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Water-soluble polyelectrolyte complexes formed by poly(diallyldimethylammonium chloride) and poly(sodium acrylate-*co*-sodium 2-acrylamido-2-methyl-1-propanesulphonate)-*graft*-poly(*N*,*N*-dimethylacrylamide) copolymers

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Abstract

The formation of polyelectrolyte complexes (PECs) between the cationic homopolymer poly(diallyldimethylammonium chloride) (PDADMAC) and the anionic graft copolymers poly(sodium acrylate-*co*-sodium 2-acrylamido-2-methyl-1-propanesulphonate)-*graft*-poly(*N*,*N*-dimethylacrylamide) (P(NaA-*co*-NaAMPS)-*g*-PDMAM) was studied in aqueous solution in comparison with the PECs formed between PDADMAC and the graft copolymer backbone poly(sodium acrylate-*co*-sodium 2-acrylamido-2-methyl-1-propanesulphonate). The turbidimetric study of the PECs formed revealed that associative phase separation is prevented when the anionic polyelectrolyte is grafted with the nonionic hydrophilic poly(*N*,*N*-dimethylacrylamide) side chains. The PECs are formed through a charge neutralisation process and they adopt a compact structure, as shown by conductivity and viscometry measurements respectively. The water-insoluble PEC core seems to be stabilised by a hydrophilic PDMAM corona, leading to the formation of nanoparticles with a hydrodynamic radius of some decades of nanometers as determined by quasi-elastic light scattering measurements.

Keywords: Water-soluble polyelectrolyte complexes; Associative phase separation; Core-corona nanoparticles

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1. Introduction

Polyelectrolyte complexes (PECs), formed by the electrostatic interactions between oppositely charged macromolecules [1], are of a permanently growing significance, due to their high potential for possible applications. Among other applications, they have been proposed for separation or purification processes, for drug delivery systems, for the design of membranes with special separation abilities or for microencapsulation. [2–7].

Although rare exceptions from the 1:1 stoichiometry have been reported in some cases [8,9], in general, associative phase separation leads to the formation of insoluble stoichiometric (1:1) polyelectrolyte complexes (SPECs) [10]. However, water-soluble aggregates are formed by mixing non-stoichiometric amounts of polyanions and polycations, corresponding to the formation of soluble non-stoichiometric polyelectrolyte complexes (NPECs), that have a net charge of the same sign as this of the component in excess [11–17]. A NPEC can be considered as a peculiar block copolymer comprised by water-insoluble blocks, consisted by neutralised polysalts, and soluble charged blocks, comprised by the polyelectrolyte in excess [13].

The use of block ionogenic copolymers instead of charged homopolymers, led to a new class of water-soluble stoichiometric PECs. Covalent binding of both the polyanion and polycation [18,19] or of one of them [20,21] to a nonionic hydrophilic block, such as poly(ethylene glycol) (PEG), results in the formation of a finally water-soluble

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product, comprised by a water-insoluble core (the insoluble PEC) and surrounded and stabilised by a hydrophilic PEG corona. Such core-shell supramolecular assemblies formed by mixing poly(ethylene oxide)-*block*-poly(α,β-aspartic acid) and poly(ethylene oxide)-*block*-poly(L-lysine) diblocks have been shown to present chain length recognition properties [22]. Due to their composition of a hydrophobic insoluble part and a hydrophilic soluble one, these interpolymer complexes self-associate in aqueous solution in supramolecular assemblies of some decades of nanometers in size [22]. Recently, the reversible formation of water-soluble complexes between sodium poly(4-styrenesulfonate) and a poly(2-vinylpyridinium)-*block*-poly(ethyleneoxide) copolymer at low pH has been reported by Jérôme et al. [23]. Moreover, for the supramolecular assemblies formed at pH $= 3$ in dilute solutions, various structures have been observed, extending from spherical to rodlike micelles and vesicles [24]. If the second block of the block ionomers is organosoluble, the formation of vesicular structures based on PECs can also occur in organic solvent, as it has been reported very recently [25]. Finally, the formation of water-soluble PECs between block ionomers and enzymes [26,27] or oligonucleotides [28–33] has been proposed for potential applications in enzyme entrapment or gene therapy, respectively.

