M. J. Tiera
V. Ap. de Oliveira Tiera
E. C. de Toledo
G. L. de Sena

Aggregation behaviour of hydrophobically modified poly(allylammonium) chloride

Abstract The behaviour of hydrophobically modified poly(allylammonium) chloride having octyl, decyl, dodecyl and hexadecyl side chains has been studied in aqueous solution using fluorescence emission techniques. Micropolarity studies using the $I_1/I_3$ ratio of the vibronic bands of pyrene show that the formation of hydrophobic microdomains depends on both the length of the side chain and the polymer concentration. The $I_1/I_3$ ratio of the polymers with low hydrophobe content (less than 5% mol) changes substantially when reaching a certain concentration. These changes are assigned to aggregation originating from interchain interactions. This behaviour is also confirmed by the behaviour of the monomer/excimer emission intensities of pyrene-dodecanoic acid used as a probe. For polymers having dodecyl side chains and hydrophobe contents higher than 10%, aggregates are formed independently of the polymer concentration. Anisotropy measurements show that microdomains resulting from the inter- and/ or intramolecular interactions are similar to those observed for cationic surfactants. Viscosity measurements show that the coil dimensions are substantially decreased for the polymers having high hydrophobe contents, indicating intramolecular associations.

Key words Cationic amphiphilic polymers · Aggregation · Pyrene fluorescence spectroscopy · Hydrophobic microdomains

Introduction

Polyelectrolytes bearing hydrophobic substituents bound to the main chain have been the subject of many investigations because of their ability to associate in aqueous solutions forming aggregates, which have potential applications in pharmaceutical, paint and cosmetics industries [1].

The association in aqueous solutions is due to intramolecular or intermolecular interactions and is related to polymer architecture. An entropic gain has been observed as a consequence of the modification of polyelectrolytes by introducing hydrophobic groups. This behaviour, known as hydrophobic interaction, leads to a reorganization of the polymer conformation to form hydrophobic microdomains. Conversely, the electrostatic repulsion between the fixed charges on the polymer chain plays an important role in the overall process, hindering the coil contraction. For copolymers having carboxylic groups, like ethyl methacrylate – acrylic acid copolymers [2], methacrylic acid – methyl methacrylate [3] and others [4], the “intramolecular aggregates” are progressively destroyed when the charge density on the polymer chain is increased by ionization of the carboxylic groups. However, with copolymers having a higher hydrophobic character, the hydrophobic microdomain is not disrupted and chains self-organize forming an aggregate with hydrophobic and hydrophilic...
domains (charged interfaces) [5]. Similar systems have been constructed with hydrophobically modified polysulfonates by controlling their hydrophobic content [6, 7].

Besides the formation of intramolecular aggregates, intermolecular interactions can also assist the formation of microdomains resulting from interchain associations. It has been shown recently that cationic copolymers with different alkyl groups on the chain associate to form intermolecular aggregates [8].

The tendency to associate depends on both the hydrophobe content and the flexibility of the macromolecule, which in turn determines their properties. Hydrophobically modified poly(allylamine) in nonprotonated and partially protonated states has been the subject of recent studies aiming to evaluate its self-organization in aqueous solutions and its capability to bind small molecules [9, 10].

Knowledge of the contribution of the polymer structure to the interactions may provide further insight into the importance of the effects of hydrophobic and electrostatic interactions on the aggregates properties. This idea led a number of workers to study hydrophobically modified polyelectrolytes in order to obtain more information about the aggregation process [11].

The present work examines the association behaviour of hydrophobically modified poly(allylammonium) chloride (PALA) in aqueous solutions using several fluorescent probes. Hydrophobically modified PALA polymers containing octyl, decyl, dodecyl and hexadecyl side chains have been studied in aqueous solution. The formation of aggregates by self-association was investigated using pyrene, pyrene-3-carboxaldehyde (PyC), pyrenedodecanoic acid (PyDod) and trans, trans, trans-1-[4-(3-carboxypropyl)phenyl]-6-(4-butylphenyl)-1,3,5-hexatriene (4H4A), which was used in fluorescence depolarization measurements to obtain information on the aggregates. The chemical structures of the probes and polymers used in this work are shown in Fig. 1.

**Experimental**

Materials $M_w =$ weight average molecular weight

The PALA used in this work was supplied by Polysciences ($M_w = 60,000$) and purified by double precipitation in methanol. PyDod was purchased from Molecular Probes and was used without further purification. Pyrene was recrystallized twice from ethanol. The 4H4A probe was prepared as reported previously [12].

Synthesis of polymers

PALA derivatives having alkyl side chains were prepared by reaction of the nonprotonated polymer with $n$-bromoalkanes. Typically, PALA was dissolved in a KOH/methanolic solution under stirring. The resulting solution was cooled to $5 \degree C$ and the KCl formed was separated by centrifugation. $n$-Bromododecane was added to the solution and was left to react for $48 h$ at $50 \degree C$. The methanolic solution containing the polymer was acidified with

![Fig. 1 Chemical structures of the probes and polymers used in this work: pyrene-3-carboxaldehyde (PyC), pyrenedodecanoic acid (PyDod), trans, trans, trans-1-[4-(3-carboxypropyl)phenyl]-6-(4-butylphenyl)-1,3,5-hexatriene (4H4A)](image)