

Charged starch nanoparticles prepared by polyelectrolyte complex formation

Ramunė Rutkaitė*,

Joana Bendoraitienė,

Rima Klimavičiūtė,

Edita Lekniūtė,

Indrė Narmontaitė,

Virginija Šinkūnaitė

*Laboratory of Biopolymer Research,
Faculty of Chemical Technology,
Kaunas University of Technology,
Radvilėnų pl. 19,
Kaunas LT-50254,
Lithuania*

Cationic and anionic starch nanoparticles were obtained by aqueous polyelectrolyte complex formation between cationic quaternary ammonium substituted starch and anionic sodium triphosphate as well as anionic hydroxyethyl starch and cationic poly(diallyldimethylammonium chloride), respectively. The formation of nanosized starch particles of a spherical shape was verified by dynamic light scattering, scanning electron microscopy and atomic force microscopy measurements. The cationic starch nanoparticles of different constitution and containing various contents of quaternary ammonium groups were produced and their zeta potential was modulated between +4 mV and +14 mV by varying polycation / polyanion ratio. Negatively charged starch nanoparticles of different constitution and containing various contents of carboxyl groups were produced and their zeta potential was modulated between –3 mV and –11 mV by varying polyanion / polycation ratio. Moreover, aqueous dispersions of cationic starch nanoparticles were stable for 2–12 days at the room temperature and the stability at 4 °C was 3–22 days. Meanwhile, aqueous dispersions of anionic starch nanoparticles were stable for 3–8 days at the room temperature and the stability at 4 °C was 6–10 days.

Key words: cationic starch, anionic starch, nanoparticles, polyelectrolyte complexes

INTRODUCTION

Colloidal particles made under mild conditions by complexation of charged natural polymers, natural polyelectrolytes, represent a promising area of investigations in terms of their attractive biodegradable, nontoxic and biocompatible properties and the use for biomedical, pharmaceutical and food applications [1–3]. Oppositively charged polyelectrolytes (polyanions and polycations) dissolved in water form polyelectrolyte complexes (PEC) that could be divided mainly into three different classes: a) soluble PEC, i. e. macroscopically homogenous systems without aggregation; b) turbid

colloidal systems with suspended PEC particles in the transition range to phase separation; c) two-phase systems of supernatant liquid and precipitated PEC which is readily separated as a solid. Regarding applications, stable homogenous dispersions of PEC are needed to make homogenous modifying polymer solutions, coatings or carriers from the complexes. It is well known that stable PEC with no phase separation during complexation can be formed under certain conditions, i. e. using polyelectrolytes with weak ionic groups and significantly different molecular weights at non-stoichiometric mixing ratios [4–9]. Those PECs consist of a long host molecule and shorter sequentially attached guest polyions of the opposite charge. In dependence on ionic sites at the polyelectrolyte chains and the mixing conditions

* Corresponding author. E-mail: ramune.rutkaite@ktu.lt

the formed stable PEC contain single stranded hydrophilic and double stranded hydrophobic sections. Soluble PEC could be prepared from copolymers which macromolecules consist of hydrophilic ionic and nonionic blocks [10–12]. PECs of low hydrophilicity (low enough to permit precipitation) result in supermolecular structures. As shown and discussed in different studies [5, 13, 14], the formed PEC particles consist of a neutralized, hydrophobic core and a shell of the excess component which stabilizes the particles against further coagulation. The systems with PECs are very sensitive to the low-molecular salts added [15, 16].

The use of the nanosized particles is of particular interest because the behaviour of the nanoparticles can be significantly different from the bulk original material. With regard to medical, biotechnological and food applications, nanoparticle-forming polymers need to be non-toxic, biocompatible and functional. Consequently, biopolymers, in particular polysaccharides are of high value. The amphiphilic character of their derivatives makes easier self-assembling to nanospheres. Until now most of the nanoparticles from biopolymer formation studies are dedicated to dextrane, chitosan or alginate compounds [17–28]. However, the formation of nanoparticles based on starch derivatives is poorly reported in the literature except several communications on starch ester nanoparticles prepared by the dialysis method [29, 30] and a comprehensive work of A. Dufresne et al. [30–34] on preparation of starch nanocrystals by hydrochloric acid hydrolysis.

