Influence of Stereoregularity of the Polymer Chain on Interactions with Surfactants: Binding of Cetylpyridinium Chloride by Isotactic and Atactic Poly(methacrylic acid)

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Association of a cationic surfactant cetylpyridinium chloride, CPC, with isotactic and atactic poly(methacrylic acid), i-PMA and a-PMA, respectively, in aqueous 0.01 M NaCl solutions was studied by pH and fluorescence measurements in conjunction with potentiometric studies using a surfactant-sensitive membrane electrode. pH measurements have demonstrated that the presence of an oppositely charged surfactant increases ionization of carboxyl groups on PMA at low degrees of neutralization. The increase is more pronounced in the case of i-PMA. The isotactic form of PMA is not soluble in water at zero degrees of neutralization but can be rendered soluble by the addition of CPC at the surfactant to a polyion molar ratio of around 0.4. In the solubilized complex, the positive charge of the CPC molecule is facing the polar solvent, whereas surfactant tails are oriented toward the i-PMA compact coil. Binding isotherms and cooperativity parameters show that chain tacticity has an important influence on the interaction of cetylpyridinium cation with polymethacrylate anion. At the onset of cooperative binding, the association is stronger with i-PMA than with the atactic form, as demonstrated by lower CAC values and higher values of the cooperativity parameters. In contrast, more surfactant is bound by a-PMA in the region where polyion becomes saturated with surfactant ions. Results are interpreted by taking into account local chain conformations as obtained from quantum mechanical semiempirical molecular orbital calculations. Greater hydrophobicity and possibly higher charge density of i-PMA on one hand and more flexibility of the a-PMA chain on the other are held responsible for these observations.

Introduction

The association of ionic surfactants (for example, cationic ones, S^+) with oppositely charged polyelectrolytes (anionic ones, P^-) is a subject of considerable interest due to its importance in biological systems as well as in industrial applications.[1−3] The biological significance arises from the fact that many biomacromolecules are polyelectrolytes whereas, for instance, membrane-forming lipids are surfactants.[3] The technological relevance of such studies is a consequence of an extremely wide range of applications of mixed surfactant−polymer systems.[1,2] The main result obtained from numerous studies of systems involving synthetic polyelectrolytes is that interaction in the pair S^+/P^- is very strong. This is a consequence of strong electrostatic attraction between charged surfactant aggregates and the polyion and is demonstrated in the most straightforward way by the very low critical aggregation concentration, CAC, values observed. CACs are usually orders of magnitude lower than the surfactant critical micelle concentrations, CMCs.[4,5] It also has been recognized that detailed properties of the surfactant ion and more particularly of the polyion have to be taken into account in the interpretation of results. The relevant characteristics related to the polyelectrolyte chain are its charge density, chain flexibility, and hydrophobicity.[4−6] These properties are determined by the structure of the polymer backbone and by the nature of the attached groups and are reflected in the equilibrium conformation of the polymer chain in solution.

It has been demonstrated that stereoregular polymers often have characteristic local conformations in solution, although their overall conformation can well be approximated by random coils.[7,8] For example, syndiotactic poly(methyl methacrylate), s-PMMA, in benzene has a locally preferred curvature[7] and appears to be more strongly coiled than isotactic PMMA, i-PMMA.[8] However, i-PMMA has a rather random overall conformation[7,8] with local helical sequences.[9−11] Furthermore, it has been shown[7] that local conformations are not much affected by the presence of charges; i.e., they are similar for the corresponding stereoregular poly(sodium methacrylates) in aqueous solution.[7] Differences in chain conformation for different stereoregular forms of the same polymer may lead to distinctly different solution properties, as is the case with isotactic and atactic poly(methacrylic acid), i-PMA and a-PMA, respectively.[9,12−15] The isotactic PMA, for example, is a weaker acid than a-PMA,[13,14] and it is practically insoluble in water below a certain critical degree of neutralization.[9,12] It displays irreversible potentiometric behavior in aqueous solutions in contrast to its atactic counterpart.[15] On the basis of these observations for pure PMA solutions it is reasonable to expect that polymer tacticity may influence also the association behavior of PMA with surfactants. The present study addresses this subject.

The majority of studies on polyelectrolyte/surfactant interaction until now have been restricted to the so-called conventional polymers with no control of tacticity. These polymers are usually the atactic variety, but no effort was generally devoted to the determination of their composition with respect to triad content.

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Recently, Guenet and co-workers[16,17] have investigated the molecular structure of stoichiometric complexes formed between cetyltrimethylammonium bromide, CTAB, and atactic and isotactic polystyrene sulfonates, a-PSS and i-PSS, respectively. They have demonstrated that tacticity has no influence on the molecular structure of the complex in *n*-butanol solution, whereas it plays a role in the gel state, which forms in nitrobenzene. Unfortunately, these authors do not report the composition in triads for their PSS samples, and the study is limited to nonaqueous media due to insolubility of the complex in water. As far as we could ascertain, there are no studies of association between surfactants and stereoregular polyelectrolytes that would cover surfactant-to-polyion molar ratios other than the stoichiometric one, and that would apply to aqueous solutions.

In this paper, we report the first studies of association of a cationic surfactant cetylpyridinium chloride, CPC, with i-PMA and a-PMA in aqueous solutions. Special care is devoted to careful characterization of the polymers with respect to chain tacticity, for both the isotactic and the atactic forms. This was usually not the case in former studies involving PMA.[18,19] First, we address the influence of surfactant on ionization of carboxylic groups on both PMAs and on the solubility of i-PMA at degree of neutralization, α_N, equal to zero ($\alpha_N = 0$). Second, we investigate the effect of surfactant on the conformational transition of the PMA chain with the help of fluorescence spectroscopy measurements. In this case, a quaternary ammonium bromide surfactant is employed. Finally, we report isotherms for the binding of CPC by both polymers in dependence on α_N in a very broad range of surfactant concentrations, from below the CAC to stoichiometric conditions. Estimated binding parameters for CPC binding by i-PMA and a-PMA are compared with each other and discussed in light of the results obtained in other systems including carboxylic polyelectrolytes.[19,20] Results are interpreted from the viewpoint of the characteristics of the polymer chain by applying quantum mechanical semiempirical molecular orbital calculations to predict local conformations of PMAs with different tacticities. Purely isotactic and syndiotactic chains, i-PMA and s-PMA, respectively, are modeled.

Materials and Methods

1. Materials. Isotactic poly(methacrylic acid), i-PMA, was prepared by the hydrolysis of isotactic poly(methyl methacrylate), i-PMMA (Aldrich Chem. Co.; weight-average molar mass of the starting ester form, as given by the supplier, is M_w = 690 kg/mol) following the procedure reported previously.[9,12,21] The tacticity of the starting i-PMMA and the degree of hydrolysis of the ester groups for the hydrolyzed product i-PMA were determined from the ^{1}H NMR spectrum in a $CDCl_3$ and in a D_2O solution, respectively.[9,22] The polymer contains 91.6% isotactic triads. This result is in excellent agreement with the data provided by the supplier (91.8%). The degree of hydrolysis was greater than 98%. For final purification of i-PMA, dialysis was used. The polymer was first dialyzed against 0.02 M HCl to obtain i-PMA at a degree of neutralization equal to 0 and then against water. The pure product was dried by lyophilization and stored in a desiccator.

Because i-PMA is practically insoluble in water at degrees of neutralization lower than 0.2,[9,12] i-PMA solution with α_N = 0.3 was prepared as the stock solution. For this purpose, a calculated amount of 0.1 M NaOH was slowly added to a weighed amount of solid polymer in a certain volume of solvent (0.01 M NaCl) in a volumetric flask; the solution was thoroughly stirred to ensure complete dissolution of the polymer and then diluted to a desired concentration with 0.01 M NaCl. Solutions with other degrees of neutralization were prepared by adding a calculated amount of either 0.1 M NaOH (for α_N = 0.4, 0.5, 0.75, and 1.0) or 0.1 M HCl (for α_N = 0.001, 0.1, and 0.2). Since polymer concentrations used in this study were rather low and crystallization is likely to be kinetically controlled, precipitation of the polymer in pure i-PMA solutions with $\alpha_N \leq$ 0.2 was in this way delayed for some time (i.e., for several hours or even days). This time was sufficient to carry out the experiments. There are indications obtained by scattering measurements[23] that nonnegligible intermolecular association between i-PMA chains is present in these solutions, which ultimately leads to precipitation at $\alpha_N = 0$. This observation implies that such solutions are unstable in the thermodynamic sense.

