

# Self-assembly of four- and two-antennary oligoglycines in aqueous medium



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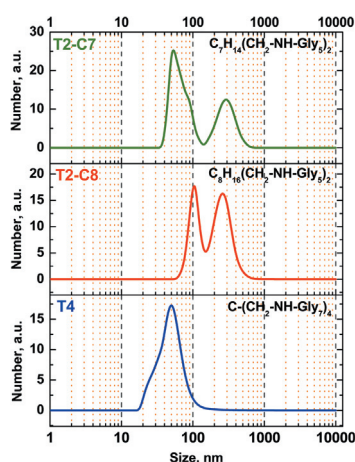
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## HIGHLIGHTS

- Tectomer nanoaggregates of T4, T2-C8 and T2-C7 are detected in aqueous solutions.
- The size distributions of the T2-Cx self-assemblies are bimodal.
- The size distributions of the T4 self-assemblies are predominantly monomodal.
- The self-assemblies are positively charged.
- Addition of NaCl shifts size distributions to smaller tectomers but does not change modality.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In aqueous media synthetic antennary oligoglycine molecules self-assemble into supramolecular structures like bulk hydrophilic aggregates (tectomers), vesicles, etc. The innate reason for the self-organization is the onset of highly cooperative network of intra- and intermolecular hydrogen bonds, resulting in 'recognition-type' interactions. The present study deals with the detailed investigation of the onset, the time evolution and the properties of the tectomers, formed from three types of synthetic oligoglycines: four-antennary (T4), two-antennary with octyl chain (T2-C8) and two-antennary with heptyl chain (T2-C7). Detailed size distributions and the electrophoretic mobilities of the aggregates are presented. The pH and the temperature of the investigated samples are strictly monitored and kept within prescribed value ranges. The impact of the addition of low molecular mass electrolyte (NaCl) on the size distributions of the obtained self-assemblies is also clarified. The basic result is the registration of predominantly bimodal size distribution of the self-assembled nanoaggregates. Only at high oligoglycine concentration the sizes distribution becomes monomodal. Insofar as the antennary oligoglycines are biocompatible, the pool of attained systematic data will be further implemented in the design and fine-tuning strategies of complex fluid formulations aimed at the entrapment of charged

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and/or hydrophobic nanospecies of various origin. The obtained results suggest that the self-assembled nanostructures of antennary oligoglycines have high potential for e.g. biomedical and water-purity-control applications.

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## 1. Introduction

Self-assembly in aqueous media is a very important phenomenon in material sciences and in various innovative technologies. Its main characteristics include spontaneous formation of complex (nano)structures under the action of weak, non-covalent interactions (hydrophobic, van der Waals and capillary forces, hydrogen bonds, molecular recognition, etc.). The obtained species are thermodynamically stable at given conditions and by changing the parameters of the environment (pH, temperature, ionic strength, etc.) the formation process can be guided and monitored [1,2]. One important class of self-assemblies in aqueous media is nanoaggregates which appear under the action of hydrogen-bonding type of interactions. H-bonding is well direction-defined and the self-assembly based on it could lead to a very precise ordering into one-, two- or three-dimensional structures (bands, sheets, helices, etc.) [3]. This bonding type is found in many bio-materials (proteins, saccharides, nucleic acids, peptides, etc.); it is also useful in the design of novel structures and products, as for example, nanotubes of peptides which can function as artificial membrane channels, etc [4].

The present study deals with the detailed investigation of aggregate size distribution in aqueous systems, containing self-assemblies of symmetric antennary oligoglycines [5–7]. The particular focus is on four- and two-antennary oligoglycines, namely C-(CH<sub>2</sub>-NH-Gly<sub>n</sub>)<sub>4</sub> (T4) and C<sub>x</sub>H<sub>2x</sub>(CH<sub>2</sub>-NH-Gly<sub>n</sub>)<sub>2</sub> (T2-Cx). Their molecules have either 4 or 2 oligoglycine tails (antennae) of identical lengths, with variable number (n) of glycine (Gly) units, bonded to a common center (C-atom or an alkyl segment). It is known that the four-antennary species with n ≥ 7 and the two-antennary class with n ≥ 4–5, are able to self-organize into aggregates and to form extra-regular adsorption layers at solid interfaces (e.g. mica) [6,7]. The Raman spectra of the four-antennary oligoglycine (T4), confirmed also by Fourier-transformation infrared spectroscopy, have evidenced that both at the solid interfaces, and in a crystalline form, T4 tectomers have Polyglycine II architecture (PG-II) [6,7]. PG-II structural motif is characterized by a highly coordinated network of intra- and inter-molecular hydrogen bonds between the CO- and NH- groups of the antennae. This architecture induces a hexagonal order in the resulting self-assemblies: each molecule is surrounded by six parallel neighbors. Bovin et al. have studied the assembly of the above-mentioned types of oligoglycines on hydrophilic negatively-charged mica surfaces using Atomic Force Microscopy [6]. and Scanning Force Microscopy [7]. The results have shown that out of three possible molecular conformations (“2 ⊥ 2”, “2 + 2” and “4 + 0”, the figures denote the number of antennae which participate in intramolecular H-bonding interaction) the four-antennary oligoglycines (T4) self-associate into an extra-regular monolayer with thickness ~4.5 nm which corresponds to “2 + 2” conformation of the monomer tails within the PG-II structure.