On the contrary to block ionomers, studies on water-soluble PECs involving polyelectrolytes of a comb-type structure are very rare [34], although the basic concept behind the possible water-solubility of such complexes remains similar. Thus, the molecular design of such comb-type copolymers consisting of various polyelectrolyte backbones and water-soluble nonionic graft chains provides a novel flexible strategy to prepare a large variety of novel water-soluble PECs. Moreover, the features of the complexes can be tuned at will by choosing the copolymer components (charged backbone and nonionic side chains) among the vast variety of water-soluble polymers with no essential synthetic restrictions.

We have recently synthesised an anionically charged graft copolymer, poly(acrylic acid-*co*-2-acrylamido-2-methyl-1- propanesulphonic acid)-*g*- poly(*N*,*N*-dimethylacrylamide), by grafting poly(*N*,*N*-dimethylacrylamide) (PDMAM) chains onto an acrylic acid-*co*-2-acrylamido-2-methylpropane sulphonic acid copolymer P(AA-*co*-AMPSA) backbone [35]. In that work, we investigated the formation of hydrogen-bonding interpolymer complexes between the PDMAM side chains and a weak polyacid, namely poly(acrylic acid) (PAA), at low pH. It was shown that the compact hydrogen-bonding interpolymer complexes formed are water-soluble due to the copolymer backbone with strongly charged sulphonate groups.

In the present work we use such graft copolymers in their sodium salt form, poly(sodium acrylate-*co*-sodium 2-acrylamido-2-methyl-1-propanesulphonate)-*graft*-poly(*N*,*N*-dimethylacrylamide) (P(NaA-*co*-NaAMPS)-*g*-PDMAM), in order to study the PECs formed between their anionic backbone and a polycation, namely poly(diallyldimethylammonium chloride) (PDADMAC), both shown in Scheme 1. It is shown that water-soluble SPECs are formed. In this case, the neutral PDMAM side chains of the graft copolymer play the role of the hydrophilic constituent, serving to keep in solution the aggregates formed due to the attractive Coulombic interactions between the anionic backbone of the graft copolymer and the cationic homopolymer.

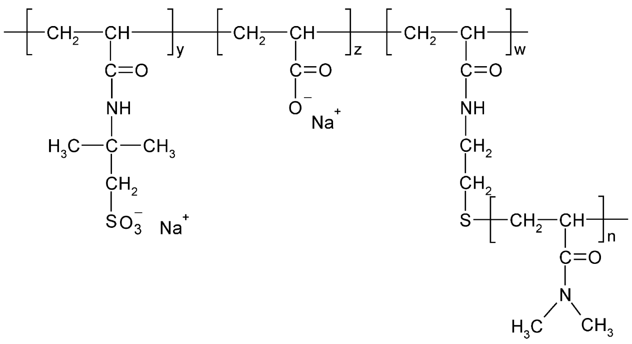
2. Experimental

2.1. Materials

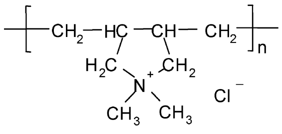
The PDADMAC sample used was a 20 wt% solution in water (Aldrich). It was purified with an ultrafiltration Pellicon system equipped with a Millipore tangential flow filter membrane with a molecular weight cut off (MWCO) = 100 kD and freeze dried. Its molecular weight was viscometrically determined in 0.5 M NaCl at 25 °C through the Mark–Houwink–Sacurada equation, $[\eta](\text{ml} \times \text{g}^{-1}) = 6.1 \times 10^{-3}\ \text{M}^{0.82}$ [36], and was found equal to 1.3×10^5.

