

Structure and Phase Behavior of Interpolyelectrolyte Complexes of PDADMAC and Hydrophobically Modified PAA (HM-PAA)

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By combining oppositely charged polydiallyldimethylammonium chloride (PDADMAC) and sodium polyacrylate (NaPA), interpolyelectrolyte complexes (IPECs) can be formed in aqueous solution. Such IPECs are studied for rather short NaPA and under variation of the *M_w* of PDADMAC. The focus is on elucidating the effect of having a hydrophobic modification of the NaPA, which is introduced by having 10 mol% of the monomeric units substituted by ones carrying a dodecyl alkyl chain. This modification renders the complexes more hydrophobic, which is seen in the fact that precipitation of the complexes occurs at a lower mixing ratio and the biphasic region is also wider. The structures of the soluble IPECs are studied by a combination of light and neutron scattering (SANS). It is observed that the complexes formed possess typical radii of gyration of $\approx 30\text{--}40$ nm, which become somewhat smaller with increasing length of the PDADMAC chain. The SANS data can be described well with the Beaucage model for complexes, where locally small hydrophobic domains of cylindrical shape are formed, whose persistence length decreases with increasing content of NaPA in the complexes. In contrast no such structures are seen for NaPA without the hydrophobic modification. The cylindrical domains are then arranged within larger-sized clusters of $30\text{--}40$ nm, which become more compact with reduced length of the PDAMAC chains. The structure of the IPECs is largely determined by the presence of the hydrophobic modification of the NaPA and is further controlled by the length of the hydrophobic modification. Such IPECs of controlled structure, relatively small size, and containing hydrophobic domains are potentially interesting as delivery systems due to having domains of variable polarity.

1. Introduction

The formation of complexes of oppositely charged polyelectrolytes, so-called interpolyelectrolyte complexes (IPECs) has been a topic of scientific investigation for more than four decades.^[1–5] Typically, around charge neutralization precipitation of insoluble complexes is observed, while for excess charge of one of the polyelectrolytes soluble complexes are formed. Their size depends on the length of the polyelectrolytes employed, their individual molecular architecture, and on the interactions between them.^[4,6–9] For the phase separation one may observe the formation of solid precipitates or alternatively a liquid-liquid phase separation, coacervate formation, may take place. Ionic assembly of oppositely charged polyelectrolytes leads to the formation of a rich variety of structures that show largely variable properties, as one can combine many different polyelectrolytes with different *M_w* or molecular architecture (e.g., branching), which leads to an enormous number of possible combinations.^[3,10–14]

According to the richness of structures and properties of IPECs they are also interesting for a number of potential applications. This applies particularly to drug

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delivery^[15] but also a number of other fields of applications have been described.^[16]

From the many polycations available polydiallyldimethylammonium chloride (PDADMAC) has been one of the most intensively studied ones and is also one that is frequently employed in practical applications, e.g. in water treatment in the context of precipitating anionic natural organic matter (NOM).^[17–19]

Koetz and Kosmella^[20] studied the phase diagram of the ternary system PDADMAC, poly(acrylic acid, sodium salt) (PAA), and water using polyelectrolytes with different molecular weights. It was found that using low molecular weights of 5 and 6 kDa for PDADMAC and PAA, respectively, the range of composition where phase separation occurs is rather narrow compared to higher molecular weights. Moreover, for the phase-separated region, only coacervation was observed without flocculation. An increase of the molecular weight of PAA resulted in a broader phase-separated region. An increase of the molecular weight of PDADMAC to 40 kDa had a similar effect. Phase separation was observed already at lower concentrations of PDADMAC. This was attributed to a «bridging flocculation». Dautzenberg et al.^[21] were investigating the effect of salt on IPECs of PDADMAC with, among others, poly (methacrylic acid, sodium salt) (Na-PMA). The addition of salt to the IPEC in the polyanion excess region resulted in flocculation already at an ionic strength of 0.1 M. Addition of salt to the IPEC in the PDADMAC excess region up to 0.43 M ionic strength, resulted in the increase of the formed complexes mass by 2 orders of magnitude and increase of the particle size from 60 to almost 400 nm, as was deduced with static light scattering. Above an ionic strength of 0.68 M almost a complete dissolution of all IPEC particles was taking place. In general, the phase boundary to the biphasic region will depend on pH and ionic strength and this dependence can also be described theoretically.^[22]

Liu et al.^[23] were investigating early stage kinetics of IPECs with high molecular weight (100–200 kDa) PDADMAC and low molecular weight (2 kDa) PAA at different charge ratios both in the polycation and polyanion excess region. From light scattering experiments it was observed that in the polycation excess region up to a charge ratio of 0.6 the scattered intensity and the hydrodynamic radii (7 nm) showed only slight increase, followed by a spike in their values when approaching the charge equilibrium, where the hydrodynamic sizes reached ≈ 2000 nm. At charge neutrality coacervation was observed. The addition of the excess of PAA resulted in the partial redissolution of IPECs and a decrease in the scattered intensities and hydrodynamic sizes, the latter ones showing values of ≈ 100 nm. In situ light scattering combined with stopped-flow (SF) revealed the presence of three distinct kinetic stages in the investigated system. The first stage at times below 1 s is related to the relaxation and reorganization of soluble IPECs, the second stage was attributed to the aggregation and/or rearrangement of the initial IPECs into larger structures. The last stage, the coacervation stage, was happening upon redistribution of the excess charges in the formed IPECs, resulting in some neutral condensed coacervate droplets that are coexisting with IPECs in a wide range of mixing ratio.

Starchenko et al.^[24] were investigating PDADMAC complexes with poly (styrene sulfonic acid) (PSS) and reported the influence of salt concentration, polyanion concentration, and polyanion molecular weight concentration on the formed complexes in

the polyanion excess region. Authors used a two-stage IPEC formation approach^[25] for the explanation of the observed trend in dependence of the formed IPECs mean particle radius (estimated as a hydrodynamic radius via the Stokes–Einstein equation) on the NaCl salt concentration and PSS concentration. According to this approach, the first stage on the molecular level involves the formation of primary IPEC particles from the oppositely-charged polyelectrolytes, and the second stage takes place on the colloidal level where the secondary IPEC particles are formed through the aggregation of the primary particles. Hence, both the aggregation process and conformation of the polyelectrolytes play an important role in the IPEC formation process. In the case of the increasing NaCl salt concentration, the mean particle radius would go through a minimum reaching higher values for the very low or very high salt concentrations. This is an indication of a competition between the two aggregation processes. As a result of changing electrostatic screening, there are changes induced in the aggregation rates of the primary colloidal particles as well as in the conformation (swelling or shrinking) of the IPEC outer shell formed from the polyanion in excess. The increase in the polyanion concentration also resulted in the increase of the IPECs mean radii for all Mw PSS grades, as the concentration of the primary particles would increase accelerating their aggregation and forming bigger particles. An increase in Mw of PSS resulted in increase of IPEC radii, that was interpreted through the common size parameters increase of the uncomplexed polymers with increase in their degree of polymerization. Interestingly, despite the influence on the size, all IPECs with different Mw PSS showed the minimum in the radii-salt concentration dependence described above, indicating that the competition between the primary particles aggregation and the polyanion shell swelling (excess component in IPEC) remains, independent of the Mw of the polyanion. Jemili et al.^[26] varied the charge density of PSS via different sulfonation rates and studied IPECs of the respective poly (styrene-co-sodium styrene sulfonate) (P(St-co-SSNa)) with PDADMAC at the polycation excess region, polyanion excess region and at the charge equimolarity (1:1) via a number of complementary techniques, including DLS, zeta-potential measurements, ITC and binding experiments with a dye. It was found that despite the previously proposed pearl necklace conformation of P(St-co-SSNa), implying that a number of the charges might be trapped in the hydrophobic domains, close to the equimolar charge concentration the hydrophobic effect responsible for the pearl formation was overcome by the electrostatic interaction, as confirmed by the above-mentioned techniques indicating the charge stoichiometry of 1:1. Moreover, it was found that the difference in the charge density of the polyions does not have a significant impact on the efficiency of the complexation, indicating that the polyions are able to rearrange bringing the oppositely charged units together also the sulfonation rate did not have an impact on the size of the IPECs with diameters ranging from 100–300 nm as deduced via DLS. The two-step IPEC formation process described above^[24,25] was observed where primary complex particles with sizes below 50 nm were formed, followed by their aggregation into bigger clusters.

While complexes formed from PDADMAC and sodium polyacrylate (NaPA) have been studied before over a wide range of Mw^[20,21,27] the effect of hydrophobically modifying NaPA has not been explored, so far. This paper aims at filling this gap.

