexB-200	0.18	1.46	1.48	20.37

electrolyte CD leads to an increased fraction of segments adsorbed in loops and tails and favors bridging interactions in colloidal dispersions. The effect of surface curvature and size ratio of polymer to particle on polyelectrolyte adsorption is often neglected, since in most systems size of adsorbent particles is significantly larger than that of polyelectrolyte molecules. However, geometrical constraints induced by high curvature and limited surface area of the single particle can significantly effect adsorption behavior of polyelectrolytes. While highly charged polyelectrolytes tend to adsorb at the planar surface in very thin layer with majority of segments in trains, higher number of loops and tails can be formed if the same polyelectrolyte adsorbs on particles with size smaller or comparable to the dimensions of the polyelectrolyte in solution. This difference in conformation of adsorbed polyelectrolyte can significantly influence flocculation mechanisms in colloidal dispersions.

To address this phenomenon in more detail, we have investigated adsorption of low and high molecular weight cationic polyelectrolytes (PDADMAC) at latices varying in particle size and surface CD. The adsorption isotherms were all of high affinity type (not shown), allowing precise determination of adsorption value at saturation region. Table III summarizes data extracted from adsorption isotherms and parameters calculated using surface CD and molecular structure of polyelectrolyte. One can see that the plateau value of adsorption isotherms of PDADMAC on all types of latices correspond to significant overcharging (charge ratio CR > 1), i.e., more polyelectrolyte was adsorbed than it was necessary to neutralize the surface charge. Since contour length of low molecular weight PDADMAC (approximately, 21 nm), as can be estimated¹⁴ from PDADMAC structure (Fig. 1), is smaller than radius of the latex particles, there should be no constraints for the polyelectrolyte to adsorb in a flat conformation.

It was recently shown¹⁵ that nonstoichiometric interaction between particles and polyelectrolytes is rather general tendency, although the charge ratio

strongly depends on the type of the system. For instance, overcharging in a polycation/silica system has been related to ionization of extra surface functional groups upon approaching of highly charged polycation to the anionic surface.¹⁶ This explanation can be adequate for systems with weak surface functional groups, while for the studied latices complete ionization of sulfate functional groups is expected and is very unlikely to increase upon polycation adsorption.

The most relevant explanation for the studied system is mismatch in polyelectrolyte and surface charge separation. As one can see (Table I) for all PS-latices, distance between surface charges varies from 1.4 to 2 nm what is significantly larger than charge spacing in PDADMAC, which is about 0.55 nm.¹⁴ Thus, positive charges of at least two PDADMAC monomers lying flat at latex surface will remain uncompensated due to the mismatch in charge separation in polyelectrolyte and substrate. Data in Table IV show that when the distance between surface charges decreases (latices B-60 and B-200), charge ratio also proportionally falls down. It should be mentioned that surface coverage degree estimated from differences in theoretically predicted (0.2 nm²) and experimentally found values of area per monomer was not higher than 25%. This, most likely, results from strong repulsion between non-neutralized charged segments of PDADMAC preventing adsorption of the next macromolecule in close proximity to already adsorbed ones. For latices with higher surface charge densities, coverage degree increases due to the higher contribution of segment-surface attraction into the force balance.

If polyelectrolyte adsorbs flat at the surface and possess uncompensated charges even at low surface coverage, fast aggregation of dispersed particles through charge patch mechanism is usually expected. However, investigations of flocculation behavior (Fig. 2) show that low molecular weight PDADMAC is an efficient flocculant only at doses close to the surface saturation. This is in disagreement with the concept of "charge patch" flocculation, which assumes that aggregation of particles occurs at intermediate coverage

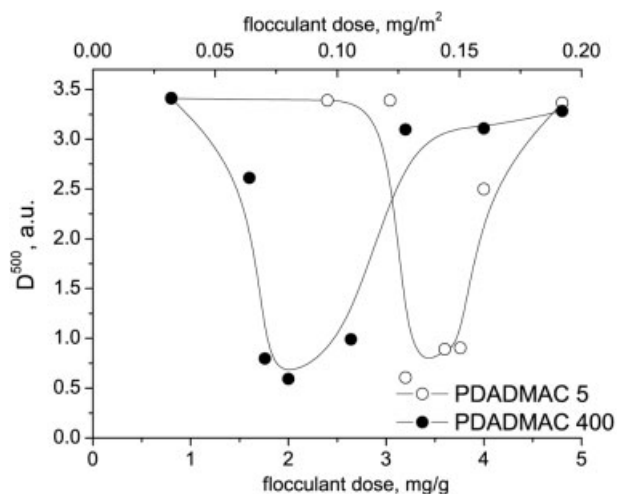


Figure 2 Flocculation of LatexA-200 by PDADMAC.

