



# Synthesis, characterization, and solution behavior of pullulan functionalized with tertiary amino groups

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## Abstract

The synthesis of cationic amphiphilic pullulan having dimethylaminopropyl groups was performed in dimethyl sulfoxide using *N,N'*-carbonyldiimidazole as activator. The pullulan derivatives with three different substitution degrees were characterized by FTIR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, elemental analysis, and conductometric titrations. The aggregates characteristics were determined by steady-state fluorescence (critical aggregation concentration and polarity) and capillary viscometry measurements. Their behavior in aqueous dilute and semidilute solutions was investigated by viscosimetric experiments and fluorescence technique over the concentration range of  $0.01\text{--}10\text{ g dL}^{-1}$ , as a function of the degree of substitution with pendant groups. Intrinsic viscosity determined using Wolf equations provided information on the conformation of polymer chains. The results highlight the appearance of intramolecular and intermolecular aggregates and the dependence of their characteristics on the degree of substitution with pendant groups.

## Keywords

Pullulan, cationic amphiphilic polymers, viscosity, fluorescence.

## Introduction

Over the past years, water-soluble polysaccharides received great attention due to their many applications as a result of the biocompatibility, biodegradability, and no toxicity aspects. Recently, nanoparticles-containing natural polysaccharides are intensively used for drug delivery applications.<sup>1,2</sup> However, in most cases, the need to incorporate organic solvents represents an obstacle from a formulation point of view. To overcome these drawbacks, the polysaccharides can be chemically modified by grafting hydrophobic groups located on side chains.<sup>3</sup> Amphiphilic polyelectrolytes obtained by chemical derivatization of water-soluble polymers can have the hydrophobic groups distributed either randomly or as blocks along the polymer backbone. The charges can be located on the same side chain as the hydrophobe or in different positions. In the first case, low-molecular amphiphiles are bound as side groups to a polymer backbone via either their headgroup or their hydrophobic tail. All these parameters control the final conformation and aggregate architecture of amphiphilic polyelectrolytes.<sup>4,5</sup> By analogy with the phenomena of micelle formation of small surfactants or lipids, aggregation of amphiphilic polymers is controlled by the balance between the interactions of the hydrophobic groups and the

hydrophilic chains. The concentration at which the polymer aggregation starts is usually called the critical aggregation concentration (CAC). At relatively high polymer concentrations, intermolecular associations of polymers are induced through the association of hydrophobic groups, resulting in a remarkable increase in solution viscosity. For this reason, these types of polymers are called associating polymers and are used as thickeners to modify solution viscosity.

Pullulan is a nonionic water-soluble polysaccharide, which is produced from starch by the yeast-like fungus *Aureobasidium pullulans*.<sup>6,7</sup> Pullulan is known for its non-toxicity and biocompatibility.<sup>8</sup> Most pullulan modifications are intended to reduce its water solubility or to introduce charged or reactive groups for functionality.<sup>9,10</sup> Up to now, various amphiphilic pullulan derivatives have been prepared by introducing long alkyl,<sup>11,12</sup> cholesterol,<sup>13–15</sup>

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