The method of PEC formation can be characterized by the diversity of products with desired properties (solubility, hydrophobicity, particle charge, etc.) which could be obtained from the same initial components by using simple procedures. The studies of PECs obtained by using biopolymers due to the structural defects undoubtedly are incomplete. Accessible ionic groups in non-stoichiometric PEC induce the charge to the particles and offer the possibility for subsequent derivatization. Employment of starches with hydroxyethyl groups enlarges the zone of mixing ratios where the soluble PECs or stable colloidal PEC systems could be obtained. Recently, we have reported on formation of nanoparticles from cationic hydroxyethyl starches of different degree of substitution [35]. The ability of those nanoparticles to entrap hydrophobic molecules was tested by using fluorescence probe experiments. The capability to accommodate hydrophobic pyrene guest molecule was decreasing with the increasing number of cationic groups in cationic starches and little depended on the polyanion/polycation ratio in starch nanoparticles. These special features and further modification possibilities distinguish starch nanoparticles as very promising nanosized carrier materials with great potential in health care and environmental sciences.

The present work involves the preparation of both positively and negatively charged nanoparticles from cationic or anionic starches by polyelectrolyte complex formation in aqueous media, their characterization and stability studies.

EXPERIMENTAL

Materials

Hydroxyethyl starch (HES), Kollotex 1250 ($[\eta] = 0.136 \times 10^3$ ml/g), was supplied by Avebe (Netherlands). Glycidyltrimethylammonium chloride (GTAC) (90%, Sigma-Aldrich), pentasodium tripolyphosphate (NaTPP) (98%, Fluka), monochloroacetic acid (99%, Sigma-Aldrich), poly(diallyldimethylammonium chloride) (PDADMACl) ($M_w < 100\,000$, 35% aqueous solution, Sigma-Aldrich) were used without purification. All other chemicals were of analytical grade or purified by standard procedures.

Synthesis of cationic and anionic hydroxyethyl starches

Cationic hydroxyethyl starch (CHES) (Fig. 1a) was prepared by the reaction of HES with GTAC in the presence of sodium hydroxide at 45 °C for 24 h. The molar ratio of the hydroxyethyl starch: epoxy compound: NaOH was 1 : 0.35 : 0.04 aiming to obtain CHES with a degree of substitution (DS) of 0.33. The reaction mixture was prepared as follows: a concentrated solution of GTAC, an aqueous solution of 2M NaOH and H₂O were thoroughly mixed, then starch was added, the reaction mixture homogenized and left for one day at 45 °C. After the reaction, the CHES was purified by Soxhlet extraction with methanol for 16 h. The nitrogen content in the CHES was estimated by the Kjeldahl method. The degree of substitution (DS) of the modified polymer was calculated from the nitrogen content:

$$DS = \frac{(162 + a) \times N}{1400 - 151.5 \times N}, \quad (1)$$

where N is the nitrogen content estimated by the Kjeldahl method (%), 162 is the molecular weight of anhydroglucoside unit, a is the content of hydroxyethyl substituent equal to 3.22 for Kollotex 1250 and 151.5 is the molecular weight of GTAC.

DS of CHES was found to be 0.33 and the prepared cationic starch was denominated as CHES_{DS=0.33}.

Anionic hydroxyethyl starch (AHES) (Fig. 1b) was prepared by the reaction of HES with monochloroacetic acid in the presence of sodium hydroxide at 55 °C for 5 h. The molar ratio of the HES: monochloroacetic acid: NaOH was 1 : 1 : 2.4. After the reaction, the AHES was dialyzed against pure water for several weeks using a cellulose acetate membrane. DS of AHES was calculated from the carboxymethyl group content that was established by titration with an aqueous PDADMACl solution using eosine as the indicator:

$$DS = \frac{(162 + a) \times CM}{5800 - 58 \times CM}, \quad (2)$$

where CM is the carboxymethyl group content estimated by the titration method (%), 162 is the molecular weight of anhydroglucoside unit, a is the content of hydroxyethyl substituent equal to 3.22 for Kollotex 1250 and 58 is the molecular weight of carboxymethyl unit.

DS of AHES was found to be 0.26 and the prepared anionic starch was denominated as AHES_{DS=0.26}.

