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Topologically Controlled Interpolyelectrolyte Complexes

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ABSTRACT: The complexation of a cylindrical polyelectrolyte−brush−surfactant complex (PMMPSS−C_{12}) and an oppositely, highly charged cylindrical polyelectrolyte−brush (PMMPEI−PEO) in dimethylformamide (DMF) leads to the formation of kinetically controlled interpolyelectrolyte complexes. In contrast, complexation employing a slightly charged PMMPEI−PEO results in topologically controlled complexes possessing cylindrical morphologies. The composition of the complexes is analyzed by light scattering and atomic force microscopy. In the investigated range of composition, the complexes consist of one PMMPSS−C_{12} and, with increasing content of PMMPEI−PEO, a growing number of PMMPEI−PEO. The results indicate—in contrast to the commonly described interpolyelectrolyte complexation—that the formed complexes are independent of the polymer concentration and the sequence of addition. Also, from detailed analysis of the light scattering data it can be argued that the complexes are able to equilibrate.

Introduction

Interpolyelectrolyte complexes (IPEC), also sometimes called simplexes, are spontaneously formed upon mixing of solutions of polyelectrolytes of opposite charges. They are present both, in nature as well as in many technical applications.[1,2] The main driving forces for the complex formation are the gain of entropy due to the release of bound counterions, as well as the strong interionic interactions of the polyions leading to kinetically controlled complex formation.[3,4] This effect is increasing with increasing charge and molecular weight of the polyelectrolytes. Typically, the IPECs possess a compact, globular shape and consist of several molecules of each component. The closer the charge ratio to 1, the less defined the complexes are, until finally—depending on the overall concentration—macroscopic precipitation is observed.[1,5–7]

So far, the influence of the topology of the starting components on the structure of the complexes has not been investigated. Synthetic complexes of defined molecular structure have rarely been observed, even with semiflexible polyelectrolytes such as DNA.[8–10] An interesting example is the complex formation between DNA and cylindrical polymers possessing dendritic, cationic side chains by Goessl et al.[11] Within a narrow concentration range and depending on the sequence of addition, helical complexes with a core of the cylindrical polymer and the DNA wrapped around this core have been observed. In addition to the intended topological control of the complex formation, it is interesting to investigate the question, whether equilibrium-like structures can be obtained, independent of polymer concentration and sequence of addition.

This will be investigated in the following employing cylindrical polyelectrolytes based on semiflexible polymacromonomers. Polymacromonomers are obtained typically by free radical polymerization of macromonomers.[12] Wintermantel et al. showed that the steric overcrowding of the oligomeric side chains leads to a stretching of the main chain and therefore to a semiflexible, cylindrical structure. The influence of the topology on the complexation is studied using negatively charged polystyrenesulfonate polymacromonomers (PMMPSS) and positively charged polyethyleneimine polymacromonomers (PMMPEI). If the complexation is performed in water, the typical kinetically controlled complex formation as described above is observed. In order to decrease the number of effective or dissociated charges, the complexation is going to be undertaken in an organic solvent such as dimethylformamide (DMF), which has a lower dielectric constant. Unfortunately, the polyelectrolytes are not soluble in DMF. Therefore, instead of using the polyelectrolytes directly, the PMMPSS was first fully complexed with the surfactant dodecyltrimethylammonium bromide (PMMPSS−C_{12}), which leads to solubility in DMF.[13] In order to achieve solubility in DMF in case of PMMPEI, it also has been modified by grafting an average of six poly(ethylene oxide) chains to each PEI side chains (PMMPEI−PEO). With these, the complex formation is investigated in organic solvents. The employed polymacromonomers are shown schematically in Figure 1.

Experimental Part

Materials. All chemicals have been employed in p.a. quality (Aldrich), water was purified with a Milli-Q system (Waters).