The atactic form of PMA, a-PMA, was obtained by polymerization of methacrylic acid using a standard procedure and was characterized previously by light scattering measurements, providing the value for the weight-average molar mass of this a-PMA sample as M_w = 131 kg/mol and the polydispersity index as 2.44.[22] The sample is predominately syndiotactic; it contains around 49% syndiotactic, 39% heterotactic, and 12% isotactic triads. This is a typical composition of triad content when PMA is obtained by direct polymerization of methacrylic acid. The polymer was purified by dialysis and stored in the refrigerator as a concentrated stock solution.

In contrast to i-PMA, the atactic form of PMA dissolves in water at $\alpha_N = 0$. Therefore, the degree of neutralization of a-PMA solutions was varied with the addition of 0.1 M NaOH to the stock solution of the polymer with $\alpha_N = 0$. In the case of a-PMA, solutions with α_N = 0.1, 0.25, 0.5, 0.75, and 1.0 were prepared.

The cationic surfactants cetylpyridinium chloride (CPC, Kemika Zagreb, Croatia) and dodecylethyldimethylammonium bromide (DEDMAB, Fluka) were purified as reported previously.[24,25] Note that the solution behavior of DEDMAB in pure surfactant solutions and in solutions containing polyelectrolytes is very similar to the one of a closely related surfactant dodecyltrimethylammonium bromide, DTAB,[5,25] which is more often encountered in binding studies. Surfactant stock solutions were prepared by dissolving weighed amounts of dried substances in the solvent.

2. pH Measurements. The influence of bound surfactant on the ionization of both forms of PMA was investigated by pH measurements. pH was measured by using a combined pH electrode from Mettler-Toledo (InLab 406) in solutions with $\alpha_N = 0$, 0.1, and 0.25 for a-PMA and with α_N = 0.001, 0.1, and 0.2 for i-PMA. It has previously been demonstrated[26,27] that the influence of the surfactant on the ionization of polyelectrolytes with carboxylic groups is negligible at degrees of neutralization greater than 0.25. The polymer concentration for pH measurements was 5×10^{-4} mol COOH/L, expressed in moles of carboxylic groups per liter of solution; this is also the so-called monomer concentration. Measurements were carried out for various surfactant-to-polymer molar ratios (S/P) that corresponded to points on binding isotherms in the cooperative region of binding just above the CAC for each α_N (Results and Discussion). All solutions containing polyelectrolyte and surfactant were prepared by slowly adding, with vigorous stirring, a surfactant stock solution to a polyelectrolyte solution, both in 0.01 M NaCl.

3. Fluorescence Measurements. Pyrene (Aldrich, optical grade) was used as the external fluorescence probe to monitor

the conformational transition in pure a-PMA and i-PMA solutions and the formation of polyelectrolyte−surfactant aggregates in solutions of i-PMA with added DEDMAB. The preparation of water saturated with pyrene was as reported previously.[18,25] The fluorescence emission spectra of pyrene were recorded on a Perkin-Elmer model LS-50 luminescence spectrometer at 25 °C following the experimental details reported in our previous studies.[25] From the spectra, the ratio of intensities of the first and the third vibrational peak of pyrene, I_1/I_3, was calculated.

The concentration of the polymer for fluorescence measurements was 0.005 mol COOH/L, and the surfactant-to-polyelectrolyte molar ratio in these solutions was $S/P = 0.3$. Fluorescence measurements on mixed polyelectrolyte−surfactant solutions were performed immediately after preparation. In mixed i-PMA/DEDMAB solutions with degrees of neutralization lower than 0.15, precipitation and phase separation of a polyelectrolyte−surfactant (PMA/DEDMAB) complex occurred. Concurrently, the fluorescence intensity of pyrene in the clear equilibrium solution decreased considerably, because all pyrene was taken up by the i-PMA/DEDMAB complex. Therefore, more pyrene was added to the equilibrium aqueous phase, and the emission spectra were recorded again. Quite clearly, the pyrene emission spectrum for the precipitated complex could not be measured. Phase separation was observed also in the a-PMA/DEDMAB system, but in this case solutions only turned turbid (see also comments in Results and Discussion, section 2), and the spectra could be recorded with such solutions.

4. Binding Measurements. The surfactant binding data were obtained by a potentiometric technique using a surfactant-selective membrane electrode as reported previously.[28,29] All measurements were performed at 25 °C in 0.01 M NaCl at a constant concentration and degree of neutralization of the polymer. The response of the electrode to the surfactant ion concentration was Nernstian in a wide concentration range (from below 1×10^{-6} mol/L to the CMC) with a slope around 60 mV/decade. The voltage difference E reached a constant value a few minutes after the change in the surfactant concentration. The concentration of the polymer for all binding studies was 5×10^{-4} mol COOH/L. In the case of i-PMA, $\alpha_N = 0.001$, 0.1, 0.2, 0.4, 0.5, 0.75, and 1.0 were studied, whereas for a-PMA $\alpha_N = 0$, 0.1, 0.25, 0.5, 0.75, and 1.0 were investigated.

Binding isotherms (i.e., plots of the degree of binding β as a function of free surfactant concentration, c_s^f) were treated by the Satake−Yang model,[28] which is the most frequently employed model in the treatment of surfactant binding by polyelectrolytes.[20,28−30] The authors[28] considered nearest-neighbor interactions in a linear lattice between bound surfactant molecules and arrived at an exact solution for the degree of binding as a function of the free surfactant concentration

$$\beta = \frac{1}{2}\left\{1 + \left[\frac{(Kuc_s^f - 1)}{((1 - Kuc_s^f)^2 + 4Kc_s^f)^{1/2}}\right]\right\} \quad (1)$$

In this equation, K is the constant of surfactant binding to an isolated site on the polymer. According to Satake and Yang, it reflects mainly Coulomb interactions in a certain polyion−surfactant ion pair. The parameter u is the so-called cooperativity parameter, which represents the equilibrium constant for the aggregation process of bound surfactant ions, thus reflecting hydrophobic interactions between surfactant hydrocarbon tails. The product Ku is then the combined contribution of electrostatic and hydrophobic interactions to surfactant binding by polyelectrolytes. Both u and Ku can be obtained from the experimental isotherms; the measure for u is the slope of the isotherm at the half-bound point where $\beta = 0.5$ (see equations below), while Ku is proportional to the inverse of the free surfactant concentration when half of the sites on the polyion are occupied.[28] This model was later extended by Delville[31] to allow for the second-nearest-neighbor interactions between surfactants. This approach[31] led to some improvement in the calculated isotherms for high degrees of binding, that is in the post-cooperative region. Another approach to model binding isotherms has been presented lately by Hansson and Almgren,[32] who have introduced a simple law of mass action model for the interpretation of the cooperative binding of surfactant to a polyelectrolyte of opposite charge. Instead of the cooperativity parameter u, the aggregation number N is therein a measure of the degree of cooperativity. Interestingly, the Satake−Yang model[28] and the mentioned approach[32] arrive at virtually the same result for the special case when $\beta = 0.5$, which can be seen by comparing eq 2 (the slope of the isotherm at the half-bound point from the Satake−Yang model) with eq 3 (the slope of the isotherm as a function of N from the law of mass action model)

$$\left(\frac{d\beta}{d \ln c_s^f}\right)_\beta = 0.5 = \frac{u^{1/2}}{4} \quad \text{or} \quad \left(\frac{d\beta}{d \ln c_s^f}\right)_{\beta=0.5} = \frac{N-1}{4} \quad (2)$$

$$\left(\frac{d\beta}{d \ln c_s^f}\right)_\beta = 0.5 = \frac{N}{4} \quad (3)$$

Obviously, the aggregation number correlates with the cooperativity of binding isotherms so that steep isotherms (large u) correspond to large micelles (large N).

In this paper, we have decided to use in the first place the Satake−Yang model for the interpretation of the data. The Satake−Yang equation was used to treat binding to a very similar carboxylic polyelectrolyte poly(acrylic acid), PAA,[20] and in this way presents a convenient basis for comparison. The Satake−Yang approach, and also the one of Hansson and Almgren, fails to predict two-step isotherms, which were observed in some cases of CPC binding by PMA. The bases for comparison in the case of two-step isotherms were the initial slope of the isotherm ($d\beta/d \log c_s^f$) above the CAC[32] and the slope in the second step of binding.

