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Body-Centered-Cubic Phases Derived from *n*-Dodecylurea Functionalized Poly(propylene imine) Dendrimers

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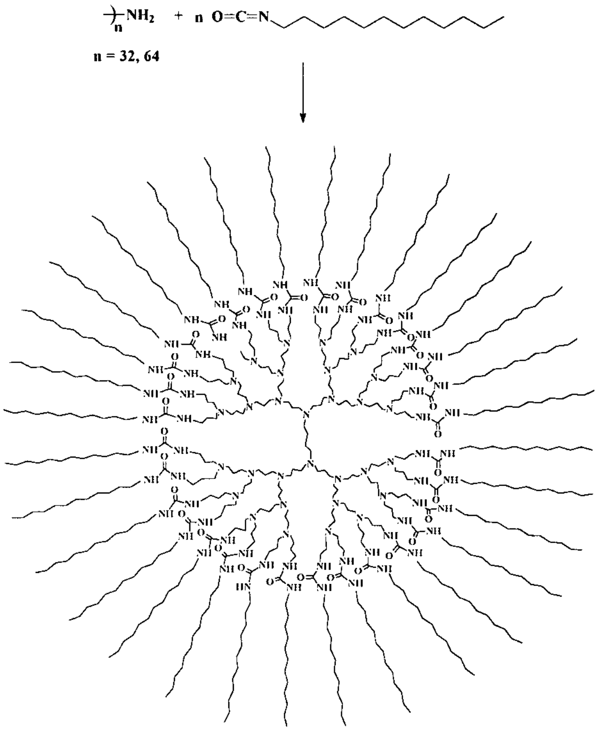
ABSTRACT: The self-organization of *n*-dodecylurea poly(propylene imine) dendrimeric derivatives of the fourth and fifth generation has been investigated using differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. The nonprotonated derivatives melt into isotropic liquids on heating. However, upon protonation of the tertiary amino groups in the interior of the dendritic moieties, a body-centered-cubic phase of *Ia*3*d* space group symmetry is observed. It is proposed that the polar segments have a nearly spherical conformation and are located on the axes of the gyroid surface, while the alkyl chains are in a disordered conformation extending on each side of the minimal surface.

Introduction

The functionalization of dendrimers[1] is nowadays a preferred strategy for obtaining a variety of novel materials serving various scientific and technological applications. In this respect various functional groups have been introduced at the external surface of the molecules, imparting to the parent dendrimers properties associated with the nature of the functional group. Thus, a diversity of materials has been prepared by covalent attachment at the dendrimeric end groups of a variety of functional moieties. The latter include carbohydrate moieties,[2] chiral groups,[3] polymerizable groups,[4] paramagnetic nitroxide moieties,[5] and recognizable groups,[6] groups that give to dendrimers the property to organize at interfaces or to form organized supramolecular structures[7] and also mesogenic moieties leading to the preparation of thermotropic liquid crystals.[8] For the latter materials another strategy has also been followed according to which liquid crystal phases are induced by self-assembling fan-shaped and cone-shaped monodendrons into columnar and cubic liquid crystalline phases.[9]

In this connection and aiming at the formation of novel liquid crystals through a facile functionalization procedure, the alkylation of diaminobutane poly(propylene imine) dendrimers of the fourth and fifth generation was undertaken by reacting all the amino end groups of the parent dendrimers with *n*-dodecyl isocyanate (Scheme 1), affording *n*-dodecylurea functionalized poly(propylene imine) dendrimers. Protonation of their tertiary amino groups affords the protonated derivatives. The structure of the parent dendrimer is modified to such an extent with this two-stage functionalization procedure that segregation of the lipophilic alkyl chains from the hydrophilic core of the dendrimer may occur. As it has long been established, the segregation of the molecular segments in certain compounds is crucial for the formation of thermotropic liquid crystals including other supramolecular organizates as liposomes and cell membranes. The materials obtained were investigated as far as their thermotropic liquid crystalline character is concerned by polarized optical microscopy, differential scanning calorimetry, and X-ray diffraction studies.