Methods. Static (SLS) and dynamic (DLS) light scattering were performed at 20 °C using an ALV-SP-86 goniometer, an ALV-3000 Correlator, a 25 mW Uniphase HeNe laser ($\lambda_0 = 632.8$ nm) and an ALV/High-QEAPD-Avalanche diode fiber optics detection system. Each sample was filtered with Millex-LG filters (pore size 0.2 μm, Millipore). A Nanoscope IIIa Multi-Mode instrument (Digital Instruments) was used in tapping mode for AFM pictures. The solutions were spin cast onto freshly cleaved mica. A Millipore Ultracel PLGC membrane (MWCO 10 kDa) was employed for ultrafiltration. Dialysis was performed with Spectra/Por Float-A-Lyzer (reg. cellulose, MWCO 10 kDa).

Synthesis. For the synthesis of PMMPEI−PEO, poly(*N*-benzoyl ethylene imine) macromonomers possessing a *N*-(4-vinylbenzyl)piperazine end group have been synthesized first according to the literature.[14] Molecular weight determination of the macromonomers by MALDI−TOF mass spectrometry yielded an number average molecular weight of $M_n = 4290$ g/mol and $M_w/M_n = 1.04$ (weight average degree of polymerization $P_w = 28$). The macromonomers have been homopolymerized radically,[15] resulting in the formation of polymacromonomers with $M_w = 1.5 \times 10^6$ g/mol (main chain $P_w = 340$, results from SLS in chloroform, dn/dc = 0.145 mL/g).[16] Because free radical polymerization is employed, it should be mentioned that the polydispersity of the main chain is rather high and typically small fractions of spherelike polymacromonomers will still be present in the sample.[12] Subsequent polymer analogous hydrolysis resulted in the formation of polymacromonomers with poly(ethylene imine) side chains. Elemental

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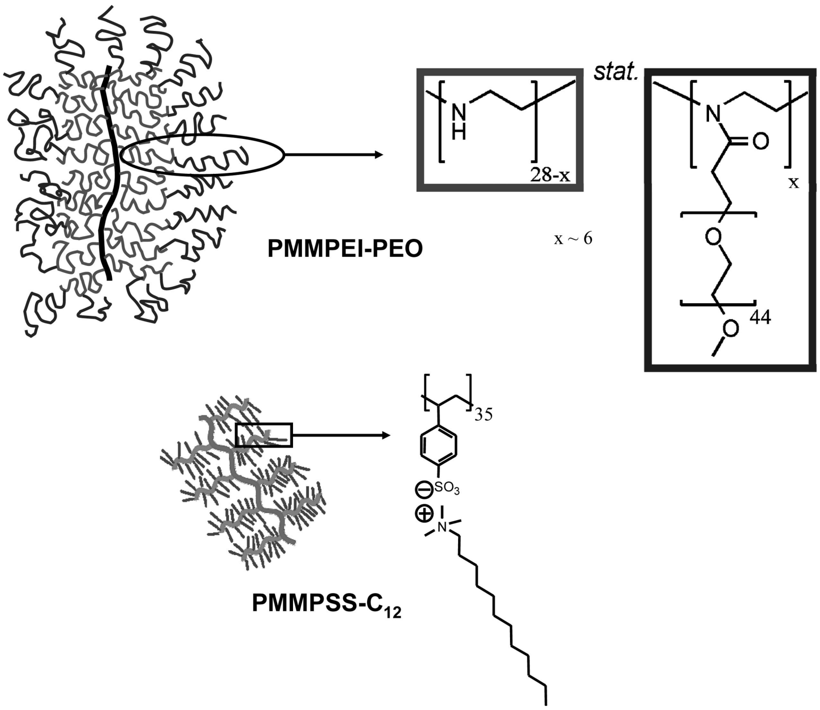

Figure 1. Schematic pictures of the employed cationic and anionic polymacromonomers.