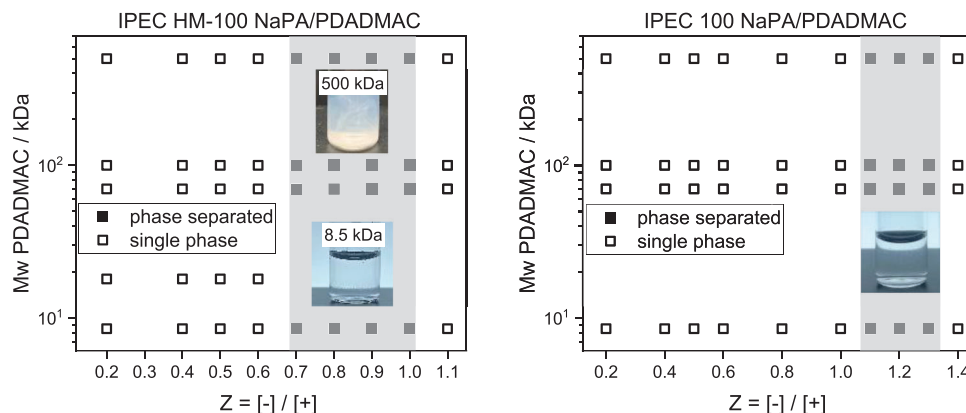


Figure 1. Phase behavior of IPECs based on modified HM-100 NaPA and unmodified 100 NaPA and PDADMAC of different Mw at varying charge ratio Z .

We compare the structure and phase behavior of complexes formed from PDADMAC with a wide range of Mw with short chain NaPA with ≈ 100 monomeric units and hydrophobically modified NaPA (HM-NaPA) with the same number of monomeric units and ≈ 10 mol% of dodecyl alkyl side chains. The hydrophobic modification was simply introduced by means of copolymerizing dodecyl acrylate as a monomer within the polymerization procedure for synthesizing the NaPA. In our investigations, we then studied first the phase behavior and then elucidated in detail the structure of the soluble complexes that are formed upon addition of the NaPA or HM-NaPA, which was done by a combination of static and dynamic light scattering (SLS, DLS) and small-angle neutron scattering (SANS).

2. Results and Discussion

2.1. Phase Behavior

Phase behavior of the samples was examined on the next day after the preparation, the nominal charge ratio Z is defined in this work as $Z = [\text{polyanion charges}]/[\text{polycation charges}]$. Visually, prepared IPECs of HM-100 NaPA with varying molecular weight PDADMAC would show a remarkable increase in turbidity upon increasing the HM-100 NaPA content from $Z = 0.2$ to $Z = 0.4$ (for the sample appearance see Figure S1 in Supporting Information), whereas following change in the sample appearance was not easily spotted by visual inspection, but was reflected in the increased scattering intensities as discussed in the following chapters. The formed IPECs exhibit phase separation within a region of charge ratios $Z = 0.7$ to $Z = 1.0$, as indicated in **Figure 1** that was independent of the Mw of used PDADMAC. Interestingly, for the 8.5 kDa, PDADMAC coacervation was observed at $Z = 0.8$, whereas for all higher Mw PDADMAC a very fine white precipitate was observed. This agrees with a report by Koetz et al.^[20] who also observed coacervation for very low and similar Mw PDADMAC and NaPA complexes.

In contrast for IPECs formed with unmodified NaPA visually transparent samples are formed within the range of charge ratios $Z = 0.2$ to $Z = 0.6$ (for the sample appearance see Figure S2 in Supporting Information). Phase separation occurs here only in a narrower region of charge ratios from 1.1 to 1.3. IPECs based on the lowest 8.5 kDa and the highest 500 kDa Mw PDADMAC

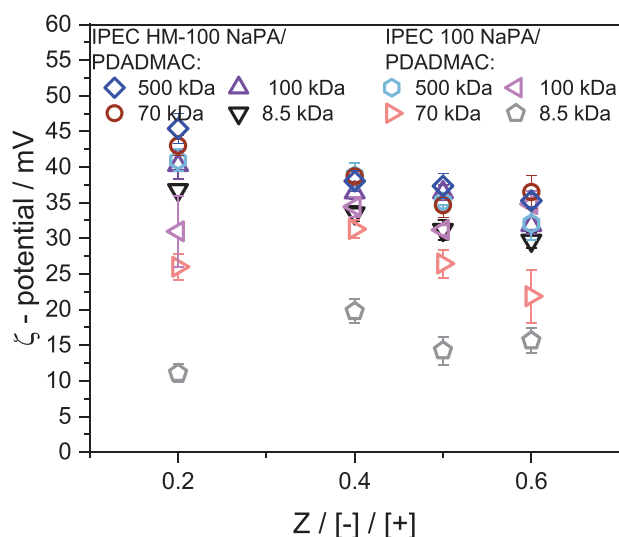


Figure 2. ζ -potential for complexes of modified HM-100 NaPA and unmodified 100 NaPA and PDADMAC of different Mw at varying charge ratio Z .

form an opalescent dispersion of coacervate droplets, while both of the medium Mw PDADMAC-based complexes form coalesced coacervate phases at $Z = 1.3$. All of the single-phase systems were of water-like viscosity.

In comparison, it is interesting to note that the hydrophobic modification leads to phase separation at low Z values, i.e., for lower amounts of added polyanion. In addition, the width of the biphasic region is smaller, where both changes confirm that the hydrophobic modification of the NaPA enhances the propensity of precipitation.

2.2. Zeta-Potential

The zeta potential allows to estimate the charge of the complexes, which is very important for estimating their colloidal stability. It was calculated from the measured electrophoretic mobility of all IPECs given in **Figure 2** and shows positive values as expected for the polycation excess region. Tabulated values are given in Table S4 in Supporting Information. IPECs based on the HM-NaPA

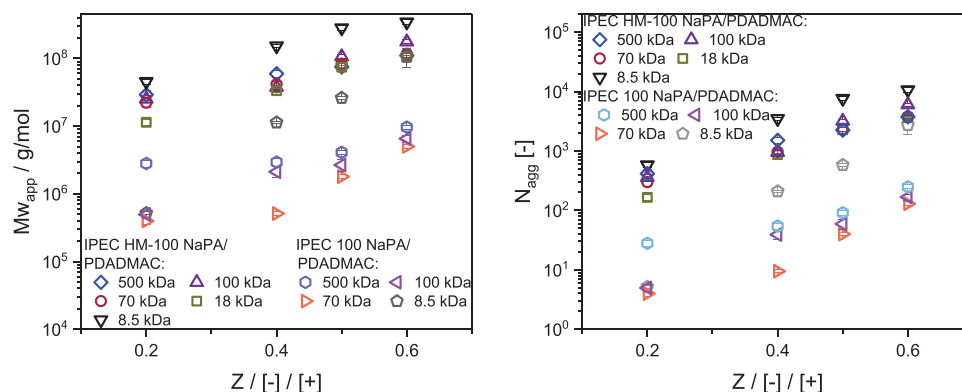


Figure 3. Apparent molecular weight Mw_{app} and effective polyanion aggregation number N_{agg} [-] for complexes of modified HM-100 NaPA and unmodified 100 NaPA and PDADMAC of different Mw at varying charge ratio Z , as determined from the SLS experiments.

show a consistent decrease of ζ -potential for all PDADMAC grades upon approaching a charge equilibrium which verifies an excess charge neutralization. The values of ζ -potential of PDADMAC with Mw 70 kDa and above are rather similar, whereas those of 8.5 kDa are slightly lower, the corresponding curve of ζ -potential versus the Mw of PDADMAC can be found in Figure S3 in Supporting Information. However, all remain above 30 mV, that is considered as a threshold value characteristic for stable colloidal particles. In the reference IPECs system based on unmodified NaPA, the ζ -potential is systematically becoming lower with decrease in Mw of PDADMAC (see Figure S3 in Supporting Information), getting well below 30 mV for 70 kDa and 8.5 kDa PDADMAC, which may indicate that here only a relatively small amount of PDADMAC is bound in the IPECs.

2.3. Static Light Scattering

For obtained structural information regarding the soluble IPECs formed light scattering experiments were done. From the static light scattering intensity (full set of scattering data given in Figure S4 and S5 in Supporting Information), the corresponding values for the apparent molecular weight Mw_{app} and the resulting effective aggregation numbers of polyanion chains N_{agg} [-] (with an assumption that formed IPEC is homogeneous) were calculated (see Equation (4) and Equation (9)) and are given in Figure 3 and in Table S5 and Table S6 in Supporting Information, for the effective aggregation numbers of polycation see Figure S6 in Supporting Information. All PDADMAC grades show a similar trend – an increase in the apparent molecular weight of the formed aggregates with increasing charge ratio Z . Moreover, 8.5 kDa PDADMAC shows the highest Mw_{app} of the formed aggregates and this is also the case for the reference system of unmodified NaPA. For longer PDADMAC, Mw_{app} shows only minor changes with variation of the molecular weight of the used polycation, the trend can be found in Figure S7 in Supporting Information. Incorporation of the dodecyl alkyl side chains into the polyanion backbone resulted generally in the increase of Mw_{app} weight by up to two orders of magnitude. Correspondingly, the effective polyanion aggregation numbers are the highest for 8.5 kDa PDADMAC both in the studied and in the reference systems and show only minor changes for higher Mw PDADMAC. Interestingly, the trend of

the highest Mw PDADMAC follows next to the one of the lowest Mw PDADMAC, which might be an indication of branching in PDADMAC internal chain structure at such high molecular weights. An increase in the IPECs effective polycation aggregation numbers with decreasing molecular weight of PDADMAC is observed (see Figure S6 in Supporting Information) as a result of fewer but much longer chains. Hence, the SLS shows that upon variation of the molecular weight of PDADMAC, the complexes formed for a given polyanion are rather similar in their overall structure and apparent molecular weights with somewhat enhanced incorporation of the polyanion chains into IPEC for the lowest Mw PDADMAC. SLS also confirms an influence of a hydrophobic modification of the polyacrylic acid on the complex formation, as is reflected in the strong increase of the two parameters Mw_{app} and N_{agg} [-] by a factor of 20–100 compared to the reference system with no hydrophobic modification (Figure 3).

