Nonstoichiometric Interpolyelectrolyte Complexes as Colloidal Dispersions Based on NaPAMPS and Their Interaction with Colloidal Silica Particles

Simona Schwarz,[1] *Stela Dragan**[2]

[1]Institute of Polymer Research, Hohe Strasse 6, 0 1069 Dresden, Germany
[2]"Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41 A, 700487 Iasi, Romania

Summary: Preparation and characterization of some nonstoichiometric interpolyelectrolyte complexes (NIPECs) as stable colloidal dispersions by the interaction between poly(sodium 2-acrylamido-2-methylpropanesulfonate) (NaPAMPS) and three strong polycations bearing quaternary ammonium salt centres in the backbone, poly(diallyldimethylammonium chloride) (PDADMAC) and two polycations containing N,N-dimethyl-2-hydroxypropyleneammonium chloride units (PCA_5 and PCA_5D_1), have been followed in this study as a function of the polycation structure and polyelectrolyte concentration. Complex characteristics were followed by polyelectrolyte titration, turbidity and quasi-ellastic light scattering. Almost monodisperse NIPECs nanoparticles with a good storage stability were prepared when total concentration of polyelectrolyte was varied in the range 0.85-6.35 mmol/L, at a ratio between charges (n^-/n^+) of 0.7. NIPECs as a new kind of flocculants were used to flocculate a stable monodisperse silica suspension. The main advantage of NIPECs as flocculants is the broad flocculation window, which is a very important aspect for industrial applications.

Keywords: dispersions; flocculation; nonstoichiometric interpolyelectrolyte complexes; particle size; polyelectrolytes; silica

Introduction

Nonstoichiometric interpolyelectrolyte complexes (NIPECs), either soluble[1-12] or stable colloidal systems[13-22] have been obtained up to date, by the interaction between oppositely charged polyelectrolytes, depending on different factors such as: nature of the ionic groups, polymerization degree, flexibility, charge density, and the concentration of the opposite polyelectrolytes, molar ratio between opposite charges, properties of the reaction medium (pH, temperature, ionic strength, dielectric constant). NIPECs as stable colloidal dispersions bearing positive or negative charges in excess proved to be of a great interest for some main practical areas such as flocculants for

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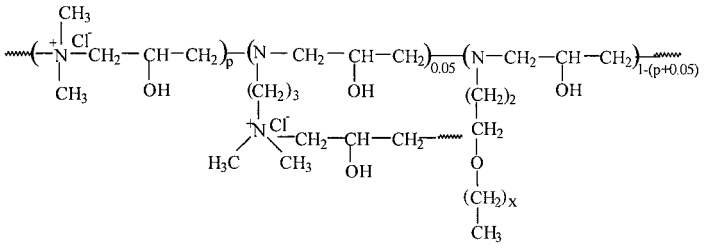
cellulose and clay dispersions, and organic compounds (dyes and surfactants) from the waste waters as well as for surface modification of different solid substrates.[13-18,20,22] The surface charge and sizes of the IPECs nanoparticles could be influenced by the structure of opposite polyions, polyions mixing ratio, polyions concentration, to mention a few among different parameters which can be varied. Formation and properties of the NIPECs obtained by the interaction between strong oppositely charged polyelectrolytes have been less investigated up to date.[23] Therefore, the aim of this study was to obtain first NIPECs as stable colloidal dispersions employing poly(sodium 2-acrylamido-2-methylpropanesulfonate) NaPAMPS as a strong polyanion and three strong polycations containing quaternary ammonium salt centres in the backbone, poly(diallyldimethylammonium chloride) PDADMAC and two polycations containing N,N-dimethyl-2-hydroxypropyleneammonium chloride units and different hydrophobic substituents (PCA_5 and PCA_5D_1), and then to use these reactive colloidal dispersions in the separation of silica nanoparticles comparative with polycations alone.

Experimental

Materials

PDADMAC[27] with a molar mass of 240000 g/mol, purchased from Aldrich, has been used as received. Polycations PCA_5 and PCA_5D_1 were synthesized and purified as it was presented before.[28] The intrinsic viscosity in 1 M NaCl at 25 °C of the samples employed in this study were as follows: 0.46 dL/g and 0.41 dL/g, respectively.



p = 0.95, PCA_5; p = 0.94, x=9, PCA_5D_1

Scheme 1

NaPAMPS, synthesized and purified according to the method previously reported,[29] has been used as a strong polyanion, with a molar mass of 170000 ,g/mol, viscometrically determined.[30] Polyions characteristics were summarized in Table 1.

Table 1. Characteristics of opposite polyions employed in the IPECs preparation.

