

Nanoscale Solution Structure and Transfer Capacity of Amphiphilic Poly(amidoamine) Dendrimers Having Water and Polar Guest Molecules Inside

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Introduction

Dendrimers^{1,2} with well-defined, highly branched architectures are potential candidates for well-varied technological applications including drug delivery, catalysis, gene therapy, light-harvesting antennae, chemical sensors etc. In this study, we synthesize hydrophobically modified third (**P3**) and fourth (**P4**) generation poly(amidoamine) (PAMAM) dendrimers with stearyl acrylates (SA) as hydrophobes via Michael addition reaction and investigate the structural behavior of these amphiphilic dendrimers in a selective solvent, toluene by SAXS measurements. Our focus is addressed on elucidating the fundamental aspects of the change in the conformation of the dendritic micelles before and after encapsulation of water molecules, polar dye, Acid Red 1(AR-1), and Cu (II) salt.

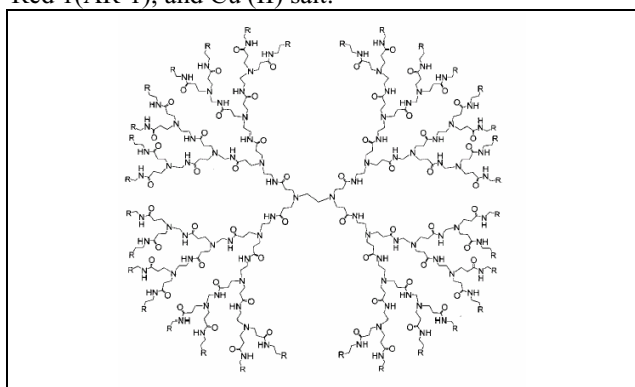


Fig.1 Structure of Amphiphilic Dendrimer **P3** .

Experimental

Synthesis. **G3** PAMAM dendrimer solution in methanol or **G4** in methanol, sufficiently molar excess of SA and dry THF were introduced in the reaction vessel, fitted with a condenser. The reaction was carried out under nitrogen atmosphere and with magnetic stirring in a water bath at 50 °C. After 7 days reaction the solvent was evaporated and the mixture was heated under reflux in diethyl ether. It was then filtered to remove excess SA and the same process was repeated thrice. The residue was treated thrice, each time with water under refluxing condition, in order to remove any water-soluble unreacted dendrimers present in it. The residue was then dried in a vacuum oven at 40 °C for 48 hours and the products were obtained as white solid materials. The products obtained (**P3** and **P4** respectively) were insoluble in water,

methanol or diethyl ether but were highly soluble in chloroform, THF, and toluene.

SAXS Measurements. SAXS measurements were carried out at 25 °C, using BL-10C with a synchrotron orbital radiation as an X-ray source set up in the Photon Factory of the High Energy Accelerator Organization at Tsukuba, Ibaraki, Japan. The wavelength of the X-ray was 1.488 Å. The scattered intensity was recorded by a position-sensitive proportional counter (PSPC) with 512 channels over a scattering vector range from 0.02 to 0.30 Å⁻¹. The scattered vector was calibrated using a sixth peak of dry collagen.

Results and Discussion

Table 1 shows R_g values for **P4** in toluene after solubilization of H₂O, AR-1, and Cu (II) salt. It is clear that the dendrimer molecules in toluene are remarkably expanded by encapsulation of the polar molecules. Water molecules, selective solvent for the core, increase the volume of **P4** by 4-fold. They may diffuse into the originally globular core in toluene to solvate and swell it, and concurrently push the buried long alkyl chains out the toluene phase. Since the numbers of AR-1 molecules inside the core are mostly 8-24, AR-1 molecules are thought to be not so effective in the core chain expansion. Further chain expansion by the presence of Cu (II) ions are likely due to complex formation with amine groups in the dendritic core. The comparison in Kratky plots of the experimental data of **P3** and **P4** with the theoretical curve calculated for the sphere model with constant density clearly demonstrates that the experimental scattering profile of **P3** and **P4** molecules after solubilization of polar molecules can be semi-quantitatively described by the sphere model.

Table 3. Characteristics of **P4** with encapsulated polar guest molecules inside at 25 °C.

Cp/mg/mL	Guest Molecule	$R_g/\text{Å}$
0.00	-	25.9
8.60	AR1	37.6
8.60	Cu	43.2
8.60	H ₂ O	37.0

References

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