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Ion-specific antipolyelectrolyte effect on the swelling behavior of polyelectrolyte layers

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ABSTRACT

In this study, we systematically investigate the interactions between mobile ions generated from added salts and immobile charges within a sulfobetaine-based polyelectrolyte film in the presence of five salts (KCl, KBr, KSCN, LiCl, and CsCl). The sulfobetaine groups contain quaternary alkyl ammonium and sulfonate groups, giving the positive and negative charges. The swelling of the polyelectrolyte film in the presence of different salts is compared with the swelling behavior of a polycationic or polyanionic film containing the same charged groups. For such a comparative study, we design crosslinked terpolymer films with similar thicknesses, crosslink densities, and charge fractions, but with varying charged moieties. While the addition of salt in general leads to a collapse of both cationic and anionic films, the presence of specific types of mobile anions (Cl^- , Br^- , and SCN^-) considerably influences the swelling behavior of polycationic films. We attribute this observation to a different degree of ion-pair formations between the different types of anionic counterions and the immobile cationic quaternary alkyl ammonium groups in the films where highly polarizable counterions such as SCN^- lead to a high degree of ion pairing and less

polarizable counterions, such as Cl^- , cause a low degree of ion pairing. Conversely, we do not observe any substantial effect of varying the type of cationic counterions (K^+ , Li^+ , and Cs^+), which we assign to the lack of ion pairing between the weakly polarizable cations and the immobile anionic sulfonate groups in the films. Further, we observe that the zwitterionic films swell with increasing ionic strength and the degree of swelling is anion dependent, which is in agreement with previous reports on the “antipolyelectrolyte” effect. Herein, we explain this ion-specific swelling behavior with the different cation and anion abilities to form ion pairs with quaternary alkyl ammonium and sulfonate in the sulfobetaine groups.

Introduction

Polyzwitterions are polymers containing functional groups, which carry both positive and negative charges. In their simplest form, as seen for polymers containing, e.g., phosphorylcholine or sulfobetaine groups, each chain carries an equal number of positive and negative charges and is therefore overall electrically neutral. This overall electrical neutrality will provide such polymers with unique hydration and swelling properties compared with uncharged polymers or polyelectrolytes that carry an overall positive or negative charge. Polyzwitterions also provide several interesting properties that make them interesting when used in films and coatings, e.g., antifouling applications and in aqueous lubricating systems.^{1–6} One of the unique properties of some polyzwitterionic films is the so-called “antipolyelectrolyte effect,” which refers to the aqueous swelling behavior of polyzwitterionic films in response to changes in the ionic strength. As implied by the term, the antipolyelectrolyte effect means that the swelling response is opposite to the response of the polyanionic or polycationic films. More specifically, polyzwitterionic films

often swell with increasing ionic strength, whereas polyanionic or polycationic films collapse with increasing ionic strength.^{7–10}

At low ionic strength, owing to the strong dipole–dipole pairing of zwitterionic groups on either the same polymer chain or on neighboring chains, the polyzwitterionic films are normally found in a collapsed state. Therefore, a zwitterionic film comprises a tight bond network with a high number of interchain and intrachain physical crosslinks, resulting in a low ability of the film to swell even if the polymers are hydrophilic. However, the dipole–dipole interactions are disrupted and the film is able to swell when the ionic strength is increased. As discussed by Wang et al., this disruption can occur either in a symmetric manner, where both internal ions in the zwitterionic ion pair are similarly affected by the increasing ionic strength (e.g., by electrostatic screening), or in an asymmetric manner, where the positive and the negative charges in the zwitterionic group are differently affected by the external salt (e.g., through the chemisorption of mobile ions).^{11–13}

To further explain the molecular mechanisms of the “antipolyelectrolyte effect,” it is interesting to mention that the swelling induced by increasing ionic strength has been found to be strongly dependent on the type of the added salt.^{14,15} Most experimental studies have focused on varying the anions of the added salt,^{7,8,16–18} for which parallels have been drawn to the Hofmeister series, where varying the type of anions has been shown to have a crucial effect on the solution behavior of both charged and uncharged macromolecules.^{19–23} This is, for example, the case for several studies of polymer films containing sulfobetaine groups, where the exact degree of swelling with increasing ionic strength has been shown to be strongly dependent on the specific type of anions. However, the fact that the swelling behavior is ion type-dependent shows that the electrostatic screening of the dipole–dipole interactions cannot be the only reason for swelling. Yet, a full molecular understanding of the “antipolyelectrolyte effect” is still lacking, especially, when it

comes to how specific types of ions affect the swelling behavior. To this end, we believe that comparing this swelling behavior with the swelling behavior of structurally simpler cationic and anionic analogs is the key to understanding the complex swelling behavior of polyelectrolytic films.

For polycationic and polyanionic films, the swelling behavior is caused by a balance between counterion-induced osmotic pressure, polymer–polymer and polymer–solvent nonelectrostatic interactions, and chain entropic elasticity.^{24–27} The response of the polycationic and polyanionic films to changes in ionic strength is derived from the variation in the counterion-induced osmotic pressure. This arises from the excess counterion concentration within the film compared with the concentration in the bulk solution, which is required to compensate the charges on the polyelectrolyte chains and causes swelling of the film at low salt concentrations. This swelling regime is known as the osmotic regime. With increasing ionic strength of the medium, the difference between the ion concentration inside and outside the film decreases; thus, the osmotic pressure decreases and the film collapses accordingly in the so-called salted regime. Finally, when the salt concentration reaches a high level, the osmotic pressure is supposedly no longer effective for the swelling of the film and the film enters a regime with a low, ionic strength-independent thickness, known as the quasineutral regime.^{24,28–30}