Sample	M_v, g/mol	M_u, g/charge	B[1)], nm
NaPAMPS	170000	229	0.25
PDADMAC	240000	162.7	0.5
PCA_5	-	140.35	0.57
PCA_5D_1	-	141.68	0.57[2)]

[1)] distance between charges;
[2)] it was assumed to be the same like in PCA_5.

IPECs preparation

Aqueous solutions of the complementary polyelectrolytes with different concentrations were prepared by adequate dilution of the stock solutions (10 mM) with water deionized and purified by a Milli-Q system (Millipore, Eschborn, Germany). Variable volumes of the aqueous solution of the titrant (always NaPAMPS), were slowly dropped into the aqueous solution of polycation, under magnetic stirring, at room temperature (about 25 °C), until a certain ratio between opposite charges was achieved.[31] The IPECs dispersions were still stirred for 2 h, and were characterized after 24 h of storage, if other conditions were not mentioned.

Complex characterization

The NIPECs properties as a function of the polycation structure were followed first by the optical density of the IPECs nanoparticles at λ = 500 nm (OD_{500}). OD_{500} measurements were carried out with a Lambda 900 UV/Vis spectrometer (Perkin Elmer, UK). Quantitative determination of the polyelectrolyte in the starting solutions and the detection of free charges in the NIPECs dispersions were performed with a particle charge detector PCD 02, Müteck, Germany using either poly(sodium ethylenesulfonate) (PES) or PDADMAC with a concentration of 10^{-3} M, in dependence on the nature of the charges in excess. Quasi-elastic light scattering measurements were performed with a Zetasizer 3000 (Malvern Instruments Ltd, UK) at a scattering angle of 90°. The operating wavelength was 633 nm. Z-averaged particle sizes (R_h) and polydispersity index of the nanoparticles were evaluated by this method.

Flocculation test

Model suspensions of silica (Geltech Inc.) with a particle size of 200 nm were used for the flocculation tests. The flocculation studies were carried out with a conventional test equipment for the characterization of the flocculation and sedimentation process under static conditions. With a pivoted frame, the stirring conditions can be hold the same for the six graduated glasses of this equipment. After the addition of the appropriate amount of polycation solution or NIPEC-dispersions, followed by stirring and 20 minutes sedimentation, the supernatant fraction was separated and then, the efficiency of flocculation was determined by measuring the OD_{500} (Lambda 900, Perkin Elmer, UK) and the height of the precipitated solid fraction.

Results and Discussion

Information on the influence of polycation structure, polyanion molar mass and polyion concentration on the formation and characteristics of the complex nanoparticles based on NaPAMPS, at different ratios (n^-/n^+: 0.5 – 1.4) between opposite charges, have been already presented in detail elsewhere.[31] The main conclusions resulted from that study were used in the present work to prepare reactive NIPECs nanoparticles with positive charges in excess. Thus, OD_{500} values as a function of the ratio between opposite charges for the complex formation between NaPAMPS as a titrant and different polycations as starting solutions showed that the IPECs dispersions had a low turbidity before the complex stoichiometry, correlated with the abscisa values of the rising curves corresponding to the one-half of the turbidity maximum, and reflects a small influence of the polycation structure, OD_{500} values being a little lower for the complex formed with PDADMAC than those prepared with PCA_5 and PCA_5D_1 as polycations. Close to the isoelectric point (iEP), the OD_{500} values strongly increased, mainly because the sizes of the complex particles increased. Polyion concentrations strongly influenced nanoparticle sizes, R_h, both before and after the complex stoichiometry.[31] NaPAMPS with a molar mass of 170000 g/mol has been selected to prepare NIPECs dispersions with different concentrations in polyelectrolytes because, at this molar mass, polyanion concentration could be varied in a large range.

A very important aspect related to the possible applications of the NIPECs as reactive nanoparticles is their stability in dependence on the polyelectrolyte structure and the total concentration of the polyelectrolytes. NIPECs nanoparticle characteristics prepared with NaPAMPS as added polyion, at a constant ratio between charges, $n^-/n^+ = 0.7$, in

dependence on the polycation structure and the total concentration of polylectrolyte, were measured after 24 h and 48 h, the values being collected in Table 2.

Table 2. Characteristics and stability of the nonstoichiometric polyelectrolyte complexes based on NaPAMPS.