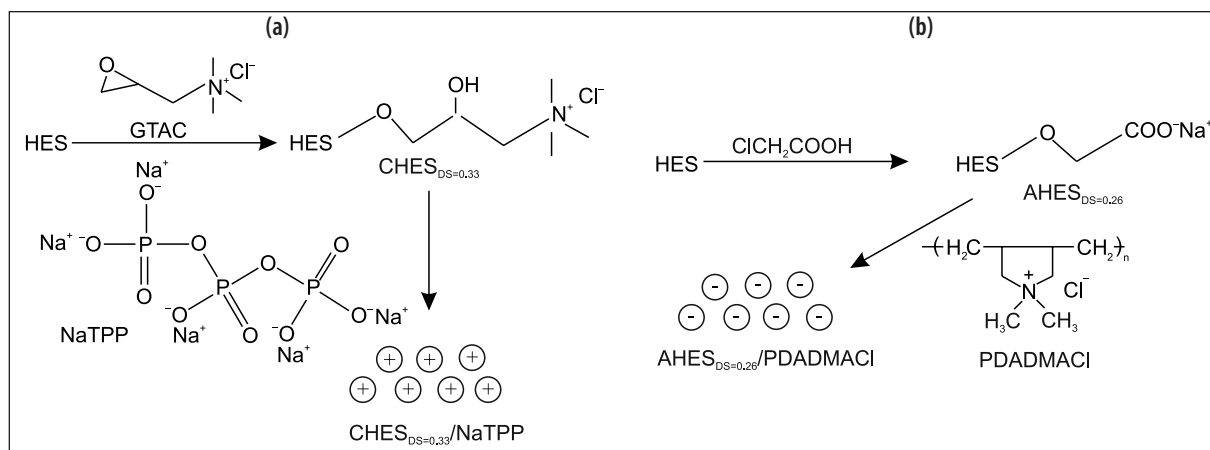


Fig. 1. Synthesis scheme for preparation of: (a) – cationic hydroxyethyl starch (CHES) and cationic starch nanoparticles (CHES/NaTPP); (b) – anionic hydroxyethyl starch (AHES) and anionic starch nanoparticles (AHES/PDADMACI)

Preparation of starch nanoparticles by polyelectrolyte complex formation

Cationic starch nanoparticles were prepared by ionotropic gelation between CHES and NaTPP as is shown in Fig. 1a. Meanwhile, the anionic starch nanoparticles were prepared by mixing the aqueous solutions of AHES and PDADMACI (see Fig. 1b). Preliminary experiments were done in order to determine the production zone of nanoparticle formation. For this purpose CHES or AHES were dissolved in water at various concentrations: 10, 8, 6, 4; 2; 1 g/l. Then, NaTPP and PDADMACI aqueous solutions were prepared analogically to modified starch solutions. Finally, the variable volume of the NaTPP or PDADMACI solution was added dropwise, at the rate of 1 ml/min, to the

CHES or AHES solution, respectively, under vigorous stirring at room temperature and pH 7. Then samples were visually analyzed and three different systems were identified: a clear solution, an opalescent suspension, and aggregates. The zones of the opalescent suspension formation for both CHES_{DS=0.33} and AHES_{DS=0.26}, which should correspond to a dispersion of very small particles, are illustrated in Fig. 2a and 2b as functions of CHES or AHES and the counterion concentration in the final sample. This opalescent dispersion zone was further investigated as a zone of nanoparticle formation. Nanoparticles were concentrated by centrifugation at 10 000 g for 3–4 hours. The supernatants were discarded and nanoparticles re-suspended in water and centrifuged again several times, separated and,