The two-antennary class (T2-Cx) can form both monolayers of thickness (~2 nm) and bilayers (~3.7 nm) on mica surfaces [6,8,9]. This is a sign that the tails of the monomers on a solid plate are packed in “2 + 0” conformation. Specifically, the formation of a bilayer in the T2-Cx case is possible only due to the presence of

the hydrophobic (alkyl) portion in the structure of the oligomer molecule.

As already mentioned, on hydrophilic solid surfaces situated in aqueous media the self-assemblies for these types of oligoglycines appear predominantly under the action of hydrogen-bonding type of interactions. Due to the particular conformation of the antennae the hydrogen bonding in these cases invoke recognition-type interactions which is expected to result in a very precise ordering into one-, two- or three-dimensional structures (bands, sheets, helices, etc.) [4]. From this point of view, the molecules of the investigated oligoglycines might be regarded as specific ‘tectones’ and the resulting self-assemblies (aggregates) are named tectomers [6].

The antennary oligoglycines are biocompatible and nontoxic for living organisms and therefore are potentially very suitable for medical applications, waste water purification, etc. For example, it has been shown that T4 possess antiviral activity because of their ability to inhibit the adhesion of the influenza virus to the host cells [5]. Besides, in a recent study [10] it has been established that aqueous solutions of the salt form of T4 (C-(CH<sub>2</sub>-NH-Gly<sub>7</sub>)<sub>4</sub>\*4HCl) can capture trace quantities of lipopolysaccharides (LPS) from bacteria *Escherichia coli* EH100 (*E. coli*). A significant decrease in the dynamic and equilibrium surface tension values has been registered upon raising of the content of T4 in the T4/LPS mixtures, despite the hydrophilic nature of the oligoglycine and the ultralow quantities of LPS. The obtained results implicate that the components of the system interact in such a way that amphiphilic T4/LPS complexes are formed. Drainage properties of the microscopic foam films and surface dilational rheology of the adsorption layers at the air/solution interface have supported the idea about the possible onset of such surface active entities in the mixed T4/LPS systems. The driving force of this complex formation is most probably of electrostatic origin: due to charging of some amino-groups (NH<sub>3</sub><sup>+</sup>) at the end of the antennae T4 favors the electrostatic interactions with the negatively charged LPS. Moreover, the analysis of the obtained data implies that the main effect of the interactions could be assigned not to single T4 molecules but to the existence of bulk tectomeric aggregates [10]. However, previous studies claimed that the salt (hydrochloride) forms of T4 are not able to self-assemble due to the electrostatic repulsion between the charged antennae ends (NH<sub>3</sub><sup>+</sup>) [5,7]. In addition, although the mentioned above investigation [10] suggests that T4 in aqueous solutions might be used for the registration and effective capture of trace quantities of LPS from bacteria *E. coli* EH100, there has not been an information about the size distribution and other properties of these oligoglycine aggregates (tectomers).

Recently an idea about innovative application of some two-antennary oligoglycines in view of possible anticancer drug delivery has been proposed [8]. The suggestion is to utilize the pH-responsivity of the bulk-solution aggregates for possible encapsulation and controlled release of some hydrophobic drugs. Again there is no systematic investigation on the formation and properties of the bulk self-assemblies so as to optimize the design of the proposed formulation.

To summarize, due to their specific properties and biocompatibility the tectomers from four- and two-antennary oligoglycines might have an important role in e.g. capturing bacterial endotoxins, drug encapsulation and release, water purification devices, etc.

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