

Detection of hydrophobic microdomains in anionic polyelectrolytes with tris-(4,7-diphenyl-1,10-phenanthroline)₃Cr(III)

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Abstract

This paper describes the changes in the luminescent properties of the tris-(4,7-diphenyl-1,10-phenanthroline)₃Cr(III), [Cr(dip)₃]³⁺ complex in an aqueous solution of three polyelectrolytes containing cyclohexyl, phenyl or 1-naphthyl groups in the side chain. When the polyelectrolytes form hydrophobic microdomains the luminescence of [Cr(dip)₃]³⁺ is affected. The luminescence increases in the presence of cyclohexyl groups in the side chains, but decreases in the presence of phenyl and naphthyl groups (in that order). This fact can be explained in terms of a reductive quenching mechanism between the complex and the aromatic groups. Indeed, experiments performed with the complex and the alcohols corresponding to the functional groups, i.e., cyclohexanol, phenol, and naphthol, also show the same behavior, confirming the interaction with the functional groups and not other components of the polyelectrolyte. The luminescent properties of the [Cr(dip)₃]³⁺ complex allow the detection of hydrophobic microdomains arising from the host–guest interaction. Moreover, the complex is able to distinguish between a nonaromatic hydrophobic microdomain and an aromatic one.

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1. Introduction

Synthetic polyelectrolytes have gained particular importance in the last decade because of their use as simple models of biological macromolecules and their technological applications [1–5]. Polyelectrolytes with hydrophobic groups attached to the side chain may form hydrophobic microdomains under appropriate conditions [6–11]. Typical examples are amphiphilic copolymers of maleic acid with alkyl vinyl ethers, styrene [1,6–10,12,13] and derivatives, methacrylic acid [14], etc. These copolymers are widely used as surfactants and materials for biomedical applications [15–17]. Poly(styrene-co-maleic anhydride) is a commercially available polymer that has

several desirable properties such as solubility, filming and miscibility when mixed with styrene polymers and is widely used in industry [2]. It can be modified because of the presence of anhydride functional groups in the backbone. The stabilization of these polymers in bulk solution is related to their ability to hypercoil by hydrophobic interactions. These micro aggregates contain a variable number of monomer units ranging from 20 to 100 depending on the type of monomer, the side chain length, the degree of neutralization of the polyelectrolyte, and also on their concentration. The concentration at which these quasicelle aggregates occurs is known as critical aggregation concentration, CAC. There are some systems [7] in which these aggregates are present over a wide pH range, from 3 to 11, and they have usually been detected by fluorescence probing measurements of the I_3/I_1 ratio and/or the lifetime of the pyrene fluorescence [6,9]. So far, these kinds of studies have mainly focused on anionic polyelectrolytes and practically no work has

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been described in cationic systems [18]. On the other hand, the association of metal ions with polyelectrolytes, gels and water soluble neutral polymers has been extensively studied mainly for use in wastewater treatment for the selective removal of toxic metal ions. In fact, Varghese et al. [19] studied the role of the hydrophobicity of polymer gels on the structure of the metal–gel complexes. These authors reported that in the case of Cu(II) uptake for polymer gels, the hydrophobicity of the gel affects not only the amount of Cu(II) associated with the polymer but also the structure of the polymer–Cu(II) complex, increasing metal uptake as the hydrophobicity of the polymer gel increases. Recently, fluorescence experiments showed that modified cationic glucans containing hydrophobic regions can interact with polynucleotides in water and also with hydrophobic guest molecules such as single-walled carbon nanotubes, polysilanes, functional molecules, etc. [20]. The interaction of conjugated polymers and cationic and anionic surfactants has been studied by fluorescence, spectroscopic and conductivity methods [21]. Both anionic and cationic surfactants quench the emission intensity of the conjugated polymer, while with the cationic ones a new emission band at low energy is observed that is attributed to a polymer agglomeration as a consequence of the interaction with the cationic surfactant.