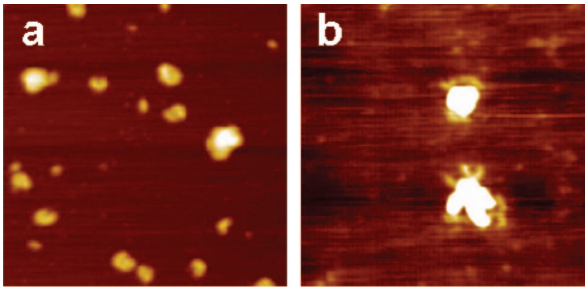

Figure 2. AFM pictures (height, 0.5 × 0.5 μm^2) of the complexes obtained from PMMPSS−C_{12} and highly charged PMMPEI−PEO, synthesized at 1.0 mg/L and spin cast from DMF (2 mM LiBr): (a) starting with a solution of PMMPSS−C_{12}, *w*(PMMPEI−PEO) = 0.1; (b) starting with a solution of PMMPEI−PEO, *w*(PMMPEI−PEO) = 0.5. The corona of PMMPEI−PEO can clearly be seen in part b.

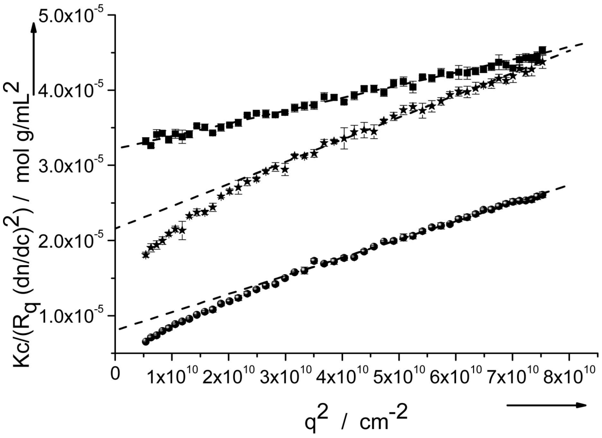

Figure 3. Static light scattering of complexes of PMMPSS−C_{12} and highly charged PMMPEI−PEO, synthesized in DMF (*c* = 0.2 g/L, 2 mM LiBr), not d*n*/d*c* corrected. Key: square, *w*(PMMPEI−PEO) = 0; star, *w*(PMMPEI−PEO) = 0.27; circle, *w*(PMMPEI−PEO) = 0.50.

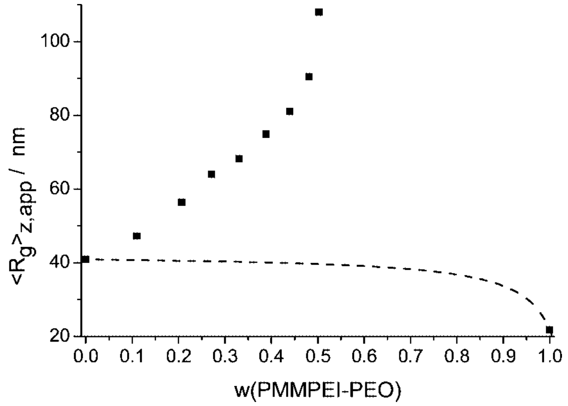

Figure 4. Radius of gyration determined for the complexes of PMMPSS−C_{12} and highly charged PMMPEI−PEO in DMF (2 mM LiBr). The dashed line corresponds to the expected values for a hypothetical homopolymer mixture.

Table 1. Determined Radii of Gyration of the Complexes of PMMPSS−C_{12} and Highly Charged PMMPEI−PEO

w(PMMPEI−PEO)	$\langle R_g \rangle_{z,\,app}$/nm
0.00	40.9
0.11	47.2
0.21	56.4
0.27	64.0
0.33	71.9
0.39	74.9
0.44	81.0
0.48	90.5
0.50	94.8
1.00	21.8

analysis confirmed 100% hydrolysis.[17] Reactive poly(ethylene oxide) oligomers (mPEG−SPA-2000, *M* = 2000 g/mol, Nektar, Huntsville, AL) have been statistically grafted to the side chains (PMMPEI−PEO).[18] Subsequently, the sample has been dialyzed against Milli-Q water (pH = 7.0). Elemental analysis yielded an average grafting density of six ethylene oxide chains per ethylene imide side chain. This sample refers to the slightly charged PMMPEI−PEO. Literature indicates a residual chemical charge of still approximately 50% of the imine functionalities at pH = 7.0.[19] Highly charged PMMPEI−PEO was obtained by addition of 15-