The monomers, acrylic acid (AA), 2-acrylamido-2-methyl-1-propanesulphonic acid (AMPSA), *N*,*N*-dimethylacrylamide (DMAM) were purchased from Aldrich. Ammonium persulphate (APS, Serva), potassium metabisulphite (KBS, Aldrich), 2-aminoethanethiol hydrochloride (AET, Aldrich) and 1-(3-(dimethylamino) propyl)-3-ethylcarbodiimide hydrochloride (EDC, Aldrich) were used for the synthesis of the graft copolymers.

Water was purified by means of a Seralpur Pro 90C



Graft copolymers P(NaA-co-NaAMPS)-g-PDMAMx



PDADMAC

Scheme 1.

apparatus combined with an ultrafiltration USF Elga laboratory unit.

2.2. Polymer synthesis and characterisation

Amine-terminated PDMAM was synthesised by free radical polymerisation of DMAM in water at 30 °C for 6 h using the redox couple APS and AET as initiator and chain transfer agent, respectively. The polymer was purified by dialysis against water in a tubing with MWCO 12000 (Sigma) and then freeze-dried. Its weight average molecular weight was determined viscometrically in methanol at 25 °C by means of the equation $[\eta] = 1.75 \times 10^{-2} M_v^{0.68}$ [37] and was found equal to 3.1×10^4. Its number average molecular weight was determined by an acid–base titration of the amine end groups and was found equal to 1.6×10^4.

A copolymer of AA and AMPSA, was prepared by free radical copolymerisation of the two monomers dissolved in water in a 1:5 mole ratio, respectively, after a partial neutralisation (85–90% mole) with NaOH at pH ~ 5–6, at 30 °C for 6 h, using the redox couple APS/KBS. The product was obtained in its sodium salt form, poly(sodium acrylate-*co*-sodium 2-acrylamido-2-methyl-1-propanesulphonate) (P(NaA-*co*-NaAMPS)), after being fully neutralised with NaOH (pH = 11), ultrafiltrated and freeze-dried. Its composition was determined by an acid–base titration and it was found to contain 11 mol% of acrylate units.

The graft copolymers P(NaA-*co*-NaAMPS)-*g*-PDMAMx, where *x* is the weight percentage feed composition in PDMAM, were synthesised by means of a coupling reaction between the P(NaA-*co*-NaAMPS) copolymer and the amine-functionalised PDMAM. In a 5% aqueous solution of the polymer mixture, a fivefold excess of the coupling agent, EDC, was added and let under stirring for 6 h at room temperature. Addition of EDC was repeated for a second time. The products obtained were purified by water with the Pellicon system and freeze-dried. The completion of the grafting reaction was confirmed by size exclusion chromatography, by means of a Waters system equipped with two Shodex OH-pak columns, B804 and B805. The water content of the products was estimated at ~5%, after drying the samples in high vacuum at 80 °C.

Table 1 summarises the polymers synthesised or used in the present study. The molar mass of all the products was determined by static light scattering measurements of aqueous 0.1 M NaCl polymer solutions, while the PDMAM content of the graft products was determined by elemental analysis.

2.3. Techniques

2.3.1. Turbidimetry

The change in transmittance at 490 nm of dilute aqueous polymer mixtures was monitored as a function of the polymer mixture composition at room temperature by means of a Hitachi spectrophotometer model U 2001.

2.3.2. Viscometry

Reduced viscosity studies and intrinsic viscosity determination were carried out with an automated viscosity measuring system (Schott-Geräte AVS 300, Germany) equipped with an Ubbelohde-type viscometer (Capillary No I, Capillary diameter 0.63 mm), at 25 ± 0.02 °C.

2.3.3. Conductimetry

Conductivity measurements were performed with a Metrohm 660 conductometer (Switzerland). The cell constant was $0.79\ \mathrm{cm}^{-1}$.

2.3.4. Quasi-elastic light scattering

The intensity time correlation functions $G_2(t)$ of the polarised light scattering were measured at $\theta = 90°$ at 25 °C with a full multiple tau digital correlator (ALV-5000/FAST) with 280 channels. The excitation light source was an argon ion laser (Spectra Physics 2020) operating at 488 nm, with a stabilised power of 30 mW. The incident beam was polarised vertically with respect to the scattering plane using a Glan polariser. The scattered light from the sample was collected through a Glan-Thomson polariser (Halle, Berlin) with an extinction coefficient better than 10^{-7}. The samples used were dust-free and optically homogeneous [38]. From the dependence of $G_2(t)$ on the scattering vector, the diffusion coefficient D of the particles was determined and their hydrodynamic radius, R_H, was obtained [19,23], using the Stokes–Einstein equation.

