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Concentration- and pH-Dependent Conformational Changes and Aggregation of Block Copolymers of Poly(methacrylic acid) and Poly(dimethylsiloxane) in Aqueous Media, Based on Fluorescence Spectra of Pyrene and Potentiometry

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ABSTRACT: Block copolymers of poly(dimethylsiloxane) and poly(methacrylic acid) (PDMS-*b*-PMA) with different molar ratios and lengths of the hydrophobic PDMS and hydrophilic PMA blocks were synthesized by radical polymerization of methacrylic acid (MA) in the presence of siloxane macroazoinitiators. Conformational changes and aggregation of the copolymers were examined by fluorescence spectroscopy of pyrene (P) as a probe and by potentiometric measurements. Fluorescence spectra were measured as a function of polymer concentration (range from 1×10^{-8} to 0.1 M COOH) and pH (range 3−11), in the absence and presence of NaCl (0.05 M), and the results were compared with the behavior of PMA as a reference. The most important parameters deduced from the spectra were the intensity ratio of the first (∼373 nm) to the third (∼383 nm) vibronic bands (the "polarity ratio" I_1/I_3 in the emission spectra) and the intensity ratio I_{338}/I_{333} in the excitation spectra for $\lambda_{em} = 373$ and 383 nm. As the probe is insoluble in the PDMS blocks, data reflect probe sites associated with the PMA blocks. Conformational changes suggesting a transition from a compact to an expanded coil were detected, based on the increase of I_1/I_3 for pH > 5. The variation of I_1/I_3 with pH is strongly affected by the PDMS blocks. The increase of I_1/I_3 was less than that in PMA at the same pH; and the pH interval characterizing the expanded coil was narrower in the block copolymers compared to PMA; moreover, in the limits of high and low polymer concentrations, the local site for P was more hydrophobic in the copolymers than in PMA. The critical aggregation concentration of the copolymers, CAC, was determined as a function of pH and the presence of salt by two methods: based on the intensity of the first vibronic peak, I_1, in the emission spectra and on the ratio I_{338}/I_{333} in the excitation spectra. CAC values are significantly higher at pH = 8 compared to pH = 3, typically by 1 order of magnitude. The CAC results are difficult to correlate with the structural differences such as MA/DMS ratios in the three copolymers. This conclusion may be a result of the hydrophobic interactions between the methyl groups of PMA and siloxane groups and of pyrene location in a range of sites that differ in their distance to the hydrophobic core of the aggregates. This study provided evidence for the role played by the PDMS blocks and polymer concentration on the process of chain uncoiling at higher pH values, on the appearance of hydrophobic domains, and on the hydrophobicity of these domains.

Introduction

Conformations of polyelectrolytes such as poly(acrylic acid) (PA) or poly(methacrylic acid) (PMA) in aqueous media depend on their chemical structure and concentration, presence and nature of counterions, and pH. Major driving forces for conformational changes and microphase separation are electrostatic interactions between the ionic groups and hydrophobic interactions that trigger self-assembling into aggregates. Solution properties of PMA have been extensively studied in pure water,[1−5] water solutions of simple salts,[6−11] and water solutions containing multivalent cations.[12−15] Modification of solubility and solution behavior of PMA chains is achieved by linking hydrophobic sequences, for instance, poly(dimethylsiloxane) (PDMS), to the PMA chains.[16−20] In solvents selective for one of the two blocks, the block copolymers self-assemble into micellar aggregates consisting of a core of the insoluble blocks surrounded by the soluble block corona.

Self-assembly of block copolymers consisting of hydrophobic and hydrophilic segments has attracted much attention in recent years because of the potential to provide control of solution properties and to investigate in detail the driving forces that determine aggregation.[21−25] Structural modifications include the molar ratio between hydrophobic and hydrophilic segments, the charge (anionic, cationic, or amphoteric), the chemical nature of the substituents attached to the main chain, and the molecular mass of each block. Self-assembling, dynamics, and transport in these systems are of great interest for basic studies, because the results can be used to build models for, and anticipate the behavior of, the more complicated biological systems, and in applications such as coatings, inks, oil recovery, and drug delivery systems.

Self-assembling of block copolymers and formation of hydrophobic domains in polymer solutions can be followed using pyrene (P) as a fluorescent probe; the major advantages of this probe are its relatively long lifetime

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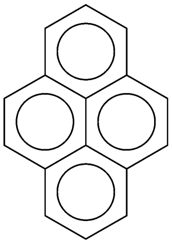
Chart 1. Pyrene (P) Fluorescent Probe



in the excited singlet state that leads to a well-resolved vibronic spectrum and its high sensitivity to the local environment. The local polarity is normally determined from the intensity ratio of the first to the third emission maxima (I_1/I_3, referred to as the polarity ratio).[26−34] The I_1/I_3 ratio varies from ∼1.85 in water to 0.95 in polystyrene and to 0.5 in nonpolar solvents.[21,28,35] Variation of the probe environment can be deduced also from the intensity ratio I_{338}/I_{333} in excitation spectra, which measure the emission at fixed wavelength, typically λ_{em} = 383 or 373 nm for P, as a function of excitation wavelength.[21,28] The I_{338}/I_{333} ratio in the excitation spectra for λ_{em} = 383 nm ranges from ∼0.2−0.4 in water to 2.4 in a highly hydrophobic environment.[21,28,36] The pyrene (P) probe is shown in Chart 1.

PDMS chains are above the glass-transition temperature at room temperature, have a weak cohesive energy, and are known as modifiers of polymer properties; a recent study of polyoxyethylene-PDMS diblock copolymers has reported the formation of various liquid crystalline phases in water *and* oils.[37] Aqueous solutions of PMA and its block copolymer with PDMS have been studied recently in our laboratories using P and 1,3-bis(1-pyrenyl)propane (P3P) as fluorescent probes.[35] The most important parameters measured as a function of pH in the range 3−13 were the polarity ratio I_1/I_3, the excimer to monomer intensity ratio I_E/I_M, and the total integrated intensity. For both probes, the conformational transition of PMA blocks at pH > 5 was reflected in the dramatic decrease of the total fluorescence intensity. In addition, data for P3P have clearly indicated that the siloxane blocks can markedly facilitate these conformational transitions, even for the low molar DMS/MA ratio in the copolymer, 1:34. Some measurements of P in PMA solutions, studied as a reference, have indicated that the I_1/I_3 ratio varies with both polymer and P concentrations, even for a constant polymer/P ratio.

Table 1. Polymer Characteristics

			mol wt			
sample	DP_{DMS}[a]	MA/DMS (molar ratio)[b]	M_n (triblock, calcd)	M_n[c] (GPC)	M_w/M_n (GPC)	c^* (M)
COP1	5	73	37 580	52 500	1.761	0.295
COP2	22	42	95 260	92 250	1.555	0.123
COP3	22	157	350 810	314 050	1.390	0.062
PMA				100 000[d]		0.144

[a] Degree of polymerization of PDMS blocks, determined from ^{1}H NMR spectra of the bishydroxypropyl-terminated PDMS precursor. [b] Determined from integrated intensity ratios of characteristic peaks for MA and DMS in the ^{1}H NMR spectra. [c] Determined from esterified copolymer. [d] Provided by the manufacturer.

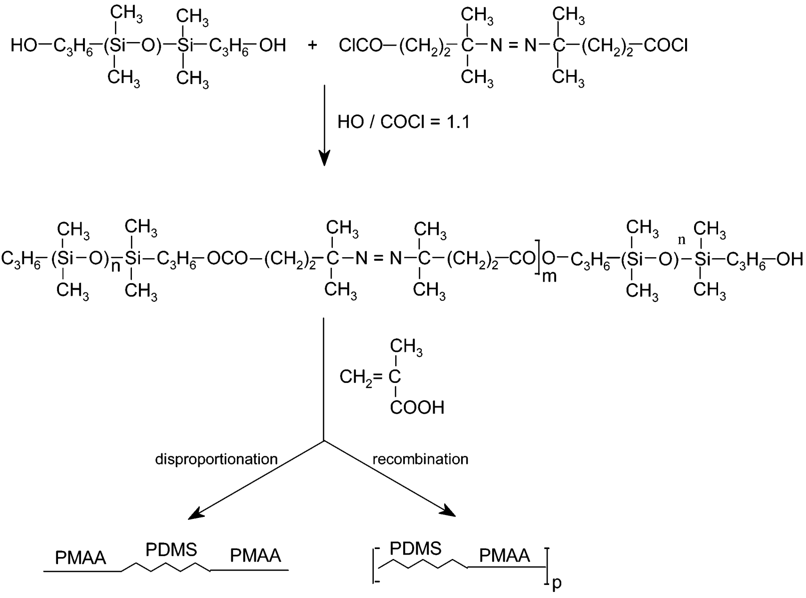
This paper focuses on conformational changes and aggregation behavior in aqueous solutions of three PDMS−PMA triblock copolymers differing in the size of the PDMS and PMA blocks. Fluorescence spectroscopy based on pyrene as a probe and potentiometry were used as the main methods of study. The objectives of this study were to assess the effects of the siloxane moiety, pH, and presence of salt on the conformational changes and aggregation of the block copolymers in aqueous media at ambient temperature.