On the other hand, the emission properties of tris(polypyridine) chromium (III) complexes, $[\text{Cr}(\text{LL})_3]^{3+}$, (LL = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 4,7-dimethylphenanthroline (dim), and 4,7-diphenylphenanthroline (dip)), in air-saturated aqueous solutions are dramatically modified in the presence of anionic acrylic and sulfonate-type polyelectrolytes [22]. In all cases the chromium complexes displayed tunable emission properties in the polyelectrolyte microenvironments, to an extent depending on the hydrophobic character of both the polyamine and the polyelectrolytes. Consequently, the photophysical and photochemical properties of chromium(III) polypyridyl complexes have been the subject of extensive investigation [22–27]. The hydrophobic polyelectrolyte microenvironment modifies different steps associated with photoinduced processes, such as (i) rates of forward and back reactions; (ii) luminescence quantum yields; and (iii) decay lifetimes. Electrostatic interactions between positively charged transition metal complexes and anionic polyelectrolytes have been used to enhance the rate of photoinduced electron transfer processes and retard recombination reactions. Binding affinities of chromium(III) complexes with the polyelectrolytes depend on a series of experimental parameters in which the hydrophobic character of both the ligand and the macromolecule play a major role [22].

In this work we use tris-(4,7-diphenyl-1,10-phenanthroline)₃-chromium(III), $[\text{Cr}(\text{dip})_3]^{3+}$, to probe the presence of hydrophobic sites in aqueous solutions of anionic amphiphilic polyelectrolytes derived from poly(maleic anhydride-alt-styrene) with two different molecular weights and cyclohexyl, phenyl, or naphthyl as side chain groups. The influence of pH and concentration of the polyelectrolyte on the luminescent properties of the Cr(III) complex is determined. This is the first time that hydrophobic microenvironments of this kind of an-

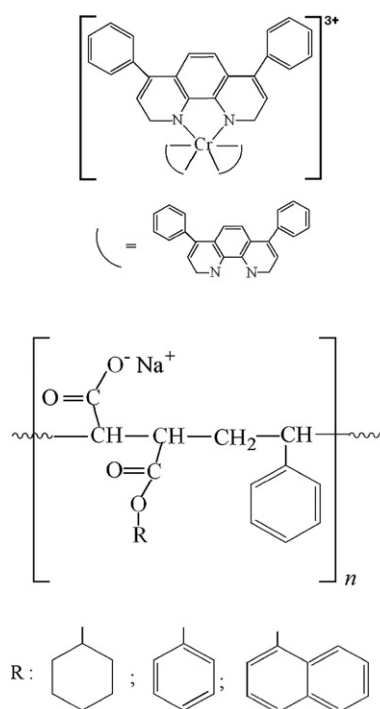
ionic polyelectrolytes containing bulky groups in the side chain have been studied by means of fluorescence measurements.

2. Experimental

2.1. Synthesis and materials

High molecular weight ($M_v = 125,000$ g/mol) poly(maleic anhydride-alt-styrene), P(AM-alt-Sty), was synthesized as described in the literature [28]. Average molecular weight was determined by solution viscosity measurements in THF at 30 °C, considering the Mark–Houwink–Sakurada constants [28] as $a = 0.81$ and $k = 5.07 \times 10^{-5}$. The polydispersity index was 1.85, and it was determined from the classical height-slices GPC treatment. Low molecular weight ($M_v = 1600$ g/mol) polymer was a commercial sample from Aldrich, Milwaukee, USA. P(AM-alt-Sty) samples were functionalized with cyclohexyl (C), phenyl (Ph) or 1-naphthyl (N) groups, by refluxing with the respective alcohol in a mixture of acetonitrile/THF (80/20). Reactions were considered to be complete when the IR band of the carbonyl group of maleic anhydride at 1825 cm^{-1} disappeared completely and the IR band of the ester carbonyl group at 1625 cm^{-1} appeared. In order to obtain the sodium salts, the polymers were treated with 10% w/v aqueous NaHCO_3 and the resulting solutions dialyzed and lyophilized. The tris-(4,7-diphenyl-1,10-phenanthroline)₃-chromium(III), $[\text{Cr}(\text{dip})_3]^{3+}$, complex was prepared and purified as described in the literature [22,26].

The polyelectrolytes used were coded as PPh16, PPh1250, PN16, PN1250, PC16, and PC1250, where 16 and 1250 correspond to molecular weights of 1600 and 125,000 g/mol. The corresponding chemical structures are shown in Scheme 1.



Scheme 1. Structures of the polyelectrolytes and the Cr(III) complex used in this work.

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