2.3.5. Preparation of the solutions of the polymer mixtures

The parent solutions of PDADMAC, the backbone and the graft copolymers at the desired concentrations were prepared by dissolution of the polymers in water under gentle agitation for 24 h. The mixtures were prepared by adding the solution of PDADMAC into the solution of the negatively charged polymer. Then the solutions of the mixtures were let under agitation for 24 h before performing the measurements. The influence of the order of mixing was checked for some samples. With the exception of mixtures of PDADMAC with the backbone P(NaA-*co*-NaAMPS), the results were quite reproducible regardless of the order of mixing.

3. Results and discussion

Fig. 1 shows the turbidimetric behaviour of the dilute aqueous solutions of polymer mixtures of PDADMAC with the backbone P(NaA-*co*-NaAMPS) or the three graft products, P(NaA-*co*-NaAMPS)-*g*-PDMAMx, as a function of their composition, expressed by their weight fraction in PDADMAC, W_{PDADMAC}. The total polymer concentration of the solutions is constant and equals 1 g/l. As shown, upon mixing the solution of the positively charged PDADMAC with that of the negatively charged P(NaA-*co*-NaAMPS) copolymer, the solutions turn strongly turbid and the

Table 1
The polymers synthesised and used in the present study

Polymer	Feed composition	Composition	Intrinsic viscosity (ml g^{-1})	$M_v \times 10^5$	$M_w \times 10^5$
PDADMAC	–	–	95^{c}	1.3	–
PDMAM	–	–	19.9^{d}	0.31	–
P(NaA-*co*-NaAMPS)	80 mol% NaAMPS	89 mol% NaAMPS^{a}	42.5^{c}	–	2.9^{e}
P(NaA-*co*-NaAMPS)-*g*-PDMAM25	25 wt% PDMAM	20 wt% PDMAM^{b}	47.5^{c}	–	3.6^{e}
P(NaA-*co*-NaAMPS)-*g*-PDMAM50	50 wt% PDMAM	48 wt% PDMAM^{b}	51^{c}	–	5.4^{e}
P(NaA-*co*-NaAMPS)-*g*-PDMAM75	75 wt% PDMAM	74 wt% PDMAM^{b}	67^{c}	–	9.9^{e}

[a] Determined by an acid–base titration.
[b] Elemental analysis results.
[c] In 0.5 M NaCl at 25 °C.
[d] In CH_3OH at 25 °C.
[e] Static light scattering results.

transmittance decreases sharply, indicating that the polyelectrolyte complex formed separates out from water, as expected. The minimum transmittance is observed when the composition of the mixtures approaches the value $W_{\mathrm{PDADMAC}} = 0.43$. In fact, this value corresponds to the charge neutralisation composition, as it can be estimated from the chemical structure of the two polymers (Table 1). When PDADMAC is mixed with the graft copolymers the solutions are much more transparent. In fact, when the copolymer P(NaA-*co*-NaAMPS)-*g*-PDMAM25 is used, containing only 25% of the neutral hydrophilic PDMAM chains, the lower transmittance value is around 72%, whereas for the PDMAM-richer graft copolymers the transmittance is higher than 90%. These results show that, when the anionic copolymer P(NaA-*co*-NaAMPS) is decorated with hydrophilic nonionic polymer chains like PDMAM, the PECs possibly formed with the oppositely charged PDADMAC remain soluble in water and not present any macrophase separation. Apparently, the neutral hydrophilic PDMAM side chains stabilise sterically the water-insoluble PECs formed, inhibiting their further aggregation to larger particles and their final precipitation. Therefore, the size of the particles formed is probably smaller and decreasing as the graft copolymers are getting richer in PDMAM chains.