degrees due to attraction between oppositely charged patches of bare surface and adsorbed polymer. The “charge patch” mechanism is typical for highly charged polyelectrolytes, which usually adsorb with local surface overcharging. Despite the detected charge mismatch during PDADMAC adsorption, we can suggest that its patch dimensions are too narrow and small for providing strong attractive interactions with wide uncovered areas. Thus, effect of PDADMAC 5 is more close to that of low molecular electrolyte, which causes flocculation due to the screening of surface charge.

Adsorption and flocculation behavior of high molecular weight PDADMAC 400 is noticeably different. When the particles are significantly larger than the polymer coils, adsorption on sphere surface is close to the case of adsorption on planar surface, for which adsorbed amount of highly charged polyelectrolyte is independent on its molecular weight.¹⁷ This is usually explained by the flat conformation of polyelectrolyte and constant number of segments required for surface charge neutralization. However, data in Table IV show that the adsorbed amount of high molecular weight PDADMAC is generally lower compared with that of low molecular weight polymer. If we assume that because of the size mismatch between particle and polymer coil, PDADMAC adsorbs at a latex particle with numerous loops and tails, as suggested in Ref. 18, much more significant overcharging at adsorption isotherm plateaus can be expected due to the lower contribution of loops and tails to surface charge compensation, and thus, higher polyelectrolyte amount required for complete charge neutralization. Contrary, calculated charge ratio is noticeably lower for PDADMAC 400 that allows conclusion that formation of loops on the surface of a single particle is rather unlikely under the studied experimental conditions.

Theoretically estimated from monomer structure, contour length of PDADMAC 400 is ~1800 nm, which

is significantly larger than particle dimensions of both types of latices. Reis et al. have previously shown¹² that semiflexible highly charged polymers adsorb flat and wrap around particles only when polymer contour length is comparable with particle diameter. For longer chains, part of the segments tends to adsorb flat, while nonadsorbing segments dangle in the dispersion and can adsorb on neighboring particles to cause bridging effects. If one compares adsorption data for 60 and 200 nm latices (Table IV), one can see that when the surface CD of 60 nm latex is almost doubled, only slight increase in adsorption value is observed, while for 200 nm latex, the adsorbed amount of PDADMAC 400 is roughly proportional to surface CD.

Calculations show that the value of PDADMAC 400 maximum adsorption on 60 nm latex corresponds to about 2 chains per particle. Most likely, because of geometrical constants, particles can not accommodate higher amount of 1800-nm long polymer chains, even if the surface CD is doubled. Increase of particle size from 60 to 200 nm corresponds to a 10-fold increase in surface area, thus a substantially higher number of polyelectrolyte chains can be accommodated at the particle surface and adsorption behavior becomes more sensitive to the surface CD.

Excluded surface area effect can also contribute to a lower adsorbed amount of PDADMAC 400 compared to PDADMAC 5. Because of the fast bridging flocculation, a part of the surface area becomes inaccessible for further polyelectrolyte adsorption, when the critical coverage degree is reached. Contrary, as we have seen in flocculation tests, aggregation of latex particles induced by adsorption of PDADMAC 5 starts at doses close to the plateau of adsorption isotherms. Thus, excluded surface area effect due to flocculation is not very likely to interfere with evaluation of maximum adsorption.

In comparison of PDADMAC 5 and 400 maximum adsorption values (Table IV) with optimum floccula-

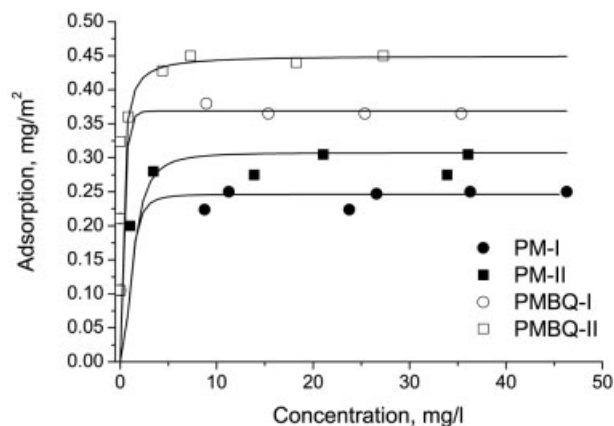


Figure 3 Isotherms of PM and PM BQ adsorption on latex B-60.