Experimental Section

Materials. PMA of molecular weight 100 000 was from Polysciences Inc., Warrington, PA. NaCl from Aldrich was 99.99% pure. Pyrene from Kodak was dissolved in cyclohexane, passed through silica gel, and recovered by solvent distillation.[26] The I_1/I_3 ratio in the fluorescence spectra of P in water was in the range reported in the recent literature.[28,35]

Synthesis of PDMS-*b*-PMA Copolymers. Polymers with DMS and MA sequence lengths and MA/DMS molar ratios given in Table 1 were obtained by precipitating radical polymerization of MA in toluene at 80 °C for 18 h (monomer concentration 20% w/w), in the presence of azoester−siloxane macroinitiators, as seen in Scheme 1.[17] The copolymers were removed from the reaction mixture by filtration and purified by extraction with petroleum ether in order to remove the

Scheme 1. Synthesis of PDMS−PMA Block Copolymers



unreacted PDMS. Copolymers of high siloxane content were separated by centrifugation of a concentrated aqueous solution of the copolymers in order to remove the PMA homopolymer and/or copolymers of low siloxane content. The products were then filtered and atomized from ethanol solution of copolymers (10% w/v), using the Mini Spray Dryer Buchi 190 apparatus. Purified samples were dried at 50 °C in a vacuum for 48 h. The notation for the three block copolymers is COP1, COP2, and COP3, with average degrees of polymerization of the PDMS blocks 5, 22, and 22, respectively.

The copolymers were characterized by ^{1}H NMR as solutions in DMSO-d_6, using the Bruker DRX 500 spectrometer. The appropriate chemical shifts, 0.9−2.1 ppm for $-CH_2-C(CH_3)-$ and 0.1 ppm for $Si-CH_3$ groups, were used to determine the molar DMS/MA ratio: 5/365 (COP1), 22/924 (COP2), and 22/3454 (COP3).

The molecular weights of the copolymers were determined by GPC analysis of the esterified copolymer in THF solution, using Waters Associates 440 equipment. To this end, the polyacid sequences were completely esterified with diazomethane in benzene solution to yield the corresponding methyl esters.[38] The products were precipitated with ethyl ether, redissolved in chloroform, reprecipitated with ethyl ether, and finally dried in a vacuum at 100 °C. It was assumed that the degree of polymerization of the polyesters was identical to that of the original polyacid. The number-average molecular weights of copolymers determined by GPC were close to the calculated values for a triblock structure, as expected for the synthesis conditions. Data for the three block copolymers are given in Table 1.

The viscosity of the copolymers was determined in 2 M $NaNO_3$ aqueous solution at 25 °C with a Ubbelohde viscometer to determine the critical concentration for chain overlap, c^*, which is related to the intrinsic viscosity, $[\eta]$, by the equation $c^* = A/[\eta]$, with $A \cong 1$.[39] For PMA with a molecular weight of 100 000, we determined $[\eta] = 79.8$ mL/g and $c^* = 0.144$ M; the corresponding values for the copolymers are 0.295 M (COP1), 0.123 M (COP2), and 0.062 M (COP3), respectively (Table 1). The determination of c^* can be based on data for the COOH concentration because the PDMS content is low: 1%, 1.7%, and 0.5% w/w in COP1, COP2, and COP3, respectively. Fluorescence spectra and potentiometric response were registered in the dilute regime for the copolymers, except for COP3 at the highest concentration, 0.1 M COOH.

Sample Preparation. Stock solutions of pyrene were prepared by adding it to doubly distilled and deionized water and refluxed for several days under magnetic stirring; the P excess was then removed by filtration at room temperature. The final solutions contained a probe concentration of 5.0×10^{-7} M, based on $\epsilon = 45\,700$ M^{-1} cm^{-1} at $\lambda_{max} = 338$ nm.[40] Stock solutions of P in water containing 0.05 M NaCl were prepared by adding the appropriate quantity of salt.

Copolymer stock solutions were prepared by dissolution in stock P solutions, followed by sonication for 10 min.[25] The concentration of COOH groups, determined by titration with NaOH, was kept at 0.11 M for all copolymers. Fluorescence experiments were performed on solutions obtained by dilution with the appropriate probe stock solutions. The pH was adjusted by addition of highly concentrated NaOH solutions prepared in P-saturated aqueous solution. These procedures ensured that all polymer solutions had the same probe concentration, 5×10^{-7} M, and the same salt concentration, 0.05 M NaCl, when salt was present.

Fluorescence Measurements. Fluorescence spectra of P in aqueous solution were measured at 25 °C as a function of polymer concentration and pH in the presence or absence of salt, using the Perkin-Elmer LS50−B spectrofluorimeter. The optical path was 1 cm. Emission and excitation spectra were measured in the range 350−500 and 300−350 nm, respectively, for identical sample volumes. For series that included pH variation, the reversibility of pH variation was checked by addition of HCl, and no differences were recorded. The experiments were performed in both air and nitrogen atmosphere with identical results. Most of the spectra were collected with the following parameters: excitation wavelength, $\lambda_{exc} = 334$ nm; emission wavelength, $\lambda_{em} = 383$ nm; excitation slit width, 2.5 nm; emission slit width, minimum (0 nm); emission filter, 350 nm cutoff; scan speed, 50 nm/min, and 2 scans. For the homopolymer (PMA) and copolymer (COPn) solutions, some fluorescence was detected in the absence of P. This background contribution was ≤2% for samples at pH = 3 and only slightly higher at the highest pH examined. Emission and excitation spectra recorded in the presence of the probe were corrected for the background signals.

The effect of pH and salt on the I_1/I_3 ratio in the emission spectra of pyrene was checked to establish a reference. The I_1/I_3 ratio in water at pH = 3 was the same as that in pure water, 1.85, and only slightly higher, ~1.87, for pH = 8. The effect of NaCl addition was checked for salt concentrations of 0.005, 0.05, and 1 M, and all I_1/I_3 ratios were 1.9. Possible

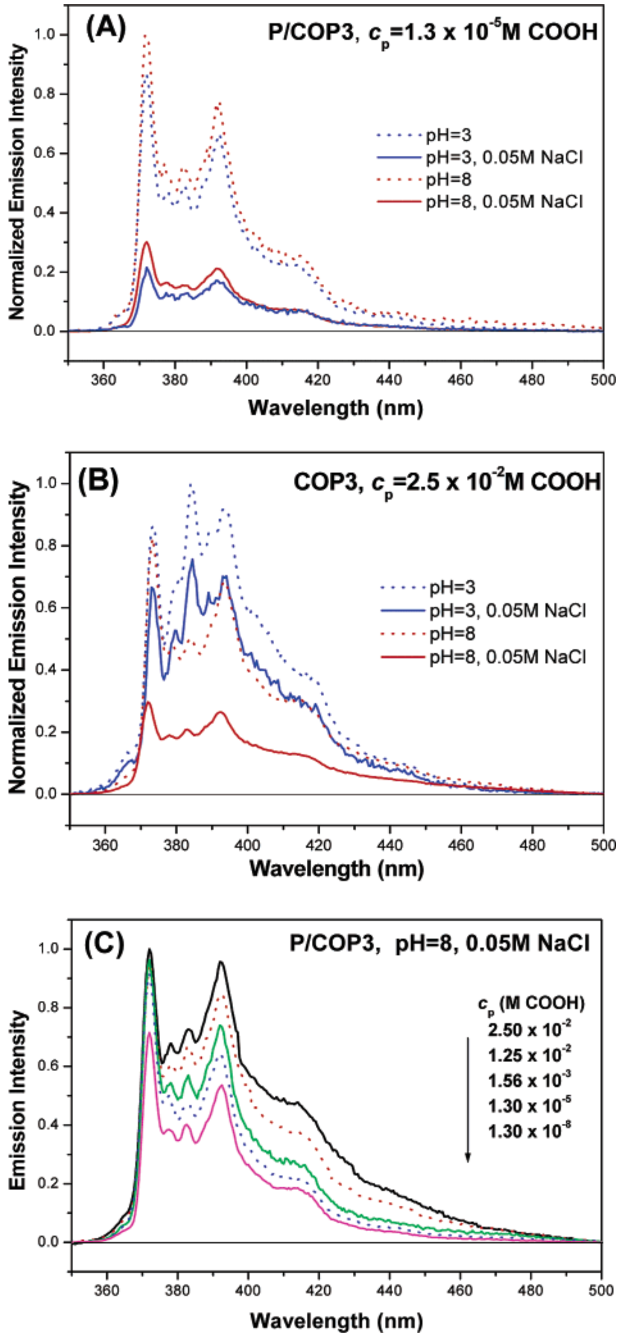


Figure 1. Emission spectra (normalized to the most intense spectrum) of pyrene in aqueous solution of COP3, $\lambda_{ex} = 334$ nm: (A) $c_p = 1.3 \times 10^{-5}$ M COOH, for the indicated pH and in the presence or absence of NaCl; (B) $c_p = 2.5 \times 10^{-2}$ M COOH, for the indicated pH and in the presence or absence of NaCl; (C) pH = 8, 0.05 M NaCl, for the indicated c_p values.