The values for the gyration radii R_g can be found in the SI (Figure S8, Supporting Information) and generally show similar values for HM-100 NaPA and NaPA of 70–80 nm that become somewhat smaller with an increase of Z , thereby indicating a tendency for compaction.

2.4. Dynamic Light Scattering

All IPECs exhibit a monomodal relaxation of the intensity autocorrelation function (see Figure 4 and S9 in Supporting Information), which was fitted with a stretched exponential model, where the fitted stretched exponent, α , deviates just a little from 1, laying in the range of 0.90–0.96, thereby indicating a rather low polydispersity. The second-order cumulant expansion (see Equation (11, 12)) was used to determine the polydispersity indices PDI of the IPECs^[28] (for the fits see Figure S10 and S11 in Supporting Information). PDI values below 0.08 are characteristic for nearly monodisperse samples, whereas values above 0.7 indicate a very broad size^[29] distribution in the system. IPECs based on hydrophobically modified HM-100 NaPA showed mid-range values of PDI varying between 0.7 and 0.5 that were similar for the different Mw PDADMAC within the error bars (see Figure S10 in Supporting Information). Moreover, the PDI would systematically decrease upon approaching the charge equilibrium, as the system would become more compact and less and less dangling

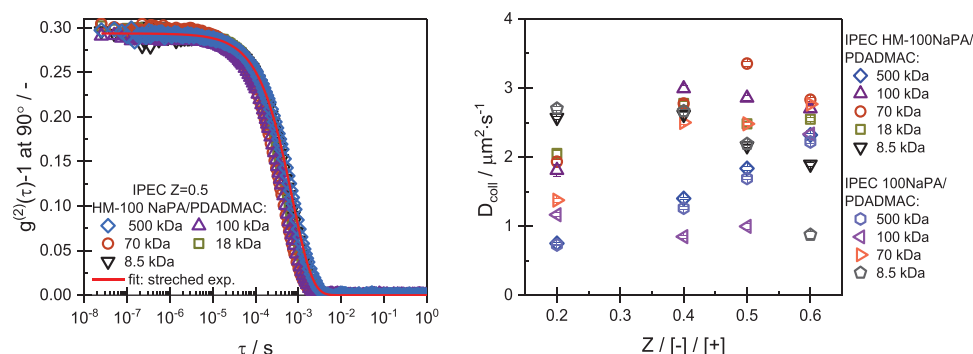


Figure 4. Intensity auto-correlation function at 90° for complexes of modified HM-100 NaPA and PDADMAC of different Mw at the charge ratio $Z = 0.5$ as determined from the DLS experiments with a stretched exponential fit; Collective diffusion coefficients D_{coll} for complexes of modified HM-100 NaPA and unmodified 100 NaPA and PDADMAC of different Mw at varying charge ratio Z , as determined from the DLS experiments.

free segments of PDADMAC chains were present in the system. PDI of the IPECs based on the unmodified NaPA showed on average higher values of PDI (see Figure S11 in Supporting Information), which also tend to decrease with the increase in the charge ratio Z .

From the slope of the fitted with the stretched exponential function decay rates Γ versus Q^2 curves the collective diffusion coefficient D_{coll} was deduced, which is shown in Figure 4 and Table S7 in Supporting Information.

The collective diffusion coefficients of the IPECs show a distribution between 0.5 and $3 \mu\text{m}^2 \times \text{s}^{-1}$. Upon approaching the charge equilibrium, at $Z = 0.6$ the spread of the parameter of IPECs based on the PDADMAC of different Mw becomes narrower with values close to $2.5 \mu\text{m}^2 \times \text{s}^{-1}$. In general, the hydrodynamic size of the IPECs is becoming smaller with increasing Z . As the SLS data in Figure 3 shows that at the same time their Mw_{app} is increasing, the complexes are apparently becoming more compact. Calculated apparent hydrodynamic radii R_h Equation (13) lay in the range of 70 – 90 nm for IPECs at $Z = 0.6$ (see Figure S12 in Supporting Information), that is similar to the extracted radii of gyration R_g (see Figure S8, Supporting Information). An effective density is calculated as $\rho_{\text{eff}} = \frac{Mw_{\text{app}}}{N_{\text{Av}} \cdot \frac{4}{3} \cdot \pi \cdot (R_h)^3}$, can be used as another measure to quantify the IPECs compactness. The variable (see Figure S13 in Supporting Information) once again confirmed the increased compactness of the formed aggregates upon approaching the charge equilibrium, as deduced for IPECs based on the HM-100 NaPA, without any clear trend for the variation in the Mw of PDADMAC. Interestingly, IPECs based on the unmodified NaPA show much lower effective densities of the aggregates. Apparently, the presence of the hydrophobic dodecyl alkyl moieties has an impact on the overall complex compactness.

2.4.1. Small-Angle Neutron Scattering (SANS)

As light scattering can only deliver a large-scale structural picture, SANS experiments were performed to obtain more detailed structural information. SANS data for IPECs formed by PDADMAC of different Mw with different amounts of HM-100 NaPA, mixing ratio described by Z , as well as for the reference IPECs formed by 8.5 kDa PDADMAC and NaPA are shown in Figure 5. It should be noted that in the SANS experiments, due to the

limited access to such experiments, we focused on the HM-100 NaPA and had only the option for one series with unmodified NaPA. For the plots of similar Z for the different Mw of PDADMAC see Figure S14 in Supporting Information. In general, it can be noted that the progression of the scattering curves for the HM-100 NaPA system with increasing Z looks rather similar, irrespective of the Mw of PDADMAC. The complexation leads to a substantial increase of scattering intensity at lower Q and a kink $\approx Q = 0.2$ – 0.3 nm^{-1} , where the slope of the curve becomes substantially reduced again. The scattering at higher Q follows a Q^{-1} behavior, potentially indicating a locally rod-like structure. Also, at this Q range the 8.5 kDa PDADMAC samples tend to show much lower (by a factor of ≈ 4) scattering intensity, thereby indicating of smaller or less local structures. However, the overall scattering curves remain rather similar, except for the 8.5 kDa PDADMAC samples, which at the same time show a bit higher intensity at low Q , which is in agreement with the higher intensity (and Mw_{app}) seen by SLS (Figure 3). Moreover, with increasing Mw of PDADMAC the shape of the scattering curve at low Q becomes somewhat more indicative of globular aggregates, i.e., it appears that the complexes become more compact, which is also in good agreement with the light scattering data.

As was already observed in SLS, the SANS once again confirms a strong influence of a hydrophobic modification of the polyacrylic acid on the complex formation. In contrast to the studied system where a substantial increase of scattering intensity at low Q is observed, the system with NaPA does not show this pronounced upturn at all, and correspondingly does not form any larger compact aggregates. This much enhanced tendency for aggregate formation then has to be attributed to the presence of the hydrophobic dodecyl alkyl side chains in the polyanion backbone. Here it might be noted that the formation of well-defined globular domains has been observed before by SANS experiments for the solutions of pure dodecyl-modified NaPA at lower and high pH.^[30]

SANS data was first analyzed in the low Q range via a shape-independent Guinier model. Calculated apparent molecular weights of the aggregates Mw_{app} (from the extrapolated I_0) and the effective polyanion aggregation numbers are given in Figure 6 and in Tables S8 and S9 in Supporting Information, respectively.