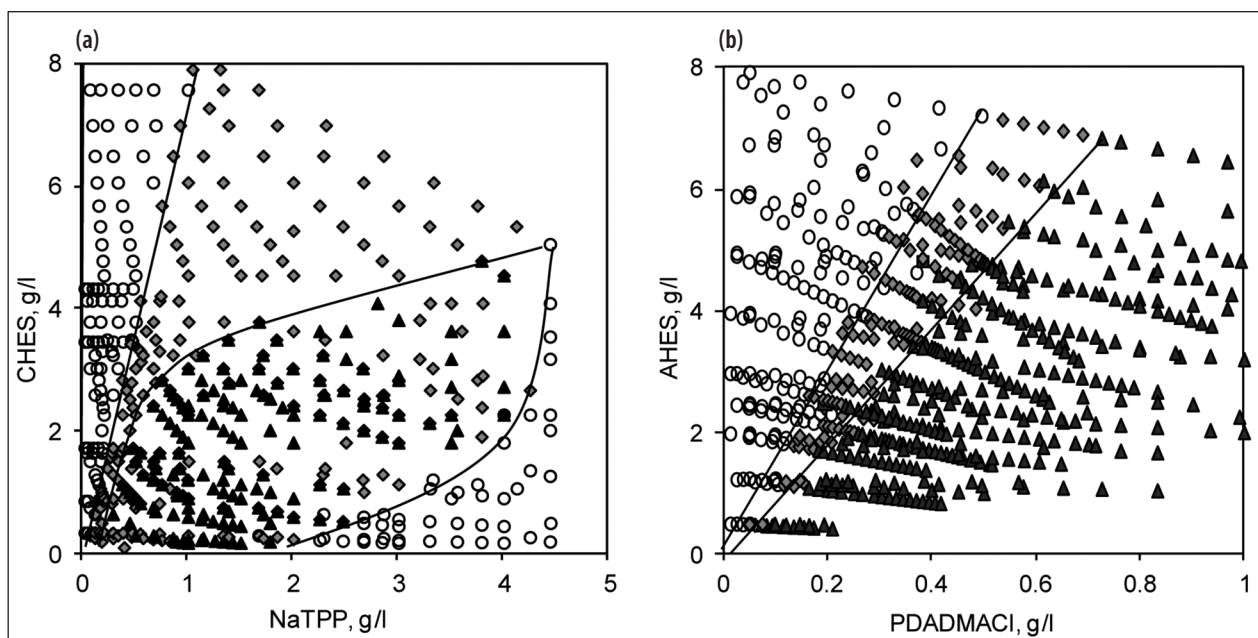


Fig. 2. Polyelectrolyte complex formation conditions for CHES_{DS=0.33} (a) and AHES_{DS=0.26} (b): circle – clear solution; diamond – opalescent dispersion; triangle – aggregated particles. NaTPP was used as a polyanion in the case of CHES and PDADMACI was used as a polycation in the case of AHES

finally, lyophilized. The yield of nanoparticles was determined by comparing the expected mass of the product with the actual mass of obtained nanoparticles, giving the percentage figure.

Characterization of starch nanoparticles

The CHES concentration in the cationic nanoparticles and the PDADMACl concentration in the anionic nanoparticles was calculated by measuring nitrogen content in the samples using a CE-440 Elemental Analyzer (Exeter Analytical Inc.). Alternatively, the NaTPP concentration in the cationic nanoparticles was determined by assessing phosphorus content spectrophotometrically after burning and reaction with ammonium molybdate. The standard sample of KH_2PO_4 was used as a reference compound.

Particle size distribution of starch nanoparticles was determined using the Zetasizer Nano-S (Malvern Instruments) in an aqueous solution at pH 7. The analysis was performed at a scattering angle of 173° at a temperature of 20°C . 4 measurements were performed for each sample and an average particle diameter was calculated. Zeta potential measurements were performed using an electroacoustic spectrometer DT-300 (Dispersion Technology Inc.) in an aqueous solution at pH 7 and at a temperature of 20°C . For SEM analysis, nanoparticles were mounted on metal stubs using an adhesive tape, gold coated under vacuum and examined on a Quanta 200 FEG (FEI Ltd). AFM measurements of the particles were performed on a NT-206 (Microtestmachines Co.) by using the contact scanning regime.

The stability of aqueous nanoparticle dispersions was assessed by monitoring the optical density of the samples at the 500 nm wavelength at temperatures of 4 and 20°C . The stability was estimated as the onset time of the decrease in optical density which accompanies full phase separation and precipitation of the particles.

RESULTS AND DISCUSSION

Formation of cationic and anionic starch nanoparticles

Cationic starch derivative containing quaternary ammonium groups (CHES) with high degree of substitution were prepared and used in the polyelectrolyte complex formation studies in order to obtain nanosized positively charged starch particles

(see Fig. 1a). Given that CHES is a cationic polyelectrolyte, our study was based on inducing its gelation by controlling its interaction with counterion NaTPP. In this sense, it is obvious that electrostatic interaction between the anionic phosphate groups of NaTPP and the positively charged quaternary ammonium groups of CHES would be responsible for the success of complex formation. Primary assays were done in order to establish the range of polyelectrolytes concentration to produce nanoparticles with an appropriate submicron size. From the results presented in Fig. 2a it could be seen that the formation of nanoparticles is possible in the case of mixing of some specific amounts of CHES and NaTPP. Further, the factors affecting the characteristics of CHES/NaTPP nanoparticles were studied. Accordingly, the nanoparticle dispersions with varying concentration and stoichiometry of the components were obtained and their constitution alongside with the size and charge of particles were assessed (Table 1).