The specific ion type can affect the counterion-induced osmotic pressure and polymer–solvent nonelectrostatic interactions. However, these effects are different depending on whether the ion is a counterion or a coion. Even when the salt concentration in bulk is low, the counterions inside the polymer film are always present in a high amount, and are therefore always affecting the film. According to the Boltzmann distribution caused by the chemical potential difference, the coion concentration inside the film is considerably lower than that in the bulk.³¹

In the present study, we aim to decouple the interactions between mobile ions generated from the added salt and two immobile charges in the zwitterionic group. This was achieved first by studying the specific ion and ionic strength–dependent swelling behavior of polycationic films containing positively charged quaternary alkyl ammonium groups and polyanionic films containing negatively charged sulfonate groups. These films’ swelling behavior was directly compared with the swelling behavior of polyzwitterionic films containing sulfobetaine groups that are zwitterionic owing to a combination of quaternary alkyl ammonium and sulfonate groups. Thus, we were able to study the effects of different counterions and coions on the quaternary alkyl ammonium and the sulfonate groups, separately, and use this knowledge to predict how different mobile cations and anions would interact with the positive and negative charges in the zwitterionic groups.

Experimental Section

Chemicals

[2-(methacryloyloxy)ethyl]trimethylammonium chloride (METAC, 75 wt.% in H₂O), 3-sulfopropyl methacrylate potassium (SPMAK, 98%), 2-(dimethylamino)ethyl methacrylate (98%), 1,4-butane sultone (BS, ≥99%), 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDPA, 97%), allyl methacrylate (AMA, 98%), *n*-butyl methacrylate (*n*-BMA, 99%), 3-mercaptopropyl trimethoxysilane (MPTMS, 95%), 2,2,2-trifluoroethanol (TFE, ≥99%), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP, ≥95%), 4,4'-azobis(4-cyanovaleric acid) (ACVA, ≥98%), potassium chloride (KCl, 99.5%), potassium thiocyanate (KSCN, 99%), potassium bromide (KBr, 99%), lithium chloride (LiCl, 99%), and cesium chloride (CsCl, 98%) were purchased from Sigma-Aldrich Denmark. *N,N*-Dimethylformamide (≥99.9%), diethyl ether (≥99.9), toluene (≥99.8), and acetonitrile (≥99.9) were received from VWR Chemicals BDH and

passed through activated basic aluminum oxide (Brockman I, Sigma-Aldrich) before use to remove any inhibitors. Zwitterionic monomer *N*-(2-methacryloyloxyethyl)-*N,N*-dimethylammonium butanesulfonate (MABS) was prepared beforehand using the procedure reported in a previous study.³² Ultrapure water (Sartorius Arium Pro; 18.2 MΩ·cm) was used for preparing aqueous salt solutions.

Polymer films

Polymer films were produced through a stepwise process: reversible addition–fragmentation chain-transfer (RAFT) polymerization, surface functionalization of the substrate, and then spin coating and curing.

First, charged terpolymers were synthesized using RAFT polymerization by incorporating 25 mol.% of charged monomer (METAC, SPMAC, or MABS) and varying amounts of AMA and *n*-BMA (corresponding to the targeted AMA composition and eventual film crosslink density). CDPA and ACVA were added in a 200:1:0.1 molar ratio (monomer:CDPA:ACVA). Cationic and anionic polyelectrolytes were synthesized using METAC and SPMAC, as the charged monomers, in a 2.5-M monomer solution in 4:1 *N,N*-dimethylformamide/H₂O. Accordingly, zwitterionic polymers were synthesized using MABS and polymerized in TFE (2.5 M with respect to the monomers). AMA contents were selected as 5, 10, or 15 mol.%, equating to *n*-BMA contents of 70, 65, or 60 mol.%, respectively, which corresponded to the eventual crosslink density of the polymer films. Ultimately, the total monomer concentration was 2.5 M, and the solution was degassed by sparging with N₂ for 30 min after which the temperature was raised to 70 °C, initiating polymerization. The polymerization was conducted under N₂ atmosphere and monitored via ¹H-NMR until completion. Then, the reaction was precipitated in cold-stirred diethyl ether. Once

collected via vacuum filtration, the product was dried overnight at 30 °C in a vacuum oven and characterized using ^1H -NMR, which confirmed the approximate composition of the polymer.

Silicon wafers were used as the substrate for the films, which needed to be functionalized before grafting the film. The wafers were rinsed with water, ethanol, and acetone, then dried under a N_2 stream, and cleaned using plasma for 180 s under a 500-mTorr water-vapor atmosphere. Then the wafers were submerged in a 15-vol.% MPTMS toluene solution and stirred at room temperature ($\sim 23^\circ\text{C}$). After 3 h, the functionalized wafers were removed from the solution, dried under an N_2 stream, and placed in a 130°C vacuum oven to induce silanization.

The polymer solution was spin coated onto the functionalized wafer and anchored via thermally initiated crosslinking. First, an ~ 1 wt.% polymer in TFE solution was prepared, and tetrafunctional thiol PETMP and a radical initiator ACVA was added. PETMP (though tetrafunctional) was loaded at a 1:1 molar ratio to that of the -ene- functionality of the polymer. After stirring for 30 min, the solution was spin coated onto the previously prepared thiol-functionalized silicon wafer (2000 rpm for 40 s) before being placed in a 90°C oven for 2 h to induce a thermally initiated thiol–ene crosslinking reaction. The wafers were then removed from the oven and cooled to room temperature. Then they were washed twice with an excess of water to remove any unattached materials and then dried under N_2 atmosphere.

Ellipsometry

The thicknesses of the films were measured using an ellipsometer (J. A. Woollam, M-2000) equipped with a liquid cell. The measurements were conducted with a fixed angle of incidence of 75° and at wavelengths of 250–1000 nm. The measurements were analyzed using the instrument's software, CompleteEase, where the sample was described with a model containing multiple layers.