	C_{PE},	OD_{500}		Rh, nm	
Polycation	mM	24 h	48 h	24 h	48 h
PDADMAC	1.59	0.0505	0.047	58.4	58.5
	3.18	0.186	0.191	76.9	76.25
	4.77	0.4494	0.449	89.2	88.55
	6.36	0.888	0.898	99.55	99.5
PCA_5D_1	3.18	0.1664	0.1705	75.45	73.5
	4.77	0.4363	0.4365	90.75	90.75
	6.36	0.6571	0.692	93.55	95.05
	1.59	0.048	0.049	61.45	60.07
PCA_5	3.18	0.1695	0.1676	76.35	76.05
	4.77	0.441	0.441	91.9	91.05
	6.36	0.759	0.759	98.45	99.25

It is well known that when polyelectrolytes are used as flocculants in waste water purification, the optimum flocculation concentration domain is usually very narrow and restabilization of the refractory pollutants can easily take place by the overdosing of the polyelectrolyte. The NIPECs colloidal dispersions synthesized up to date showed a larger optimum flocculation concentration, being considered as new reactive nanoparticles.[17,18]

Flocculation efficiency of the NIPECs dispersions synthesized in this paper has been tested, comparative with the starting polycations, in the flocculation of silica monodisperse stable nanoparticles (Figures 1, 2, 3). As one can observe from Figures 1, 2 and 3, at concentrations higher than those corresponding to the optimum concentration for flocculation, redispersion took place very quickly, when polycations where used alone. PDADMAC and PCA_5 alone show a very narrow range of flocculation and the residual turbidity corresponding to the optimum flocculation concentration remained about 0.4 g/mg for PDADMAC. PCA_5D_1, containing 1 mol % hydrophobic side chains, shows a broader flocculation range with a low residual turbidity. For industrial applications it is very important to have a broad flocculation window because the main parameters of the waste waters (solid content, ionic strength, pH, presence of

surfactants, which act as stabilisators for the fine suspensions) could change in very large limits in one day.

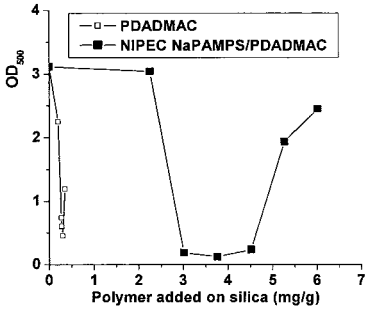


Fig. 1. Flocculation test of silica nanoparticles with PDADMAC comparative with NIPEC prepared with NaPAMPS added on PDADMAC.

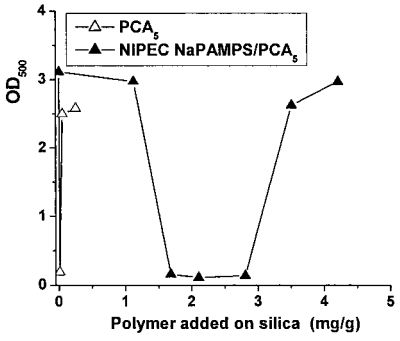


Fig. 2. Flocculation test of silica nanoparticles with PCA_5 comparative with NIPEC prepared with NaPAMPS added on PDADMAC.

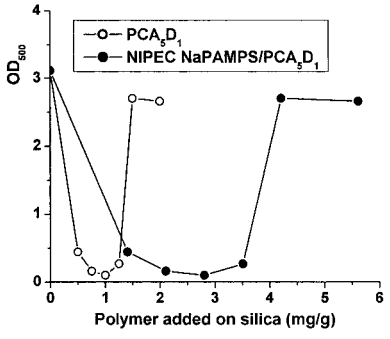


Fig. 3. Flocculation test of silica nanoparticles with PCA_5D_1 comparative with NIPEC prepared with NaPAMPS added on PCA_5D_1.

The main difference showed by the NIPECs dispersions used as flocculants compared with pure polycations was the much larger window of flocculation. The amount of polyelectrolytes corresponding to the optimum flocculation concentrations is higher because at a molar ratio of 0.7 the excess of positive charges is not so high. On the other hand, the residual turbidity is much lower than in the case of the polycation alone since the hydrophobic parts from the complex itself have also a contribution.

The influence of the polycation structure was clearly observed in the flocculation process of silica. Thus, the window of the optimum flocculation concentration was broader in the case of PCA_5D_1 because of the higher hydrophobicity induced by the presence of 1 mol % of decyloxypropylamine side chains. The largest range concentrations where the flocculation took place were found in the case of the polycation PCA_5D_1, both for pure polycation and for the NIPEC prepared on its basis. These results show that the presence of a small content of hydrophobic side chains has a positive influence on the flocculation window. Concerning the values of the optimum concentration, the higher values found in the case of NIPECs are explained by the lower amount of charges, which result from the difference between the ratio n^-/n^+ corresponding to the iEP and the ratio n^-/n^+ of 0.7 selected for the NIPECs preparation. But, even if the amount of flocculant is very important, NIPECs can be used as specialized flocculants for wastes containing nanoparticles with low charge such as disperse dyes from the textile factories or slurries from microelectronics, which could be considered as "refractory pollutants". Such solid-liquid separation processes are not well solved by the comercial polycations up to date.

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