The molar content of cationic starch derivative in the initial mixture and final particles was calculated taking into account the molecular weight of the repeat unit of CHES. Meanwhile, the molar content of polysalt was evaluated by using the molecular weight of NaTPP. The total initial concentration of the components in the solution was varied from 0.93 to 9.53 g/l to obtain $\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ nanoparticles. By keeping the molar ratio of the components in the mixture at $[\text{CHES}]/[\text{NaTPP}] \approx 2.6/1$ approx. 65% yield of $\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ particles was obtained. The limited yield of PEC nanoparticles could be related to equilibrium between insoluble PEC, soluble PEC and non-reacted individual polyelectrolyte molecules in aqueous dispersion. The electrostatic interaction between the anionic phosphate groups of NaTPP and the positively charged quaternary ammonium groups of CHES might be also suppressed because of limited access of the cationic groups due to their uneven distribution in CHES macromolecules. Thus, the extent of PEC formation between individual components might be also reduced. NaTPP is the sodium salt of the polyphosphate penta-anion, however, it is rather unlikely that all five anionic groups would be taking a part in the complex formation at the same time. The molar composition of the components in the obtained nanoparticles was similar to that in the initial mixture.

Table 1. Preparation conditions, composition, particle size and zeta potential characteristics of $\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ nanoparticles

Sample	CHES, mmol/l	NaTPP, mmol/l	Total concentration of components in the solution, g/l	Particle yield, %	Molar ratio of components in starch nanoparticles		Average particle diameter, nm	Zeta potential, mV
					CHES	NaTPP		
$\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ -1	1.18	0.46	0.93	64	2.12	1	127 ± 22	$+10.4 \pm 0.31$
$\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ -2	2.37	0.92	1.86	65	2.12	1	145 ± 15	$+14.4 \pm 0.52$
$\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ -3	4.72	1.82	3.70	66	2.18	1	139 ± 22	$+14.49 \pm 0.48$
$\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ -4	7.58	2.91	5.94	66	2.14	1	136 ± 12	$+12.26 \pm 0.35$
$\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ -5	7.55	5.44	6.85	44	1.20	1	87 ± 11	$+8.45 \pm 0.25$
$\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ -6	7.45	9.05	9.40	27	0.82	1	85 ± 11	$+6.79 \pm 0.16$
$\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ -7	7.46	12.88	9.53	9	0.53	1	75 ± 10	$+4.34 \pm 0.20$

Table 2. Preparation conditions, composition, particle size and zeta potential characteristics of AHES_{DS=0.26}/PDADMACI nanoparticles

Sample	AHES, mmol/l	PDADMACI, mmol/l	Total concentration of components in the solution, g/l	Particle yield, %	Molar ratio of components in starch nanoparticles		Average particle diameter, nm	Zeta potential, mV
					AHES	PDADMACI		
AHES _{DS=0.26} /PDADMACI-1	2.76	0.97	2.03	3	1.86	1	345 ± 4	-10.21 ± 0.18
AHES _{DS=0.26} /PDADMACI-2	4.03	1.36	2.96	4	1.95	1	291 ± 1	-7.34 ± 0.03
AHES _{DS=0.26} /PDADMACI-3	6.38	2.06	4.66	8	2.10	1	372 ± 12	-4.57 ± 0.01
AHES _{DS=0.26} /PDADMACI-4	7.44	2.43	5.45	12	1.99	1	482 ± 31	-4.67 ± 0.01
AHES _{DS=0.26} /PDADMACI-5	8.47	2.49	6.16	22	1.93	1	327 ± 14	-4.01 ± 0.01
AHES _{DS=0.26} /PDADMACI-6	8.43	2.80	6.18	41	1.87	1	427 ± 11	-3.82 ± 0.01
AHES _{DS=0.26} /PDADMACI-7	8.38	3.13	6.21	50	1.70	1	910 ± 15	-3.75 ± 0.01

Alternatively, anionic starch derivative containing carboxyl groups (AHES) with high degree of substitution was prepared and used in the polyelectrolyte complex formation studies aiming to obtain negatively charged starch particles (see Fig. 1b). PDADMACI was chosen as a cationic polyelectrolyte in this case. The electrostatic interaction between cationic quaternary ammonium groups of PDADMACI and the negatively charged carboxyl groups of AHES would be important for the complex formation. The range of polyelectrolytes concentration to produce the particles with an appropriate submicron size was established. From the results presented in Fig. 2b it could be seen that the formation of nanoparticles is possible in the case of mixing of some specific amounts of AHES and PDADMACI. It should be noted that the window of AHES nanoparticle formation is narrower compared to that of CHES and lower concentration of counterion (PDADMACI) should be used in order to obtain stable starch particle dispersion. The factors affecting the characteristics of AHES/PDADMACI nanoparticles were also studied. Thus, the nanoparticle dispersions with varying concentration and stoichiometry of the components were obtained and their constitution, size and charge of the particles were evaluated (Table 2).

