

# Columnar and smectic self-assembly deriving from non ionic amphiphilic hyperbranched polyethylene imine polymers and induced by hydrogen bonding and segregation into polar and non polar parts

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## ABSTRACT

A series of hyperbranched polyethylene imine (PEI) polymers functionalized with long aliphatic chains has been prepared and characterized. Their self-organization as a function of temperature has been investigated using differential scanning calorimetry, thermogravimetry and X-ray diffraction. Both lamellar (SmA, SmB) and columnar (rectangular) mesophases have been identified. From the detailed study of the parameters of these mesophases it turns up that hydrogen bonding between amide groups and the ordering of the long alkyl chains are the critical factors that determine the organization of the molecules and the formation of the mesophases.

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## 1. Introduction

Liquid crystalline character is one among the most interesting properties of dendritic polymers [1] (i.e. symmetrical dendrimers and non symmetrical hyperbranched polymers). A detailed characterization of multiple mesophase formation deriving from diversified molecular architecture, and investigation of their properties for prospected applications is developing as a consequence of the increasing scientific research for these macromolecules during the previous two decades [2]. In order to achieve liquid crystallinity, a variety of strategies have been employed. The most typical methods for the induction of mesophases are the development of dendritic polymers that self assemble into cylindrical [3] or spherical [4] shapes, suitable "promesogenic" branches [5] and the functionalization of the periphery [6] of these dendrimers or hyperbranched polymers with groups that induce liquid crystalline character such as rigid rod or disk shaped molecules or cholesterol derivatives [7]. The latter strategy is commonly employed to polypropylene imine (DAB) dendrimers and polyethylene imine hyperbranched polymers (PEI) giving rise to a variety of mesophases covering a wide range of liquid crystalline phases. Thus

when the terminal amino groups are substituted with appropriate groups, nematic (N) [8], chiral nematic (N\*) [9], smectic A (SmA) [8a,9,10], smectic C (SmC) [8a,9,10], chiral smectic C (SmC\*) [9], columnar hexagonal (Colh) [8a,10,11], columnar rectangular (Colr) [6k,p,11b] and cubic [11b,12] phases are formed. Apart from these classical strategies where the dendritic polymer is provided with characteristic groups which introduce mesophase formation another approach has been described that does not necessitate the presence of "promesogenic units" [11]. It is related to the intrinsic property of dendritic macromolecules such as hyperbranched poly(ethylene imine) and dendrimeric poly(propylene imine), to form a polar inner part (core) and an outer non polar shell when suitably functionalized with lipophilic aliphatic chains. The polarity of the core can be enhanced by the direct protonation of nitrogen groups [11,12] or by the spontaneous assembly of carboxylic acids bearing long aliphatic chains onto the surface of the amino terminated polymers [13]. The interaction between polar and non polar parts leads to microphase separation which is regarded as the main factor inducing mesomorphic character in simple low molecular weight molecules. In addition inter and intra molecular hydrogen bonds are reported to contribute to the rigidity of the internal core, resulting in improved liquid crystalline properties with wide mesophase temperature range and high clearing temperature [8a].

In this context, we aimed to investigate the synergistic effect of these two factors, hydrogen bonding and microphase separation on mesophase formation. For this reason the thermotropic behaviour of poly(ethylene imine) hyperbranched polymer functionalized

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with long aliphatic chains has been examined. Hyperbranched poly(ethylene imine) in contrast to the symmetric propylene imine dendrimers possesses secondary amino groups which reside not only at the periphery but even near the core of the molecule. These secondary amino groups are also functionalized (alkylated) as the primary amino groups. This introduction of the aliphatic chains via the  $\text{-HN-(CO)-NH-}$  or  $\text{>N-(CO)-NH-}$  groups results in hydrogen bonding formation throughout the interior of the hyperbranched polymer, and due to their non polar character, in segregation of polar and non polar segments (Scheme 1). Due to the above mentioned reasons “amide dendrons” with long aliphatic chains have already been found to exhibit lyotropic liquid crystalline phases [14]. As it has long been established, understanding and control of the organization of such amphiphilic molecules is of crucial importance for the formation of not only liquid crystalline phases but also in most other cases other supramolecular organizes as liposomes cell membranes and organic–inorganic nano-hybrids [15]. The materials obtained were investigated as far as their thermotropic liquid crystalline character is concerned by thermogravimetric analysis (TG), differential scanning calorimetry (DSC), and X-ray diffraction studies (XRD).

