

# NMR Paramagnetic Probing of Polymer Solutions Using Manganese(II) Ions

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**Abstract**—Nuclear magnetic relaxation studies show that manganese(II) ions can serve as paramagnetic probes for investigation of aqueous solutions of polyelectrolytes (polystyrene sulfonate and polyethylenimine) and their mixtures. The analysis of the measured rates of spin–lattice ( $R_1$ ) and spin–spin ( $R_2$ ) relaxations reveals the differences in the binding character of manganese(II) ions with polystyrene sulfonate and polyethylenimine. In a mixture of the polymers in acidic and neutral media, manganese(II) forms two types of ternary complexes. Using the suggested method for definition of the hydration degree of a coordination sphere of the bound probe ions, the number of water molecules in the first sphere of the polymer-bound manganese(II) ions is found on the basis of the value of the  $R_2/R_1$  ratio.

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## INTRODUCTION

The interaction of polyelectrolytes with charged low- and high-molecular compounds is of particular interest owing to the possibility of formation of strong complexes, including interpolyelectrolyte complexes (IPEC) [1, 2]. Polyelectrolytes and IPECs find application in solution of environmental problems [3]. In particular, the interaction of metal complexes with polyelectrolytes provides the basis for a technology of extraction of target cations from polymer-containing solutions during their membrane filtration [4]. Polyelectrolytes and their compounds are used in production of medicines as additives [5] and biocompatible materials [6]. Furthermore, nanocapsules prepared by layer-by-layer application of oppositely charged molecules of polyelectrolytes can be used as drug carriers [7]. These nanocapsules can include metal complexes of different nature, which allows them to combine different functions, for example, paramagnetism and luminescence required for diagnostic purposes in biomedicine [8–10].

Traditionally, the investigation of macromolecules and their complexes in solutions is carried out using the methods such as viscometry, gel permeation chromatography, and light scattering, which give the characteristics of macromolecules and their complexes as a whole. The spectral methods using probes allow one to obtain additional information at the level of local fragments of macromolecules. One of the tools that make it possible to reveal the regularities of interaction of polyelectrolytes with each other and with other

compounds is the method of NMR paramagnetic probing. The paramagnetic probes can be metal ions ( $Gd^{3+}$ ,  $Mn^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ , and others). Upon interaction of these paramagnetic ions with macromolecules or aggregated particles (surfactant micelles), a growth in the relaxation efficiency is observed that is caused by deceleration of the probe rotation upon binding with such large aggregates (an increase in the relaxation efficiency occurs in solutions of paramagnetic cations whose relaxation time is controlled by correlation rotation time  $\tau_c$ ) [11–13]. Earlier, they were used, for example, to study the solutions of ionic and non-ionic surfactants [14–17], lipophilic macrocycles [18, 19], and solubilization ability of micelles [20]. For polymer solutions, this approach was used more rarely; in particular, there are reports on solutions of some peptides, for example, albumin [21–24]. NMR spectroscopy with paramagnetic probes ( $Gd(III)$ ,  $Cu(II)$ , and  $Mn(II)$ ) was utilized to study solutions of a series of polymers and different mixtures on their basis in deuterated solvents using rather complex technical instrumental methods [25].

To study the solutions of polyelectrolytes, the most efficient paramagnetic cation probes are gadolinium(III) and manganese(II) ions, which possess the highest values of relaxation efficiencies and are hydrolytically stable in acidic and neutral media (unlike  $Fe(III)$  probes). This work presents the results of NMR paramagnetic probing of aqueous solutions of sodium polystyrene sulfonate (PSS) (anionogenic, strong electrolyte) and polyethylenimine (PEI) (cat-