The molar content of anionic starch derivative in the initial mixture and final particles was calculated by taken into account molecular weight of the repeat unit of AHES. The total initial concentration of the components in the solution was varied from 2.03 to 6.21 g/l. By having the molar ratio of the components [AHES]/[PDADMACI] in the mixture from 3.4/1 to 2.7/1 approx. 20–50% yield of AHES/PDADMACI particles was obtained. Quite low particle yield (see samples 1–4 in Table 2) was obtained when the total concentration of the components in solution was lower than 6 g/l. The concentration of AHES in the obtained nanoparticles was lower compared to that in the initial mixture. The limited yield of PEC nanoparticles could be related to equilibrium between insoluble PEC, soluble PEC and non-reacted anionic polyelectrolyte molecules in aqueous dispersion as it was mentioned above. It is also obvious that PDADMACI macromolecules are more “active” in the complex formation. Consequently, higher content of this component is present in starch nanoparticles compared to that in initial preparations.

Characterization of starch nanoparticles

Zeta potential measurements confirmed the formation of positively and negatively charged starch particles. Positive values of zeta potential were characteristic of cationic CHES_{DS=0.33}/NaTPP nanoparticles. Their zeta potential was modulated between +4 mV and +14 mV by varying polycation/polyanion ratio. By increasing the concentration of NaTPP in the nanoparticles (see samples No. 4–7 in Table 1) still positively charged starch particles were obtained. Thus, one can deduce that cationic groups of CHES are placed mainly on the surface of the nanoparticles. By having an excess of polyanion (samples No. 6 and 7 in Table 1) lower zeta potential values were measured indicating higher degree of incorporation of negatively charged NaTPP in the nanoparticles. It is worth to notice that particle yield for CHES_{DS=0.33}/NaTPP was also reducing with the increasing concentration of NaTPP in the initial mixture. Meanwhile, negative values of zeta potential were measured for AHES_{DS=0.26}/PDADMACI nanoparticles. Their zeta potential was modulated between -3 mV and -11 mV by varying polyanion/polycation ratio. By increas-

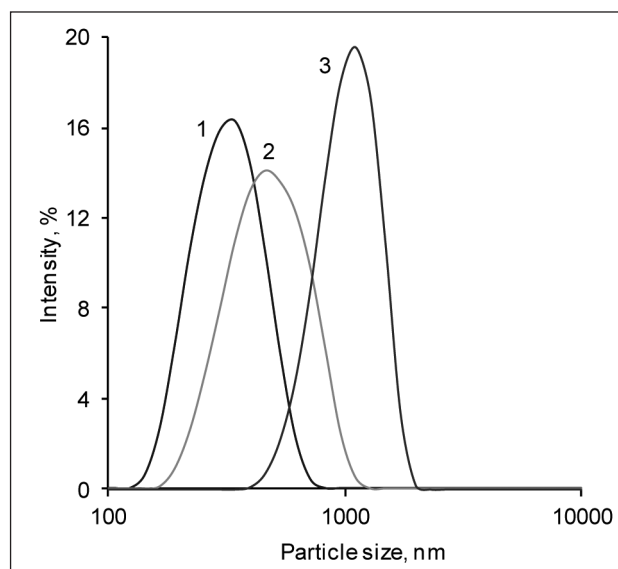


Fig. 3. Size distribution by volume diagrams of AHES_{DS=0.26}/PDADMACI nanoparticles. Molar ratio AHES_{DS=0.26}/PDADMACI in the solution: 1 – 3.4 : 1; 2 – 3.02 : 1; 3 – 2.68 : 1. Total concentration of components in the solution is 6.16–6.21 g/l

