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Optical study and structure modelling of PPI liquid crystalline dendrimer derivatives

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Abstract

Optical study of two families of poly(propylene imine) (PPI) dendrimers ($G = 1–5$) are reported. The enlarging of the chain number (generations) of the PPI dendrimer leads to the spectra shift to IR region in solvent until 8 and 19 nm for both families, respectively. The theoretical modelling of the dendrimer structure was performed. The geometric characterization of dendrimer structure demonstrates that the preferable free space for encapsulation is periphery of the PPI dendrimer.

Keywords: Nanostructures; Modelling; Geometric structure; Optical study; Dendrimer structure; Poly(propylene imine)

1. Introduction

Dendrimers are artificially made macromolecules self-assembled in three-dimensional structures with well-ordered architectures. The structure is always built around a central multi-functional core molecule, with branches and end-groups. The highly branched 3D structure provides a high degree of surface functionality and versatility [1]. Soft self-assembly of dendrimers allows the tailoring of molecular properties during synthesis because the locations of the core, branches, and periphery of dendrimers can be controlled and tuned with high accuracy. The possibility to control the structure during synthesis has created substantial interest in application of dendrimers [2]. However, the geometric characterization of dendrimer structure has lagged behind the rapid progress in synthesis and design [3]. From theoretical studies [4] it followed that dendrimers evolved in concentric shells enclosing empty spaces. Other theoretical studies questioned these assumptions and arrived at the conclusion that dendrimers were indeed the structures with filled interior [5]. Experimental evidence is also not adequate. By using X-ray diffraction and the atomic PDF technique, it was shown [6] that PAMAM dendrimers are well ordered structures at atomic scale with relatively open interior. The empty spaces within dendrimer structure are important aspect for understanding of physical properties and possible applications of dendrimers. Another exceptional feature of the dendritic architecture is monodispersity. As a whole, it is essential to obtain a comprehensive understanding of dendrimer structure and dynamics [7,8]. Properties such as the shape and size of the dendrimers as a function of generation, solvent accessible surface area and distribution of terminal groups as well as elastisity of

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dendrimer structure with respect to surface interaction [9] are all critical for some applications of dendrimers [7]. The shape persistence of dendrimer molecules and three-dimensionality of structure are very important features for photonics and other applications like drug-delivery agents in medicine [10,11], nanoscopic containers [12], light-harvesting cells [13–15] and OLEDs [16–18], catalysts [19], sensors and detectors [20].

The main goal of the present work was to investigate the optical properties of the poly(propylene imine) (PPI) LC dendrimer and to calculate the dendrimer structure. Two families of covalently functionalized liquid crystal poly(propylene imine) (PPI) dendrimers generations ($G = 1$–5) were synthesized. First and second family were derived from 4-(4′-decyloxybenzoyloxy)-2-hydroxybenzaldehyde with different mesogenic units OC_2H_5 and OC_5H_{11}, respectively. The optical properties of two families of PPI dendrimers were investigated by measuring and analysing the UV–vis spectra in chloroform solution and in solid state. The structure of the first family of PPI dendrimer was studied by SEM. The theoretical calculation of the structure of PPI dendrimer was performed.

2. Experimental

Two families of poly(propylene imine) (PPI) dendrimers with different number of flexible chains, $n = 4$, 8, 16, 32 and 64 ($G = 1$–5 generations) were synthesized. The synthesis of dendrimers was carried out in two steps following the method described previously [21]. Commercial dendrimers (PPI) have been functionalised at the periphery with mesogenic units (shorter – OC_2H_5 and longer – OC_5H_{11}, first and second family, respectively) containing different structural features, namely, the number of terminal alkyloxy chains and the position of attachment of the mesogenic units to the dendrimeric core [22,23].

The UV–vis spectra were recorded on a Perkin-Elmer UV–vis Lambda 19 spectrophotometer in solid state and in solvent using chloroform as solvent. The prepared concentration varied from 1×10^{-8} to 8×10^{-8} mol/ml for every generation, where cuvette thickness 1 cm. Thin film (thickness 20 μm) of the PPI dendrimer ($G = 5$) was prepared between two quartz platelets and oriented in strong magnetic field.

The theoretical search of the geometrical structure was performed by Hartree-Fock/6-31G basis sets by applying Berny geometry optimization which enable to describe geometrical and electronic structures enough well. The theoretical study of optical spectra were investigated by TD B3LYP/6-31G approach. This is a promising technique for the evaluation information of molecules in excited electronic states.

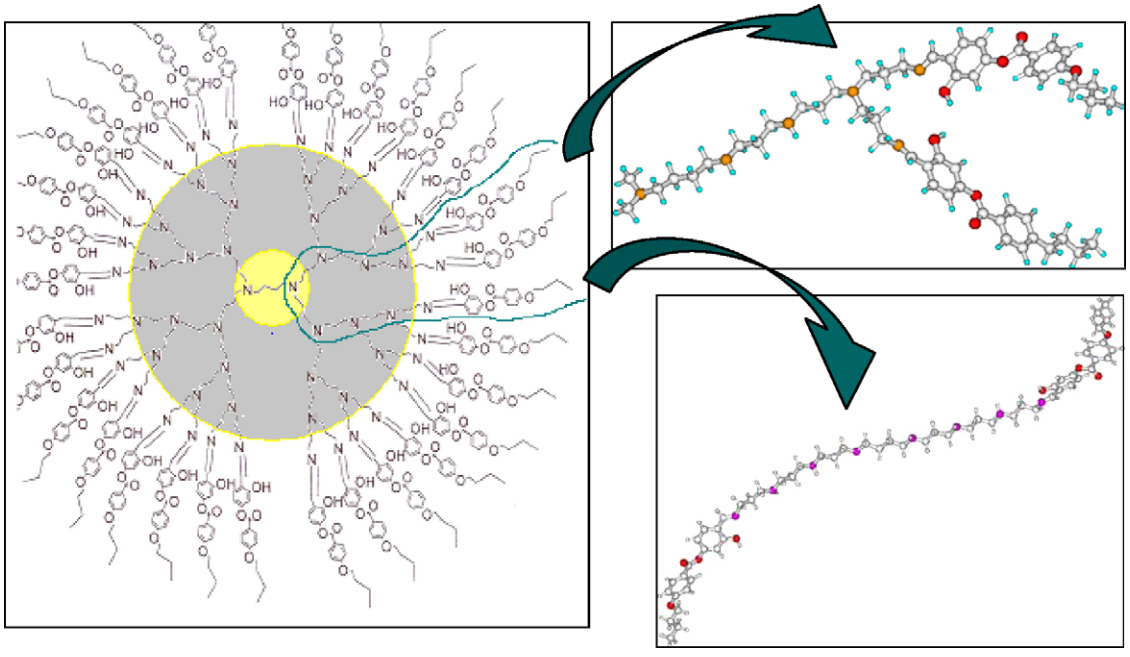

Fig. 1. PPI dendrimer structure with $n = 64$ flexible chains (left). Calculated structure from core to the periphery of one (bottom right) and two (top right) chains.