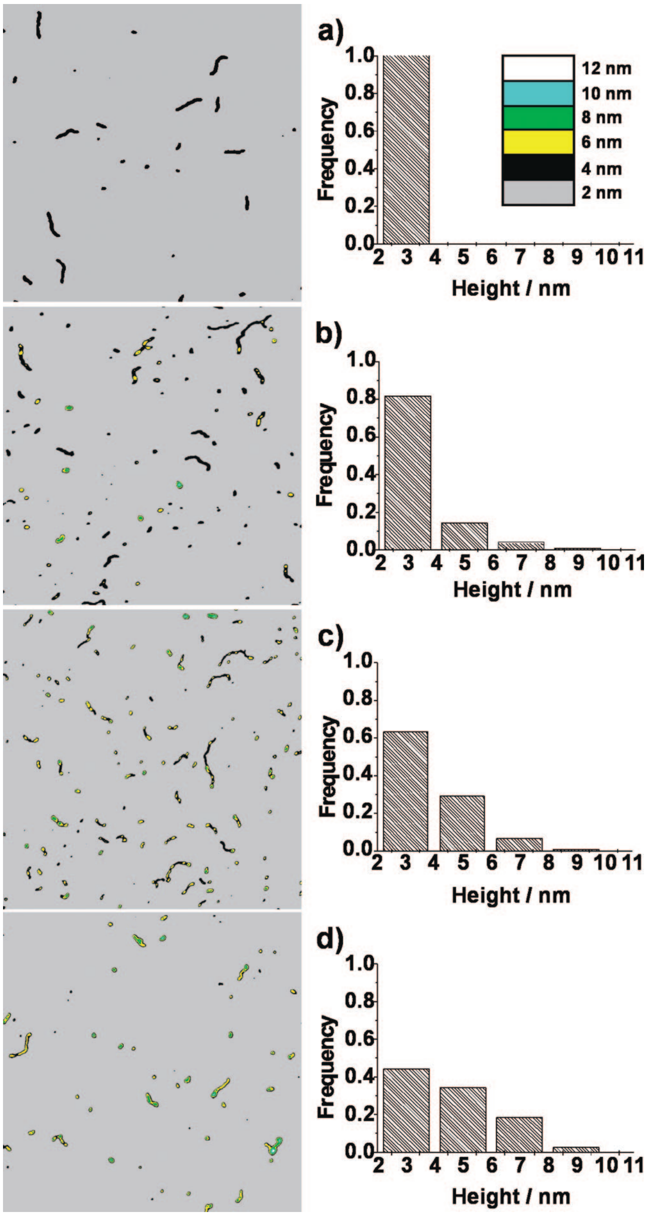

Figure 5. AFM pictures (height, left, size: 1.5 × 1.5 μm^2) of complexes of PMMPSS−C_{12} and slightly charged PMMPEI−PEO and the corresponding height frequencies determined (right): (a) *w*(PMMPEI−PEO) = 0.00; (b) *w*(PMMPEI−PEO) = 0.33; *w*(PMMPEI−PEO) = 0.70; *w*(PMMPEI−PEO) = 0.87. Upper right corner: height scale.

fold molar excess (per N) of concentrated HCl (0.2 vol %) to PMMPEI−PEO in DMF (c = 1 g/L).