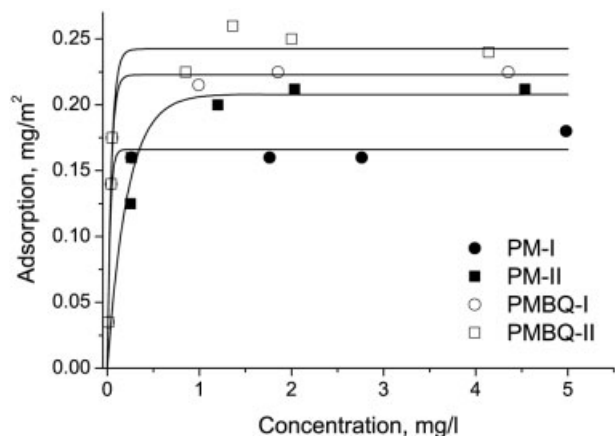


Figure 4 Isotherms of PM and PM BQ adsorption on Silica 200.

tion doses and widths of flocculation window (Fig. 2) clearly proves that higher molecular weight polyelectrolyte is efficient at lower doses and that the upper limit for efficient flocculation coincides with the value of maximum adsorption.

Effect of polyelectrolyte hydrophobicity

Introduction of hydrophobic fragments into polymer backbone by chemical grafting¹⁹ or copolymerization procedures²⁰ is a powerful tool to control interfacial and rheological properties of polyelectrolytes in numerous industrial applications. Increase of flocculant hydrophobicity can be beneficial for phase separation in hydrophobic, colloidal dispersions, such as emulsions, latices, or certain cell cultures. It was shown²¹ that at the same surface CD and polymer segment CD, adsorption of polyelectrolytes increases with increase of nonelectrostatic affinity to the surface.

Figures 3 and 4 show that adsorption isotherms of PM and PM BQ of different molecular weight are of high affinity type for both latex and silica substrates, indicating no remarkable difference in affinity of these polymers to highly hydrophilic and partially hydrophobic surfaces. To follow peculiarities of PM and PM BQ adsorption behavior on silica and latices in more detail, we have summarized the experimental results in Tables V and VI. One can see that for all substrates, PM BQ adsorbs at somewhat higher amounts than PM of comparable molecular weight. Besides, adsorption of PM only slightly depends on molecular weight, while adsorbed amount of PM BQ increases with increase of molecular weight.

Maximum adsorption values given in Tables V and VI can mislead to the conclusion that the possibly more hydrophobic character of latex surfaces significantly promotes adsorption of PM and PM BQ. How-

TABLE V
Adsorption of PM and PMBQ on Latex Particles

Polymer	Substrate	Adsorption (mg/m ²)	Charge stoichiometry (n ⁺ _{polymer} /n ⁻ _{substrate})
PM-I	LatexA-60	0.22	2.73
	LatexB-60	0.25	1.40
	LatexA-200	0.15	1.43
	LatexB-200	0.16	1.01
PM-II	LatexA-60	0.23	2.79
	LatexB-60	0.29	1.63
	LatexA-200	0.15	1.44
	LatexB-200	0.29	1.63
PMBQ-I	LatexA-60	0.27	2.49
	LatexB-60	0.37	1.53
	LatexA-200	0.14	0.99
PMBQ-II	LatexB-200	0.16	0.74
	LatexA-60	0.37	3.40
	LatexB-60	0.45	1.85
	LatexA-200	0.20	1.41
	LatexB-200	0.24	1.11

ever, if we take into account differences in surface CD of substrates, which is slightly higher for studied latices, the obtained values for adsorption isotherm plateau will be rather close for hydrophilic silica and more hydrophobic latices. Thus, most likely, the difference in adsorbed amounts of PM and PM BQ, first of all, originates not from the higher surface-segment interactions but from the difference in solution properties of hydrophilic and hydrophobically modified polyelectrolytes.