The model was created with Si as the substrate, a 1 nm-thick Si-SiO₂ transition layer, a 100 nm-thick SiO₂ layer, a uniform polymer film without absorption of light, and finally ambient conditions matching the refractive index of the solvent. The properties of the polymer film were described using a Cauchy model with the form $n(\lambda) = A + B/\lambda^2$ where n and λ are the refractive index and the wavelength, respectively, and A and B are fitting parameters. The fitting parameters for the film were A and B from the Cauchy model and the thickness of the polymer film. The refractive index of the salt solution changed with the concentration and type of the salt, which was adjusted accordingly in the model. See supporting information Section S1 for details on the procedure of performing the measurements and the optical model.

Results and Discussion

In this study, we have used random terpolymers comprising three repeating units: a noncharged unit (*n*-butyl methacrylate), a crosslinkable unit (allyl methacrylate), and a charged unit (Figure 1). While the fraction of the charged units was kept constant (25 mol.%) for all polymer films, the fraction of crosslinkable units was systematically varied between 5, 10, and 15 mol.% to obtain polymer films with various crosslink densities. Three types of charged units were chosen: either a positively charged unit (METAC), a negatively charged unit (SPMAK), or a zwitterionic unit (MABS) (Figure 1). With such molecular designs, we were able to first systematically vary the crosslink density for the polyelectrolyte systems while keeping the charge fraction constant. Second, we were able to compare the swelling behavior of the polycationic, polyanionic, and polyzwitterionic films, which have the same fraction of charged units, similar crosslink density (controlled via the fraction of crosslinkable units), and controlled nonelectrostatic interactions arising from the fraction of noncharged units. Dry-film thicknesses determined using the

ellipsometry and topographical information from AFM images of the prepared polymer films are provided in Supporting Information Section S2.

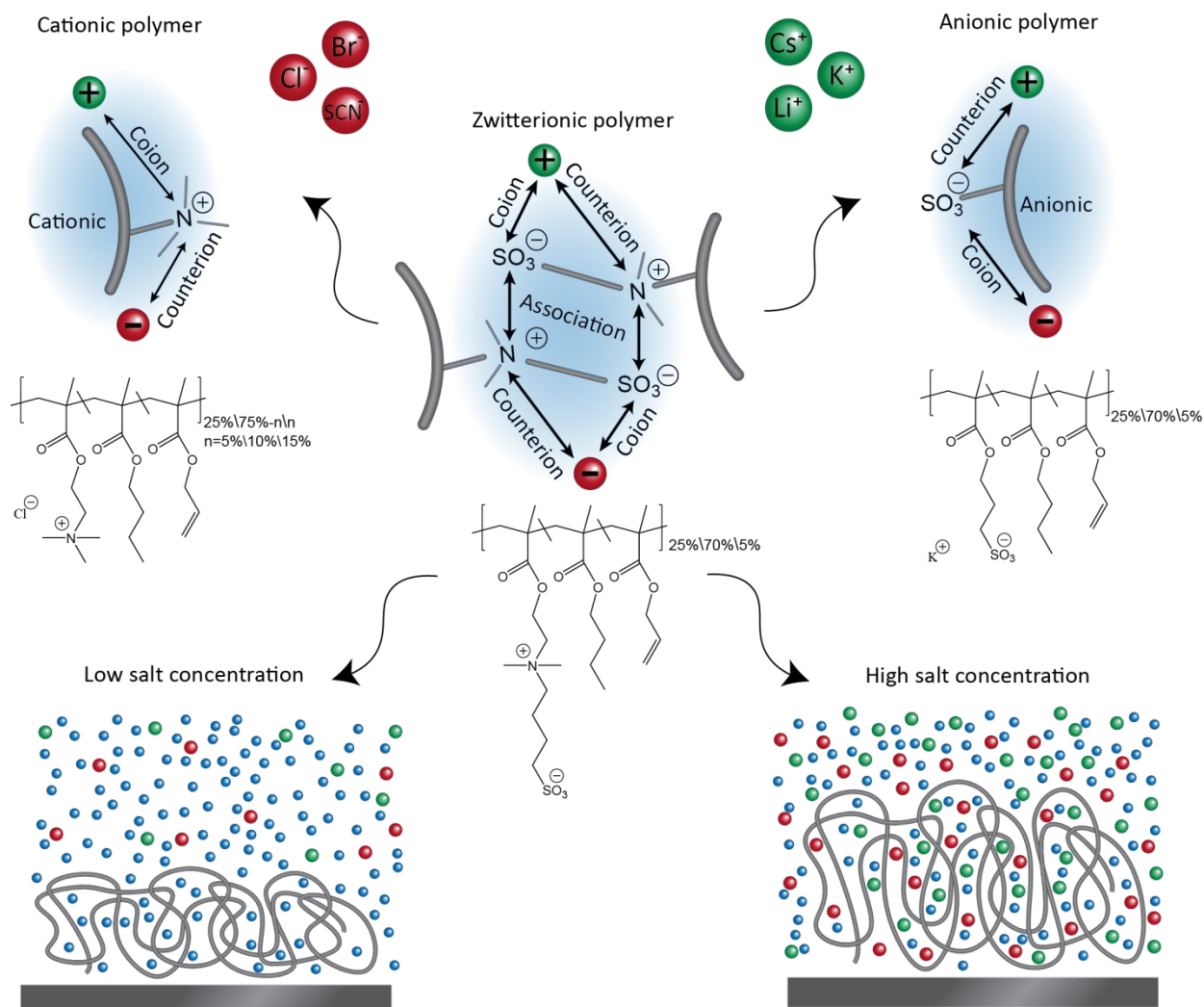


Figure 1. Schematic of the investigated systems and relevant ionic interactions. Three random terpolymers with cationic, anionic, and zwitterionic groups were used to prepare surface grafted, crosslinked polymer films. Swelling behavior was investigated as a function of the concentration of added salts (KCl, KBr, KSCN, LiCl, and CsCl), corresponding to three different anions and three different cations. Then, the different cations and anions worked as counterions, coions, or both, depending on the ionic nature of the polymers.