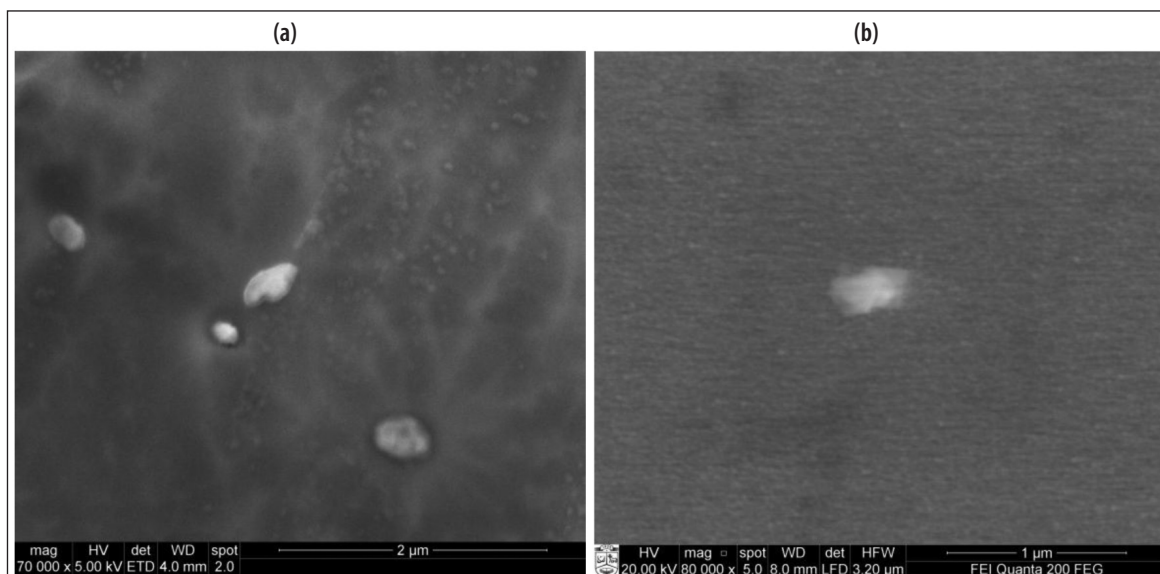


Fig. 4. SEM micrographs of $\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ (a) and $\text{AHES}_{\text{DS}=0.26}/\text{PDADMACI}$ (b) nanoparticles. Magnification $\times 70,000$ and $\times 80,000$, respectively

ing the concentration of PDADMACI in the samples (see samples No. 4–7 in Table 2), the aggregation of the particles was observed and slightly lower zeta potential values were obtained. The particle yield for $\text{AHES}_{\text{DS}=0.26}/\text{PDADMACI}$ was increasing with the increasing concentration of PDADMACI in nanoparticle preparations.

The formation of nanosized particles was revealed by light scattering, SEM and AFM measurements. Size distribution by volume diagrams showed that only one fraction was characteristic of $\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ particle dispersion and the particles with an average diameter of about 75–145 nm were obtained (see Table 1). The particle size was reducing by the increasing concentration of NaTPP in the nanoparticles (see samples No. 4–7 in Table 1). The average particle diameter was reducing from 136 to 75 nm for $\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ samples. Presumably, more compact and, consequently, smaller particles were formed by increasing the number of NaTPP molecules and reducing the content of bulky CHES molecules in PEC. Size distribution by volume diagrams (Fig. 3) show that only one fraction was characteristic of anionic starch particle dispersion and the particles with an average diameter of about 290–910 nm were obtained (see Table 2). Furthermore, it can be noted that the particle size was dramatically increasing by the increasing concentration of PDADMACI in the nanoparticles (see Table 2 and Fig. 3). This finding is in good agreement with the previous data and confirm the formation of aggregates of PEC.

Meanwhile, SEM and AFM images (see Figs. 4 and 5) revealed well-defined spheroidal nano-sized starch particles. In summary, it can be concluded that aqueous dispersions of charged starch nanoparticles could be obtained and the positive or negative charge of the particles surface can be also modulated from higher to lower values by changing the ratio of the components.

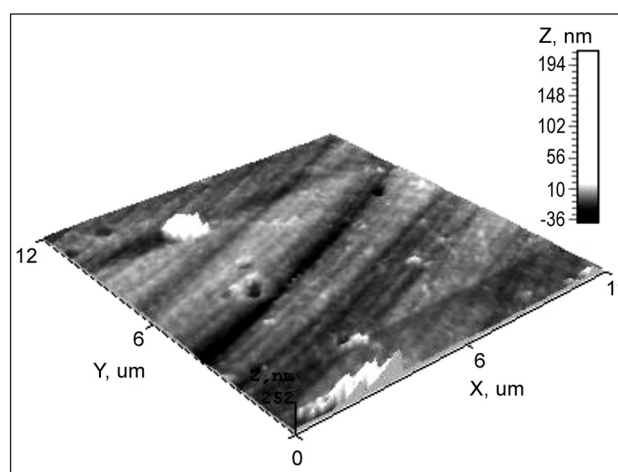


Fig. 5. AFM image of $\text{AHES}_{\text{DS}=0.26}/\text{PDADMACI}$ nanoparticles

Stability of aqueous starch nanoparticle dispersions

The stability of aqueous anionic and cationic starch nanoparticle dispersions was assessed by monitoring the changes in turbidity of the samples at 4 °C and at the room temperature (Table 3).

