Nanoparticles tailored by polyelectrolyte self-assembly approach

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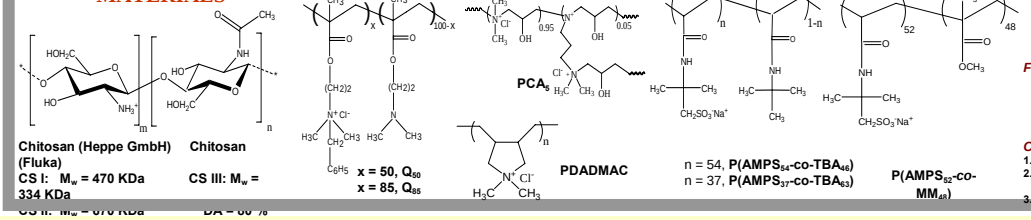
Aim: Self-assembly processes of polymers involving electrostatic interactions can be used to design materials with unique properties, with various structures ranging from the nanometer sizes (water-soluble aggregates, nanoparticles of polyelectrolyte complexes - PEC) to the macroscopic state (physical gels, films). The preparation of PEC as dispersions with a narrow distribution of the nanoparticle sizes and a high storage colloidal stability was a central task last decade [1-5]. In the followings, some results obtained in our research group, concerning the design of some nanoparticles based on synthetic and natural polyelectrolytes, have been summarized [6-10]. Nonstoichiometric PEC (N-PEC) nanoparticles were prepared by controlled mixing of some random anionic/nonionic copolymers with synthetic or natural polycations, their structural characteristics being deeply investigated by dynamic light scattering and atomic force microscopy. The effect of preparation conditions, such as the polyelectrolyte structure and the molar ratio between charges, on the particle sizes was studied in detail. The nonstoichiometric complex nanoparticles, with positive charges in excess, were tested in the destabilization of kaolin model dispersion and proved to be more efficient than polycations alone, especially as concern the broadness of the flocculation window [8-10].

MATERIALS



IPECs preparation. Specific volumes of the aqueous solution of polyanion, having a constant concentration of 5 mM, were continuously added to the aqueous solution of polycation, having a constant concentration of 0.5 mM, with a constant addition rate, under magnetic stirring, at room temperature, to obtain a certain molar ratio between opposite charges, n^-/n^+. After mixing, the formed dispersions were stirred 60 min and were characterized after 24 h.

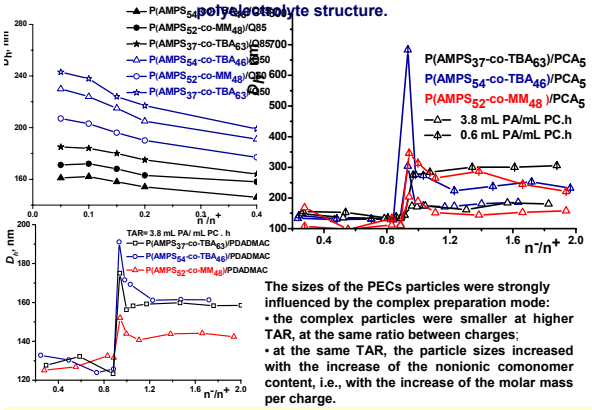
Flocculation tests. Volumes of 50 ml Kaolin suspension were stirred at 120-150 rpm in beakers and then different volumes of flocculant solution were added. Stirring was continued with the same speed for about 2 min, and then decreased to about 50 rpm for 15 min. After a settling time of about 20 min the supernatant was characterized by OD_{500}.

Characterization methods

1. Dynamic light scattering - Zetasizer 3000 (Malvern Instruments, UK)
2. Atomic Force Microscopy - Nanoscope IIIa Dimension 3100 SPM (Digital Instruments Veeco Metrology Group, Woodbury, NY, USA).
3. UV-Vis spectrometry for turbidimetric measurements - SPECORD M42

New N-PEC nanoparticles based on synthetic polyelectrolytes

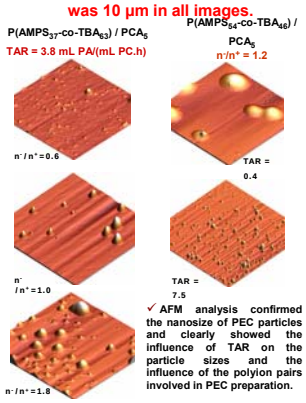
Dependence of hydrodynamic diameter, D_h, on the molar ratio between charges, n^-/n^+, and polyelectrolyte structure.



The sizes of the PECs particles were strongly influenced by the complex preparation mode:

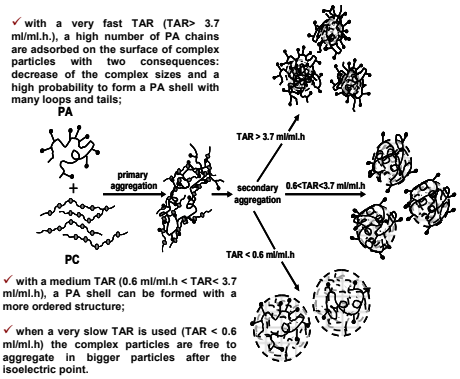
- the complex particles were smaller at higher TAR, at the same ratio between charges;
- at the same TAR, the particle sizes increased with the increase of the nonionic comonomer content, i.e., with the increase of the molar mass per charge.