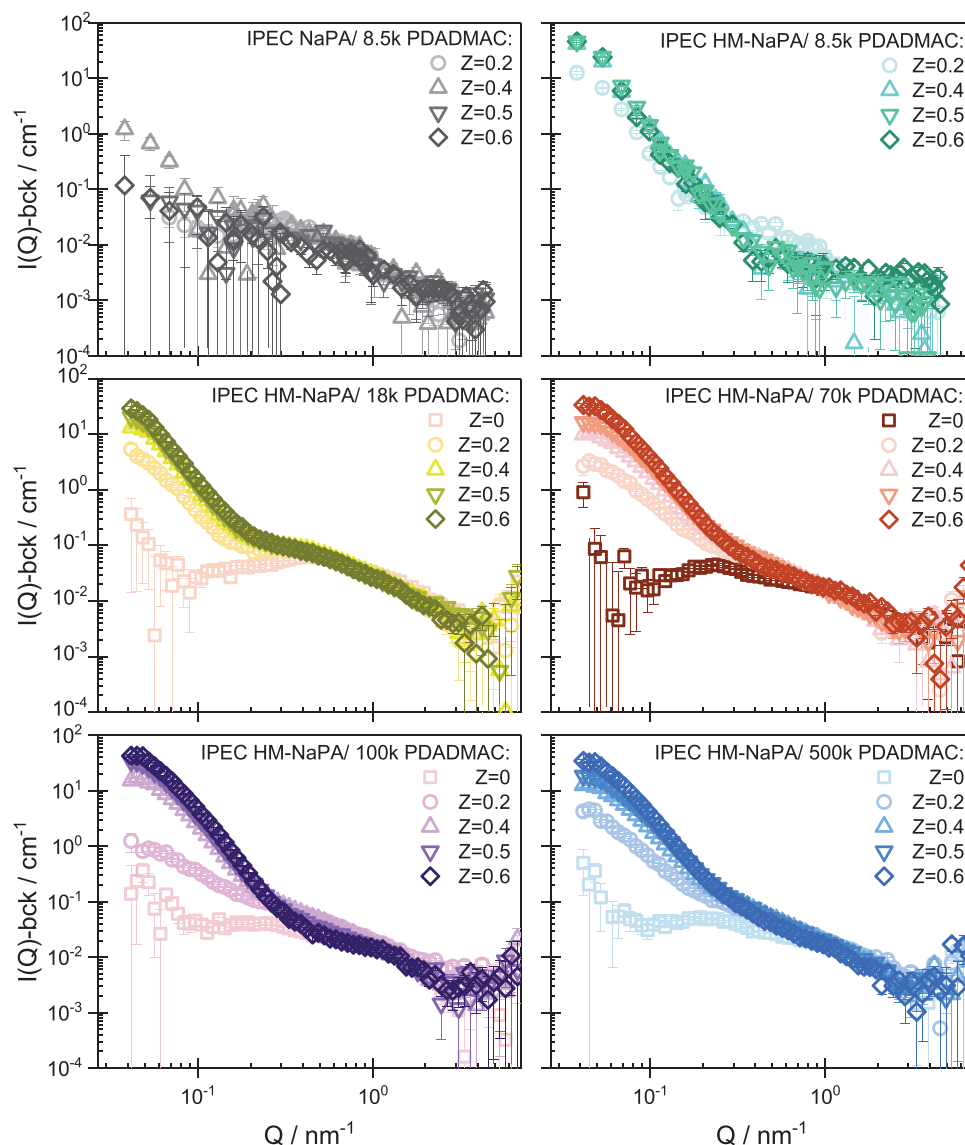


Figure 5. SANS intensity as a function of the magnitude of the scattering vector Q for complexes of HM-100 NaPA and PDADMAC of different M_w and a reference system with the lowest M_w PDADMAC. The mixing ratio $Z = [AA]/[DADMAC]$ was systematically varied.

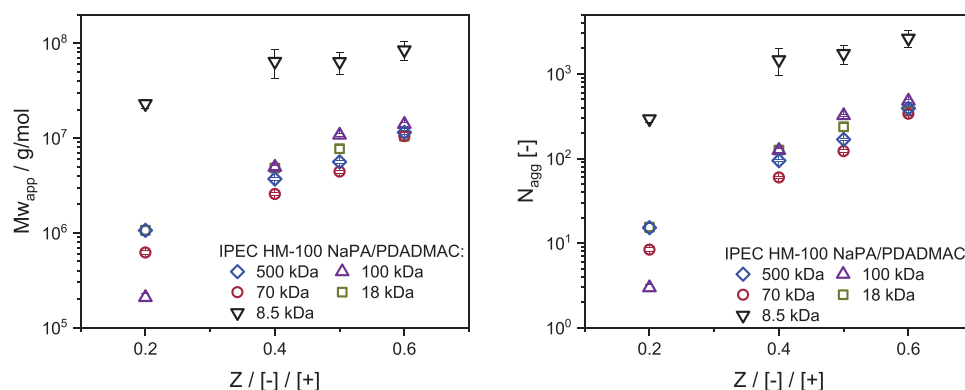


Figure 6. Apparent molecular weight $M_{w,app}$ and effective polyanion aggregation number N_{agg} for complexes of modified HM-100 NaPA and PDADMAC of different M_w , as determined from the SANS experiments.

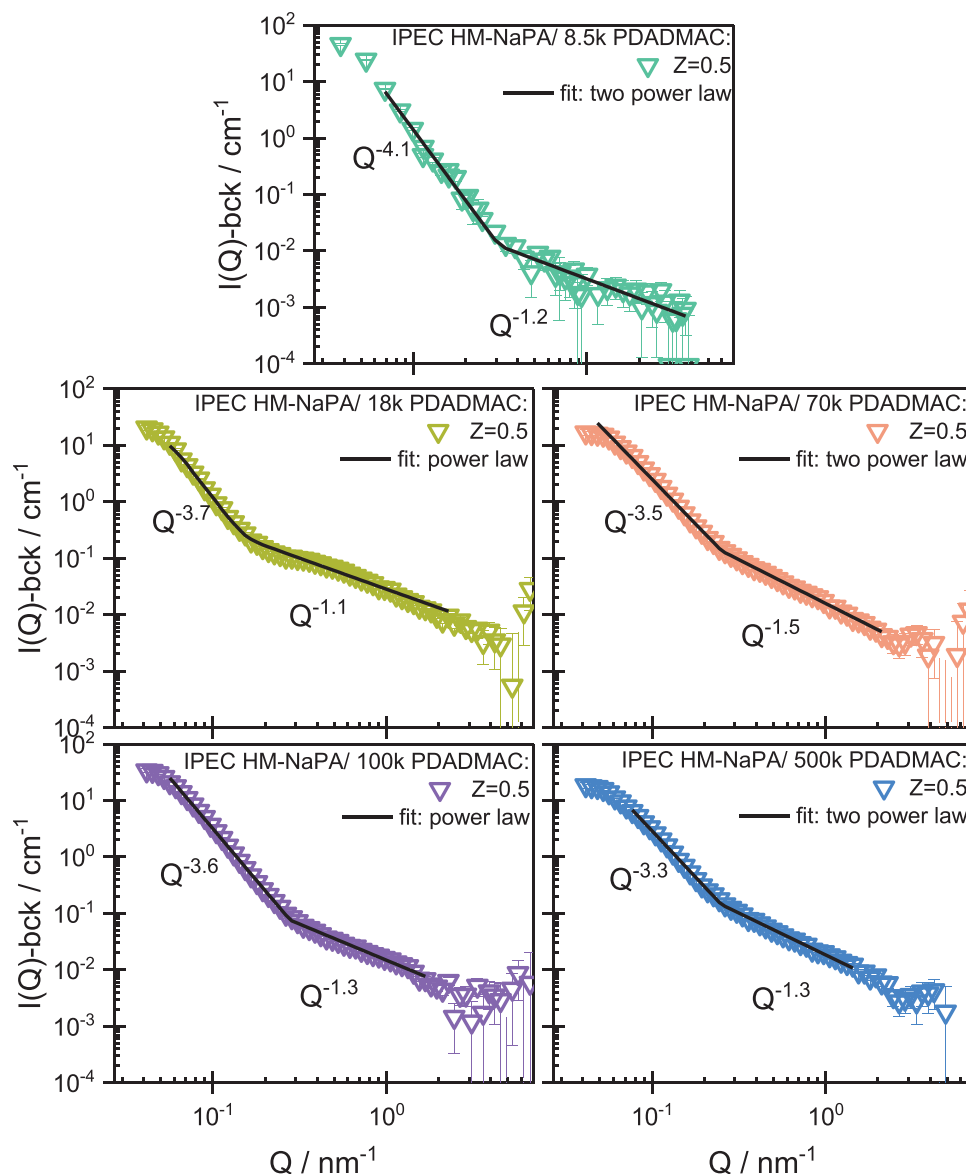


Figure 7. Fit of SANS data with the power law model for the case $Z = 0.5$ (other fits are given in the SI).

The trend is similar to that observed in the static light scattering experiments. The apparent molecular weights of formed aggregates increase when approaching the charge equilibrium, i.e., with increasing Z , showing the highest values for 8.5 kDa PDADMAC, which is also exhibiting the highest effective aggregation number of polyanion chains, and only slight dependence on the molecular weight of other used PDADMAC grades. Once again, the effective polycation aggregation numbers in Figure S15 in Supporting Information decrease with increase in Mw of PDADMAC, as a result of fewer but longer chains in the system. However, the obtained numbers are by about one order of magnitude lower than those determined from the static light scattering (Figure 3), which may be attributed to the different Q -range probed via each method, where in light scattering one naturally sees more the larger scale structures.