5. Molecular Modeling. The low-energy conformations accessible to the oligomer chains of i-PMA and s-PMA have been investigated by using quantum mechanical semiempirical molecular orbital (MO) calculations. Calculations were carried out by building the chains unit by unit, optimizing the geometry at each step using the Broyden−Fletcher−Goldfarb−Shanno (BFGS) optimization algorithm.[33−36] No constraints or restraints were imposed on the system. The maximal number of monomer units in the investigated oligomer chains was $n = 15$. The self-consistent-field (SCF) energy was calculated with the AM1 semiempirical method.[37] The segments of i-PMA and s-PMA were fully protonated and terminated with methyl groups. The calculations were performed in vacuo and in an implicit solvent with a dielectric constant of 78.4. The effect of the solvent was mimicked by using the COSMO solvation model.[38] Throughout the study, the MOPAC 2002, version 5.04, suite of programs (MOPAC 2002, Fujitsu Limited, Tokyo, Japan) was used.[39] The results of the calculations are discussed in terms of geometrical and energetical properties of the modeled configurations and are then used for the interpretation of experimental results obtained from binding studies.

TABLE 1: Calculated Degree of Ionization, α, in Solutions of a-PMA and i-PMA ($c_p = 5 \times 10^{-4}$ mol/L) without and with Added CPC for Different Degrees of Neutralization α_N

		α	
	α_N	without CPC	added CPC
a-PMA	0.0	0.044	0.074
	0.10	0.108	0.138
	0.25	0.253	0.256
i-PMA	0.001	0.014	0.065
	0.10	0.102	0.125
	0.20	0.202	0.203

Results and Discussion

1. Influence of CPC on Solubility and Ionization of PMA. From the measured pH and the known degree of neutralization, the degree of ionization, α, of COOH groups can be obtained by taking into account the condition of electroneutrality. The following equation can be derived

$$\alpha = \alpha_N + \frac{[H^+] - [OH^-]}{c_p}$$

where α_N is calculated from the known concentration of the polyelectrolyte, c_p, and the amount of added NaOH, and $[H^+]$ and $[OH^-]$ are the activities of hydrogen and hydroxide ions obtained from pH measurements. The calculated degree of ionization α is reported in Table 1 for α_N values lower than 0.25 and presents an average value of several measurements (Materials and Methods). Results show that the addition of an oppositely charged surfactant leads to an increase in degree of ionization in a-PMA and i-PMA solutions. This is in accordance with previous studies involving poly(acrylic acid).[26] The change in α is especially noticeable in cases of unneutralized and partly neutralized polyacids. In unneutralized pure a-PMA solution ($\alpha_N = 0$), the degree of ionization is 0.044, indicating that around 4% of COOH groups are ionized. Upon the addition of CPC, α increases to 0.074, revealing that the binding of surfactant leads to a nearly 70% increase in the ionization of carboxylic groups. As the degree of neutralization is increased, this effect becomes smaller; the increase of ionization at $\alpha_N = 0.1$ is 28%, and at $\alpha_N = 0.25$ it is only 1%.

In the case of i-PMA with the lowest degree of neutralization studied, that is with $\alpha_N = 0.001$, the difference between degrees of neutralization and ionization is even larger. Only about 1.4% of carboxylic groups are ionized in a solution of pure i-PMA. This low value might be a consequence of the position of COOH groups in the compact state of i-PMA. Fluorescence measurements indicate (see below) that more COOH groups hide in the interior of the compact coil in the case of i-PMA as compared with a-PMA. The degree of ionization is increased 5 times (to 6.5%) when CPC is added. The effect is much larger than that in the a-PMA case at $\alpha_N = 0$, but it becomes comparable with a-PMA at higher degrees of neutralization; at $\alpha_N = 0.1$ and 0.2, ionization in i-PMA solutions increases by around 23% and by less than 1%, respectively. As it will be discussed later, this increase in ionization may have an important effect on the interaction between the polymethacrylate chain and the cetylpyridinium cation, CP^+, at low degrees of neutralization.

In addition, we have explored the possibility to induce the solubility of i-PMA in water at zero degrees of neutralization by the addition of CPC. The concentration of i-PMA for this experiment was 0.01 mol COOH/L (this is considerably higher than the solubility limit), and $S/P = 0.2$ and 0.4 were tested. It was found that the addition of CPC at $S/P = 0.4$ has led, after prolonged mixing of the solution overnight, to the solubilization of the polymer. This phenomenon is attributed to the preferential orientation of the hydrophobic surfactant tails toward the hydrophobic i-PMA coil, with CPC charges facing the solvent. This leads to an aggregate with a hydrophilic (charged) surface and thus to an effective solubilization of i-PMA.

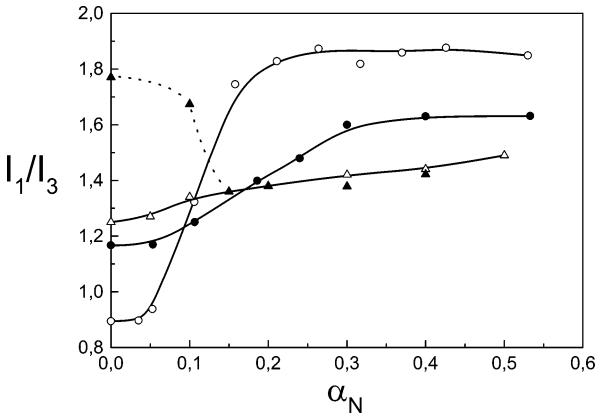

Figure 1. Intensity ratio I_1/I_3 of the fluorescence of pyrene in dependence on degree of neutralization, α_N: full symbols, i-PMA; open symbols, a-PMA; circles, solutions of pure a-PMA and i-PMA; triangles, polyelectrolyte solutions with added DEDMAB at $S/P = 0.3$. The polyelectrolyte concentration is in all cases $c_p = 0.005$ mol COOH/L.

2. Fluorescence. Figure 1 shows the fluorescence ratio, I_1/I_3, of pyrene as a function of the degree of neutralization for both forms of PMA in water and in aqueous solutions where a fixed amount of a cationic surfactant was added. For these measurements, dodecylethyldimethylammonium bromide was used (Materials and Methods) due to the fact that pyridinium surfactants quench the fluorescence of pyrene. In contrast to CPC, DEDMAB is a C_{12} chain length surfactant. It is well documented that surfactants with shorter hydrocarbon chains exhibit higher CMC values and bind less strongly to polyelectrolytes in comparison with longer-chain analogues.[1−5] As a consequence of this, precipitation of the polyelectrolyte−surfactant complex is not so extensive or it can even be avoided in specific cases. Our intention in taking DEDMAB for fluorescence experiments was also to bring precipitation to a minimum (Materials and Methods). Note, however, that DEDMAB nevertheless forms micellar aggregates in conjunction with polyelectrolytes at concentrations below its CMC.[5]

The I_1/I_3 in pure a-PMA solutions shows a sharp increase from a value around 0.9 to a value around 1.8, which takes place in the region $0.05 \leq \alpha_N \leq 0.2$. This α_N region corresponds to the well-known pH-induced conformational transition of the PMA chain from a compact conformation to an extended one,[13,14,40] which is accompanied by a release of pyrene from the hydrophobic environment of rather low polarity to very polar aqueous surroundings.[18] From potentiometric measurements, one usually observes this transition in a somewhat higher pH region ($0.1 \leq pH \leq 0.3$).[13,14,40] However, it is possible that the method based on pyrene fluorescence is more sensitive to detect the loosening up of the compact coil than the potentiometric one. The value $I_1/I_3 = 0.9$ at $\alpha_N \leq 0.05$ indicates a fairly nonpolar environment of the interior of the compact a-PMA coil, less polar than, for example, the one sensed by pyrene in toluene ($I_1/I_3 = 1.03$[41,42]) or in 2-propanol ($I_1/I_3 = 1.07$[42]). However, the I_1/I_3 value above $\alpha_N = 0.2$ reflects the highly polar environment of aqueous 0.01 M NaCl[41] into which pyrene is liberated when the a-PMA coil opens up.

