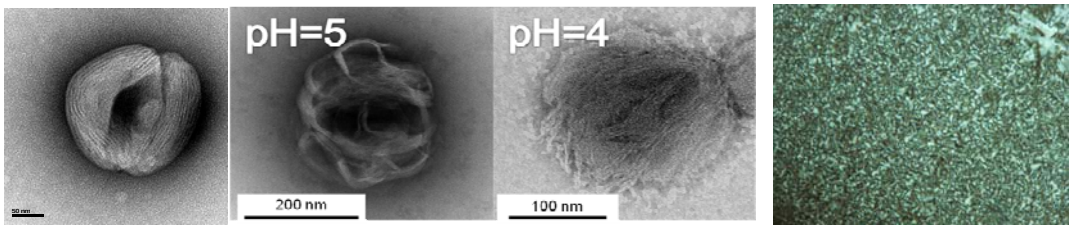
pH-RESPONSIVE "ONION NANOSPHERES" COMING FROM IONIC LIQUID CRYSTAL PAMAM DENDRIMERS

Silvia Hernández-Ainsa[1,3], Joaquín Barberá[1], Mercedes Marcos[1], José Luis Serrano[2], Teresa Sierra[1]
[1]. Instituto de Ciencia de Materiales de Aragón (ICMA), Universidad de Zaragoza–CSIC, Pedro Cerbuna 12, 50009, Zaragoza, Spain. [2]. Instituto Universitario de Nanociencia (INA), Universidad de Zaragoza, Pedro Cerbuna 12, 50009, Zaragoza, Spain. [3]. Current address: Biological and Soft Systems, Cavendish Laboratory, JJ Thomson Avenue, Cambridge, CB3 0HE.

Liquid crystal order allows the control of the supramolecular arrangement, thus providing a powerful tool to obtain ordered structures capable of executing a function. For instance, many lyotropic liquid crystals have been studied as bioinspired synthetic materials mimicking cellular membranes. In this way, supramolecular self-assembly in water constitutes an active topic of research because the possibility to produce a variety of nanoobjets with different shapes. These structures have opened a wide range of potential applications in fields as different as Material Science or Biomedicine.

Among the great variety of molecules investigated in this context, dendrimers posses some specific characteristics that make them of great relevance to address the desired self-assembly process. Nearly all amphiphilic dendrimers for guest encapsulation have been obtained by means of covalent bonds, which is laborious and require several purification steps. The preparation of dendrimers by non-covalent self-assembly processes, such as the ionic interaction, is a very convenient synthetic method due to its simplicity, (it is made in one-step) and its versatility because variation of the functional groups can easily be carried out. Some of these ionic dendrimers have shown liquid crystalline properties.

With the aim to obtain amphiphilic molecules a series of ionic amphiphilic dendrimers constituted by the grafting of poly(amidoamine) (PAMAM) of different generations (G=0-4) with linear carboxylic acids bearing hydrophobic chains has been prepared. Almost all of the compounds present liquid crystalline behaviour as shown by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffractometry (XRD) studies. Smectic A mesomorphism has been found for most of the compounds and a rectangular columnar mesophase is displayed for the highest generation compound at low temperature. Interestingly these amphiphilic dendrimers are also capable to self-assemble in water depending on their hydrophobic/hydrophilic balance forming some nanoobjects. In most of the cases these nanoobjects resemble nanospheres whose morphology has been studied by means of transmission electronic microscopy (TEM). The stability of these nanospheres is disrupted in acid or basic media and their amphiphilic nature makes them suitable for trapping both hydrophobic (β-carotene) and hydrophilic (Rhodamine B) molecules. These features make these easy to synthesize systems promising and versatile candidates as molecular nanocarriers for a number of biomedical and technological applications.



a b c d

a), b), c) Representative TEM images of nanospheres formed by self-assembly in water of the ionic dendrimer derived from PAMAM and myristic acid., d) POM textures of G4(C14) at 59ºC in the first cooling process.