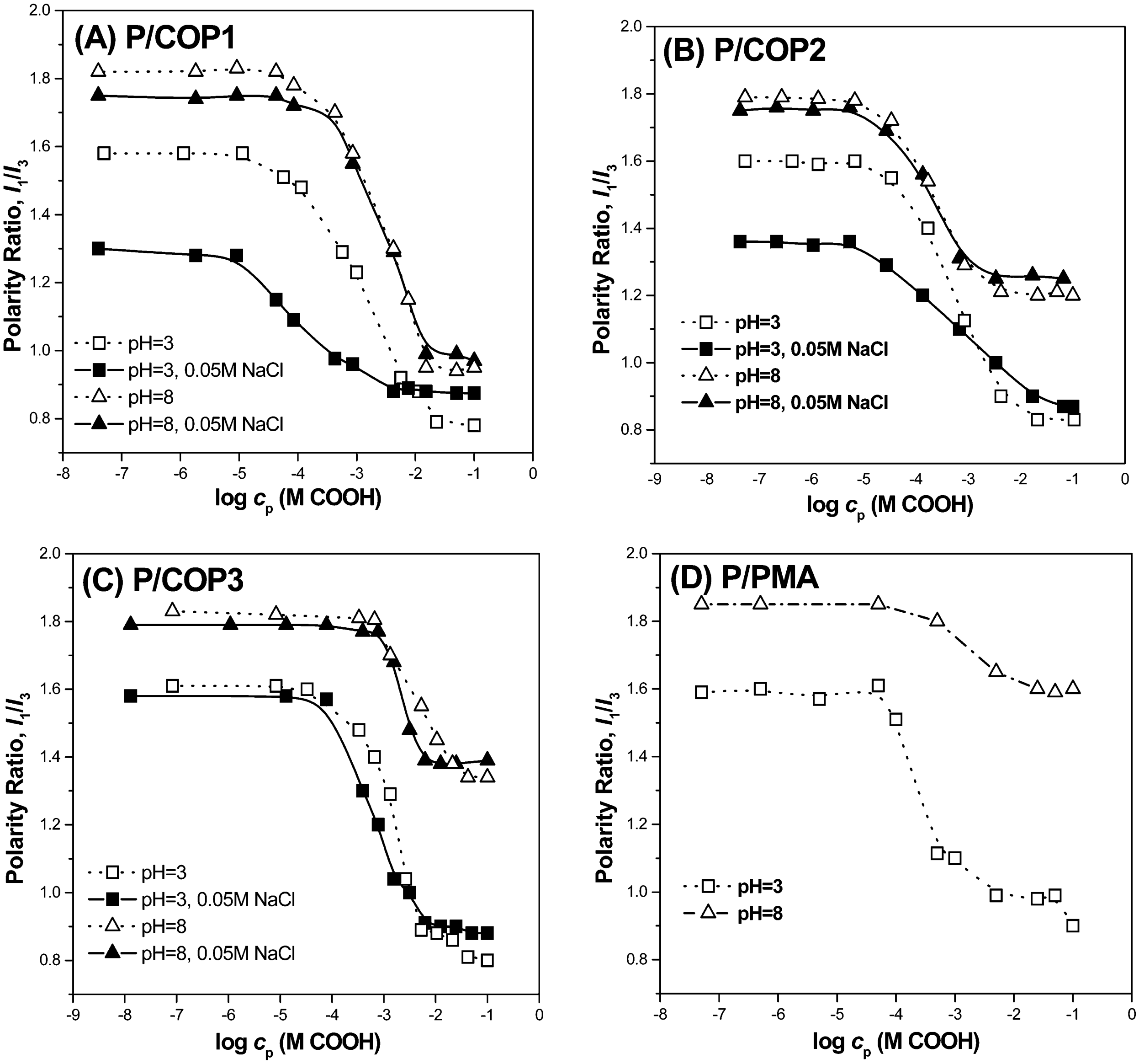


Figure 2. Variation of the I_1/I_3 ratio in the emission spectra of P as a function of polymer concentration for the indicated pH and in the presence or absence of NaCl: (A) COP1, (B) COP2, (C) COP3, and (D) PMA.

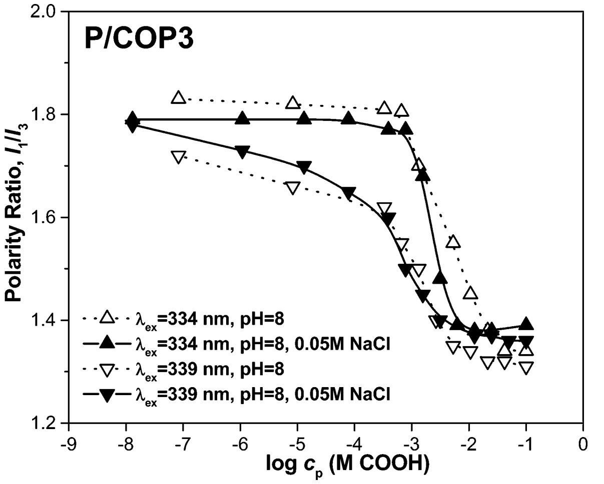


Figure 3. Variation of the I_1/I_3 ratio in the emission spectra of P in COP3 with excitation wavelength (λ_{ex} = 334 and 339 nm) for the indicated pH and in the presence or absence of NaCl.

emission quenching by Cl^- ions is under investigation in our laboratory.

Deconvolution of excitation spectra was performed using the ORIGIN 6.1 software.

Potentiometry. The copolymer solutions were prepared in doubly-distilled water and titrated with NaOH solutions. Measurements were performed at 25 °C with the 716 DMS TITRINE instrument.

Results and Discussion

Because pyrene (P) is insoluble in the PDMS blocks,[41] it can be assumed that it is located in PMA domains and reflects the local polarity. This assumption implies that emission and excitation spectra of the copolymers can be compared with PMA data in order to assess the effect of PDMS blocks.[42]

Emission Spectra. Figure 1A–C presents emission spectra of pyrene in aqueous solutions of COP3 for selected copolymer concentrations, c_p, at pH = 3 and 8 in the presence or absence of salt. At lower copolymer concentrations, no pronounced intensity variations with pH increase were detected (Figure 1A). At higher copolymer concentration, however, the emission intensity decreased significantly with increase of the pH from 3 to 8, indicating disruption of intermolecular hydro-