Next, we investigated the swelling behavior of the systems: polycationic, polyanionic, and polyzwitterionic films. For this, we first considered the effect of the ionic strength on the swelling behavior of the polymer films in the presence of KCl and then determined how this response is affected by the type of counterions and coions. To later provide a detailed discussion of the polyzwitterionic films based on these understandings, we studied the polycationic and polyanionic films to investigate the interactions between the mobile ions and the immobile charged groups in the films

Effects of ionic strength and crosslink density on polycationic films

For the polycationic films with different crosslink densities, the swelling ratios (relative to the dry-film thickness) are plotted in Figure 2 as a function of the KCl concentration. The overall swelling behavior of the polycationic film follows the typical behavior of strong polyelectrolyte films with respect to ionic strength.^{10,25,33} We observed that this film exhibited a high and constant thickness at low salt concentrations, from 0.01 to 10 mM, which corresponds to the osmotic regime, where the counterion-induced osmotic pressure caused considerable swelling of the film.^{24,29,30} From ~10–30 mM, the salted regime started, where a decline in swelling was observed because the osmotic pressure difference decreased due to the addition of external salts. In addition to the osmotic and salted regimes, a quasineutral regime is sometimes observed for polyelectrolyte films at very-high salt concentrations, depending on the films properties.^{25,34,35} In the current case, this regime is, however, not manifested below 3 M KCl.

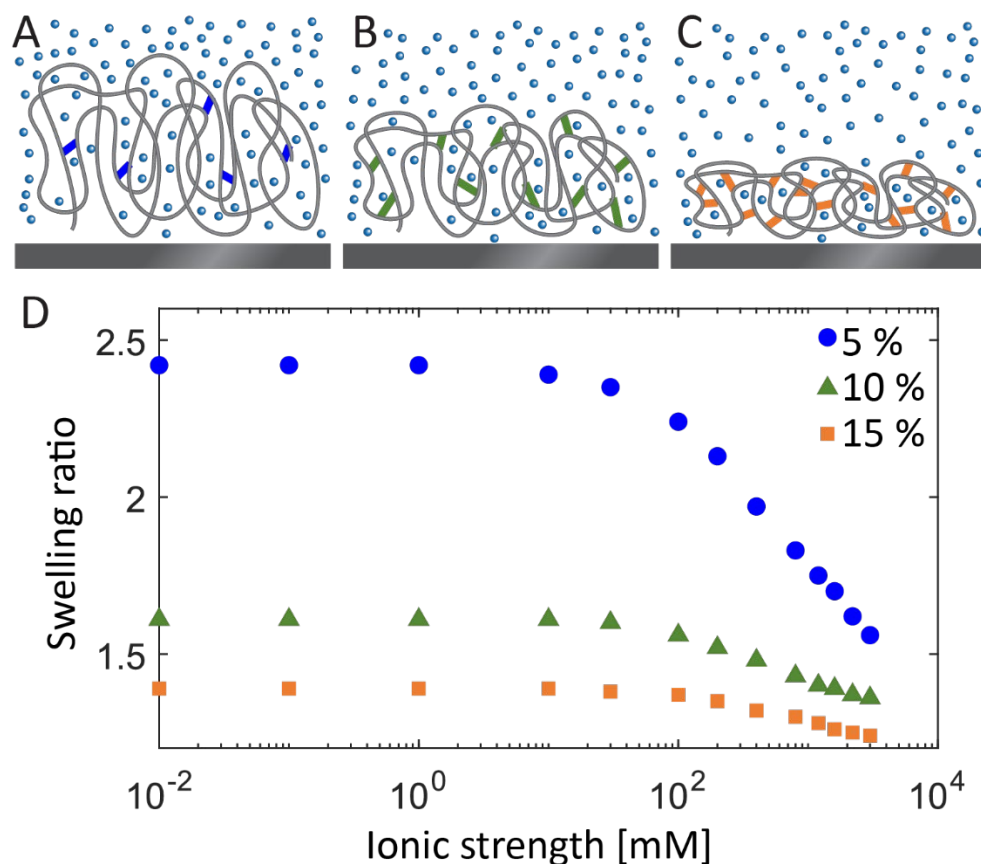


Figure 2. Illustration of the crosslinking effect for (A) low, (B) intermediate, and (C) high crosslinking degrees. (D) Swelling ratios of hydrated polycationic films (hydrated-film thickness compared with dry-film thickness, see Supporting Information S2 for dry-film thicknesses) as a function of KCl concentration for films with either 5, 10, or 15 mol.% of the crosslinked monomer.

Films of different degrees of crosslinking but with the same charge density were investigated to show how the degree of crosslinking can influence the swelling behavior. As shown in Figure 2, all the three films qualitatively followed the same trends with an osmotic regime in the first part (constant thickness) and a salted regime in the last part (declining thickness). However, with increased crosslink density, chain stretching became restricted; thus, the swelling decreased in the osmotic regime. This observation is not surprising; however, it is important for the interpretation of the zwitterionic films' swelling, where it is expected that dipole–dipole intrachain and interchain

bonds will also limit the swelling due to a similar effect (although the effect is caused by a different type of crosslinking).

Specific ion effects on polycationic films

Five monovalent salts KCl, KBr, KSCN, LiCl, and CsCl were chosen to demonstrate how swelling of the polycationic film depends on the specific types of ions. Here, it is possible to systematically vary either the coions or the counterions.