The change of I_1/I_3 in i-PMA solutions is less sharp than that in the a-PMA case; the initial I_1/I_3 is around 1.17 whereas the final one is around 1.6. The increase takes place in a broader α_N region, between $\alpha_N = 0.05$ and $\alpha_N = 0.3$. These observations point to some important differences in the micropolarity that is detected by pyrene in a-PMA solutions on one hand and in the i-PMA ones on the other, both in the compact and in the extended conformations of the polymer chain. First, the interior of the compact coil in the case of i-PMA is more polar (less hydrophobic) than in the case of a-PMA. Second, in the extended conformation the i-PMA chain makes the microenvironment that is sensed by pyrene less polar (more hydrophobic) than is the case with the a-PMA chain. One can put it the other way around; the interior of the a-PMA compact coil is more hydrophobic (less polar), whereas the extended state is more hydrophilic than the corresponding states of i-PMA. This leads to a larger overall change in I_1/I_3 in a-PMA solutions. Possible molecular origins for this observation are given below.

More polar interior of i-PMA compact coil could be explained by presuming that the hydrophobic methyl groups on the isotactic chain, due to their highly regular orientation, which presumably makes the chain more rigid, cannot hide as effectively into the compact coil as can the ones on the atactic chain. As a consequence of this, a larger number of CH_3 groups cover the surface of the i-PMA coil in comparison with the atactic form, whereas more COOH groups reside in the interior. This makes the compact state of i-PMA ($\alpha_N < 0.1$), as compared with a-PMA, more hydrophobic from the outside and more hydrophilic from the inside and explains the higher value of I_1/I_3 in the unneutralized state. Along with this, the insolubility of i-PMA at $\alpha_N = 0$ can be attributed to its predominantly hydrophobic surface whereas the lower ionization degree is a consequence of the inaccessibility of the COOH groups (see also the discussion above in connection with pH measurements). However, when the polyion expands ($\alpha_N > 0.3$), the i-PMA chain seems to be more hydrophobic than the a-PMA one. This is ascribed to the possibility of a locally helical conformation of the i-PMA chain in aqueous solution[9−11] and will be discussed in more detail when presenting the quantum mechanical semiempirical molecular orbital calculations of isotactic and syndiotactic oligomers of PMA.

A completely different behavior of the I_1/I_3 ratio is observed in the presence of DEDMAB. For $\alpha_N \geq 0.15$, the I_1/I_3 value lies between 1.36 and 1.42 and is practically independent of α_N. In a-PMA/DEDMAB solutions with $\alpha_N < 0.15$, the ratio decreases slightly to 1.25 at $\alpha_N = 0$. The value of I_1/I_3 between 1.1 and 1.35 is typical for pyrene solubilized in micelles or similar surfactant aggregates.[25,42−44] The precipitation of an insoluble i-PMA/DEDMAB complex took place for $\alpha_N < 0.15$, and the I_1/I_3 values for $\alpha_N = 0$ and 0.1 (1.77 and 1.67, respectively; cf. the dotted line) indicate the polarity of the equilibrium aqueous phase (Materials and Methods). The data in Figure 1 suggest that hydrophobic surfactant aggregates (the so-called polyelectrolyte-induced surfactant micelles) are present in mixed PMA/DEDMAB solutions at all α_N values, irrespective of chain tacticity. The eventual conformational transition of the PMA chain in the presence of surfactant can be faintly traced only in the case of the a-PMA/DEDMAB solution (see the decrease in I_1/I_3 from 1.38 at $\alpha_N \approx 0.15$ to 1.25 at $\alpha_N = 0$).

3. Surfactant Binding Isotherms. The interaction of the usual form of PMA, the atactic one, or the so-called conventional PMA, with cationic surfactants was studied previously by fluorescence[18] and by potentiometric measurements.[19] The authors[19] reported binding isotherms for the binding of tetradecyltrimethylammonium bromide, TTAB, to PMA in 0.01 M NaBr for two degrees of neutralization, i.e., for $\alpha_N = 0.26$ and 1. A more precise investigation (for more α_N) was therein[19] carried out for poly(acrylic acid), PAA. Since it was reasonable to expect that the differences between atactic and isotactic PMA might not be very large, we have decided to carry out precise measurements also for a-PMA but for more α_N values than reported in ref 19. Additional reasons for this decision were that the surfactant chain length and the headgroup are not the same in our study and that in the present case the tacticity of a-PMA was determined, in contrast to the report of Kiefer et al.[19] It will be seen that the general conclusions in our investigation of a-PMA agree with those of Kiefer et al. obtained for PAA.[19]

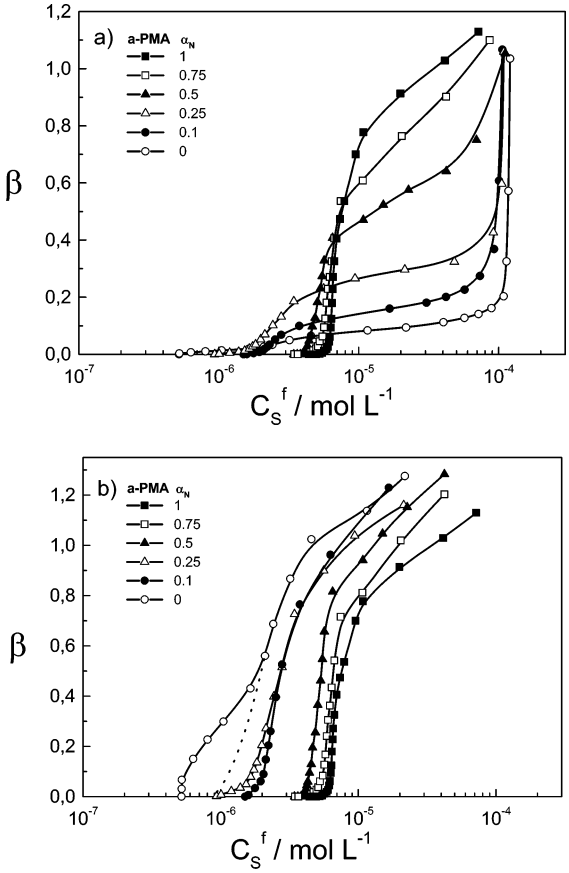

Figure 2. Binding isotherms for CPC in solutions of a-PMA in dependence on degree of neutralization of the polymer: $c_p = 5 \times 10^{-4}$ mol COOH/L, $c_s = 0.01$ M NaCl. (a) The degree of binding β is calculated per mole of all COOH groups on a-PMA; (b) the degree of binding β is calculated per mole of ionized COO^- groups on a-PMA.

Binding isotherms for the CPC binding to a-PMA and i-PMA are presented in Figures 2a and 3a, respectively. In these two figures, the degree of binding β is calculated per mole of all carboxylic groups (un-ionized, COOH, and ionized, COO^-) on the PMA chain. For a more clear interpretation, the isotherms were calculated also per mole of ionized carboxylic groups by taking into account the degree of ionization determined from pH measurements and are in terms of this plotted in Figures 2b and 3b.

The isotherms for both stereoisomers show a highly cooperative character of binding, which is summarized by the following general features.[19,20,28−32] The binding starts at very low free surfactant concentrations, typically below 1×10^{-5} M (CPC binding by a-PMA) or even below 1×10^{-6} M (CPC binding

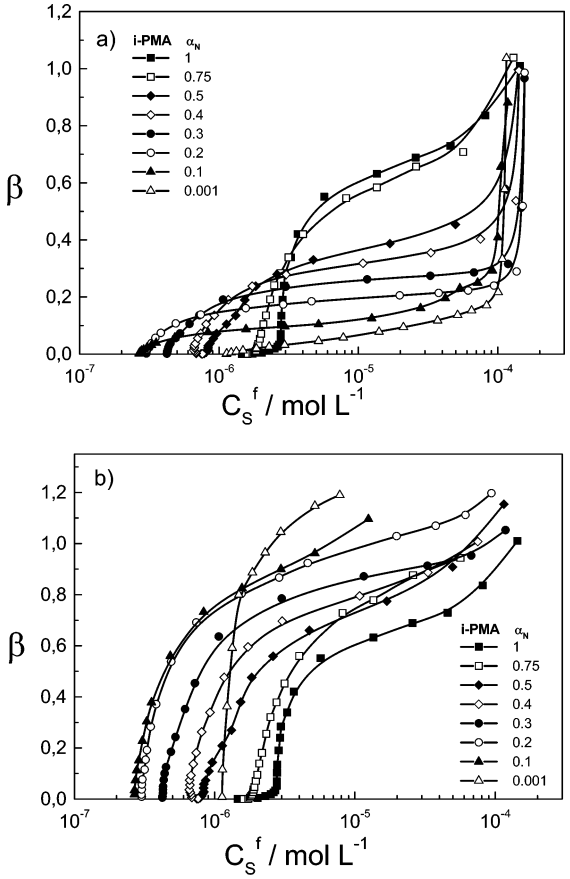

Figure 3. Binding isotherms for CPC in solutions of i-PMA in dependence on degree of neutralization of the polymer: $c_p = 5 \times 10^{-4}$ mol COOH/L, $c_s = 0.01$ M NaCl. (a) The degree of binding β is calculated per mole of all COOH groups on i-PMA; (b) the degree of binding β is calculated per mole of ionized COO^- groups on i-PMA.