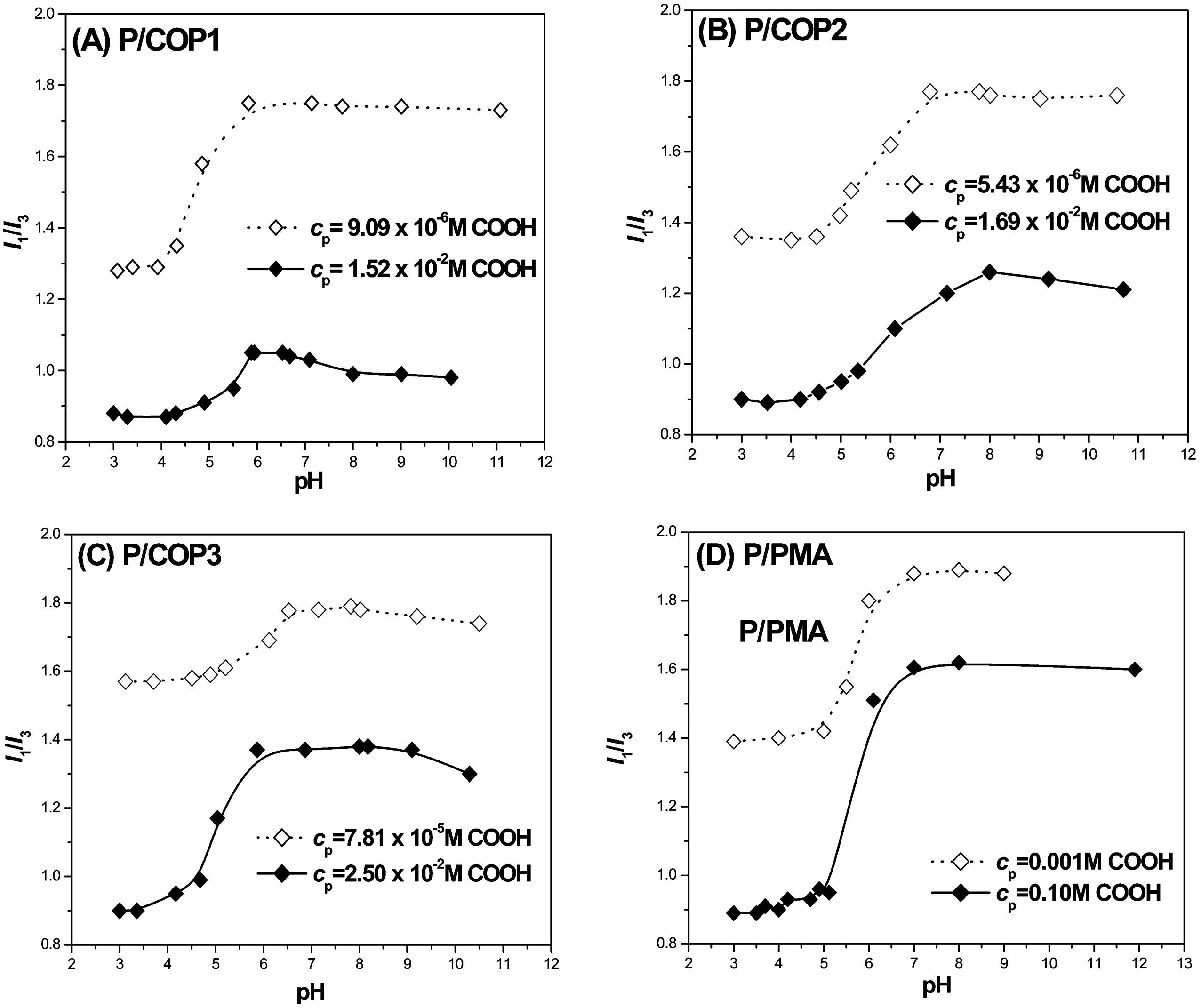


Figure 4. Variation of the I_1/I_3 ratio in the fluorescence spectra of pyrene in aqueous solutions of the polymers as a function of pH: (A) COP1 (c_p = 9.09 × 10^{-6}, 1.52 × 10^{-2} M COOH) in the presence of NaCl; (B) COP2 (c_p = 5.43 × 10^{-6}, 1.69 × 10^{-2} M COOH) in the presence of NaCl; (C) COP3 (c_p = 7.81 × 10^{-5}, 2.50 × 10^{-2} M COOH) in the presence of NaCl; (D) PMA (c_p = 0.1, 0.001 M COOH).

phobic interactions (Figure 1B). In the presence of salt the intensity decreased for both concentrations, but for the lower polymer concentration the intensity decrease was almost identical at pH = 3 and 8. The lowering of the emission intensity with salt addition suggests a higher local polarity of the probe site. The effect of c_p variation for pH = 8 and salt presence is shown in Figure 1C. The final probe environment appears to be a result of intermolecular interactions (visualized via concentration variations) and intramolecular interactions due to salt presence and pH variations. Similar trends were detected for COP1 and COP2.

The I_1/I_3 values, deduced from emission spectra as a function of polymer concentration, are shown in Figure 2A−C for the copolymers and in Figure 2D for PMA as a reference. In general terms, the behavior of P in the copolymers is similar to that in PMA. Close inspection of the I_1/I_3 ratios, however, reveals subtle effects of the PDMS block on the behavior of P in PMA. In the limit of high copolymer concentrations for both low and high pH values, the I_1/I_3 ratios are lower in the copolymers compared to PMA, suggesting a more hydrophobic environment due to the presence of the PDMS blocks. In regions of low polymer concentrations, the behavior of the copolymers is similar to that of PMA in the entire pH range; at high pH, however, the I_1/I_3 ratios are 1.75, 1.79, and 1.83 for COP1, COP2, and COP3, slightly lower than that for PMA (1.85) and close to the value of P in water, indicating that the probe is not attached to individual chains. The I_1/I_3 ratios at low copolymer concentrations and high pH are slightly lower in the presence of salt (1.75−1.79) and lower in acidic pH with or without salt (1.28−1.61). These plots reflect the conformational transition well documented for PMA and copolymers derived from PMA,[42−45] from a globule at high concentration or constant concentration at low pH to an expanded coil at low concentration or constant concentration in high pH, a transition that is accentuated by the presence of salt.

Examination of I_1/I_3 ratio for all copolymers at high concentration and low pH shows that this value is lower (0.78−0.89) than that for pyrene in PS films (0.95) and slightly lower than that for pyrene in aqueous solution of either PMA[42,43] or PS−PEO diblock and triblock copolymers[28] but always higher than that of pyrene in a nonpolar solvent (0.5).

Important differences in the I_1/I_3 ratios for the three copolymers were also detected. While the I_1/I_3 ratio at low polymer concentrations and high pH is about the same for the copolymers and only slightly lower than

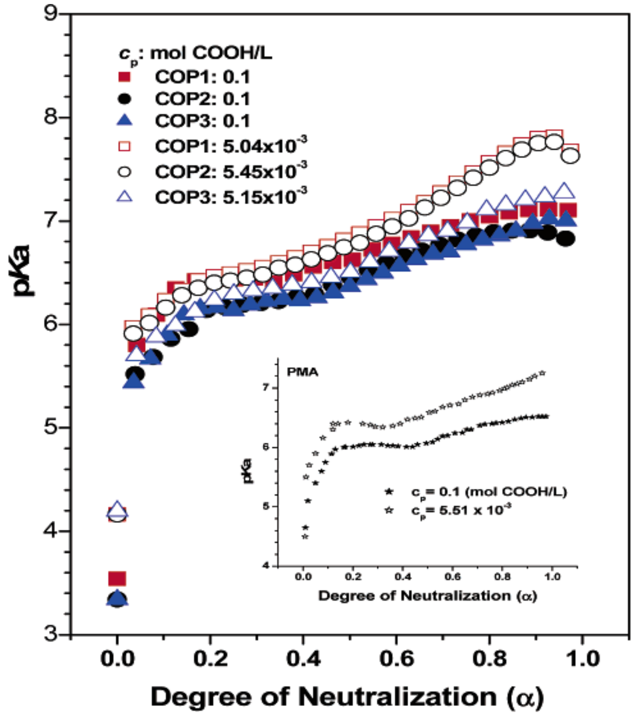


Figure 5. Variation of p*K*a in the copolymers with the degree of neutralization, α, for the block copolymers; $c_p = 0.1$ M COOH (solid symbols) and $c_p > 5 \times 10^{-3}$ M COOH (open symbols). Inset presents data for PMA at the two indicated concentrations as a reference.

the value in PMA, the effect of salt is different in the copolymers, as is the I_1/I_3 ratio at low pH values and high copolymer concentrations. In addition, the decrease of the I_1/I_3 ratios with concentration is different for the three copolymers. At high pH and high concentration, the I_1/I_3 ratio of COP1 (0.95−0.97) is close to that for pyrene in PS films (0.95) and toluene solution (1.04)[28] or PS-poly(sodium acrylate) in aqueous solution (1.05−1.12).[21] The I_1/I_3 value of COP2 (1.2−1.25) is higher and similar to that for polyisobutylene-*b*-poly(sodium methacrylate) diblock copolymer (1.2).[44] At the same time, I_1/I_3 for COP3 (1.34−1.39) is similar to the value of nonionic detergents such as Triton X-100 (1.30) or cationic detergents with large counterions (dodecyltrimethylamonium chloride, 1.37).[21] The data presented in Figure 2A−C suggest that at low pH the PDMS−PMA globule is formed by interchain association and that pyrene is located in the more hydrophobic domains of PMA sequences in the block copolymers.