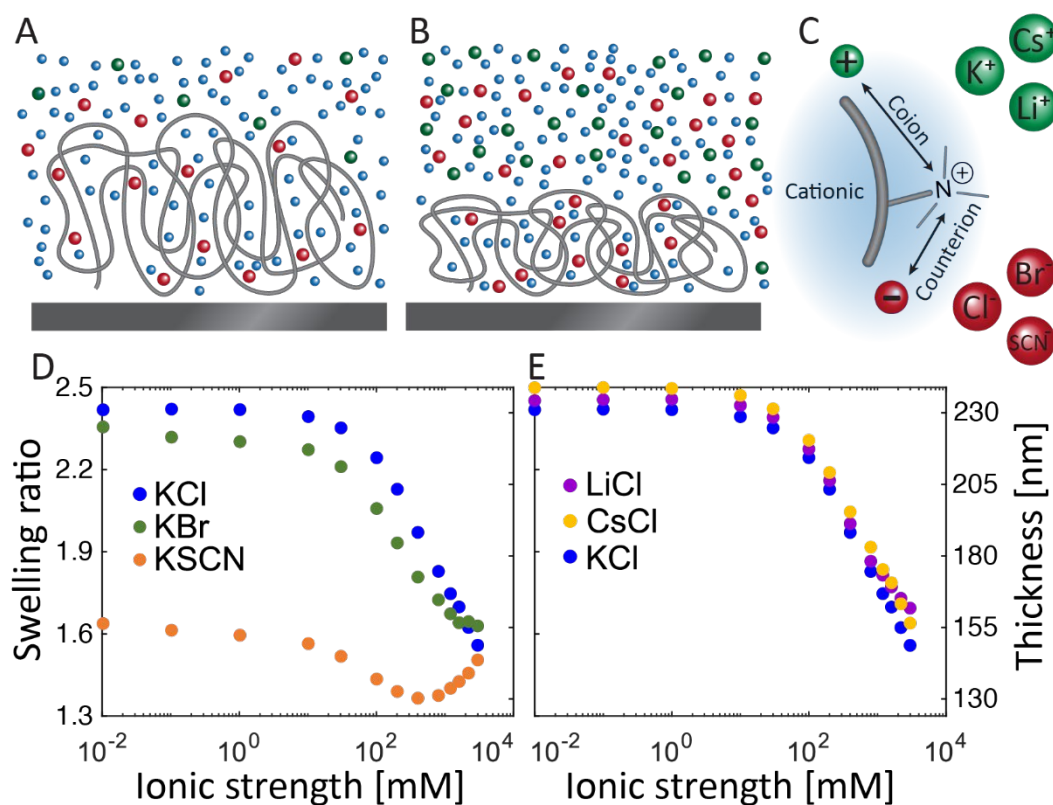


Figure 3. Illustration of polycationic film swelling when hydrated in (A) low and (B) high salt concentrations. (C) Role of ions when interacting with the charged quaternary alkyl ammonium groups (of polymers) as either cationic coions or anionic counterions. Ellipsometry-based thickness of the polycationic film as a function of salt concentration in the presence of (D) either

potassium salts with various anionic counterions or (E) chloride salts with various cationic coions. Note that both swelling ratios (left y-axes) and the absolute thickness (right y-axes) are provided.

Figure 3D shows the effect of different anions (counterions) on the swelling behavior of the polycationic film with a low crosslink density (5 mol.% of the crosslinker monomer) while keeping the cation (coion) unchanged as K^+ . Here, where the thickness of the films follows the trend $Cl^- > Br^- > SCN^-$ at low salt concentrations, in the osmotic regime, the anionic counterions considerably affect the swelling of the film. However, the thicknesses converge to an approximately similar level at high salt concentrations. This difference in the osmotic regime indicates a lower counterion-induced osmotic pressure in the case of SCN^- compared to other ions. Counterion-specific behavior has previously been observed in other cationic films, and here, it has been explained by the effect of specific types of counterions on the counterion-induced osmotic pressure and the polymer–polymer and polymer–solvent nonelectrostatic interactions.^{10,25,36–38} Thus, we have linked the trend of thickness at low ionic strength to the ability of anionic counterions to form ion pairs with the quaternary alkyl ammonium groups on the polyelectrolyte chains, and thus, become osmotically passive. To this end, based on our results, it is expected that the degree of ion-pair formation follows the trend $SCN^- > Br^- > Cl^-$, which agrees with previous reports.^{39,40} Beside this overall behavior, the film with SCN^- as counterions started to swell with increasing salt concentration, from approximately 800 mM. At such high ionic strength, the counterion-induced osmotic pressure declined and the swelling is attributed to a “salting-in” effect, similar to what is observed for many noncharged polymers, where it has been suggested that chaotropic ions like SCN^- can increase the polymer solubility through preferential partitioning around the polymer chains.^{19,41–44}

Figure 3E shows the effect of the cations (coions) on the swelling behavior of polycationic films, while the anion (counterion) was kept as Cl^- . In contrast to the drastic variations observed with varying anionic counterions, different cationic coions afforded an almost identical swelling behavior, both with respect to the overall trend (first an osmotic regime and then a salted regime) and the absolute thicknesses. However, at the highest salt concentrations ($>1\text{ M}$) a weak specific cationic coion effect was observed, and we assigned this weak effect to the influence of ions on the polymer–solvent nonelectrostatic interactions (Hofmeister effects).

To investigate the effect of crosslink density on the ion-specific response of the polycationic films, measurements on polycationic films with 10 and 15 mol.% crosslinking monomers have been conducted using the same salts specified in Figure 3 (see Supporting Information Section S3). The thickness of the hydrated films showed a similar trend with the variation of anionic counterions, as observed for the low-crosslink polycationic film ($\text{Cl}^- > \text{Br}^- > \text{SCN}^-$). Similarly, the variation of cationic coions afforded almost identical swelling behavior for each film with fixed crosslink density. However, with increasing crosslink density, the overall swelling of the films and their response to specific anionic counterion effects became less pronounced.

Most relevantly, while the cationic coions only begin to show small variations at very-high salt concentrations, these variations in coions and counterions show how the anionic counterions considerably affect the swelling at very-low salt concentrations. This agrees well with the idea that the anionic counterions are present inside the film in high concentrations at all times and affect the ion osmotic pressure. However, the concentration of cationic coions inside the film is lower than the concentration in bulk; thus, their effect on the film is negligible in this concentration range.