Tapping mode AFM images of N-PEC nanoparticles at different n^-/n^+ and different TARs, adsorbed on the silicon wafers. Scan size was 10 μm in all images.



✓ AFM analysis confirmed the nanosize of PEC particles and clearly showed the influence of TAR on the particle sizes and the influence of the polyion pairs involved in PEC preparation.

Schematic representation of PECs formation between synthetic polycations and ionic/nonionic random copolymers of AMPS



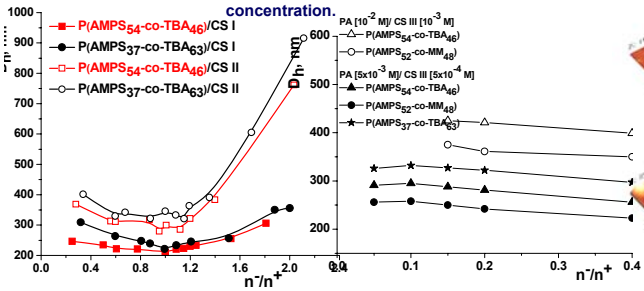
✓ with a very fast TAR (TAR> 3.7 ml/ml.h.), a high number of PA chains are adsorbed on the surface of complex particles with two consequences: decrease of the complex sizes and a high probability to form a PA shell with many loops and tails;

✓ with a medium TAR (0.6 ml/ml.h < TAR< 3.7 ml/ml.h), a PA shell can be formed with a more ordered structure;

✓ when a very slow TAR is used (TAR < 0.6 ml/ml.h) the complex particles are free to aggregate in bigger particles after the isoelectric point.

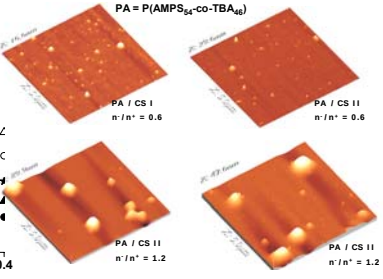
New N-PEC nanoparticles based on natural/synthetic polyelectrolytes

Dependence of hydrodynamic diameter, D_h, on the molar ratio between charges, n^-/n^+, chitosan molar mass and polyelectrolyte structure and concentration.



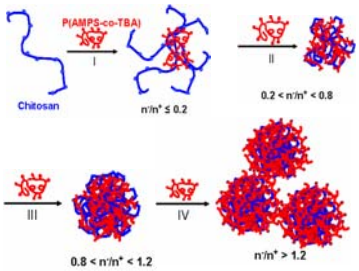
✓ The region ranging from n^-/n^+ of 0.8 up to 1.2, characterized by an almost constant size of the complex particles, for all polyion pairs, seems to be a peculiarity of the chitosan based complexes, taking into account the semi-rigid backbone of chitosan.

Tapping mode AFM images of the N-PEC nanoparticles at different n^-/n^+, adsorbed on the silicon wafers. Scan size was 10 μm in all images.



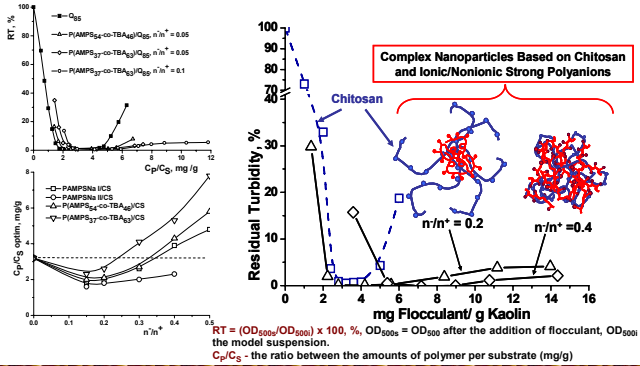
✓ The AFM images indicated that before the stoichiometry, the adsorbed particles appeared as small and individual particles, whereas aggregated structures were observed after that.

Schematic representation of the PEC formation between chitosan and ionic/nonionic random copolymers of AMPS



✓ A four step mechanism was postulated for the formation of N-PECs as colloidal dispersions from chitosan as starting polyion and ionic/nonionic random copolymers of AMPS as added polyions [8].

Flocculation test of kaolin with positive N-PECs nanoparticles



RT = $(OD_{500s}/OD_{500i}) \times 100$, %, OD_{500s} = OD_{500} after the addition of flocculant, OD_{500i} = OD_{500} of the model suspension.

C_P/C_S - the ratio between the amounts of polymer per substrate (mg/g)

✓ The N-PEC nanoparticles were more effective than the polycations alone in the kaolin separation, especially at low molar ratios between charges, when the flocculation window was more then double at an optimum dose lower than that of polycations. The main advantage of N-PECs is the increase of critical concentration for kaolin re-stabilization, the N-PEC particles adsorbed on the kaolin surface protecting them more efficient against re-dispersion.

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