The variation of the probe site with the specific copolymer seems to suggest that probes are distributed in various PMA regions: adjacent to the PDMS blocks, at the interface between the two types of blocks, or in a range of sites that vary in their distance to the PDMS blocks. The trend in the I_1/I_3 ratios at pH = 8 and high concentration (0.95−0.96 for COP1, 1.2−1.25 for COP2, and 1.34−1.39 for COP3) correlates with the length of the PMA block in the copolymer (365, 924, and 3454, respectively), suggesting that longer hydrophilic chains provide more sites for the probe and pull it away from the more hydrophobic PMA/PDMS interface. We note that a study of polystyrene-*b*-poly(acrylic acid) copolymers by ESR of nitroxide spin probes has revealed PAA sites that are dynamically slower compared to the homopolymer; this result was explained by the proximity of the probe to the PS core.[46] A spin probe study of the COP*n* systems would be useful and is planned for the future.

The increased local hydrophobicity of the probe site with polymer concentration, as reflected in the polarity ratio, was used in some publications to determine the critical aggregation concentration (CAC). This approach is problematic because I_1/I_3 values depend on the excitation wavelength, λ_{ex}. This effect is clearly seen in Figure 3 for COP3 at pH = 8: the I_1/I_3 ratio for λ_{ex} = 334 nm is higher (a more polar environment) compared to the value for λ_{ex} = 339 (a more hydrophobic environment).[28] For this reason, the I_1/I_3 ratios presented here were used only to ascertain the location of the probe; the CAC values were determined from the excitation spectra, as described below.

pH-Sensitive Conformational Changes. These effects were studied by fluorescence spectroscopy and potentiometric titration. Fluorescence spectra of P in aqueous solutions as a function of pH were measured for the copolymers and PMA. The I_1/I_3 variation as a function of pH and concentration in the presence of salt are presented in Figure 4A−D.

Data for PMA, Figure 4D, indicate a sharp increase of the I_1/I_3 ratio for pH > 5, as described in the literature.[35,42,43,47,48] The highest value of the polarity ratio for the higher concentration (0.10 M) is 1.62, lower than that for P in water or in very dilute PMA solutions (c_p range from 1×10^{-8} to 1×10^{-7} M). For PMA concentration of 0.001 M, the highest value of the polarity ratio is 1.88, as for P in salt solutions (concentrations 0.005, 0.05, and 0.1 M, see Experimental Section). Data presented in Figure 4D, together with those presented in Figure 2D, suggest a complex picture for the location of P, depending on both the pH *and* the polymer concentration. The different values for the maximum I_1/I_3 ratio as a function of polymer concentration indicate that the uncoiling of the chain as a function of the degree of neutralization is limited by interchain interactions, which become more dominant as the polymer concentration increases.

Conformational changes as a function of pH were also detected for the block copolymers (Figure 4A−C), and the results depend on polymer concentration as well as the relative length of PMA and PDMS blocks. For COP1, the data in Figure 4A indicate the decisive role of concentration on the polarity ratio. There is only a weak transition at the highest copolymer concentration ($c_p = 1.52 \times 10^{-2}$ M) in the presence of salt, but the transition is clearly visible at the lowest copolymer concentration ($c_p = 9.09 \times 10^{-6}$ M), and the maximum value of the polarity ratio is only 1.74. The absence of the transition in the most concentrated copolymer solution may be related to the inability of PMA segments to uncoil due both to chain entanglements and the blocking effect of the PDMS segments. We also note that the decrease of the polarity ratio at high pH occurs at a lower pH for COP1 (pH ≥ 8) compared to PMA (pH > 12).

The limited pH range for the existence of the uncoiled PMA chain is highlighted for COP2 and COP3 at $c_p = 1.69 \times 10^{-2}$ and 2.5×10^{-2} M, respectively (Figure 4B,C). It seems that the uncoiling of PMA chains is restrained by the presence of PDMS segments; this effect is more pronounced at higher polymer contents, and as a result the probe relocates into more hydrophobic sites.

The variation of p*K*a for PMA with the degree of neutralization, α, is associated with conformational

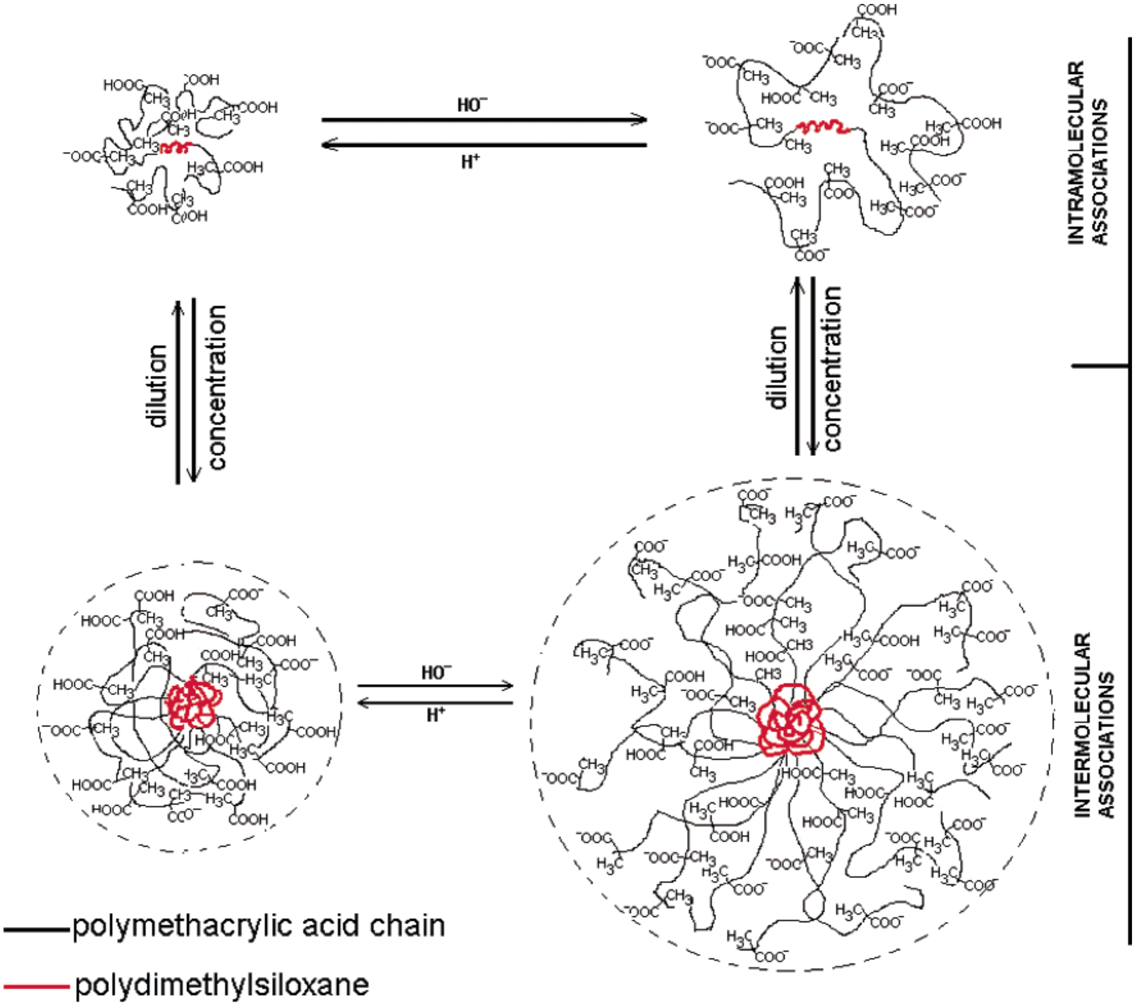


Figure 6. Schematic representation of intramolecular and intermolecular interactions in the block copolymers with increasing pH and concentration (see text).

changes due to hydrophobic interactions between methyl groups and electrostatic interactions in the polyanion.[48−51] For $\alpha < 0.15$, PMA exists in the tightly coiled conformation; at $\alpha = 0.15$ (α_1), the electrostatic energy induces a conformational transition to a more diffuse coil. As seen in the inset of Figure 5, in the range $\alpha = 0.2-0.5$ (depending on polymer concentration), pKa is essentially independent of α due to an expanded conformation that is gradually neutralized. An increase of pKa is observed for higher α values (to $\alpha_2 = 0.4-0.5$). The pKa$_0$ values (pKa values extrapolated to $\alpha = 0$) for the second interval are higher than those for the first interval; both pKa$_0$ values increase with decreasing polymer concentration and tend to stabilize to an almost constant value at high polymer concentrations.

The pKa dependence on α for the copolymers COPn at two concentrations, 0.10 and 5×10^{-3} M, is shown in Figure 5. The presence of siloxane blocks linked to PMA does not modify the general pK_a dependence on α. However, the pK_{a0} values for the copolymers are higher than the corresponding values in PMA. Moreover, the more diffuse coil of PMA blocks in copolymers appears at a higher α_1 (in the region 0.15−0.22), and the high limit of expanded coil, $\alpha_2 = 0.3-0.45$, is lower compared to PMA; these effects result from the presence of hydrophobic siloxane sequences, which are expected to lead to tighter polymer coils. The most visible effect of siloxane is registered for the COP1 and the COP2 copolymers, which have the shorter PMA blocks.