As demonstrated here, anions can interact and form ion pairs with the quaternary alkyl ammonium groups on the polycationic chain. Therefore, it is expected that in a polyelectrolyte system with the same cationic groups, these anions (Cl^- , Br^- and SCN^-) will compete with the sulfonate groups to bind with the quaternary alkyl ammonium groups. Such a competition in ion-pair formation and the resulting anion-specific behavior of polyelectrolyte systems are discussed later.

Specific ion effects on polyanionic films

Next, we investigated the swelling behavior of polyanionic films (5 mol.% of the crosslinker monomer) that were designed with similar physical properties (charge density and crosslink density) but with a sulfonate side group to develop negative charges on the chain. This makes it possible to investigate the effect of the same five salts used on the polycationic film, but this time, with the reversed roles of coions and counterions (Figure 4).

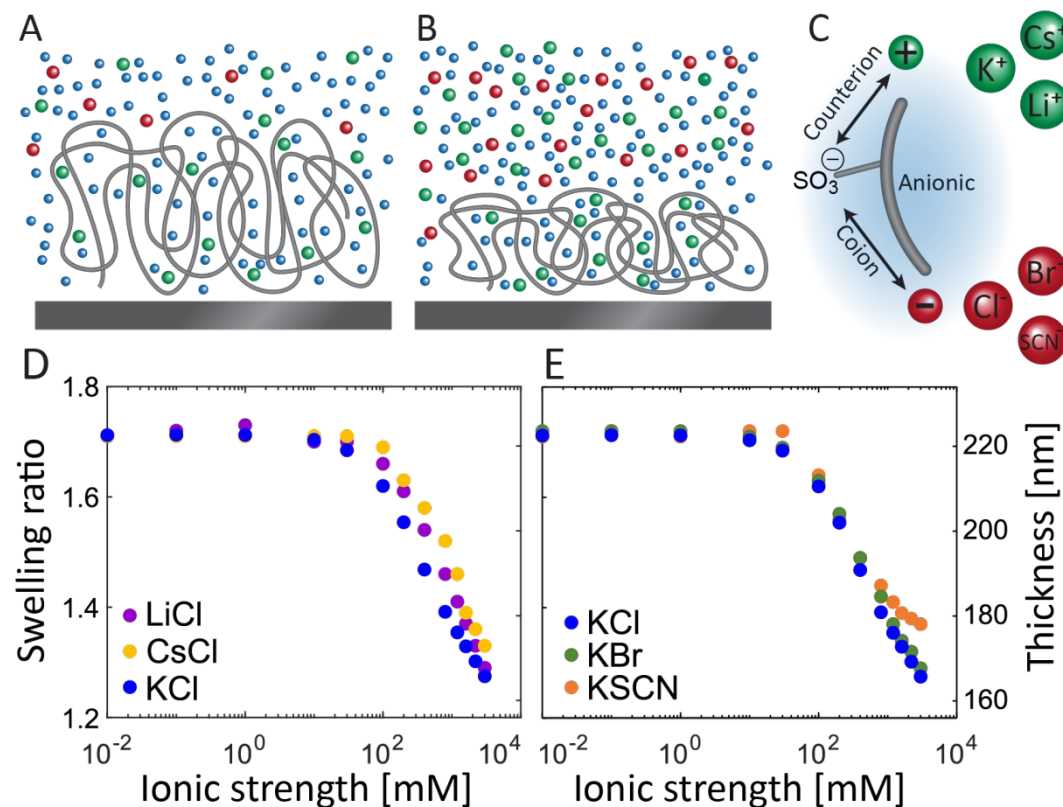


Figure 4. Illustration of polyanionic film swelling when hydrated in (A) low and (B) high salt concentrations. (C) Role of ions when interacting with the charged sulfonated groups (of polymers) as either anionic coions or cationic counterions (C). Ellipsometry-based thickness of the polyanionic film as a function of salt concentration in the presence of (D) either chloride salts with various cationic counterions or (E) potassium salts with various anionic coions. Note that both swelling ratios (left y-axes) and the absolute thickness (right y-axes) are provided.

By comparing Cs^+ , K^+ , and Li^+ , the effect of cations (counterions) on the swelling behavior of the polyanionic film was investigated (Figure 4D). A typical swelling behavior was observed for all the cases with an osmotic regime at low salt concentration, up to $\sim 10\text{--}30\text{ mM}$, followed by a salted regime with a further increase in the salt concentration. Firstly, no significant influence of the type of cationic counterions is seen in the osmotic regime at lower ionic strength. This indicates that the counterion-induced osmotic pressure is not affected by the type of cationic counterions. This can be explained by a similar degree of ion-pair formation (or no ion pairing) between the sulfonate groups in the film and these mobile cationic counterions. This is in contrast to the observed effect of the anionic counterions on the polycationic film where we observed various degrees of ion pairs with the quaternary alkyl ammonium groups in the films. It should however be noted that a weak effect of the type of cationic counterions is seen in the salted regime with a film collapse following the order $\text{K}^+ > \text{Li}^+ > \text{Cs}^+$. A similar effect of cations at high salt concentrations has previously been reported for the aggregation behavior of hemoglobin and in this case different binding affinities of the cations to negatively charged carboxylates groups and uncharged part of the protein was suggested as the explanation.^{45,46}