PMMPSS was obtained by free radical polymerization of polystyrene macromonomers having a methacrylic end group (M_n = 3640 g/mol, M_w/M_n = 1.05, both MALDI−TOF mass spectrometry).[20] Free radical homopolymerization was performed to obtain polymacromonomers with polystyrene side chains (M_w = 1.6 × 10^6 g/mol, main chain P_w = 410, results from SLS in tetrahydrofurane, dn/dc = 0.193 mL/g).[21] Sulfonation with acetyl sulfate and subsequent neutralization with excess sodium hydroxide led to the formation of PMMPSS, which was purified by ultrafiltration.[22] Elemental analysis confirmed a degree of sulfonation of 100%. To a solution of PMMPSS in water (c = 1 g/L) dodecylammonium bromide (c = 200 g/L) was added until precipitation of the complex. Subsequent washing and liophilization yielded PMMPSS−C_{12}. Elemental analysis confirmed 100% complexation.

A detailed description of the complex formation by mixing of the polymer solutions is given in the Supporting Information.

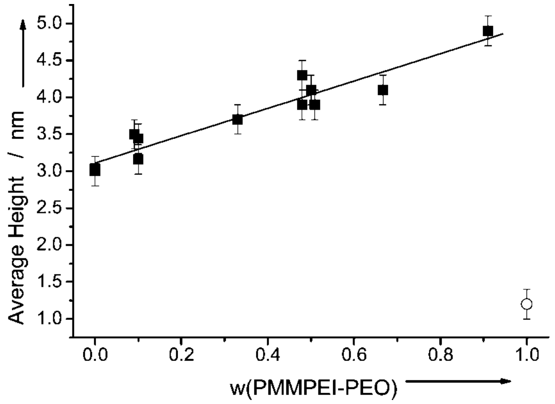

Figure 6. Average height of the complexes of PMMPSS−C_{12} and slightly charged PMMPEI−PEO, determined above a threshold of 2 nm (filled squares), and average maximum height of PMMPEI−PEO (open circle).

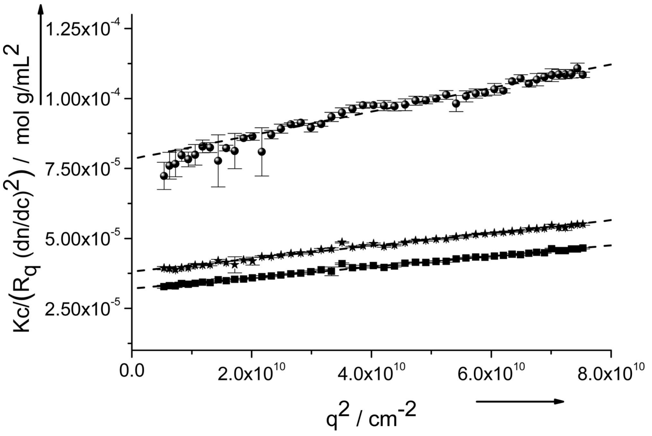

Figure 7. Static light scattering of complexes of PMMPSS−C_{12} and slightly charged PMMPEI−PEO in DMF (2 mM LiBr), not dn/dc corrected: square, *w*(PMMPEI−PEO) = 0.13; star, *w*(PMMPEI−PEO) = 0.48; circle, *w*(PMMPEI−PEO) = 0.87.

Table 2. Results Obtained from Light Scattering of Complexes of PMMPSS−C_{12} and Slightly Charged PMMPEI−PEO in DMF (2 mM LiBr)

w(PMMPEI−PEO)	$\langle R_g \rangle_{z,\ app}$/nm	$\langle R_h \rangle_{z,\ app}$/nm	$\rho = R_g/R_h$	polymer started
0	40.9	24.2	1.69	PMMPSS−C_{12}
0.13	42.4	25.4	1.67	PMMPSS−C_{12}
0.33	41.4	24.5	1.69	PMMPSS−C_{12}
0.48	42.5	26.9	1.58	PMMPSS−C_{12}
0.48	42.5	25.9	1.64	PMMPEI−PEO
0.70	39.9	25.7	1.55	PMMPEI−PEO
0.87	40.2	27.4	1.47	PMMPEI−PEO
1.0[a]	*21.8*	13.5	1.61	PMMPEI−PEO

[a] PMMPEI−PEO partly associated with larger structures, see Results and Discussion.