As it was already mentioned above, polyelectrolytes of so high CD at low salt concentration have rather extended conformation that limit accommodation of the polymer at a particle surface. Introduction of hydrophobic functionalities induces inter- and intramolecular association, which can lead to more compact polyelectrolyte structures in solution. Obviously, because of the cooperative nature of hydrophobic interactions they will be enhanced by increase of polyelectrolyte molecular weight. This can explain observed differences in PM and PM BQ adsorption behavior.

TABLE VI
Adsorption of PM and PMBQ on Silica

Polymer	Substrate	Adsorption (mg/m ²)	Charge stoichiometry (n ⁺ _{polymer} /n ⁻ _{substrate})
PM-I	Silica 200	0.166	2.68
	Silica 1000	0.192	1.61
PM-II	Silica 200	0.208	3.59
	Silica 1000	0.196	1.76
PMBQ-I	Silica 200	0.222	3.08
	Silica 1000	0.233	1.68
PMBQ-II	Silica 200	0.245	3.40
	Silica 1000	0.301	2.17

Formation of multilayers, which was suggested to be responsible for higher adsorption of hydrophobically modified polyacrylamides on clays,²² is doubtful in the studied system. Adsorption isotherms of both PM and PM BQ (Fig. 3) have distinct horizontal saturation regions, which shows that once monolayer is formed, increasing of polyelectrolyte concentration does not lead to increase of its surface content. It was previously shown^{22,23} that for associating polyelectrolytes, which tend to form multilayers on solid surface, the isotherms have a particular shape without distinct plateau region. It is interesting to note that although flocculation of latex (Fig. 5) and silica (Fig. 6) dispersions starts at nearly the same doses of PM and PM BQ, the hydrophobically modified polyelectrolyte shows a broader flocculation window in correspondence with higher value of the adsorption isotherm plateau.

CONCLUSIONS

Adsorption and flocculation behavior of PDADMAC (with molecular weights of 5000 and 400,000 g mol⁻¹), PM, and PM BQ was investigated in dispersions of silica and polystyrene latices containing surface sulfate groups to elucidate the effects of molecular weight, CD, and hydrophobicity on the performance of these industrially important polyelectrolytes.

We have found that in most cases, adsorption of the studied polycations occurred with surface overcharging up to a charge ratio of 3.6. This was related to the mismatch of charge spacing between functional groups of substrates and of highly charged polyelectrolytes. The particle size of substrate affected polyelectrolyte adsorption when it was comparable with dimensions of polymer coils in solution. In this case,

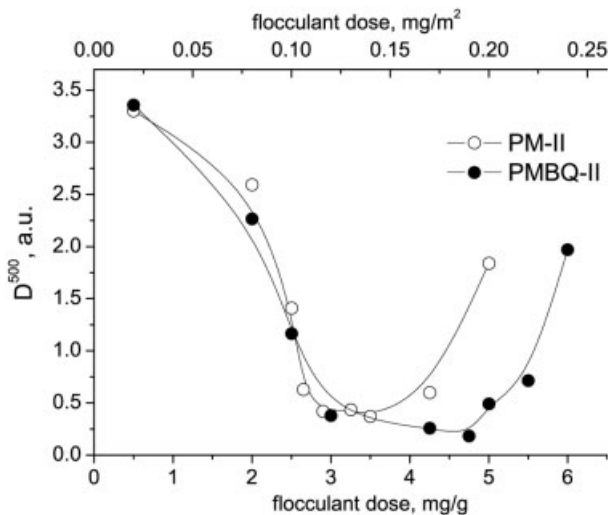


Figure 5 Flocculation of Latex A-200 dispersion.

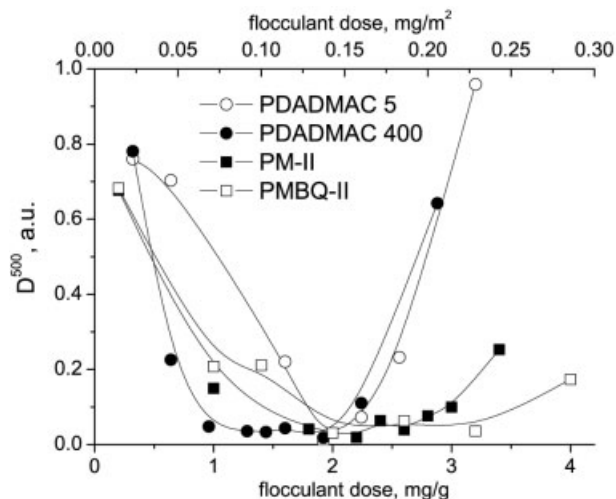


Figure 6 Flocculation of Silica 200 dispersion.

increase of substrate surface CD did not promote further polyelectrolyte adsorption as a result of geometrical constraints, leading to adsorption of most segments in loops and tails, despite the high CD of the polycation.