The turbidity of the samples was decreasing dramatically when full phase separation and precipitation of the particles in the solution was taking place. It was found that $\text{AHES}_{\text{DS}=0.26}/\text{PDADMACI}$ nanoparticle dispersions were stable for 3–8 days at the room temperature and the stability at 4 °C was 6–10 days. The stability of the dispersions was changing by varying the polyanion / polycation ratio in samples. With the increase of content of PDADMACI in the PEC particles (samples No 5–7 in Table 3), they tend to aggregate and to precipitate from the solution faster. At the same time the observation of $\text{CHES}_{\text{DS}=0.33}/\text{NaTPP}$ samples revealed that nanoparticle dispersions were stable for 2–12 days at the

Table 3. Stability of aqueous CHES_{DS=0.33}/NaTPP and AHES_{DS=0.26}/PDADMACI nanoparticle dispersions at different temperatures

Sample	Stability of aqueous nanoparticle dispersion, hours	
	4 °C	20 °C
CHES _{DS=0.33} /NaTPP-1	72	48
CHES _{DS=0.33} /NaTPP-2	120	72
CHES _{DS=0.33} /NaTPP-3	146	96
CHES _{DS=0.33} /NaTPP-4	288	168
CHES _{DS=0.33} /NaTPP-5	528	288
CHES _{DS=0.33} /NaTPP-6	480	216
CHES _{DS=0.33} /NaTPP-7	432	168
AHES _{DS=0.26} /PDADMACI-1	192	72
AHES _{DS=0.26} /PDADMACI-2	240	192
AHES _{DS=0.26} /PDADMACI-3	192	96
AHES _{DS=0.26} /PDADMACI-4	192	96
AHES _{DS=0.26} /PDADMACI-5	240	192
AHES _{DS=0.26} /PDADMACI-6	185	152
AHES _{DS=0.26} /PDADMACI-7	146	120

room temperature and the stability at 4 °C was 3–22 days. By increasing the amount of NaTPP in the PEC preparations (samples No. 5–7 in Table 3), the stability of the dispersions was reducing at both temperatures. It should be noted that the stability of the dispersions was also lower than the total concentration of the macromolecules in the preparations lower than 2 g/l.

CONCLUSIONS

Cationic starch nanoparticles were successfully produced in aqueous media by forming PEC between cationic quaternary ammonium substituted starch and anionic sodium tripolyphosphate. Meanwhile, anionic starch nanoparticles were obtained by aqueous polyelectrolyte complex formation between anionic hydroxyethylstarch and cationic poly(diallyldimethylammonium chloride). The formation of spheroidal nanosized particles was verified by dynamic light scattering, scanning electron microscopy and atomic force microscopy measurements. It was found that stable aqueous dispersions of starch nanoparticles could be obtained and the charge of the particles surface can be modulated from high to low values by changing the ratio of the oppositely charged components.

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Ramunė Rutkaitė, Joana Bendoraitienė, Rima Klimavičiūtė,
Edita Lekniūtė, Indrė Narmontaitė, Virginija Šinkūnaitė

KRŪVĮ TURINČIOS KRAKMOLO NANODALELĖS IŠ POLIELEKTROLITINIŲ KOMPLEKSŲ

S a n t r a u k a

Vandenyje sudarius katijoninio hidroksietilkrakmolo ir natrio tripolifosfato arba anijoninio hidroksietilkrakmolo ir poli(dialildimetilamonio chlorido) polielektrolitinius kompleksus gautos katijoninių arba anijoninių grupių perteklių turinčios krakmolo nanodalelės, kurių dydis patvirtintas šviesos sklaidos, atominių jėgų mikroskopijos bei skenuojančios elektroninės mikroskopijos tyrimais. Keičiant polikatijono ir polianijono molekulių santykį tirpale gautos skirtingą ketvirtinio amoniogrūpių kiekį turinčios krakmolo nanodalelės, kurių dzeta potencialas keitėsi nuo +4 mV iki +14 mV, arba skirtingą karboksigrūpių kiekį turinčios krakmolo nanodalelės, kurių dzeta potencialas keitėsi nuo –3 mV iki –11 mV. Vandeninės katijoninių grupių turinčių krakmolo nanodalelių dispersijos kambario temperatūroje buvo stabilios – nuo 2 iki 12 dienų, o –4 °C temperatūroje – nuo 3 iki 22 dienų. Vandeninės anijoninių grupių turinčių krakmolo nanodalelių dispersijos nurodytose temperatūrose buvo stabilios atitinkamai nuo 3 iki 8 dienų ir nuo 6 iki 10 dienų.