SANS data exhibit an onset of a plateau in the low- Q region, in the low- to middle- Q region the intensity shows a power law of $I(Q) \sim Q^{-3.3}$ to Q^{-4} that is an indication of cluster formation. In the low- Q region, where smaller structures are being probed, the power law flattens to $I(Q) \sim Q^{-1.3}$ what may be considered as an indication of rod-like structures in the system. The cross-point Q_{cross} of these two power law regimes can be used to estimate the persistence length as $l_p = 2.87/Q_{\text{cross}}$.^[31]

This simple model describes the experimental data quite well as shown in Figure 7 (other fits and the corresponding residuals are given in Figures S16–S20 in Supporting Information). The persistence length l_p calculated from the cross-point is shown below in Figure 8 and is also given in Table S10 in Supporting Information. The general trend for all of the investigated IPECs shows a shift of the cross-point of the two power law regimes

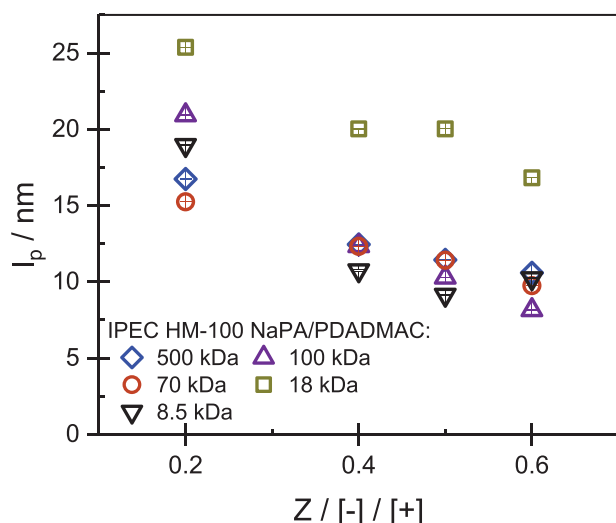


Figure 8. Persistence length l_p obtained from the SANS results for the IPECs with different Mw PDADMAC as a function of the mixing ratio Z .

to higher Q values as the nominal charge ratio Z of the IPECs increases. This shift results in a decrease in the calculated persistence length, indicating that the rigidity due to the electrostatic interactions becomes less prominent as the excess of the charges are getting more and more compensated. Moreover, for the charge ratios above 0.2 all HM-100 NaPA samples, irrespective of the Mw of PDADMAC, show very similar values, except for the 18 kDa. The origin of this deviating behavior is not absolutely clear, but appears to be related to the fact that here one sees a more prominent polyelectrolyte peak, that results in complications for the exact determination of the second power law region. This makes the deduced value for the 18 kDa PDADMAC samples much less reliable.

Another shape-independent model, the Beaucage model, can be used to describe interrelated structural levels present in a system.^[32,33] As can be concluded from the SANS data, IPECs containing hydrophobically modified polyacrylic acid exhibit cluster formation on a bigger scale with the presence of elongated substructures at larger spatial resolution. The data was fitted with the two-level Beaucage model ($N = 2$), as described by Equation (16), and which has as parameters the Guinier scaling factor G , a radius of gyration R_g , and the Porod exponent P . For the two-level Beaucage model the larger-sized structures then could be identified as the full size of the IPECs, while the smaller structures could be associated with the smaller-sized hydrophobic domains within these IPECs.

Example fits for IPECs at $Z = 0.5$ are shown in **Figure 9**, all fits and the corresponding residuals can be found in Figures S21–26 in Supporting Information. We note very good agreement for all experimental data sets. The fitted radii of gyration of the aggregates R_g and of the substructures $R_{g,s}$ are shown in **Figure 10** and are given in Table S11 in Supporting Information. The formed substructures of IPECs based on PDADMAC with molecular weight 18 kDa and higher show similar $R_{g,s}$ values of ≈ 2.5 nm, i.e., in good agreement with the expected size of the hydrophobic domains. The lowest molecular weight PDADMAC follows a similar trend up to charge ratio 0.5, where an upturn

of the parameter by a factor of 2 takes place. Interestingly, such a much larger size of the substructures (and already occurring at lower Z ratio) is seen for the case of the NaPA reference system. This indicates that for this situation of the shortest PDADMAC no well-defined compacted substructures can be formed and instead a more loose type of aggregation must take place. At the lowest charge ratio $Z = 0.2$, where the PDADMAC is in the most charge excess, the $R_{g,s}$ of the formed substructures are almost falling into one point, indicating the similarity of the units that is independent on the molecular weight of the polycation used. For all other PDADMAC systems $R_{g,s}$ is somewhat decreasing with increasing Z and becoming smaller than 2 nm, which indicates that here the structural size is increasingly dominated by the hydrophobic domains, whose size should be given by the length of the dodecyl alkyl chain. (**Figure 11**)

The size of the bigger domains R_g tends to increase with the Z ratio, as more and more charged groups are getting involved into the complex formation. PDADMAC grades of 8.5 and 18 kDa, which are the closest ones in terms of the chain length to the polyanion used, show the biggest aggregate sizes, whereas PDADMAC with higher molecular weights show similar sizes ≈ 30 nm for $Z = 0.4$ and above. Interestingly, at $Z = 0.2$ 500 kDa PDADMAC is the next after the low molecular weight grades, this might be the result of the branching in PDADMAC chains, that results in a much shorter length than what is to be expected of a completely linear architecture, and which becomes increasingly important with increasing Mw.^[34]

In order to obtain further information regarding the local structure of these aggregates, the SANS data was also fitted with a flexible cylinder model in the high Q range of $0.3\text{--}3\text{ nm}^{-1}$. For 18 kDa based IPECs the range start was shifted to 0.5, as the polyelectrolyte peak present at ca. 0.4 nm^{-1} makes data fitting complicated. The corresponding fits for $Z = 0.5$ are shown below, all further fits and the corresponding residuals can be found in Figures S27–S32 in the supporting information.

In these fits, the Kuhn length and radius of the cylinder were the only free parameters. The contour length was fixed at 100 nm for all series, since the fitted Q -range is not exhibiting a plateau, thus this parameter cannot be determined from the experimental data and must be larger than the experimental size window.

The obtained fit parameters are given in **Figure 12** and in Table S12 in Supporting Information. The radii r for IPECs based on PDADMAC grades starting from 70 kDa are similar to those we have determined before^[35] for PDADMAC cross-sectional radius of 0.6 nm. A similar value was found by Merta et al.^[36] and Patel et al.^[37] For the lowest Mw PDADMAC and its reference system as can already be qualitatively expected, fitted radii are similar and are by a factor of 2 smaller than those for 70 kDa to 500 kDa. The simple explanation is that here simply thinner rod-like domains are formed, but partly this could also arise from a more stretched shape of these domains. The Kuhn length l_b of the IPECs shows a pronounced drop from $Z = 0.2$ to $Z = 0.4$ but changes only slightly with further increase in Z . One explanation could be that at low charge ratio Z there are increasingly more PDADMAC chains in the complex that are not directly complexed and in addition there might be free PDADMAC molecules. As both are comparatively strongly charged they will be stiffer than chains complexed by oppositely charged polyelectrolyte. Hence, the higher l_b (Figure 12 right) and l_p (Figure 8) values at $Z = 0.2$