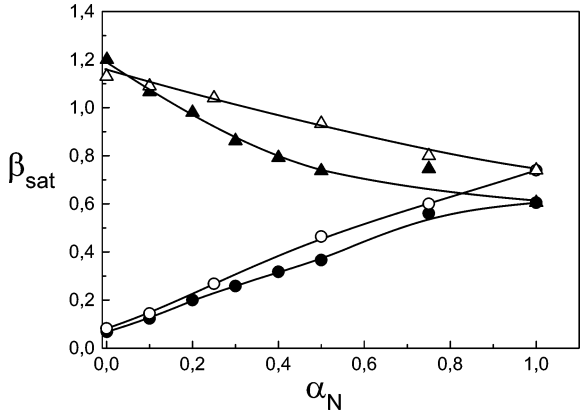

Figure 4. Degree of binding β_{sat} in the plateau region (at free surfactant concentration $c_s^f = 1 \times 10^{-5}$ mol/L) in dependence on α_N: full symbols, i-PMA; open symbols, a-PMA; circles, β calculated per mole of all COOH groups; triangles, β calculated per mole of ionized COO^- groups.

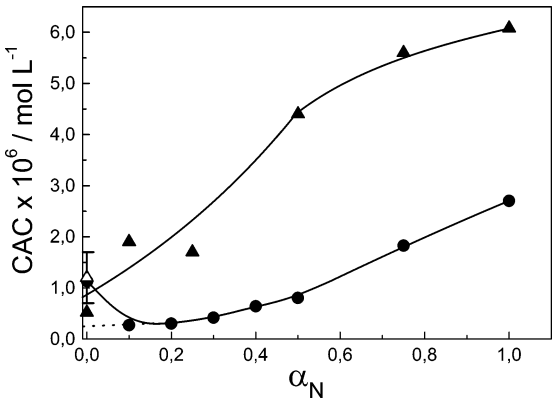

Figure 5. Dependence of the CAC values for CPC binding to PMA on degree of neutralization α_N: i-PMA (full circles), a-PMA (full triangles); a-PMA, $\alpha_N = 0$, estimated from the second binding step (open triangle).

by i-PMA), and is indicated by a steep rise of β above the CAC. It can be seen that CAC values increase with increasing α_N for both forms of PMA. More details about CAC values in dependence on tacticity will be given in the following. The degree of binding reaches a saturation limit (a plateau region[5]), which is indicated by a rapid increase of the free surfactant concentration with further additions of surfactant while β remains more or less constant.[5] The second steep increase in β at c_s^f above 1×10^{-4} mol/L indicates the formation of free CPC micelles and agrees with the CMC value of this surfactant in aqueous 0.01 M NaCl (1.6×10^{-4} M[24]).

As shown in Figures 2a and 3a the degree of binding in the plateau region, when calculated per mole of all carboxylic groups, increases with increasing α_N. This is more clearly seen from Figure 4 where the so-called β_{sat} values, taken in the saturation region at $c_s^f = 1 \times 10^{-5}$ mol/L, are plotted in dependence on α_N. We may conclude from this figure that the final amount of bound CP^+ is mainly a result of strong electrostatic interaction between the polyion and the oppositely charged surfactant ion. However, the dependence of β_{sat} on α_N becomes just the opposite when isotherms are calculated per mole of COO^- groups (Figures 2b, 3b, and 4). In this case, the degree of binding in the plateau region is the lowest for $\alpha_N = 1$ and the highest for $\alpha_N = 0$. For $\alpha_N < 0.25$, β_{sat} even exceeds unity, implying that all COO^- groups and in addition also some un-ionized carboxylic groups are occupied by the surfactant at these low degrees of neutralization. This finding suggests that hydrophobic interactions between surfactant ions and the polyion in the weakly ionized state make a very important contribution to the final degree of binding.

The following additional details are worth mentioning for the binding of CPC by a-PMA; note that these features may not be so clearly expressed in the case of i-PMA. The onset of cooperative binding at $\alpha_N = 0.5$, 0.75, and 1.0 occurs at approximately the same free surfactant concentration (the CAC), i.e., between 4.4×10^{-6} and 6×10^{-6} mol/L. For lower degrees of neutralization ($\alpha_N = 0$, 0.1, and 0.25), the CAC drops sharply to less than 2×10^{-6} mol/L. (See the plot of CAC as a function of α_N in Figure 5.) This behavior, observed for a-PMA, is in accordance with results of Kiefer et al.[19] obtained for the PAA/TTAB system. It was interpreted therein[19] by the help of Manning's counterion-condensation theory. When α_N is greater than about 0.4, the excess of simple salt (NaCl in our case) essentially controls the charge density of the polyion, keeping it at an approximately constant effective value through the counterion-condensation mechanism. The resulting effective charge density of the polyion then rules the electrostatic attraction with surfactant cations. The decrease of the CAC at α_N below 0.4 is attributed to an increased hydrophobicity of the polymer at low α_N and is very likely also to be associated with conformational change in the case of PMA.

3.1. i-PMA versus a-PMA. Comparison of binding isotherms of CPC by i-PMA with those obtained for a-PMA/CPC system shows several important differences. The most notable one is that CAC values are considerably lower in the i-PMA case

(Figure 5); at $\alpha_N = 1$, CAC is more than 2 times lower in the presence of i-PMA (compare values 2.7×10^{-6} and 6.1×10^{-6} mol/L for i-PMA and a-PMA, respectively), and at $\alpha_N = 0.5$ it is 5.5 times lower. The experimental values at $\alpha_N = 0.1$ differ by a factor of 7 (compare CAC values 0.27×10^{-6} and 1.9×10^{-6} mol/L for i-PMA and a-PMA, respectively). Lower values of CAC point to significantly stronger interactions with the isotactic form of the polymer at the onset of cooperative binding. Recalling the results of pH and fluorescence measurements (see above), this could be a consequence both of a larger increase in ionization of COOH groups induced by added surfactant and of a greater hydrophobicity of i-PMA. The main underlying reason is most probably different conformations of the i-PMA chain in comparison with that of a-PMA.

Some isotherms suggest that the binding mechanism may proceed in two steps. The most clear two-step binding isotherm was observed in a-PMA solutions with $\alpha_N = 0$ (Figure 2b). The first decrease in the slope of the isotherm is in this case indicated at β around 0.1 while the second steeper increase starts at β around 0.4 and continues up to $\beta \approx 1$. The second example that suggests a two-step binding process, but maybe not as clearly as the previous one, is the i-PMA solution with $\alpha_N = 0.5$ (Figure 3b). In this case, β increases very steeply in the initial stage up to 0.1, whereas the indication of the second increase is traced somewhat below 0.3 and keeps to $\beta \approx 0.5$. Other binding isotherms do not follow this pattern as closely as those described above; however, there are indications for such behavior also in i-PMA solutions with $\alpha_N = 0.2$, 0.3, and 0.4. For details see Figure 3b; note that the isotherm for $\alpha_N = 0.4$ initially starts with a negative slope. Interestingly, the binding isotherm for i-PMA/CPC with $\alpha_N = 0.001$ does not indicate the presence of a two-step mechanism. This finding may be a consequence of the different nature of the compact state of i-PMA in comparison with a-PMA (insolubility of i-PMA).

We attribute the first increase in the degree of binding to the increase in the ionization of COOH groups that is caused by the presence of surfactant, as demonstrated by pH measurements. In this stage, the polymer remains in a more or less compact conformation; due to this, the charge density on its surface is temporarily increased. This in consequence leads to relatively strong attractive interaction with surfactant cations. (Note that this stage exhibits a higher slope than the second one!) The accessibility of COOH groups for surfactant is more difficult in the i-PMA case than in the a-PMA one (see fluorescence measurements). This may be the reason that two-step behavior in i-PMA solutions is observed only for α_N higher than some minimum value. Low solubility of i-PMA may also play a role here. Above some critical degree of binding, the PMA chain changes its conformation (in the aggregate with surfactant) from a compact form to some more extended conformation in a way that resembles the conformational transition. Such an increase in chain dimensions (or more correctly polyelectrolyte−surfactant aggregate dimensions) leads to a decrease in the effective charge density of the polyion and consequently to some leveling off of the binding isotherm. Concurrently, new possibilities for the surfactant to bind cooperatively to the polyion appear, and the second binding step involves the interaction of surfactant cations with the previously hidden carboxyl groups on the polyion. The slope of the β versus c_s^f curve in this part is lower than in the first one, because some binding sites are already occupied by surfactant from the previous binding step. The exact interpretation of possible conformational changes in such complex systems is of course a difficult problem and requires additional research.