To understand and explain the difference of the counterion effects observed for the polycationic and the polyanionic films, focus should be placed on the mechanism through which ion pairs are formed. Ion-pair formation has been suggested to be correlated with the polarizability of the ions in the pair in such a manner that highly polarizable ions tend to interact stronger with the (also highly polarizable) quaternary ammonium groups and thus form a larger number of ion pairs compared to weakly polarizable ions with sulfonate groups.^{10,47,48} In our current study, the polarizability of the mobile anions ranged between 3.5 and 7.0 Å³, while the polarizability of the mobile cations was much lower (0–2 Å³).⁴⁹ To this end, we suggest that although the cations used here have different polarizabilities, they are all so low that the ion-pair formation in those cases is negligible (i.e., no ion pairing). Contrastingly, can the higher polarizabilities of some anions, leads to different degrees of ion-pair formation with the quaternary alkyl ammonium groups (see Supporting Information Section S4 for further details). In the case of the polycationic film it should be noted that a similar qualitative explanation of our experimental results could have been obtained using Collins' Law of Matching Water Affinities as from an argument using polarizabilities.^{50,51} Considering the quaternary alkyl ammonium group as a weakly hydrated species it should accordingly form stronger ions pairs with weakly hydrated ions like SCN[−] compared to with relatively stronger hydrated ions like Cl[−]. The Law of Matching Water Affinities seems however more difficult to apply for the polyanionic film with different cations, where, at low salt concentrations, the sulfonate groups appear to form weak (or no) ion pairs with neither the weakly hydrated Cs⁺ ions nor the more strongly hydrated Li⁺ ions. However, no matter which model is used, the formation of ion pairs is of course dependent on the properties of both the charged moieties and in polyelectrolyte films and the properties of the counterions. Thus, the same

counterions might result in different counterion-induced osmotic pressures for different polyelectrolyte systems.

In Figure 4E, the effect of changing the type of anion (coion) is shown to have an insignificant effect on the swelling of the films at low to medium ionic strength (up to around 400 mM). However, it is observed that the film with SCN^- as the counterion collapses less than those with Cl^- and Br^- as counterions, at higher concentrations of salts. Although the local salt concentrations in the films are not identical in the two situations, this observation is in line with the previously discussed behavior of SCN^- in the polycationic film at high ionic strength.

Here it was demonstrated that various cations have an insignificant ion-pair interaction with the sulfonate groups, in contrast to the various interactions of anions with quaternary alkyl ammonium groups. For the sulfobetaine, we can expect an asymmetric ion association for some types of added salts where mobile anions can form ion pairs with the positively charged quaternary alkyl ammoniums, while mobile and osmotically active cations balance the negatively charged sulfonates.

Specific ion effects on polyzwitterionic films

We next turned the focus to the swelling behavior of the sulfobetaine-based polyzwitterionic film, which contains a quaternary alkyl ammonium and a sulfonate group in each zwitterionic unit. The thickness of the polyzwitterionic film as a function of the ionic strength of the salts with systematic variations of cations and anions is shown in Figure 5.

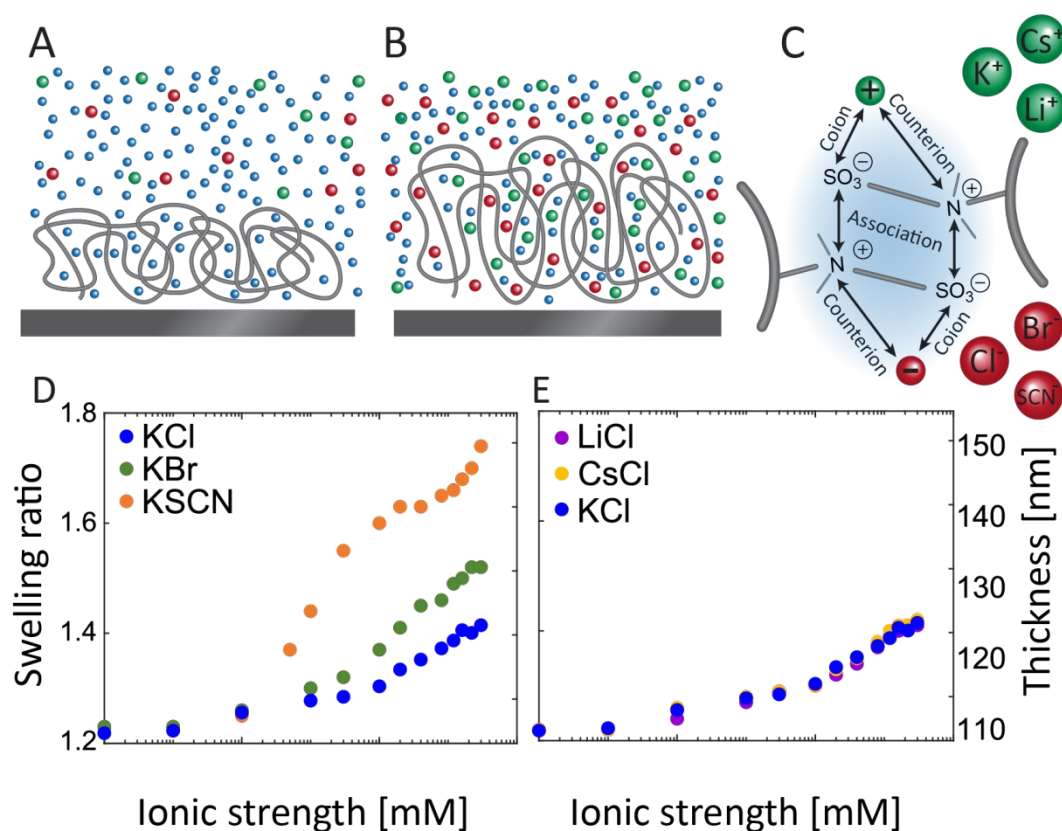


Figure 5. Illustration of polyelectrolyte film swelling when hydrated in (A) low and (B) high salt concentrations. (C) Role of ions when interacting with the charged groups (of polymers) as either coions or counterions (C). Ellipsometry-based thickness of the polyelectrolyte film as a function of salt concentration in the presence of (D) either potassium salts with various anions or (E) chloride salts with various cations.