The gradual variation of copolymer conformations with concentration and pH are represented schematically in Figure 6. In the coiled state at low pH the methyl groups of the PMA blocks are expected to form, together with the PDMS blocks, a hydrophobic interphase. The larger size of the aggregates at higher pH and high concentrations can explain the restraining effect of the PDMS blocks and the increased opportunity for chain entanglement.

Excitation Spectra. The onset of aggregation was deduced from the analysis of pyrene excitation spectra shown in Figure 7A−D for COP3 as an example, for selected polymer concentrations at pH = 3 and 8, in the absence and presence of salt, with $\lambda_{em} = 383$ nm. The emission of pyrene in water for $\lambda_{ex} = 338$ nm is weak but increases when pyrene is transferred to a less polar medium; this increase is sensitive to polymer concentration, pH, and salt presence and is polymer-specific.

The I_{338}/I_{333} ratios deduced from the excitation spectra are presented in Figure 8A−C for the copolymers and in Figure 8D for PMA. Several publications have shown that these ratios are more reliable for the determination of CAC compared to lifetime measurements of fluorescence emission.[21,28,36,44]

For *low* copolymer concentrations, the I_{338}/I_{333} ratios are in the range 0.5−0.7 at pH = 3 and 8 (no salt added) and 0.8−1.0 at pH = 3 (in the presence of salt); the salt effect is less pronounced at pH = 8. The values in the absence of salt at pH = 3 are slightly higher than those

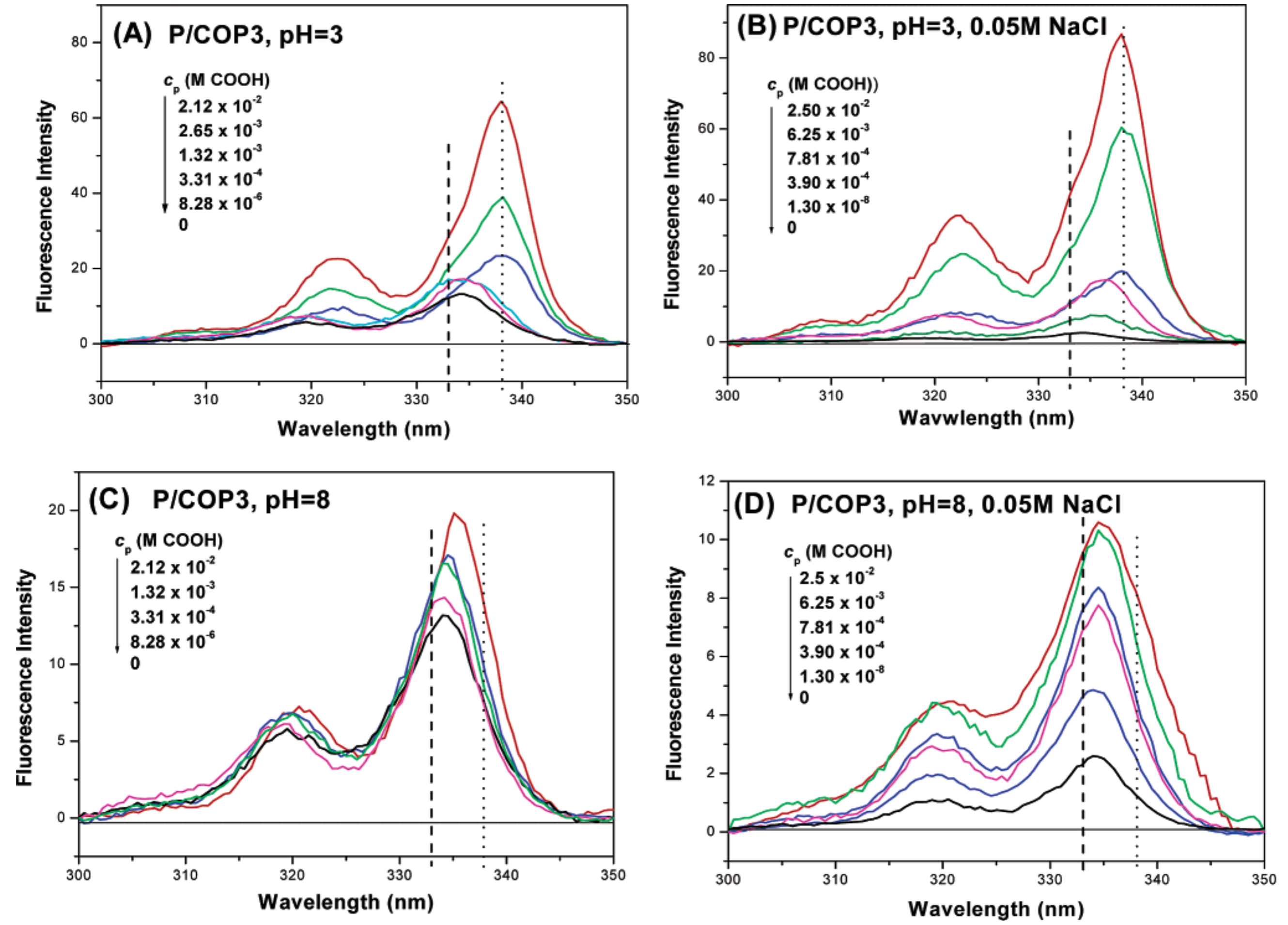


Figure 7. Excitation spectra of pyrene in aqueous solution of COP3, $\lambda_{em} = 383$ nm, for selected polymer concentrations, c_p: (A) pH = 3; (B) pH = 3, NaCl; (C) pH = 8; (D) pH = 8, NaCl. Dashed and dotted vertical lines point to $\lambda_{ex} = 333$ and 338 nm, respectively.

for PMA homopolymer (0.5, Figure 8D), and also higher than the values of 0.3−0.4 expected for pyrene in a hydrophilic environment. For high pH and no salt, the I_{338}/I_{333} ratios are close to that of PMA (0.6). For *high* copolymer concentrations and low pH, the I_{338}/I_{333} values are 2.2, 2.3, and 2.3 for the copolymers, slightly higher than that for PMA (2.2) but slightly lower than that for pyrene in a hydrophobic environment (2.4−2.5).[21,28,36] These experimental results suggest a more hydrophobic location of P in the presence of PDMS−PMA block copolymers in water media, P is located near hydrophobic domains most likely formed by methyl groups of PMA chain, but also by PDMS segments.

The corresponding I_{338}/I_{333} values for high copolymer concentration and high pH are 1.0, significantly lower than values in micellar structures and only slightly higher than that for PMA (0.9); these values reflect the insolubility of pyrene in the PDMS core of aggregates.

Critical Aggregation Concentration (CAC). CAC values for the copolymers were determined from the fluorescence intensity of the first vibronic peak, I_1, in emission spectra and the I_{338}/I_{333} ratio in excitation spectra ($\lambda_{em} = 383$ nm) by plotting these ratios vs log c and fitting the data to a sigmoidal curve.[21,28] The concentration determined by the intersection of the two branches of the I_1 or I_{338}/I_{333} dependence on copolymer concentration is taken as the CAC; this procedure is illustrated in Figure 9C for COP3 at pH = 8 and added salt (from excitation spectra) and in Figure 10 for the I_1 data of COP3 at pH = 8 with and without salt. The CAC values were almost identical when derived from excitation spectra with $\lambda_{em} = 373$ or 383 nm.[21,28]

Values of CAC were also determined by deconvolution of the excitation spectra using a nonlinear curve-fitting program. Excitation spectra of pyrene consist of peaks or pronounced shoulders at 306, 322, 333, and 338 nm, as seen in Figure 7A−D; the peak at 338 nm is characteristic of pyrene in a hydrophobic environment. Such a deconvolution is seen in Figure 9A for COP3 at pH = 3 in the presence of salt. In some samples the deconvolution also resulted in four peaks, peaks 1−4, but peaks 3 and 4 were not centered at 333 and 338 nm; this case is shown in Figure 9B for COP3 at pH = 8 in the presence of salt. As seen in Figure 9C, CAC values based on the intensity ratio of peaks 4 and 3, I_4/I_3, and on the I_{338}/I_{333} ratio in the nondeconvoluted excitation spectra are identical in this case, within experimental error.