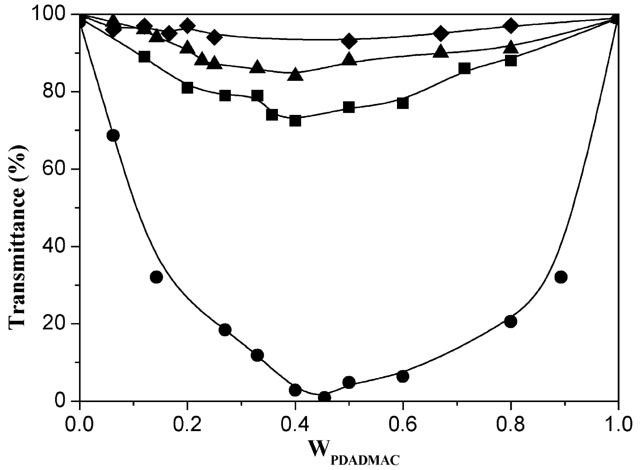


Fig. 1. Transmittance vs. the PDADMAC weight fraction, W_{PDADMAC}, for the polyelectrolyte mixtures P(NaA-*co*-NaAMPS)/PDADMAC, (●); P(NaA-*co*-NaAMPS)-*g*-PDMAM25/PDADMAC, (■); P(NaA-*co*-NaAMPS)-*g*-PDMAM50/PDADMAC, (▲); P(NaA-*co*-NaAMPS)-*g*-PDMAM75/PDADMAC, (◆). The total polymer concentration is 1 g/l. $T = 25$ °C.

Fig. 2 presents the variation of the reduced viscosity ratio, $r_{\eta\mathrm{red}}$, of the polymer mixtures in water, as a function of their molar composition, N_{PDAMAC}, based on the charged monomer units. The measurements were performed by using solutions of the same unit-molar concentration, 5 mM, on the basis of the charged units. The ratio $r_{\eta\mathrm{red}}$ is calculated by the equation

$$r_{\eta\mathrm{red}} = \eta_{\mathrm{red,mix}}/\eta_{\mathrm{red,av}} \tag{1}$$

where $\eta_{\mathrm{red,mix}}$ is the experimentally determined reduced viscosity value of each polymer mixture and $\eta_{\mathrm{red,av}}$ is the weight average of the reduced viscosities η_{red1} and η_{red2} of the two pure components, calculated by the equation

$$\eta_{\mathrm{red,av}} = \eta_{\mathrm{red1}} W_1 + \eta_{\mathrm{red2}} W_2 \tag{2}$$

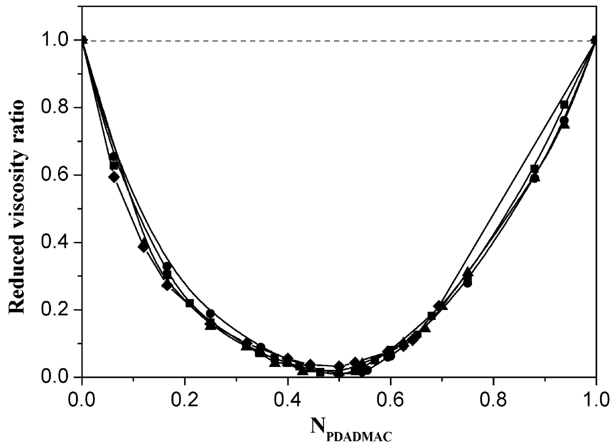


Fig. 2. Variation of the reduced viscosity ratio, $r_{\eta\mathrm{red}}$, vs. N_{PDADMAC} for the P(NaA-*co*-NaAMPS)/PDADMAC and the P(NaA-*co*-NaAMPS)-*g*-PDMAM*x*/PDADMAC mixtures at constant total unit-molar concentration in charged units, 5 mM. (●): P(NaA-*co*-NaAMPS)/PDADMAC, (■): P(NaA-*co*-NaAMPS)-*g*-PDMAM25/PDADMAC, (▲): P(NaA-*co*-NaAMPS)-*g*-PDMAM50/PDADMAC, (◆): P(NaA-*co*-NaAMPS)-*g*-PDMAM75/PDADMAC. $T = 25$ °C.