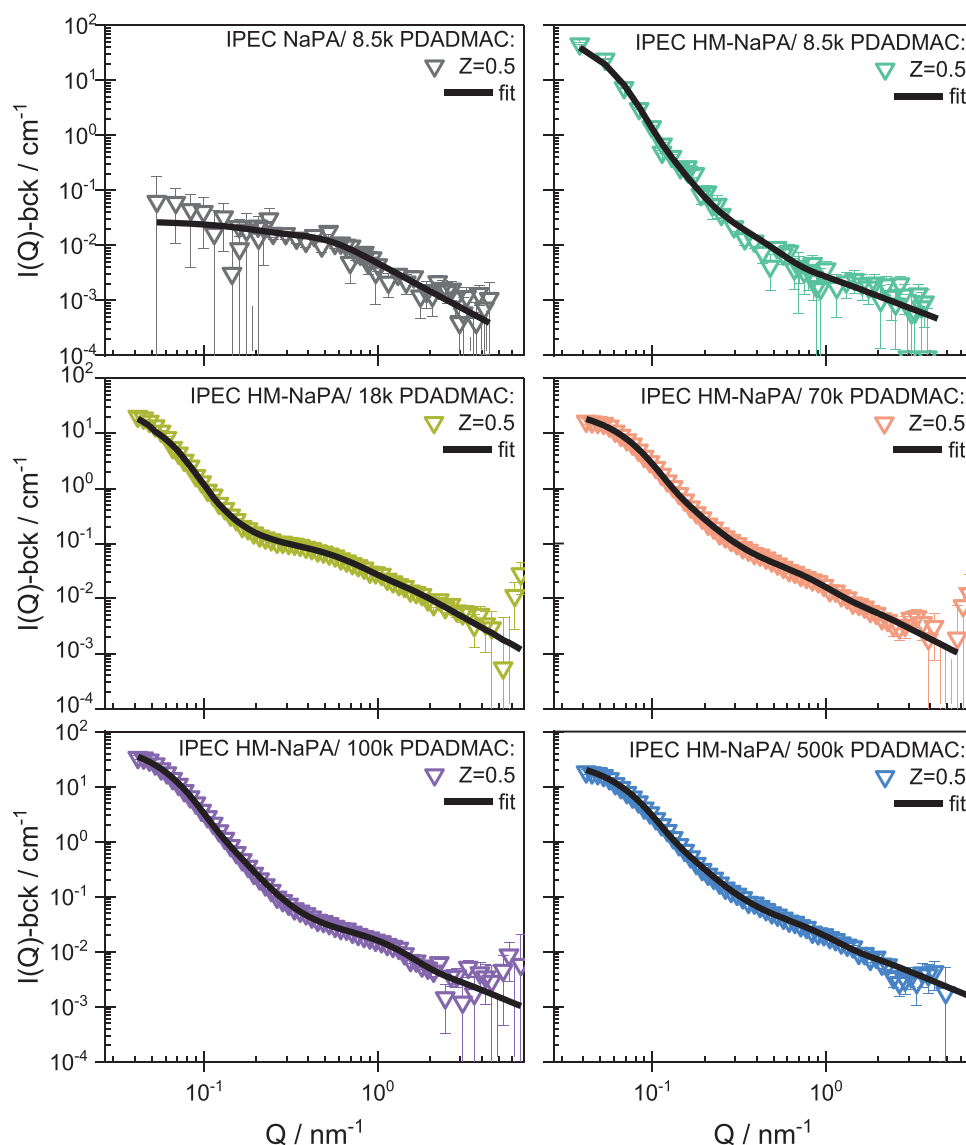


Figure 9. Fits of the SANS data by a shape-independent Beaucage model for IPECs with different Mw PDADMAC for the case of $Z = 0.5$ (fits for the other Z values are given in the SI).

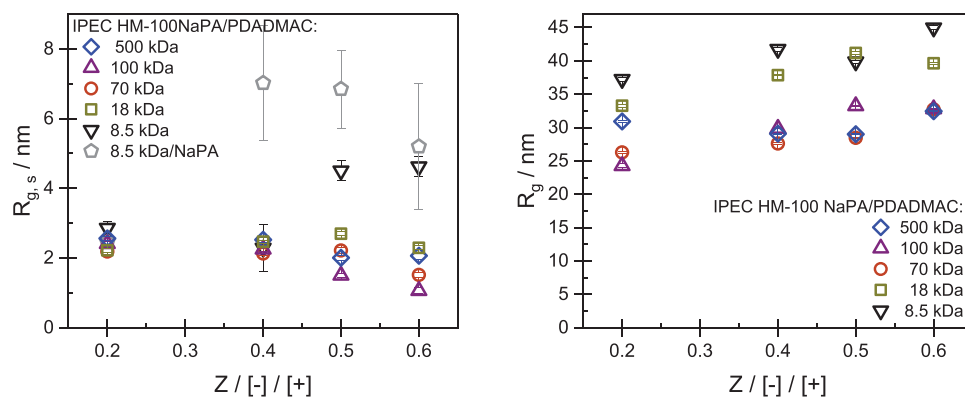


Figure 10. Radii of gyration of the substructures $R_{g,s}$ and the clusters R_g obtained from fitting the SANS data with the Beaucage model. Data are given as a function of the charge ratio Z for the IPECs with different Mw PDADMAC.

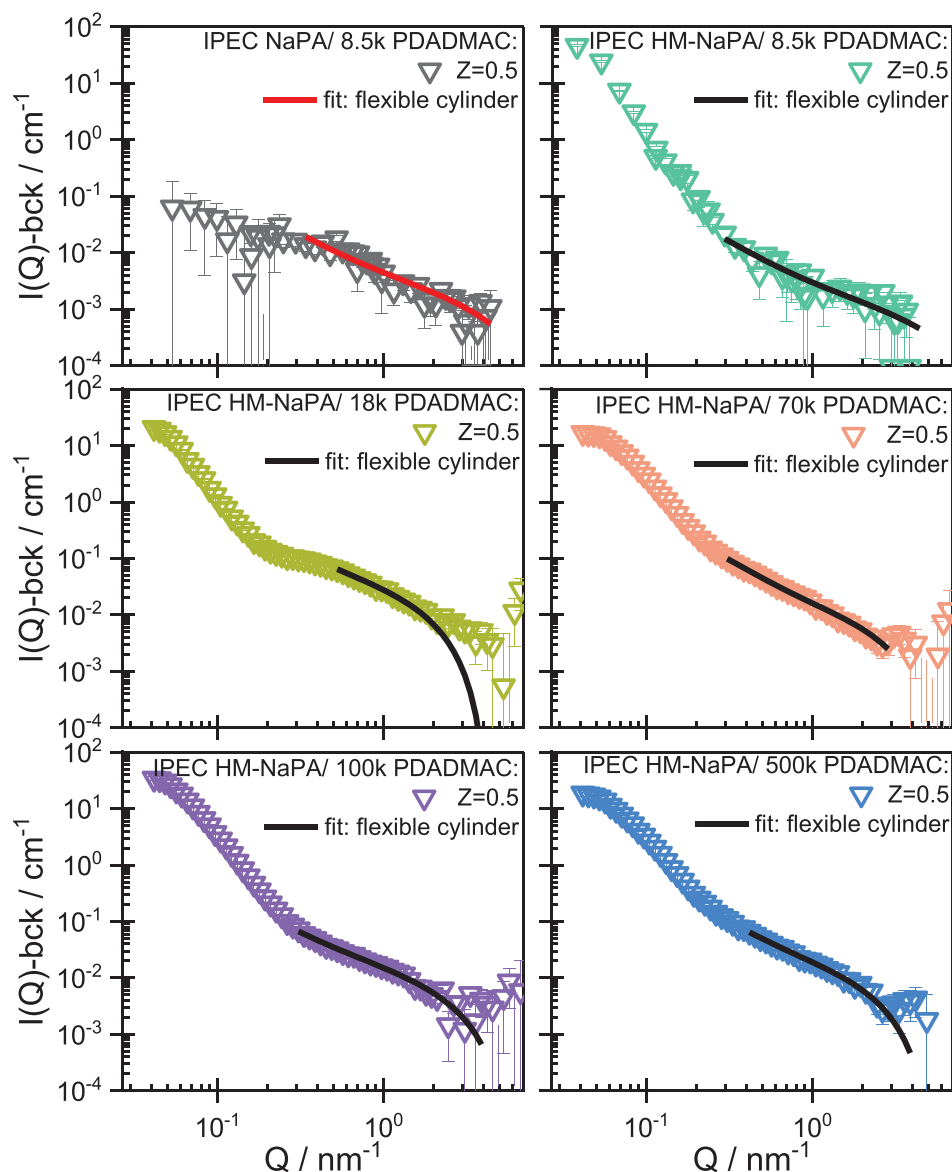


Figure 11. Fits of the high q -range of the SANS data by a model of flexible cylinders for IPECs with different M_w PDADMAC for the case $Z = 0.5$ and a reference system (fits for the other Z values are given in the SI).

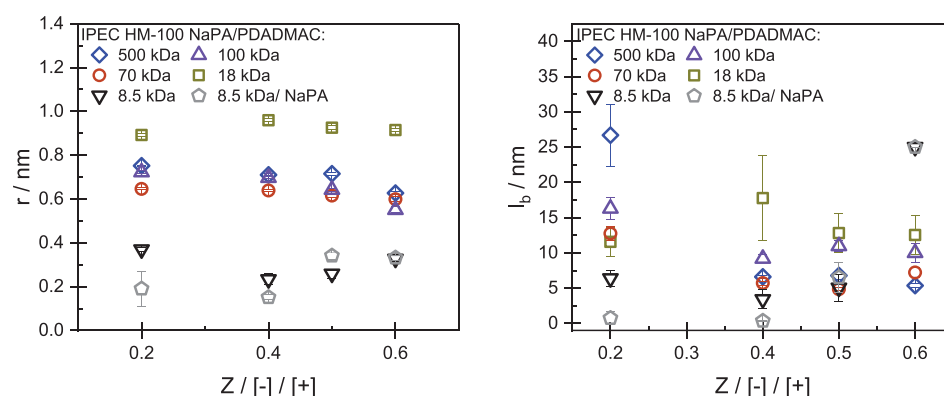


Figure 12. Fitted with a flexible cylinder model radius of cylinder r and Kuhn length l_b obtained from the SANS data for the IPECs with different M_w PDADMAC as a function of the charge ratio Z .