Starting with the effect of varying the anions, Figure 5D shows the swelling behavior of the polyelectrolyte film (5 mol.% of the crosslinker monomer) in the presence of KCl, KBr, and KSCN. For all three cases, the film was found in a collapsed state at a low salt concentration up to around 1 mM followed by an increase in thickness with a further increase in salt concentration. Secondly, it was observed that the swelling behavior of the polyelectrolyte film is strongly anion dependent. The film undergoes the most pronounced swelling in the presence of SCN⁻, while in

the presence of Br^- swelling occurs to a lower extent, and the least pronounced swelling is found in the case of Cl^- . Contrary to this observed effect of different anions, the swelling behavior of the polyelectrolytic film is shown, in Figure 5B, to be independent of the type of cation.

The swelling of polyelectrolytic films with the addition of salt is commonly referred to as the “antipolyelectrolyte” effect and has been attributed to the dissociation of intrachain and interchain dipole–dipole bonds between the zwitterionic groups.^{13–18} The electrostatic interactions between the two groups are screened upon increasing medium ionic strength, whereby these groups can undergo dissociation. However, the fact that this behavior depends on the ion type demonstrates that an electrostatic effect cannot solely explain the behavior. In particular, the specific interactions between the salt ions and the immobile ions should be considered. We can implement the learnings from the cationic and anionic systems, to explain this behavior.

In the case of interactions between the mobile anions and the sulfonate group in the anionic film, we observed no significant influence of anionic coions on the swelling behavior of films except for very-high concentrations of SCN^- , where a change in nonelectrostatic interactions was observed (the coion effect in the polyanionic film, Figure 4E). On the other hand, we concluded that the interactions between the anions and the quaternary alkyl ammonium groups in the cationic film could be ranked based on their tendency to form ion pairs with the trend $\text{SCN}^- > \text{Br}^- > \text{Cl}^-$ (the counterion effect in the polycationic film, Figure 3D). This was also the trend of swelling observed in the polyelectrolytic film, indicating that the stronger the interaction of the anions with the quaternary alkyl ammonium groups, the higher degree of dissociation of the intrachain and interchain bonds, and thus the higher swelling of the film.

Regarding the effect of cations (Figure 5E), we observed, on the other hand, no significant interaction between the cations and the immobile groups, neither in the case of the polycationic film where the cations are coions nor in the case of polyanionic films where the cations are counterions. The cations did not form strong ion pairs with the sulfonate groups, in contrast to the case of anions in a polycationic film. We, therefore, suggest that this also can explain why the type of cations does not influence the swelling behavior of the polyzwitterionic systems.

By systematically comparing specific cation and anion effects on quaternary alkyl ammonium groups and sulfonate groups, we have now demonstrated that the swelling of the polyzwitterionic films is enhanced by ions that can strongly interact with one of the charges in the zwitterionic groups (in our case, anions pairing with the quaternary alkyl ammonium groups). We can also speculate about how this dissociation induced swelling of the polyzwitterionic film. At low ionic strength, the polyzwitterionic film was found in a collapsed state due to the formation of intrachain and interchain dipole–dipole bonds. These bonds between the chains act as physical crosslinks that limited swelling of the film, similar to the case observed with varying chemical crosslinks (Figure 2 and Supporting Information Section S3). With increasing ionic strength in the medium, more ions enter the polyzwitterionic film. This phenomenon first screens the electrostatic interactions between the quaternary alkyl ammonium groups and the sulfonate groups. Second, ions with strong interactions with one of the charged moieties (e.g., SCN^- and quaternary alkyl ammonium groups) break the bond between the sulfonate and quaternary alkyl ammonium groups to bind to the favored site. Because of this dissociation, the film swells due to a combination of two effects. First, breaking the interchain bonds yields a lower degree of ionic crosslinking, which allows increased swelling. Second, when SCN^- binds to a quaternary alkyl ammonium group, it is required by electroneutrality that an oppositely charged ion (for example K^+) enters the film to compensate the

charge on the sulfonate group. Because K^+ is mobile and osmotically active (as demonstrated in the case of polyanionic film), it can induce an osmotic pressure, which further increases the swelling of the film (similar to the case of the polyanionic film).

Conclusions

We have systematically studied the effect of interactions between mobile ions and immobile charges in polycationic and polyanionic films to understand the swelling behavior of polyzwitterionic films with similar charged moieties. We observed that the change in the type of cation did not considerably influence the swelling of the films, neither when acting as coions in the polycationic film nor when acting as counterions in the polyanionic film. Changing the type of anion had an insignificant effect on the swelling of the films when the anions acted as coions in the polyanionic film but exhibited a considerable effect when they acted as counterions in the polycationic film. The counterion-specific effect in the polycationic films is explained by different abilities of anions to form ion pairs with the quaternary alkyl ammonium groups.

For the polyzwitterionic film, we observed increased swelling with increasing ionic strength in accordance with the so-called “antipolyelectrolyte effect,” and the magnitude of the swelling was found to be strongly affected by the anion types following the order $SCN^- > Br^- > Cl^-$, while it did not depend on the type of cations. By studying all the possible interactions between the mobile ions and immobile charges on the polyzwitterionic chain, we proposed that the antipolyelectrolyte effect is a complicated swelling mechanism related to the electrostatic and nonelectrostatic ion-specific interactions. Dissociation of the intrachain and interchain bonds was derived via electrostatic screening and enhanced by specific ion-pair interactions, in cases where ions from the salt could strongly bind to one of the immobile charged groups. In addition, as

another result of dissociation, the osmotic pressure of mobile counterions (which are present to compensate the charge of the immobile charged groups) increased the swelling of films.

ASSOCIATED CONTENT

Supporting Information. Expanded description of ellipsometry technique and film characterization. Expanded discussion of polarisability of ions and additional data for crosslinking dependent film swelling. (PDF)

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Notes

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