TABLE 2: Parameters Obtained from the Cooperative Binding Model (*u*, *Ku*, and *K*) for a-PMA/CPC and i-PMA/CPC Systems in Dependence on Degree of Neutralization α_N

system	α_N	*u*	*Ku*	*K*
a-PMA	0	27	5.0×10^5	1.8×10^4
	0.1	70	3.3×10^5	0.5×10^4
	0.25	30	3.7×10^5	1.2×10^4
	0.5	180	1.9×10^5	830
	0.75	190	1.5×10^5	790
	1.0	270	1.4×10^5	520
i-PMA	0.001	220	7.7×10^5	0.4×10^4
	0.1	84	2.7×10^6	3.2×10^4
	0.2	130	2.5×10^6	1.9×10^4
	0.3			
	0.4			
	0.5			
	0.75	610	4.2×10^5	690
	1.0	919	3.3×10^5	360

Finally, it is worthwhile to mention that the CAC for the i-PMA/CPC solution at $\alpha_N = 0$ is larger than that obtained for a-PMA from the first binding step. However, by extrapolation of the second binding step of the isotherm for the CPC binding by a-PMA at $\alpha_N = 0$ down to low β values (see the dotted line in Figure 2b), the projected CAC for a-PMA becomes comparable with that for i-PMA. Still, from the course of the CAC versus α_N curve for i-PMA one would expect a somewhat lower value for i-PMA/CPC at zero degrees of neutralization. The observed minimum in the CAC at α_N close to zero is very likely a consequence of the previously mentioned insolubility of the isotactic polymer. The dotted line in Figure 5 indicates the anticipated course of the curve based on the CAC data for $\alpha_N \geq 0.1$.

An additional important distinction between a-PMA and i-PMA solutions is the greater β value in the plateau region of binding (β_{sat}, Figure 4) in the case of a-PMA for all α_N values. The difference is between 20% and 30%. In contrast with the conclusion reached for the interaction in the initial stage, this result indicates stronger attractive interaction of the surfactant with a-PMA in the final region of cooperative binding, in which the polyion becomes saturated with surfactant aggregates. The reason for this behavior may lie in different flexibilities of PMA chains with different stereoregular structure. We presume that the atactic chain is more flexible than the isotactic one. A more flexible chain can wrap around charged surfactant micelle more easily than a stiffer one, thus compensating for the charges on the micelle more efficiently. This contributes to the larger stability of the surfactant aggregate with a-PMA. The local conformation was held responsible (see above) also for large differences in CAC values. This presumption will be further discussed below.

3.2. Model Treatment of Binding Isotherms. The importance of polyion hydrophobicity is additionally verified by applying the Satake−Yang model[28] (eq 1) for the treatment of experimental binding isotherms. In this treatment, binding isotherms calculated per mole of ionized carboxylic groups were considered (Figures 2b and 3b). The binding parameters *u* and *Ku*, derived from the cooperative binding model,[28] are summarized in Table 2 for a-PMA and i-PMA. Note that *u* and *Ku* values for i-PMA solutions with $\alpha_N = 0.3$, 0.4, and 0.5 where two-step isotherms were observed are not reported. The model is not able to predict such a behavior. The data given in Table 2 that refer to the a-PMA case with $\alpha_N = 0$ (this is the most typical two-step isotherm) were estimated from the second binding step.

The behavior of the product *Ku* is parallel to the reciprocal value of CAC because it reflects the position of the isotherm

on the concentration axis.[30] It can be seen that *Ku* decreases with increasing ionization, in accordance with the increasing trend in CAC. There is a well pronounced step change in *Ku* at α_N above 0.5; in a-PMA solutions, *Ku* drops by a factor of 2 in comparison with values at lower α_N, whereas in i-PMA solutions this decrease is around 6-fold. Similarly this holds true for *u*, except that *u* changes in the opposite way; it increases from around 40 and 140 (averages for $\alpha_N \leq 0.25$) to more than 180 and 610 (for α_N above 0.5) for a-PMA and i-PMA, respectively.

The cooperativity parameter *u* is proportional to the number of surfactant monomers forming an aggregate[29,32] (eqs 2 and 3), implying that larger aggregates are formed at higher α_N. This is in accordance with previous structural studies,[45] where it has been demonstrated that the characteristic distance in PMA aggregates with added alkylpyridinium surfactants increases markedly with an increasing degree of ionization. This finding was in part attributed to the increase in the micellar aggregation number of the polyelectrolyte-induced micelles[27,45] and agrees with the interpretation of binding isotherms by the law of mass action model.[32]

From *u* and *Ku*, one can obtain the values for the so-called intrinsic binding constant *K*, which describes the binding of surfactant ion to an isolated site on the polyion.[28] *K* is believed to reflect primarily the electrostatic interaction between surfactant ions and the polyion and is therefore expected to increase with increasing polyion charge density.[20] These values are reported in the fourth column in Table 2 and show a very unusual behavior. Contrary to expectations, *K* is high (around 1×10^4) at low polyion charge densities (i.e., for $\alpha_N \leq 0.25$) and drops to rather low values (below 1000) for high polyion charge densities (i.e., for $\alpha_N \geq 0.5$). This behavior suggests that the tendency of surfactant to bind to an isolated site on the polyion is much higher for the weakly neutralized polyacid, where attractive electrostatic interactions are rather weak. One may conclude that in the case of surfactant binding to PMA the main contributing factor to *K* in this α_N region is the hydrophobicity of the polyion, in accordance with previous suggestions. Thus, constant *K* from the Satake−Yang model may include primarily electrostatic contributions in surfactant binding by a typical hydrophilic polyelectrolyte, but in the case of hydrophobic polyelectrolytes it contains also other contributions, especially those originating from the large hydrophobic character of the polymer.

To include in this comparison also the two-step isotherms, the initial slope of the cooperative part of binding isotherms[32a] and the slope of the second binding region were evaluated and are plotted in Figure 6 as a function of the reduced linear charge density parameter λ. These slopes were obtained as a linear fit of the points in a β versus log c_s^f plot for β below (initial slope) and above 0.1. λ was calculated from the usual expression $\lambda = \alpha_N e^2/(4\pi\epsilon_0\epsilon_r kTb)$, in which *e* is the unit charge, $\epsilon_0\epsilon_r$ is the permittivity of the medium, *k* is Boltzmann's constant, *T* is the absolute temperature, and *b* (2.52 Å) is the structural value for the length of the repeat unit of PMA. Figure 6 displays a very similar behavior for the a-PMA/CPC system as that found previously for sodium (carboxymethyl cellulose), NaCMC, solutions with added DTAB[32a] (note that NaCMC is a rather hydrophilic polyelectrolyte); that is, the slope is initially low and increases sharply at λ around 1. The value for the first binding step in the a-PMA/CPC isotherm at $\alpha_N = 0$ (the open circle in Figure 6) is the highest one (almost 30) and secedes from this trend. Similarly, initial slopes for the two-step isotherms in i-PMA/CPC solutions are high (open triangles in Figure 6) and do not fit the pattern in NaCMC/DTAB or a-PMA/CPC solutions as they initially decrease with increasing λ. The subsequent sharp increase in slopes of i-PMA/CPC isotherms is observed at somewhat higher λ values (λ above 1.5 or α_N above 0.5) than in a-PMA/CPC solutions. Once again, by taking into account the slope of the second binding mode for two-step isotherms (full triangles in Figure 6), a similar picture is obtained also for i-PMA/CPC solutions. A reasonable explanation for these observations is that the properties of the polymethacrylate chain change in the course of surfactant binding due to the surfactant-induced conformational transition, as was suggested above. The cooperativity is higher for the polymer being in the compact form (steeper slopes) than for that in the extended conformation (lower slopes). Such a scenario is excluded for NaCMC chains, which exhibits no conformation change in solution.