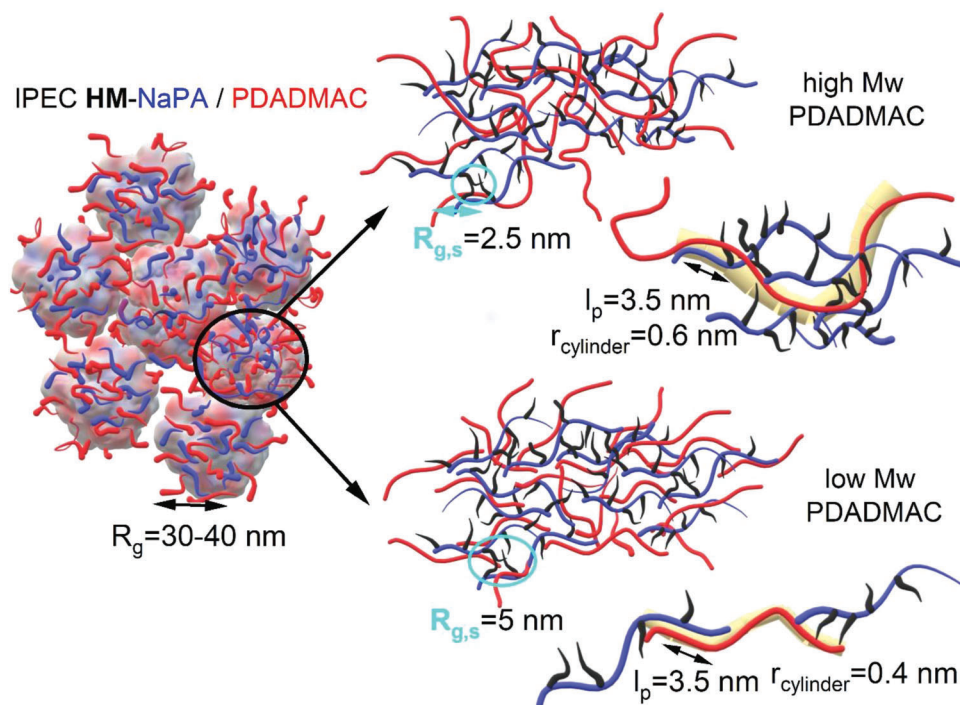


Figure 13. Structure of IPEC based on hydrophobically modified HM-100 NaPA and PDADMAC: Complexes tend to form clusters of aggregates (on the left), which are build-up from smaller sub-units, that locally have rod-like structures.

could result from this effect. For the IPECs prepared at the highest Z , the Kuhn length lays in the range of 5 to 12 nm. For 8.5 kDa the parameter at $Z = 0.6$ has too large an error bar to give a conclusive result. Given that $l_b = 2l_p$ this value is in a good agreement with the persistence length l_p calculated from the cross-point of the power law regions (Figure 8), and the overall trend as a function of Z and also with respect to the different Mw PDADMACs is quite similar.

3. Conclusions

IPECs based on hydrophobically modified polyacrylic acid sodium salt (HM-NaPA) and PDADMAC of varying molecular weight have been studied in the polycation excess region and the results were compared to the case of complexes with pure NaPA as a reference case. As seen by light scattering experiments, complexes become larger/heavier when approaching the charge equilibrium, where a biphasic region is observed, which is larger for the case of HM-NaPA. Quantitatively, SANS data of the complexes show similar trends for PDADMAC of Mw 18 kDa and above, and in addition, indicate the formation of similar local structures at the same charge ratio Z . The power law of $\approx Q^{-1.3}$ at higher Q indicates formation of rod-like structures as depicted in **Figure 13**, with fitted radii of ca. 0.65 nm for high Mw PDADMAC and 0.3 nm for 8.5 kDa as an indicator of more compact local structures. In parallel the Kuhn length is decreasing with increasing charge compensation from 12 to 5 nm for the highest Z ratio. This can be explained by a reduced chain stiffness as the initially fully charged PDADMAC chains become increasingly neutralized by oppositely charged complexing polyelectrolyte (see Fig-

ure 13). On a bigger scale these complexes tend to form clusters of aggregates with sizes in the range of 30–40 nm (see Figure 13), which are a build-up of smaller sub-units of 2.5–5.0 nm in size (see Figure 13).

The influence of hydrophobic modification of polyacrylic acid with dodecyl alkyl side chains was studied via comparison to the non-modified polyacrylic acid. SLS showed the formation of complexes with much lower Mw_{app} and a decrease of the aggregation number by almost one order of magnitude. Complementary SANS data of 8.5 kDa PDADMAC IPECs revealed differences at a larger size scale, where no substantial upturn of the scattering curves at low Q , characteristic for cluster formation, was observed for the reference system. Such cluster formation can then be largely related to the presence of hydrophobic chains in the polymer backbone. On a smaller probed domain length scale, the hydrophobically modified and the pure NaPA systems exhibit the same progression of the scattering curves, hence indicating formation of locally similar structures, which are determined by the polyelectrolyte chains.

In summary, it can be stated that the substitution of 10% of the carboxy units of NaPA by hydrophobic dodecyl alkyl side chains leads to a substantially altered aggregation behavior of complexes with PDADMAC. Much larger aggregates are formed due to the presence of hydrophobic interactions between the locally formed rod-like structures, where the length of the PDAMAC chains is another tuning parameter for the detailed structure. Accordingly, such hydrophobic interactions in IPECs allow to control structure and properties of these IPECs and this could have relevant implications for instance for their use as delivery systems.

4. Experimental Section

Materials: Polydiallyldimethylammonium chloride (PDADMAC) with an average molecular weight of 8.5 kDa was purchased from Polysciences Europe GmbH as a 28 wt.% solution in water, 18 kDa and 70 kDa PDADMAC grades were received as a gift from the Fraunhofer Institute for Applied Polymer Research (IAP), Golm, 100 kDa (very low molecular weight, <100 kDa) and 500 kDa (high molecular weight, 400–500 kDa) PDADMAC were purchased from Sigma-Aldrich as 35 wt.% and 20 wt.% solutions in water, respectively. Polymer grades purchased as solutions in water were freeze-dried before usage and redispersed in D₂O (99.9% isotopic purity, Deutero GmbH).

The polyanion HM-100 NaPA was obtained by simple copolymerisation of *tert*-butyl acrylate and dodecyl acrylate, leading to hydrophobically modified poly (acrylic acid), with a degree of polymerization DP = 100. The concentration of the dodecyl acrylate hydrophobic moiety was 10 mol% and it was statistically distributed along the polymer backbone. The polymer was synthesized in our lab via the atom transfer radical polymerization (ATRP), the details of the synthesis and molecular characterization (¹H-NMR for determining the extent of hydrophobic modification and GPC for determining Mw and Mw distribution) can be found in previously published work.^[38] Gel permeation chromatography (GPC) and ¹H-NMR spectrum of unhydrolyzed product can be found in Figures S33 and S34 in Supporting Information, respectively. The presence of hydrophobic modification was confirmed with fluorescence emission spectra shift of polarity-sensitive probe 6-propanoyl-2-dimethylaminonaphthalene, PRO-DAN shown in Figure S33 in Supporting Information. The acid was deprotonated using an equimolar (as determined from the titration) amount of NaOD.

As a reference system unmodified poly(acrylic acid, sodium salt) NaPA with average molecular weight 8 kDa was used, it was purchased from Sigma-Aldrich as a 45 wt.% solution in water. The polymer was freeze-dried before usage and redispersed in D₂O.

Stock solutions of PDADMAC were prepared at a nominal charge concentration of 0.01 M, counting a monomer unit as a single charged unit, this corresponds to the overall polymer concentration of 0.15 wt.%. A stock solution of HM-100 NaPA was prepared at the same nominal charge concentration (0.01 M), that was estimated from the molecular weight of the charged unit determined from titration. This corresponds to the overall polymer concentration of 0.10 wt.%. The ionic strength was adjusted to 5 mM via addition of NaCl. A stock solution of NaPA was prepared at a nominal charge concentration of 0.01 M, counting a monomer unit as a single charged unit, this corresponds to the overall polymer concentration of 0.07 wt.%. The ionic strength was adjusted to 5 mM via addition of NaCl. The parameters of stock solutions and IPECs are summarized in Tables S1–S3 in Supporting Information.

Prepared polyelectrolyte stock solutions were mixed at different ratios in order to obtain a certain nominal charge ratio Z, defined here as Z = [polyanion charges]/[polycation charges]. A component in deficiency was added to the component in excess as one shot and the mixture was immediately mixed using a vortex for 20 s, complexes were then let to stir overnight on a roller mixer. Complexes were prepared at least 12 h prior to measurements and at Z = 0, 0.2, 0.4, 0.5, and 0.6, in the polycation excess region. For the phase behavior studies complexes were prepared up to the charge ratios of 1.1 and 1.4 for HM-100 NaPA and 100 NaPA-based IPECs, respectively.

Methods–Zeta-Potential: Measurements were conducted on a Lite-sizer 500, by Anton Paar at 25 °C. Zeta-potential ζ was calculated from the measured electrophoretic mobility μ_E as:

$$\zeta = \frac{3\eta\mu_E}{2\epsilon_0\epsilon_r} \quad (1)$$

where η is the viscosity and ε_r is the relative permittivity of the medium, ε₀ is the permittivity of vacuum.

