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Structural changes in stimuli-responsive nanoparticle/dendrimer composite films upon vapor sorption

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Abstract

Au-nanoparticle/dendrimer composite films are stimuli-responsive materials with a potential application as highly sensitive chemiresistive sensors, since their conductance strongly changes upon sorption of chemical species from vapor phase. Here we report on the neutron reflectometry studies on such films exposed to water, methanol, and toluene vapors as external stimuli. Poly (amidoamine) (PAMAM) dendrimer third generation and poly (propylene imine) (PPI) dendrimer fourth generation were used to build up the films.

The interaction between the film and the vapor is mainly governed by the chemical nature of the dendrimer component. Both AuPAMAM and AuPPI films have well expressed affinity to water. The more hydrophilic PAMAM adsorbs about 3 times more water than the more hydrophobic PPI. In contrast, the diffusion of toluene is limited to a thin region near the film/gas phase interface where a thin wetting layer of toluene is registered. Methanol as a solvent with transitional hydrophilicity shows intermediate behavior when interacting with the films.

Since this work is largely based on neutron reflectometry we point out that this technique is outstanding in resolving fine details of film response to vapors which is important to understand the changes that occur in the vapors sensing process. ***To cite this article: N. Krasteva et al., C. R. Chimie 12 (2009).***

Keywords: Au-nanoparticle; Dendritic polymer; Neutron reflectometry; Vapor sorption; Thin composite film; Stimuli-responsive layer

1. Introduction

Over the past decade nanocomposite materials comprising metal nanoclusters embedded in an organic medium have gained considerable attention. These materials possess many specific properties, pertaining to their structure, thermodynamics and electronic, spectroscopic, optic, electromagnetic and chemical features. Composite nanoparticle/polymer materials combine the sensitivity and response of polymers to

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external stimuli (e.g., polymer swelling in the presence of vapors or gases) with the charge transport ability of the metal nanoparticles, thus allowing creation of materials with tunable stimuli-responsive conductivity. The possibility of tuning the chemical and electrical properties of these materials by systematically varying the size, structure, and composition of the constituents renders them not only interesting for scientific investigation, but makes them increasingly attractive for technological applications such as nanoelectronics, catalysis, and chemical sensing [1–5].

Au-nanoparticle/dendrimer nanocomposite films are stimuli-responsive materials. It was shown that the conductance of these films is strongly affected by sorption of chemical species from the vapor phase, which makes these materials good candidates for highly sensitive and selective chemical sensors [6–8]. Today, it is assumed that swelling and changes in the permittivity of the film as a consequence of analyte sorption are the major factors that account for the response of such nanoparticle/organic sensors to dosing with gaseous analytes. Thus, for enabling a quantitative understanding of the films' sensitivity it is necessary to quantify both the structural changes and the distribution of adsorbed vapor molecules in the film.

Here we summarize the structural changes upon vapor sorption in Au-nanoparticle films prepared with two dendrimers with different solvent affinity (Fig. 1). Poly (amidoamine) (PAMAM) dendrimer third generation was used as organic component in AuPAMAM films. Poly (propylene imine) (PPI) fourth generation dendrimer was used as organic component in AuPPI films.

Neutron reflectometry [9–11] was used as the main tool in the present study. The method has been applied for analyzing the structure and swelling of polyelectrolyte layers [12,13], composition variations in thin polymer films caused by chemical reactions [14] or solvent diffusion [15]. Neutron reflectivity (NR) experiments provide structural information in the direction z perpendicular to the film surface over a length scale of 1–500 nm with a resolution down to about 0.2 nm. Neutrons possess strong penetration power as a consequence of their weak interaction with almost any material. Their sensitivity to different isotopes allows measuring the composition profiles along the z direction. An important advantage of the methodology, as compared to X-ray methods, is the absence of sample damage, even upon prolonged exposure to the neutron beam.

The specular neutron reflectivity method is based on the variation in the specular reflection at the interface between two phases with the wave vector transfer $Q = 4\pi\sin\theta/\lambda$, where θ is the angle of incidence of the neutron beam and λ is the neutron wavelength. The variation of the reflectivity R with Q (the reflectivity profile) depends also on the scattering length density profile $\rho(z)$, according to Eq. (1) [9,16]. The scattering length density (SLD) is given by $\rho = \sum b_i N_i$, where b_i is the neutron scattering length, and N_i^i is the number density of the ith sort of nuclei.

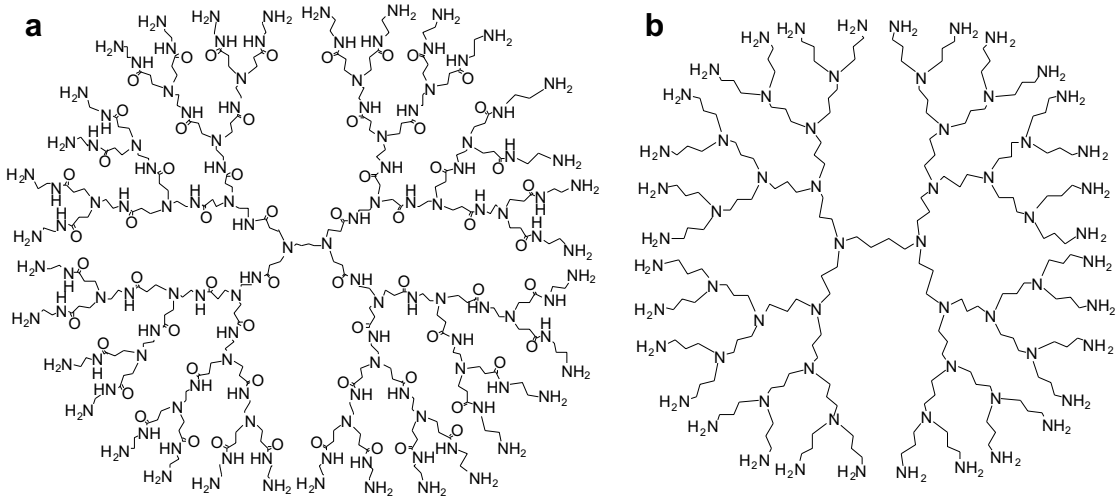

Fig. 1. Structural formulas of the dendrimers used as linkers of the Au nanoparticles: a) third generation poly (amidoamine) dendrimers (PAMAM); b) fourth generation poly (propylene imine) dendrimer (PPI).