The CAC values of the copolymers deduced from I_1 in the emission spectra (determined as shown in Figure 10) and from nondeconvoluted and deconvoluted excitation spectra for different pH values and presence or absence of salt are shown in Table 2. Values calculated from the concentration variation of I_1 are higher by a factor of 5−10 compared to values determined from the excitation spectra with the largest differences measured at lower pH and with respect to values deduced from nondeconvoluted excitation spectra. At higher pH, however, all values are in a narrow range. The discrepancy between CAC values based on I_1 data and on

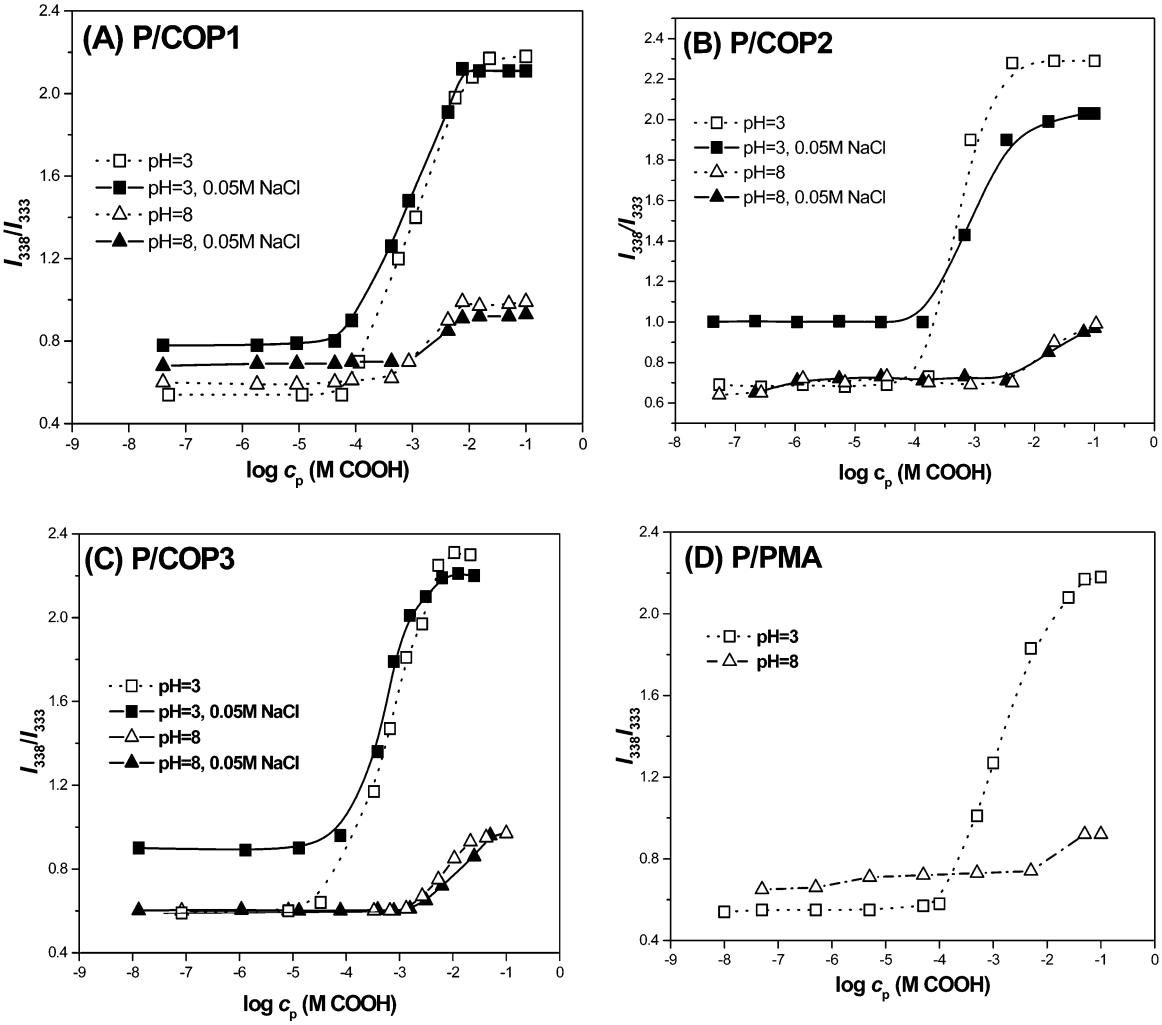


Figure 8. Variation of the intensity ratio I_{338}/I_{333} in the excitation spectra of P with polymer concentration, c_P, for the indicated pH and in the presence or absence of NaCl: (A) COP1; (B) COP2; (C) COP3; (D) PMA.

excitation spectra was reported[21] and is not completely understood. It is possible that line width variations may affect the height of the peaks, which was the parameter used for CAC determination.

CAC values determined from deconvoluted and non-deconvoluted excitation spectra are closer and vary from almost identical (in the case of COP2 at pH = 8) to a factor of up to ~3 (for COP2 at pH = 3 in the presence of salt). It is estimated that the cumulative margin of error in the determination of these values is ~20%. Data in Table 2 clearly demonstrate that the CAC values determined from excitation spectra are much higher at the higher pH, typically by a factor of ~10, and that the effect of added NaCl is small in most cases. The more solvated conformation at high pH values appears to isolate and shield the hydrophobic PDMS core, thus forcing the probe to reside in a hydrophilic environment, as clearly seen in Figure 6. At low pH the structure is compact and hydrophobic, thus providing easier access for PDMS segments in different polymer chains to interact and to aggregate; under these conditions the probe appears to reside in a range of hydrophobic sites. The scatter of CAC values for the copolymers at pH = 3 and the narrow range of CAC values measured at pH = 8 seem to support the idea of probe location in multiple sites at low pH and in one or similar sites at high pH.

Comparison of data derived from one method, deconvoluted excitation spectra, for the three block copolymers does not result, however, in a clear picture of the effect of the triblock composition, particularly the MA/DMS ratio. The behavior of block polyelectrolyte systems is considerably more complicated than that of copolymers containing nonionic water-soluble blocks. As concluded by Astafieva et al.,[21] the aggregation of block polyelectrolytes is influenced by variables such as block length, salt content, temperature, and pH values and these parameters cannot be considered independently; to these parameters we must add the nature of side groups in the polyelectrolyte. It is expected that the block copolymer become more soluble, and the CAC increase, for the same hydrophobic block length with increasing ionic block length; in other words, we expect the CAC of COP3 to be higher than that of COP2. However, CAC values for the two systems are not significantly different; in fact, for pH = 3 the CAC values of COP2 are the highest in the group. Complicating factors include the interactions between PDMS segments and the methyl groups in PMA blocks. Moreover, partition of the probe in a range of sites differing in their hydrophobicity, as suggested above, means that the I_{338}/I_{333} ratio is a result of several contributions. Similar studies for PDMS-*b*-PA may be helpful for the understanding of the methyl group effect.