where W_1 and W_2 are the weight fractions of the two pure components in the mixtures. By its definition, any deviation of the ratio $r_{\eta\mathrm{red}}$ from unity (dotted line) offers a good qualitative measure of the interpolymer interactions [39–41]. We observe that in all the systems studied the values obtained are lower than unity, indicating that PDADMAC forms PECs of a compact structure both with the backbone P(NaA-*co*-NaAMPS) and the graft copolymers P(NaA-*co*-NaAMPS)-*g*-PDMAM*x*. All the curves obtained show a minimum, of a very low value, close to zero, in a mixture composition $N_{\mathrm{PDADMAC}} = 0.5$. The composition of the minima indicates that the interaction between these oppositely charged polyelectrolytes proceeds through a charge neutralisation process. We also observe that the curves corresponding to the graft copolymers practically coincide with the curve of the backbone, a good indication that the PECs formed between PDADMAC and the copolymers grafted with the neutral hydrophilic PDMAM side chains are also as compact as the polyelectrolyte complex formed between PDADMAC and the backbone.

The formation of PECs between two oppositely charged polyelectrolytes is accompanied by the liberation of counterions in the solution, leading to an increase of the solution conductivity [1,8]. The variation of the conductivity of aqueous solutions containing mixtures of PDADMAC with the backbone P(NaA-*co*-NaAMPS) or the graft copolymers P(NaA-*co*-NaAMPS)-*g*-PDMAM*x* is shown in Fig. 3. The study has been performed at the same molar concentration, 5 mM, of charged monomer units. It is noteworthy that the conductivity of the pure copolymer solutions decreases with increasing *x*, although the molar concentration of the charges is the same for all copolymer solutions. This should be related to the higher mass per charge ratio and the expected lower mobility of the polyions as the graft copolymer becomes richer in uncharged PDMAM graft chains. By adding PDADMAC, conductivity increases and takes values higher than the weighted average of the conductivities of the two pure components at the corresponding concentration. Moreover, a maximum is observed at $N_{\mathrm{PDADMAC}} = 0.5$, i.e. at the charge neutralisation composition. Note that all the systems studied exhibit a similar behaviour, regardless of the presence of the non-complexable neutral PDMAM side chains in the graft copolymers.

The hydrodynamic radius of the colloidal polyelectrolyte complex particles formed in the mixtures of the graft copolymers with PDADMAC was determined with quasi-elastic light scattering measurements. Fig. 4 shows the obtained results vs. the mole fraction N_{PDADMAC}, based on the charged units of the polymers mixed. We see that the smallest particles for each system are formed at the mixtures with a composition corresponding to charge neutralisation, $N_{\mathrm{PDADMAC}} = 0.5$. The values of the hydrodynamic radius obtained at this point are shown in Table 2. The smallest value obtained, 38 nm, compares with the value of the fully extended PDMAM side chain, 40 nm, as it is calculated by the number average degree of polymerisation (160) and the vinyl monomer projection length (0.25 nm).

We also observe that the size of the particles decreases as the composition of the graft copolymer in neutral hydrophilic PDMAM chains increases, in agreement with the results shown in Fig. 1. Apparently, for the PDMAM-poor samples, a greater number of graft copolymer chains is required for the formation of the stabilising corona, resulting in larger PEC nanoparticles. As the PDMAM content of the sample increases, the stabilising corona can be formed by a lower number of graft copolymer chains, leading to smaller PEC nanoparticles.