Results and Discussion

The complexation of PMMPSS and PMMPEI−PEO in water also leads to the commonly observed kinetically controlled structures, independent of the degree of charges on the PMMPEI−PEO, which can be influenced by changing the pH of the solution (data not shown).

Complex Formation Using PMMPSS−C_{12} and Highly Charged PMMPEI−PEO. A comparable behavior is obtained, when the complexation between PMMPSS−C_{12} and highly charged PMMPEI−PEO is performed in DMF. As examples, the AFM pictures of the complexes obtained at two different compositions are shown in Figure 2.

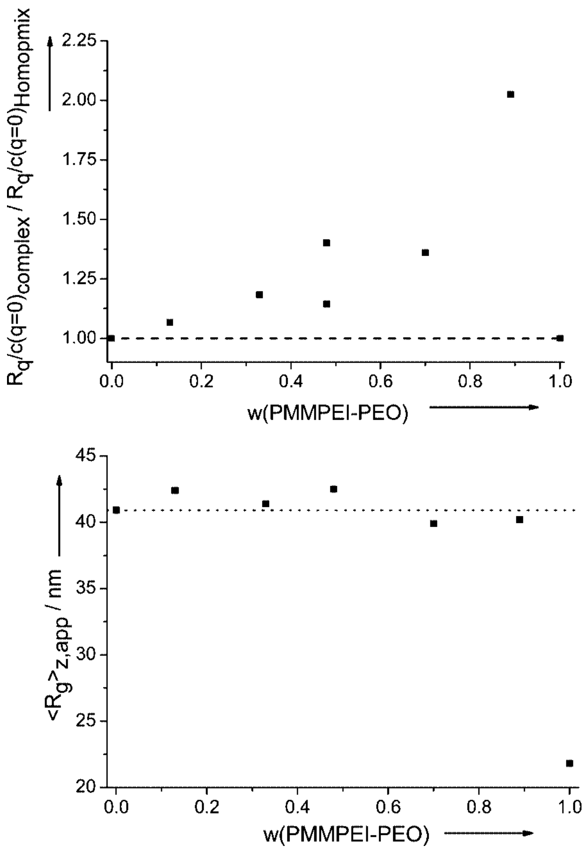

Figure 8. Concentration-normalized (extrapolated to $q = 0$) Rayleigh ratios (a) of the scattering intensities of the complexes in relation to the scattering intensity of a homopolymer mixture-and radius of gyration (b) of the complexes of PMMPSS−C_{12} and slightly charged PMMPEI−PEO in DMF (2 mM LiBr).

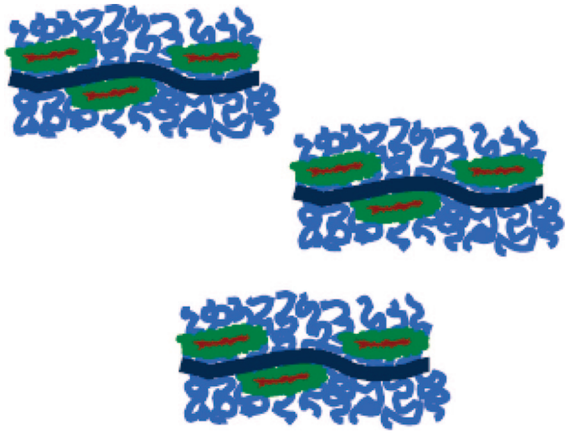

Figure 9. Schematic picture of the formed complexes of PMMPSS−C_{12} (blue) and PMMPEI−PEO (red/green). This picture should just serve as first generation model and does not intend to include details of the structure, e.g., relative orientation or distribution of the PMMPEI−PEO within the PMMPSS−C_{12}.