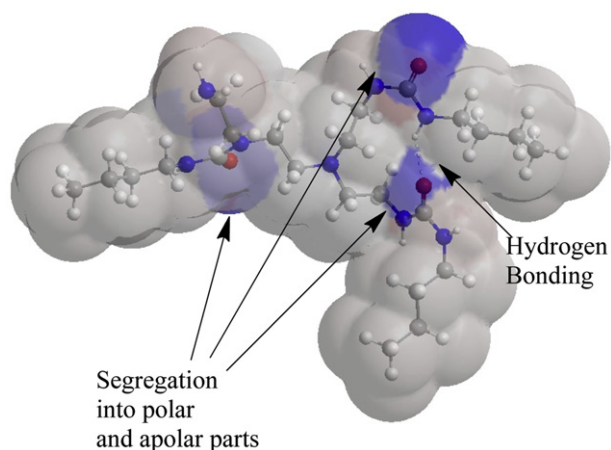
## 2. Experimental

### 2.1. Materials

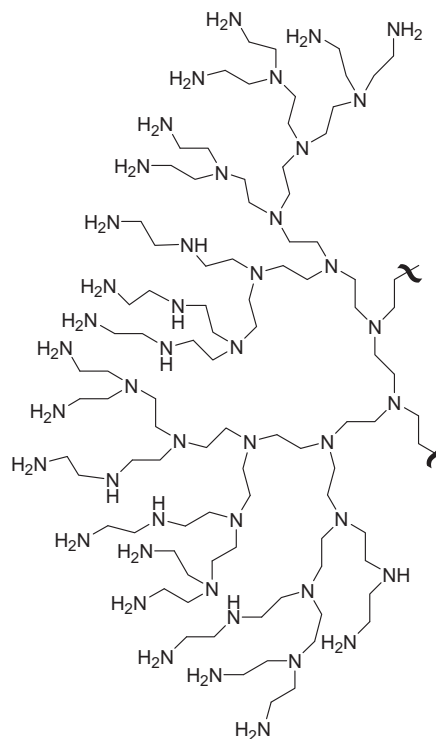
Poly(ethylene imine), PEI, polydispersity 1.3, degree of branching 65–75% ( $M_n = 5000$ ), hyperbranched polymer was obtained from Hyperpolymers INC. Dodecyl, hexadecyl and octadecyl isocyanates, were obtained from Aldrich and used as received. The chemical structure of PEI is shown in Scheme 2.

### 2.2. Synthesis of the alkyl-functionalized poly(ethylene imine) hyperbranched polymers

The amino groups of PEI were interacted with long-chain *n*-alkylisocyanates for the preparation of fully alkylated derivatives (Scheme 3) as previously described [16]. Briefly, to 1 mmol of PEI dissolved in 40 ml of dry dichloromethane, a 10% excess of *n*-alkylisocyanate (with chain length 12, 16 or 18 carbon atoms), dissolved in the same solvent, was added drop-wise, under argon, at 0 °C. The reaction mixture was kept at this temperature for half



**Scheme 1.** Representation of a portion of PEI functionalized with aliphatic chains. Blue surfaces represent negative charges, red surfaces positive charges and grey areas non polar segments. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

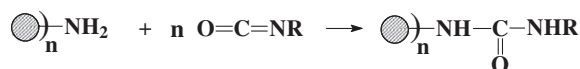


**Scheme 2.** Chemical structure of PEI hyperbranched polymer.

an hour and then allowed to reach room temperature in which it was allowed for several hours. The products obtained were precipitated with 300 ml of acetonitrile, separated from the reaction mixture by centrifugation and dried under vacuum over phosphorus pentoxide affording the alkylated derivatives PEI-*n* (*n* = 12, 16, 18). Their chemical structures were established by  $^1\text{H}$  and  $^{13}\text{C}$  NMR (Figs. S1 and S2 in the Supporting Information section).

### 2.3. Characterization of the alkyl-functionalized poly(ethylene imine) hyperbranched polymers

The chemical structure of the functionalized hyperbranched polymers synthesized was checked by proton ( $^1\text{H}$  NMR) and carbon ( $^{13}\text{C}$  NMR) nuclear magnetic resonance (AC 250 Bruker NMR Spectrometer operating at 215.13 MHz). Fourier transform infrared spectroscopy (FT-IR) was performed on a Nicolet Magna-IR Spectrometer 550. Thermotropic polymorphism was investigated by differential scanning calorimetry employing a DSC-10 calorimeter (TA instruments) at heating and cooling rates of  $10\text{ }^\circ\text{C min}^{-1}$ . The thermal stability of the functionalized hyperbranched compounds was assessed by thermogravimetry employing a TA TGA-2050 instrument. Liquid crystalline phases were investigated by X-ray diffraction using  $\text{CuK}\alpha$  radiation from a Rigaku rotating anode X-ray generator (operating at 50 kV, 100 mA) and an R-Axis IV image plate. Powder samples were sealed in Linderman capillaries and heated employing an INSTEC hot stage.



**Scheme 3.** Reaction employed for the synthesis of the alkylated hyperbranched polymers.

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