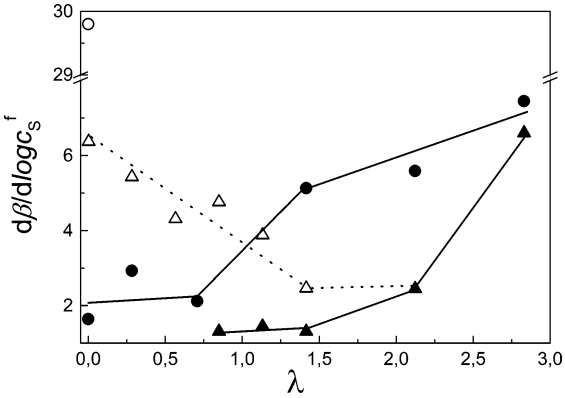

Figure 6. Dependence of the slope of the binding isotherms, dβ/d log c_s^f, for i-PMA/CPC (triangles) and for a-PMA/CPC (circles) solutions on the reduced linear charge density parameter λ. Open and full symbols indicate slopes obtained from the first and from the second binding step, respectively (see text).

An additional difference between PMA and NaCMC manifests itself in the behavior of CAC; in NaCMC/DTAB solutions, CAC decreases with increasing charge density (Figure 6 in ref 31a), whereas in PMA/CPC solutions it increases (Figure 5 in this paper). By our opinion, the reason for this contrasting behavior lies in the fact that NaCMC is a hydrophilic polyelectrolyte while PMA has an appreciable hydrophobic character.

It is reasonable to propose that in the case when polyelectrolytes have the same chemical structure (which clearly holds for a-PMA and i-PMA) differences in surfactant binding could be explained solely by proposing different local conformations of polyions. Local conformation determines the flexibility of the polymer chain, its charge density, hydrophobicity, etc., which are all crucial factors in determining polyelectrolyte−surfactant interactions. To shed more light on this point we present in the following results obtained from quantum mechanical semiempirical molecular orbital calculations.

4. Molecular Modeling of Isotactic and Syndiotactic PMA Chains. The calculations are carried out for two oligomers of PMA; one chain consists only of isotactic triads, and the other one is purely syndiotactic. The syndiotactic oligomer serves as an approximation of the atactic chain. The atactic polymer in our study contains almost 50% syndiotactic triads. It has been shown that atactic and syndiotactic PMA display similar solution behaviors.[13,14] The objective of these calculations was to reveal the conformational properties of the regular i-PMA and s-PMA oligomer chains, which would be helpful in interpretation of the experimental results. To our best knowledge, this is the first study in which the conformations of PMA have been investigated on the level of quantum mechanics. In the past, several

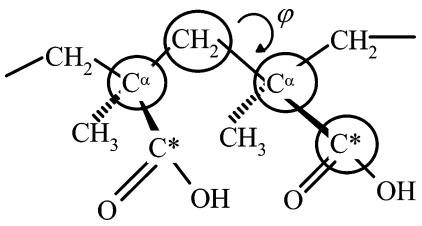

Figure 7. Schematic representation of the backbone torsion angle φ in the PMA chain, defined along the bonds $C^{\alpha}-CH_2-C^{\alpha}-C^{*}$.

conformational analyses of the ester forms of PMA, that is of the PMMA chains, have been carried out using various molecular mechanics potentials.[46−48]

The buildup of the oligomer chains as described in the Materials and Methods section leads to the following regular structures of s-PMA and i-PMA: (i) bent (curved, circular) structure of s-PMA, (ii) helical structure of i-PMA, and (iii) bent (curved, circular) structure of i-PMA. The term "bent" or "curved" aims at emphasizing the distinction between this conformation and the helical one, which is that the helical form cannot bend appreciably, whereas the "bent" one can. The expression "circular" refers to the observed local curvature of a chain segment that perfectly fits a portion of a circle (arc) when viewed perpendicularly. In this way, the term "circular" additionally clarifies the tendency of the chain to bend. The use of all these expressions will be evident in the following.

Despite the fact that the COOH and $COOCH_3$ groups are different in size and shape as well as in electronic properties, the low-energy conformations of i-PMA and s-PMA are similar to the corresponding PMMA chains.[7,46−51] The helical conformation has often been reported for the polymer chains of isotactic PMMA.[9−11,49−51] Yet, to our knowledge, the bent conformation has only been reported for the syndiotactic PMMA chains.[46] The helical and bent conformations of i-PMA, as calculated in the present study, differ in the backbone torsion angle φ, which is schematically represented in Figure 7. In the case of the helical conformation, the torsion angle φ is relaxed to the average value of 33.9° ± 0.1°. The positive sign of the torsion angle indicates that the angle was traced clockwise along the bonds $C^{\alpha}-CH_2-C^{\alpha}-C^{*}$ (Figure 7). The resulting structure corresponds to the 10/1 helix having a pitch of 20.93 Å, which is in agreement with the reported structural parameters for i-PMMA helical segments.[50] By taking into account the structural value for the length of the repeat monomer unit in vinyl polyelectrolytes ($b = 2.52$ Å, see above), one obtains for the length of a fully stretched PMA oligomer with 10 monomer units a value of 25.2 Å. The shorter distance in the helical conformation results in a higher effective value of the reduced linear charge density parameter λ (see above) for the isotactic form and consequently in stronger electrostatic attraction with oppositely charged ions, e.g., surfactant cations. This explains the stronger interaction of CPC with i-PMA, as compared with a-PMA, in the initial stage of binding that is demonstrated by lower CAC values (Figure 5).

The other possibility is that the average backbone torsion angle φ regularly alternates between −73.1° ± 0.4° and −31.6° ± 0.5°. Then the resulting low-energy conformation of i-PMA is bent. We note, however, that several combinations of bent and helical segments in the polymer chains of i-PMA can also be energetically favorable, but investigation of these, more realistic, conformations is beyond the scope of the calculations presented in this paper. In the case of the s-PMA oligomer, the assignment of the backbone torsion angle φ is unambiguous, leading to the bent conformation of the chain, which is well-known for the case of s-PMMA.[46] The average backbone torsion angle φ in s-PMA alternates between 71° ± 4° and −73° ± 4°. Large deviations in the magnitude of the torsion angle indicate higher flexibility of the s-PMA chain as compared to i-PMA. This is in good agreement with experimental observations regarding higher β_{sat} values for a-PMA, which were attributed to greater flexibility of the atactic polymer.

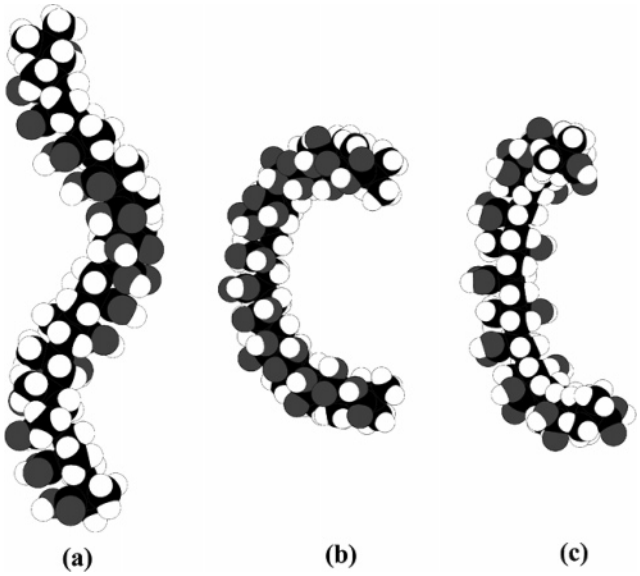

Figure 8. Low-energy conformations of the oligomer chains after geometry optimization in implicit solvent: (a) helical form of i-PMA, (b) bent form of i-PMA, and (c) bent form of s-PMA. Each chain consists of 15 monomer units. The black spheres represent the carbon atoms, the white ones the hydrogen atoms, and the gray ones the oxygen atoms.