Polycations with higher hydrophobicity adsorbed in somewhat higher amounts on both silica and latex substrates and showed better flocculation performance. All adsorption isotherms were of high affinity type, but no evidence of enhanced segment-surface interactions was observed for hydrophobically modified polycations. The shape of isotherms with clear horizontal plateau at saturation rather than constant increase of adsorbed amount imply that multilayer adsorption is not an applicable model for the studied system. More compact structure of hydrophobically associating polyelectrolytes in solution and at interface was suggested to be the main reason for higher adsorption values and better flocculation performance of PM BQ compared to PM.

References

- Hesslink, F. Th. In *Adsorption from Solution at the Solid/Liquid Interface*; Parfitt, G. D., Rochester, C. C., Eds.; Academic Press: New York, 1983; p 377.
- Muthukumar, M. In *Colloid-Polymer Interactions. From Fundamentals to Practice*; Farinato, R. S., Dubin, P. L., Eds.; Wiley-Interscience: New York, 1999; p 175.
- Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Gassgove, T.; Vincent, B. *Polymer at Interfaces*; Chapman & Hall: London, 1993.
- Dobrynin, A. V.; Deshkovski, A.; Rubinshtein, M. *Phys Rev Lett* 2000, 84, 3101.
- Taylor, K. C.; Nasr-El-Din, H. A. *J Petrol Sci Eng* 1998, 19, 265.
- Bolto, B. A.; Dixon, D. R.; Gray, S. R.; Chee, H.; Harbour, P. J.; Ngoc, L.; Ware, A. J. *Water Sci Technol* 1996, 34, 117.
- Paulke, B.-R.; Möglich, P.-M.; Knippel, E.; Budde, A.; Nitzsche, R.; Müller, R. H. *Langmuir* 1995, 11, 70.
- Zimmermann, A.; Jaeger, W.; Reichert, K. H. *Polym News* 1997, 22, 390.

9. Dautzenberg, H.; Jaeger, W.; Kötz, J.; Philipp, B.; Seidel, Ch.; Stscherbina, D. *Polyelectrolytes: Formation, Characterization and Application*; Carl Hanser Verlag: Munich, 1994.
10. Cohen Stuart, M. A.; Cosgrove, T.; Vincent, B. *Adv Colloid Interface Sci* 1985, 24, 143.
11. Claesson, P. M.; Poptoshev, E.; Blomberg, E.; Dedinaite, A. *Adv Colloid Interface Sci* 2005, 114/115, 173.
12. Netz, R. R.; Joany, J.-F. *Macromolecules* 1999, 32, 9026.
13. Joanny, J.-F.; Castelnovo, M.; Netz, R. J. *Phys B: Condens Matter* 2000, 12, A1.
14. Karibyantz, N.; Dautzenberg, H.; Cölfen, H. *Macromolecules* 1997, 30, 7803.
15. Kleimann, J.; Gehin-Delval, C.; Auweter, H.; Borkovec, M. *Langmuir* 2005, 21, 3688.
16. Shin, Y.; Roberts, J. E.; Santore, M. M. *J Colloid Interface Sci* 2002, 247, 220.
17. Durand-Piana, G.; Lafuma, F.; Audebert, R. *J Colloid Interface Sci* 1987, 119, 474.
18. Rehmert, R.; Killmann, E. *Colloids Surf A* 1999, 149, 323.
19. Yahya, G. O.; Ali, S. K. A.; Hamad, E. Z. *Polymer* 1996, 37, 1183.
20. Ternner, S. R.; Siano, D. B.; Bock, J. *US Pat.* 4,528,348 (1985).
21. van de Steeg, H. G. M.; Cohen Stuart, M. A.; de Keizer, A.; Bijsterbosch, B. H. *Langmuir* 1992, 8, 2538.
22. Volpert, E.; Selb, J.; Candau, F.; Green, N.; Argillier, J. F.; Audibert, A. *Langmuir* 1998, 14, 1870.
23. Argillier, J. F.; Audibert, A.; Lecourtier, J.; Moan, M.; Rousseau, L. *Colloids Surf A* 1996, 113, 247.