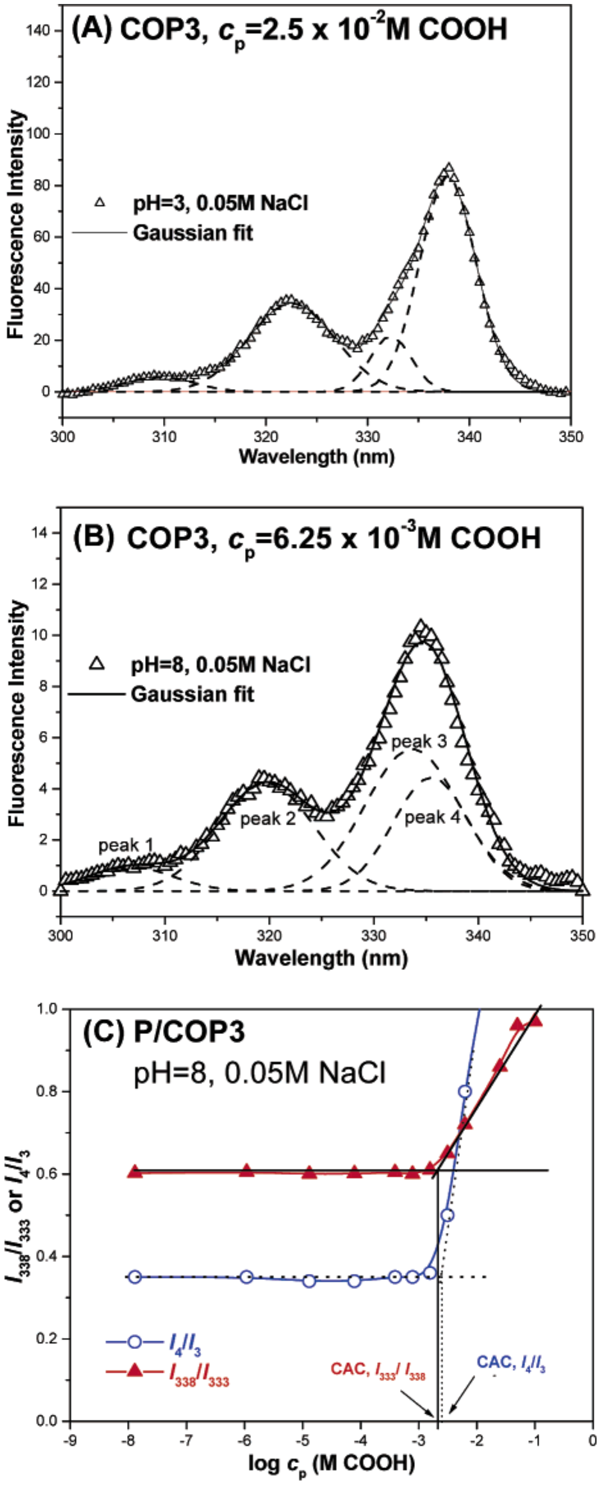


Figure 9. Deconvolution of excitation spectra of pyrene in aqueous solution of COP3: (A) $c_p = 2.5 \times 10^{-2}$ M COOH, pH = 3, NaCl; (B) $c_p = 6.25 \times 10^{-3}$ M COOH, pH = 8, NaCl. (C) Determination of CAC from the intensity ratio I_{338}/I_{333} obtained from nondeconvoluted (▲) and deconvoluted (○) excitation spectra of COP3 at pH = 8 and NaCl (see text and Table 2).

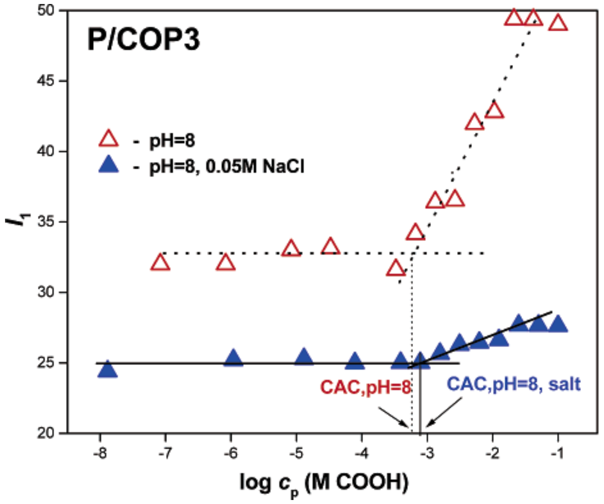


Figure 10. Determination of CAC from the height of the first vibronic peak, I_1, in the emission spectra of P in COP3 at pH = 8, $\lambda_{ex} = 338$ and λ_{em} 373 nm in the presence and absence of salt (see text and Table 2).

Absence of Excimer Peak. Pyrene association prior to or during the excited state leads to the appearance of the excimer band at 480 nm. The ability to form a pyrene dimer in the excited state depends on the number of other probes in the vicinity of the excited molecule. Excimer formation can provide information on the size of the micelle aggregates or, in the case of fluorescent probes containing two pyrenyl moieties, on the local viscosity.[31,34,35]

The signal from the excimer was not detected in the spectra reported here. This absence is assigned to the low P concentration in the polymer solutions. We note that Nakashima et al.[52] and Lee and Meisel[53] reported no excimer in aqueous PMA solution and in water-swollen Nafion ionomers when the probe concentration was 5×10^{-7} M, the same as in this study. The excimer emission *was* detected in PMA and in a PMA-*b*-PDMS copolymer when pyrene concentration was 1×10^{-6} M.[35]

Conclusions

Block copolymers of poly(dimethylsiloxane) and poly(methacrylic acid) (PDMS-*b*-PMA) with different lengths of the hydrophobic PDMS and hydrophilic PMA blocks were investigated by fluorescence spectroscopy based on pyrene as a probe and by potentiometric titration. The copolymers were triblocks with a PDMS center block, and the DMS/MA molar ratio in the three copolymers prepared was 5/365 (COP1), 22/924 (COP2), and 22/3454 (COP3). The behavior of the copolymers was compared with PMA as a reference. Since pyrene is insoluble in the PDMS blocks, the comparison provided the opportunity to assess the effect of the PDMS blocks on the aggregation of the PMA blocks.

Fluorescence spectra were measured as a function of polymer concentration (range from 1×10^{-8} to 0.1 M COOH) and pH (range 3−11) in the absence and presence of NaCl (0.05 M). Spectra were analyzed in terms of the intensity ratio of the first to the third vibronic bands, I_1/I_3 (the "*polarity ratio*") in the emission spectra, the intensity of the first vibronic peak, I_1, and the intensity ratio I_{338}/I_{333} in the excitation spectra for $\lambda_{em} = 373$ and 383 nm.

The variation of the polarity ratio with pH indicated that polymer concentration plays a major role on the formation of hydrophobic domains and on the local polarity of the domains, as reflected by the probe site. The extent of hydrophobic domains where the probe resides increased progressively with polymer concentration. This result indicates that the PMA globule in the copolymers is formed as a result of *inter*chain association, even when the polymer concentration is below the

Table 2. CAC Values Determined from I_1 in the Emission Spectra and from I_{338}/I_{333} Ratios in Nondeconvoluted and Deconvoluted Excitation Spectra of Pyrene in Aqueous Solution of the PDMS-*b*-PMA Copolymers[a]

sample	pH = 3	pH = 3, 0.05 M NaCl	pH = 8	pH = 8, 0.05 M NaCl
COP1 (DMS/MA = 5/365)	6.3×10^{-4}	7.1×10^{-4}	7.1×10^{-4}	7.9×10^{-4}
	0.6×10^{-4}	0.7×10^{-4}	6.2×10^{-4}	7.9×10^{-4}
	1.6×10^{-4}	1.6×10^{-4}	16.0×10^{-4}	10.0×10^{-4}
COP2 (DMS/MA = 22/924)	5.6×10^{-4}	6.1×10^{-4}	3.2×10^{-3}	4.3×10^{-3}
	1.0×10^{-4}	1.2×10^{-4}	3.2×10^{-3}	3.7×10^{-3}
	1.4×10^{-4}	4.0×10^{-4}	3.6×10^{-3}	4.0×10^{-3}
COP3 (DMS/MA = 22/3454)	4.5×10^{-4}	5.0×10^{-4}	0.6×10^{-3}	0.8×10^{-3}
	0.6×10^{-4}	0.8×10^{-4}	1.7×10^{-3}	2.0×10^{-3}
	0.8×10^{-4}	2.2×10^{-4}	4.0×10^{-3}	2.4×10^{-3}

[a] For each copolymer the CAC values were derived from I_1 in the emission spectra (first line), I_{338}/I_{333} ratio in the nondeconvoluted excitation spectra (second line), and I_{338}/I_{333} ratio in the deconvoluted excitation spectra (third line) as a function of copolymer concentrations.

overlap concentration, c*. In the limits of high and low polymer concentration, the fluorescence spectra indicated more hydrophobic domains in the copolymers compared to PMA.

Uncoiling of PMA segments was reflected in the sharp increase of the I_1/I_3 ratio for pH > 5, but the process appears restricted by the presence of the PDMS blocks. This conclusion was clearly seen in the lower maximum polarity at the site of the uncoiled chain, the narrower concentration range for the existence of the uncoiled chain, and even the total disappearance of the transition for COP1 at the highest concentration.

The presence of siloxane blocks in the copolymers does not modify the general feature of p*K*a versus the degree of neutralization, α, of the PMA homopolymer. However, p*K*a$_0$ values (p*K*a extrapolated to zero polymer concentration) for all copolymers are higher compared to PMA.

The critical aggregation concentration of the copolymers, CAC, was determined as a function of pH and presence of salt, based on the intensity of the first vibronic peak in the emission spectra, I_1, and on the ratio I_{338}/I_{333} in deconvoluted and nondeconvoluted excitation spectra. The CAC values for the three copolymers at 25 °C are influenced by the pH and by structural variables such as block length. CAC values are higher at pH = 8 compared to pH = 3, typically by an order of magnitude; at the same pH, addition of salt does not modify appreciably the CAC values. The CAC results are difficult to correlate with the structural differences in the three copolymers, however. This conclusion may be a result of hydrophobic interactions between the methyl groups of PMA and siloxane groups and of pyrene location in a range of sites that differ in their distance to the hydrophobic core of the aggregates, which consists of siloxane repeat units.

This study provided evidence for the role played by the PDMS blocks and polymer concentration on the process of chain uncoiling at higher pH values, on the appearance of hydrophobic domains, and on the hydrophobicity of these domains.

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