The formed spherical aggregates have diameters between 30 and 150 nm and possess at higher weight fractions of PMMPEI−PEO a compact core which is surrounded by a shell of PMMPEI−PEO. All samples were obtained at concentrations around 10^{-3} g/L, and no significantly larger aggregates have been observed. Also, the addition of LiBr (0−2 mM) did not influence the results.

Figure 3 shows the scattering behavior of the complexes, in which the PMMPEI−PEO has been added to a solution of PMMPSS−C_{12}.

If the process is reversed, i.e., the PMMPSS−C_{12} is added to a solution of highly charged PMMPEI−PEO, macroscopic precipitation is observed already at little amounts of added PMMPSS−C_{12} (weight fraction w(PMMPEI−PEO) = 0.95). As in case of other IPECs, the order of mixing heavily influences the complex formation.

The light scattering of the complex solutions according to Zimm[23] show a bending, which is highest in case of low w(PMMPEI−PEO). Principally, the origin of the bending can be attributed to two effects: (i) the molecular weight distribution and the distribution of the radii of gyration is broad or (ii) the data analysis according to Zimm does not linearize the form factor. The latter is likely to be excluded due to the fact that the bending diminishes with increasing w(PMMPEI−PEO). Thus, the bending at low scattering vector q can be attributed to the scattering of a small weight fraction of larger complexes. Upon addition of PMMPEI−PEO, the number of larger complexes increases, and therefore the bending decreases. The bending at low q has not been taken into account for the extrapolation in order to determine the radius of gyration. Therefore, the apparent radii of gyration $\langle R_g\rangle_{z,app}$ represent the major part of the sample (Table 1).

As also seen in Figure 4, $\langle R_g\rangle_{z,\ app}$ increases with increasing w(PMMPEI−PEO).

In contrast, a hypothetical homopolymer mixture would show the following decreasing behavior:[23]

$$\langle R_g^2\rangle_z = \frac{\sum_i w_i\left(\frac{R_q}{c}(q=0)\right)_i \langle R_g^2\rangle_{z,i}}{\sum_i w_i\left(\frac{R_q}{c}(q=0)\right)_i}$$

with $\langle R_g^2\rangle_z$, $\langle R_g^2\rangle_{z,i}$ the square of the z-averaged radius of gyration of the mixture or the ith component, respectively, the weight fraction of component i and $(R_{qC}(q=0))_i$ the extrapolated reduced scattering intensity at concentration c. The latter is used, because the exact determination of the absolute scattering of the polyelectrolytes as well as the complexes, which would include precise determination of dn/dc, has not been possible due to the inherent complexity of the samples. Nevertheless, it can easily be seen that the increase in the radius of gyration justifies the interpretation of the complex formation between PMMPSS−C_{12} and highly charged PMMPEI−PEO in DMF, although the observed behavior is comparable to the complex formation of PMMPSS and PMMPEI−PEO in water.

Complex Formation Using PMMPSS−C_{12} and Slightly Charged PMMPEI−PEO. Several examples of AFM pictures obtained from complexes at different compositions are presented in Figure 5.

Independent of the composition, the formed complexes possess a cylindrical morphology. Small spherical like complexes can be attributed to complexes based on shorter PMMPSS−C_{12} present due to the broad size distribution. In any case, the observed complexes differ strongly from the ones shown, e.g., in Figure 2 obtained using highly charged PMMPEI−PEO. Beneath the AFM pictures the corresponding statistical analysis of the height distributions is provided. From these it can be seen that increasing heights are populated with increasing amount of added PMMPEI−PEO, until a maximum height of 10 nm is reached. Figure 6 shows a linear dependence of the average height as function of the mass fraction of added PMMPEI−PEO.

A remarkable observation is the independence of the formed complex morphologies in case of slightly charged PMMPEI−PEO on overall concentration. A statistical data analysis of AFM pictures obtained at polymer concentrations of c_p = 0.001 g/L and c_p = 0.2 g/L showed no difference. The same holds true for the sequence of polyelectrolyte addition.