The calculated low-energy conformations of the 15-mer i-PMA and s-PMA segments in implicit water environment are shown in Figure 8. It can be seen that the so-called bent structures of i-PMA and s-PMA (Figures 8b and 8c; note that the views of the oligomers are not perpendicular to the plane of the circular chain segment) differ appreciably in the position of COOH groups. Although this position in both cases alternates, COOH groups in i-PMA are predominately gathered on one side of the curvature (the difference between the backbone torsion angles is only around 40°; see above), whereas they are much further apart in s-PMA. The difference between the backbone torsion angles in this case is more than 140°. One may conclude that due to such a distribution of COOH, and along with that of CH_3 groups, i-PMA in the bent conformation is more hydrophobic than s-PMA. This agrees with the finding that s-PMA is more extensively hydrated than i-PMA (see the discussion below on the energy differences between in vacuo and implicit solvent). The helical conformation (Figure 8a) differs from the bent ones in that the COOH groups propagate clockwise and always in the upward direction along the axis of a helix; therefore, the chain in a helical conformation shows no, or at least considerably lower, tendency to bend. It is noticeably stiffer than the bent or curved structures.

The energy of the conformations of i-PMA and s-PMA depends on the number of monomer units in the chain. The relative energies of the segments with the number of monomer units $n = 1$, 2, 3, 4, 5, 10, and 15 calculated in vacuo and in implicit solvent are summarized in Table 3. Relative values are given with respect to the energy of the monomer unit terminated with the methyl groups, after optimization in vacuo. The results show that adding extra monomer units to the chains of i-PMA and s-PMA considerably stabilizes the oligomers. Moreover,

TABLE 3: Relative Energies of the Helical (Helix), E^{Rel}_{Helix}, and Bent (Bent), E^{Rel}_{Bent}, Conformations of s-PMA and i-PMA in Vacuo (Gas) and in Implicit Solvent (Solv) for Seven Different Chain Lengths[a]

	s-PMA			i-PMA						
	E^{Rel}_{Bent}			E^{Rel}_{Helix}			E^{Rel}_{Bent}			
n	$E^{Rel}_{Bent,Gas}$	$E^{Rel}_{Bent,Solv}$	$\Delta E_{Gas\rightarrow Solv}$	$E^{Rel}_{Helix,Gas}$	$E^{Rel}_{Helix,Solv}$	$\Delta E_{Gas\rightarrow Solv}$	$E^{Rel}_{Bent,Gas}$	$E^{Rel}_{Bent,Solv}$	$\Delta E_{Gas\rightarrow Solv}$	$\Delta E^{Solv}_{Bent\rightarrow Helix}$
1	0.0	−44.3	−44.3	0.0	−44.3	−44.3	0.0	−44.3	−44.3	−0.0
2	−119302.6	−119381.6	−79.0	−119292.6	−119368.8	−76.2	−119292.6	−119368.8	−76.2	−0.0
3	−238599.4	−238714.0	−114.6	−238581.3	−238688.9	−107.6	−238576.9	−238685.0	−108.1	−3.9
4	−357895.1	−358044.7	−149.6	−357869.6	−358009.0	−139.4	−357864.0	−358003.8	−139.8	−5.2
5	−477188.6	−477375.9	−187.3	−477157.9	−477328.5	−170.6	−477150.8	−477322.4	−171.6	−6.1
10	−1073663.6	−1074028.6	−365.0	−1073599.5	−1073924.7	−325.2	−1073574.8	−1073905.8	−331.0	−18.9
15	−1670135.0	−1670675.1	−540.1	−1670041.0	−1670516.9	−475.9	−1670001.3	−1670490.6	−489.3	−26.3

[a] n stands for the number of monomer units in the oligomer chain. The energy of the monomer unit terminated with the $-CH_3$ groups is taken as a reference. $\Delta E_{Gas\rightarrow Solv}$ corresponds to the energy difference between the oligomer chains optimized in vacuo and in implicit solvent, and $\Delta E^{Solv}_{Bent\rightarrow Helix}$ corresponds to the energy difference between the bent and the helical conformation of the i-PMA chains, both optimized in the implicit solvent. All energies are in kJ/mol.

the comparison of the relative energies of the oligomers calculated in vacuo and in a water environment shows that an appreciable stabilization of the oligomers occurs in solvent as compared to the vacuum conditions. The energy differences between the oligomers in vacuo and in the solvent systematically increase with the length of the chain. In the case of the 15-mer PMA chains, the energy differences between the structures optimized in vacuo and in solvent are −475.9 kJ/mol for the helical segment of i-PMA, −489.3 kJ/mol for the bent segment of i-PMA, and −540.1 kJ/mol for the bent segment of s-PMA, showing that the stabilization due to the solvent is most pronounced in the case of s-PMA. This finding is in agreement with the discussion in the previous paragraph and suggests that s-PMA chain may be more extensively hydrated in an aqueous environment than i-PMA; i.e., i-PMA has a larger hydrophobic character. The outcome of the calculations also shows that among the investigated oligomers the bent conformation of s-PMA is the most stable one overall (see the reported relative energies in Table 3). We assume that the reason for this may be mainly due to steric hindrance between the COOH groups that are in bent s-PMA further apart than in helical or bent conformations of i-PMA. Comparison of the relative energies of the bent and helical conformation of i-PMA oligomers shows that the oligomers in the helical conformation are more stable than the oligomers in the bent conformation. The difference between the energies of the 15-mer helical and bent oligomers of i-PMA is 39.7 kJ/mol in vacuo and 26.3 kJ/mol in solution (Table 3).

From these results we can conclude that i-PMA chains in solution may consist of bent and of helical segments while s-PMA chains consist of mainly bent segments presumably making syndiotactic chains more flexible. Larger flexibility may be the reason for the larger degree of binding of CPC by the a-PMA chain at saturation (see discussion above). We note, however, that (i) the analysis of the structures was carried out on isolated molecular chains (in a vacuum and in the solvent); therefore, the interchain interactions were not taken into account; (ii) analysis has been performed on highly ordered low-energy conformations of PMA while it is clear that the structures of molecular chains in solution are affected by the polymerization reaction, which induces several small displacements from the ideal structural parameters and makes the chains more irregular; (iii) PMA in our study has been completely protonated and the potential electrostatic effects between the ionized COOH groups are not included in the model.

Conclusions

We have performed a careful study of the interaction of CPC with two stereoregular forms of PMA, the isotactic and the atactic one, for several degrees of neutralization of carboxyl groups on the chain ranging from 0 (unneutralized form) to 1 (completely neutralized form). The most noticeable distinction between i-PMA and a-PMA on the macroscopic level is the insolubility of the isotactic polyacid in water at $\alpha_N = 0$. The presence of CPC proves beneficial as it leads to the solubilization of i-PMA at a sufficiently high surfactant-to-polymer molar ratio, i.e., when S/P is equal to 0.4. In general, the binding of surfactant causes precipitation of a polymer−surfactant complex through charge neutralization. This suggests that the solubilization mechanism in the i-PMA/CPC case involves a different mode of surfactant binding. This involves the formation of a solubilization layer of CPC ions in which surfactant tails are oriented toward the hydrophobic i-PMA coil, whereas the charged headgroups are facing the solvent.

The results for the degree of binding have shown that chain tacticity plays a very important role in interactions with oppositely charged surfactant, which is demonstrated by the following findings:

(i) The cooperative binding of CPC to i-PMA starts at a lower surfactant concentration (CAC) than the binding to a-PMA. The difference in CAC values is between 2- and 6-fold.

(ii) The cooperativity parameter u is higher for i-PMA than for a-PMA, just as the cooperativity binding constant Ku. The values for the intrinsic binding constant K (binding of surfactant to an isolated site on the polyion) suggest that hydrophobic interactions between the polymer and the surfactant play a decisive role in both cases already at the initial stage of binding.

(iii) In contrast to the first two findings, more surfactant is associated with the atactic polymer in the post-cooperative region (at saturation). The difference ranges from 20% to 30%.

A reasonable presumption for the explanation of these dissimilarities is that the decisive property is the conformation of the polymer chain. Quantum mechanical semiempirical molecular orbital calculations were performed to obtain the conformations of syndiotactic and isotactic PMA oligomers. The results have revealed several distinctions between both PMA forms, which may have important significance not only for the interaction of the polymer with surfactants but also for the solution behavior of pure polymers. Two regular structures have appeared from these calculations: a 10/1 helical one for i-PMA and a bent or curved structure for both s-PMA and i-PMA. These two bent structures, however, differ appreciably in the torsion

angle, showing that the s-PMA oligomer chain is the most hydrophilic overall. The more hydrophobic character of i-PMA is further confirmed by the calculated energy differences between the oligomers in vacuo and in an implicit solvent. The outcome of these calculations has shown that the reason for stronger binding of CPC by i-PMA in the initial stage is due to its larger hydrophobic character and possibly to a higher charge density in helical segments, whereas a higher degree of binding to a-PMA at saturation is a consequence of greater flexibility of this chain.

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