Static and Dynamic Light Scattering (SLS and DLS): Light scattering was measured on ALV/CGS-3 instrument, that allows simultaneous DLS and SLS measurements. The instrument is equipped with He–Ne

laser with a wavelength λ = 632.8 nm. Samples were measured inside a temperature-controlled toluene bath. Light scattering was recorded at several scattering angles θ, ranging from 30° to 130° set by an ALV-SP goniometer. The data was analyzed with SimplotQt^[39] (Python-based in-house software for light scattering data analysis).

The relation between a scattering angle and a magnitude of the scattering vector Q is as follows:

$$Q = \frac{4\pi n_0 \sin\left(\frac{\theta}{2}\right)}{\lambda} \quad (2)$$

where n₀ is a refractive index of solvent at a given temperature, in the current study it was deuterated water at 25 °C and n₀ was taken as 1.327. Static light scattering data were analyzed with the Guinier law, that allows the extrapolation to the forward scattering intensity at zero angle I₀(Q = 0), at the same time yielding the Guinier radius R_g:

$$\lim_{Q \rightarrow 0} I(Q) = I_0 \exp\left(-\frac{Q^2 R_g^2}{3}\right) \quad (3)$$

From extrapolated I₀ and measured refractive index increment (dn/dc = 0.18 mL g^{−1} the apparent molecular weights of aggregates Mw_{app} were calculated as:

$$Mw_{app} = \frac{I_0}{K \cdot c_g} \quad (4)$$

where c_g is a mass concentration and K is an optical constant calculated as:

$$K = \frac{4\pi^2 n_0^2}{\lambda^4 N_A} \cdot \left(\frac{dn}{dc}\right)^2 \quad (5)$$

where λ is a laser wavelength, N_A is the Avogadro constant, and (dn/dc) is a refractive index increment.

The polycation chains aggregation number was calculated from the SLS apparent molecular weight based on the mole fractions of each component. First, the average molar mass of a repeating unit, consisting of the oppositely charged units was estimated, based on the mole fraction f_[+] and f_[−] and molar mass of the charged units M_[+] and M_[−]:

$$M_{ru} = M_{[+]} \cdot f_{[+]} + M_{[-]} \cdot f_{[-]} \quad (6)$$

from this and previously calculated Mw_{app} average number of charged units per IPEC was calculated:

$$N_{CU} = \frac{Mw_{app}}{M_{ru}} \quad (7)$$

Here it should be mentioned, that the calculated Mw_{app} is a (weight) average of the formed complexes, and for large excess of the polycation (Z << 1) one might have some uncomplexed PDADMAC. For this case, the real Mw of the complexes would be higher than Mw_{app}, as that would be the mass average of the complexes and free polycation.

Finally, the aggregation number of polycation and polyanion chains with a degree of polymerization of charged unit DP_[+] and DP_[−] for PDADMAC and NaPA, respectively was calculated with an assumption of the formation of a completely homogeneous IPEC as:

$$N_{agg}^{[+]} = \frac{f_{[-]} \cdot N_{CU}}{DP_{[+]}} \quad (8)$$

$$N_{agg}^{[-]} = \frac{f_{[+]} \cdot N_{CU}}{DP_{[-]}} \quad (9)$$

The DLS measurements yielded an intensity autocorrelation function $g^{(2)}(\tau)$ that was recorded via ALV 5000/E multiple τ correlator.

By means of fitting intensity autocorrelation function, a relaxation rate Γ can be determined. Functions used for fitting are stretched exponential Equation (10) and the second order cumulant expansion Equation (11):

$$g^{(2)}(\tau) - 1 = B + \beta e^{-2(\Gamma\tau)^\alpha} \quad (10)$$

here B is a baseline constant that was set to 0, β governs the intercept of the correlation function, α is a stretching exponent and $0 < \alpha \leq 1$, Γ is a relaxation rate.

$$g^{(2)}(\tau) - 1 = B + \beta e^{-2(\Gamma\tau)^\alpha} \left(1 + \frac{\mu_2}{2!} \tau^2\right)^2 \quad (11)$$

here μ_2 is the second moment of the cumulants expansion. When normalizing the second cumulant to the first, which is describing a mean diffusion coefficient, a variable describing the relative width of the distribution that is referred to as the polydispersity index PDI is obtained:

$$PDI = \frac{\mu_2}{(\mu_1)^2} \quad (12)$$

From the slope of Γ versus Q^2 a collective diffusion coefficient D_{coll} can be determined which is related to a hydrodynamic radius R_h via the Stokes-Einstein relation, with an assumption of a spherical particle:

$$R_h = \frac{k_B \cdot T}{6\pi \cdot \eta_0 \cdot D_{coll}} \quad (13)$$

where k_B is the Boltzmann constant, T is the temperature and η_0 is the solvent viscosity.

Small-Angle Neutron Scattering: SANS measurements of IPECs based on 18 kDa, 70 kDa, 100 kDa, and 500 kDa PDADMAC were performed at the ISIS Neutron and Muon Source facility on the Larmor Instrument. The experimental wave length range λ was 0.9–13.3 Å, the distance between the detector and a sample was 4.1 m, yielding the fixed Q -range of ≈ 0.004 – 0.5 Å^{-1} . Samples were measured in quartz cuvettes with an optical path length of 2 mm.

SANS measurements of IPECs based on 8.5 kDa PDADMAC were performed at the Budapest Neutron Centre on the Yellow Submarine instrument.^[40] Three configurations were used with mean neutron wavelengths λ of 4.2 Å and 12.5 Å, and sample-to-detector distances of 1.14 and 5.26 m, yielding the covered Q -range of ≈ 0.004 – 0.44 Å^{-1} . Samples were measured in quartz cuvettes with an optical path length of 2 mm.

Data analysis was performed with SasView,^[41] an open-source scattering analysis software.

SANS data was fitted with a shape-independent two-power law model, that calculates an empirical functional form for scattering data characterized by two-power laws. The scattering intensity is calculated as:

$$I(Q) = \begin{cases} A \cdot Q^{-p_1} + \text{background} & Q \leq Q_c \\ C \cdot Q^{-p_2} + \text{background} & Q > Q_c \end{cases} \quad (14)$$

where Q_c is the cross-point between the two power laws, with the p_1 and p_2 being the power law exponents at low and high Q , respectively. The parameter A is the scaling coefficient that sets the overall intensity of the lower Q power law region and the scaling for the second power law region is then scaled as:

$$C = \frac{A Q_c^{p_2}}{Q_c^{p_1}} \quad (15)$$

Upon fitting A , Q_c , p_1 , and p_2 were set as free parameters.

SANS data was fitted with the shape-independent two-level ($N = 2$) Beaucage model,^[32,33] that is able to approximate the scattering occurring

from different types of particles, including fractal clusters, random coils, ellipsoidal particles, etc. The scattering intensity is calculated as:

$$I(Q) = \sum_{i=1}^N \left[G_i \exp\left(-\frac{Q^2 R_{gi}^2}{3}\right) + B_i \exp\left(-\frac{Q^2 R_{gi}^2}{3}\right) \left(\frac{1}{Q_i^*}\right)^{P_i} \right] \quad (16)$$

$$Q_i^* = Q \left[\text{erf}\left(\frac{Q R_{gi}}{\sqrt{6}}\right) \right]^{-3}$$

with the Guinier scaling pre-factor G , a pre-factor specific to the of power law scattering B , a radius of gyration R_{gi} , and the Porod exponent P that is a scaling exponent of the power law that gives an information of the fractal dimension of the objects. In this work R_{g1} and the Porod exponents, P_1 are designated as R_g and P for the large structures and R_{g2} and P_2 are designated as R_{gs} and P_s for the smaller substructures.

For the HM-100 NaPA-based IPECs R_g and R_{gs} , B_1 , B_2 , and G_2 were the free parameters. The parameter G_1 was fixed to the forward scattering intensity extrapolated via the previously done Guinier approximation and the power laws P and P_s were fixed to the values previously obtained via the power law fit. The only exception was the 18 kDa PDADMAC system, where the P_s was set as a free parameter.

In the case of the pure NaPA reference system, the model was reduced to the one-level ($N = 1$) and all the parameters were set as free parameters.

SANS data was fitted with a flexible cylinder model that is described by Pedersen et al.^[42,43] and Chen et al.^[42,43] The model is of a number of locally stiff rods defined by the cross-sectional radius r , the persistence length l_p that characterizes the stiffness of the system and the contour length L . The mathematical description of the corresponding form factor $P(Q)$ can be found in the SI in Equation S1–S3, Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in the ISIS Neutron and Muon Source Data Journal at <https://data.isis.stfc.ac.uk/doi/STUDY/108676692/>.

Keywords

amphiphilic copolymers, complex formation, self-assembly, small-angle neutron scattering (SANS)

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