The AFM pictures suggest that the complexes of PMMPEI−PEO and PMMPSS−C_{12} are formed under maintenance of the cylindrical morphology. A driving influence of the surface can be excluded, because subsequent coadsorption of both polyelectrolytes results in the expected picture of independent and individual adsorption of the polymers (Supporting Information). In addition, the linear dependence of the average height as function of added PMMPEI−PEO implies that the complexes are formed in a rather controlled fashion, which is also deduced from the independence of the polymer concentration and the sequence of adding.

The controlled formation of complexes with cylindrical morphologies is also observed by light scattering in solution. The scattering of complexes of slightly charged PMMPEI−PEO and PMMPSS−C_{12} according to Zimm is shown in Figure 7.

The corresponding data analysis is summarized in Table 2 and Figure 8.

The radius of gyration is independent of the complex composition and corresponds to the value obtained for pure PMMPSS−C_{12}. A quantitative analysis of the molecular weight has not been possible due to the difficulties of determining correct dn/dc values for the complex system. Nevertheless, the concentration-normalized Rayleigh ratio (R_q/c) of the complexes—normalized to the individual homopolymer mixture—provides a relative trend of the evolution of the molecular weight (Figure 8). It is seen that the Rayleigh ratio of the complexes is larger than the one expected for homopolymer mixtures and increases with increasing amount of PMMPEI−PEO, indicating an increase in molecular weight of the complexes.[23] The constancy in R_g implies that the complexes contain only a single PMMPSS−C_{12}. Thus, the static light scattering confirms the AFM pictures. In addition, Table 2 also contains the results obtained from DLS, also showing that within experimental error the controlled complex formation occurs. A crude and simplistic model schematically showing the complexes is given in Figure 9, where the PMMPEI−PEO's are "attached" to the PMMPSS−C_{12}. Nevertheless, this crude picture—although describing the observations—has to be refined in the future, e.g. with respect to the distribution of PMMPEI−PEO within the PMMPSS−C_{12}, or the potential release of surfactants from PMMPSS−C_{12}.

It should be pointed out that slightly charged PMMPEI−PEO exhibits an interesting association behavior in DMF. Although this is not yet fully understood, the presently important features are shortly summarized: (i) the formed associates are instable against shearing, (ii) large associates have diameters of approximately 500 nm (as determined from DLS, data not shown), (iii) the associates tend to sediment, (iv) addition of acid leads to the dissolution of the associates, and (v) the kinetics of formation of the associates are slow. After several days, only sedimented associates are observed. Only solutions according to point v have been used for the complexation starting with PMMPEI−PEO. When beginning with PMMPSS−C_{12}, the associates have been dissolved by shearing immediately before complex formation. Both ways yielded the same complexes, i.e. the slow association of PMMPEI−PEO in DMF has no significant influence on the complex formation.

A close look to the scattering curves of the complexes sometimes shows a deviation from linearity and some downward bending at low q. This happens statistically and does not depend on the mixing ratio of the components. In addition, this deviation from linearity vanishes with time, implying that the complexes have the possibility to equilibrate. This will also be further studied in the future.

Conclusion

The presented complexes between PMMPSS−C_{12} and slightly charged PMMPEI−PEO behave substantially different as compared to the commonly described, kinetically controlled interpolyelectrolyte complexes. AFM and light scattering independently show the cylindrical morphology of the formed complexes. In addition, the sequence of addition, the polymer concentration and the presumable tendency of PMMPEI−PEO for slow association have no significant influence on the complexes formed. These results, together with the observable equilibration of the complexes, lead to the conclusion that the formed complexes are equilibrium or at least close to equilibrium structures. Putting all data together yields a crude schematic model of the complexes: PMMPEI−PEO is added to the corona of PMMPSS−C_{12} in a surprisingly controlled manner and the complexes retain the cylindrical morphology. It will be interesting to see, whether the presented results can be transferred to other polyelectrolyte systems currently under investigation.

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Supporting Information Available: Text giving the preparation of the solutions for light scattering and AFM and an AFM picture of individually coadsorbed homopolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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