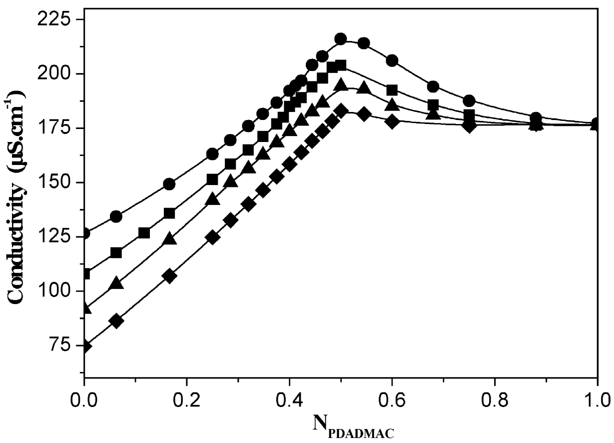


Fig. 3. Variation of the conductivity vs. N_{PDADMAC} of aqueous solutions of P(NaA-*co*-NaAMPS)/PDADMAC, (●); P(NaA-*co*-NaAMPS)-*g*-PDMAM25/PDADMAC, (■); P(NaA-*co*-NaAMPS)-*g*-PDMAM50/PDADMAC, (▲); P(NaA-*co*-NaAMPS)-*g*-PDMAM75/PDADMAC, (◆). The total unit-molar concentration in charged units is 5 mM. $T = 25$ °C.

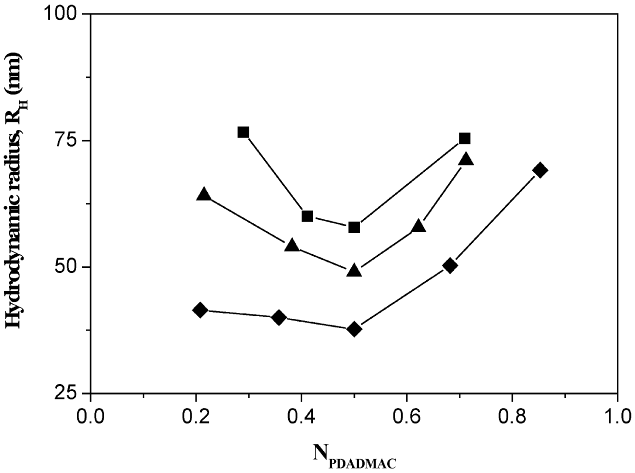


Fig. 4. Variation of the hydrodynamic radius, R_{H}, of the complexes formed between PDADMAC and P(NaA-*co*-NaAMPS)-*g*-PDMAM25, (■); P(NaA-*co*-NaMPS)-*g*-PDMAM50, (▲); and P(NaA-*co*-NaAMPS)-*g*-PDMAM75, (◆) vs. N_{PDADMAC}. The total unit-molar concentration in charged units is 5 mM. $T = 25$ °C.

Table 2
Hydrodynamic radius, R_H, of the particles formed between PDADMAC and the three graft copolymers at the charge neutralization point

Graft copolymer	R_H (nm)
P(NaA-*co*-NaAMPS)-*g*-PDMAM25	58
P(NaA-*co*-NaAMPS)-*g*-PDMAM50	49
P(NaA-*co*-NaAMPS)-*g*-PDMAM75	38

4. Conclusion

In the present work, we demonstrated the possibility to form water-soluble PECs by using graft copolymers, instead of linear ones. For this reason, we studied the PECs formed between the cationic polyelectrolyte PDADMAC and the anionic graft copolymers P(NaA-*co*-NaAMPS)-*g*-PDMAM*x*. These complexes, although highly compact (viscometry), are soluble in water (turbidimetry), and they follow a 1:1 charge stoichiometry (viscometry and conductivity). The most compact structures are observed at the charge neutralisation point, while the hydrodynamic radius of the core-corona nanoparticles formed decreases as the composition, *x*, of the graft copolymers in PDMAM increases. Apart the graft density, other structural factors possibly affecting the formation of such water-soluble PECs is the length of the side chains and their hydrophilicity. Moreover, we envisage providing the PECs formed with stimuli-responsive properties by using appropriate side chains. For instance, thermosensitivity could be introduced by using poly(*N*-isopropylacrylamide) side chains [42]. Finally, the use of biocompatible polymers, like poly(ethylene glycol), could prove these systems useful for biomedical purposes, like drug delivery.

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