Scheme 1



Experimental Section

General Procedure for the Synthesis of *n*-Dodecylurea Functionalized Diaminobutane Poly(propylene imine) Dendrimers (G4, G5). To 0.001 mol of diaminobutane poly(propylene imine) dendrimers (DSM Fine Chemicals) of the fourth (DAB-32) and fifth (DAB-64) generation,[10a] dissolved in dry dichloromethane, 0.035 or 0.070 mol of *n*-dodecyl isocyanate, dissolved in the same solvent, was slowly added at 0° C. The reaction mixture was held at this temperature for half an hour and then allowed to reach room temperature. The products obtained were precipitated with methanol and separated from the reaction mixture by centrifugation, followed by repeated washings with methanol. The materials were exhaustively dried in a vacuum over phosphorus pentoxide,

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and their structure was established by NMR[7a,10] and elemental analysis. ^{1}H NMR (250 Hz, $\mathrm{CDCl_3}$): $\delta = 6.00$ and 6.40 (s, $\mathrm{N}\mathit{H}\mathrm{CON}\mathit{H}$), 3.15 (m, $\mathrm{C}\mathit{H}_2\mathrm{NHCONH\ C}\mathit{H}_2$), 2.34 (m, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2C}\mathit{H}_2\mathrm{N}$, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{N}$, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2CH_2NHCONH}$), 1.55 (m, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2N}$, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2NHCONH}$), 1.44 (m, $\mathrm{NHCONHCH_2C}\mathit{H}_2\mathrm{CH_2}$), 1.23 (m, $\mathrm{NHCONHCH_2CH_2(C}\mathit{H}_2)_9\mathrm{CH_3}$), 0.85 (t, $\mathrm{CH_3}$). ^{13}C NMR (62.9 Hz, $\mathrm{CDCl_3}$): $\delta = 159.7$ ($\mathit{C}\mathrm{O}$), 52.5 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2N}$, $\mathrm{N}\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2N}$), 50.6 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2NHCONH}$), 42.3 ($\mathrm{NHCONH}\mathit{C}\mathrm{H_2CH_2}$), 37.8 ($\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2NHCONH}$), 31.9 ($\mathit{C}\mathrm{H_2CH_2CH_3}$), 30.6 ($\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 29.8−29.4 ($\mathrm{CH_2(}\mathit{C}\mathrm{H_2)_5CH_2}$), 27.9 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2NHCONH}$), 27.2 ($\mathrm{NHCONHCH_2}\mathit{C}\mathrm{H_2CH_2}$), 24.8 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2N}$, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2N}$), 22.7 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_3}$), 14.1 ($\mathrm{CH_3}$). Elemental analysis: G4, $\mathrm{C_{600}H_{1232}N_{94}O_{32}}$: Calcd: C, 70.12; H, 12.08; N, 12.81. Found: C, 70.02; H, 12.38; N, 12.89. G5, $\mathrm{C_{1208}H_{2480}N_{190}O_{64}}$: Calcd: C, 70.11; H, 12.08; N, 12.86. Found: C, 69.97; H, 12.35; N, 12.85.

Protonated Derivatives (G4P, G5P). The alkylated poly(propylene imine) dendrimers were dissolved in chloroform and protonated by adding excess of aqueous HBr under intense agitation. Chloroform solution was freed of HBr excess by repeated extractions with water. Following evaporation of the organic solvent, the materials were dried extensively under vacuum over phosphorus pentoxide. It should be noted that the compounds are hygroscopic and readily absorb water when exposed in the open air. Complete protonation was confirmed by NMR[10c,d] and elemental analysis. COSY and HSQC 2D-NMR experiments at 27 °C were also employed for the complete assignment of the peaks. ^{1}H NMR (500 Hz, DMSO-d_6): $\delta = 6.00$ and 6.40 (s, $\mathrm{N}\mathit{H}\mathrm{CON}\mathit{H}$), 3.15 (m, $\mathrm{NH^+C}\mathit{H}_2\mathrm{CH_2C}\mathit{H}_2\mathrm{NH^+}$, $\mathrm{NH^+C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{NH^+}$, $\mathrm{NH^+C}\mathit{H}_2\mathrm{CH_2CH_2NHCONH}$), 3.00 (m, $\mathrm{CH_2NHCONHC}\mathit{H}_2$), 3.05 (m, $\mathrm{C}\mathit{H}_2\mathrm{NHCONHCH_2}$), 2.15 ($\mathrm{NH^+}$), 1.85 (m, $\mathrm{NH^+CH_2C}\mathit{H}_2\mathrm{CH_2NH^+}$, $\mathrm{NH^+CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2NH^+}$, $\mathrm{NH^+CH_2C}\mathit{H}_2\mathrm{CH_2NHCONH}$), 1.45 (m, $\mathrm{NHCONHCH_2C}\mathit{H}_2\mathrm{CH_2}$), 1.23 (m, $\mathrm{NHCONHCH_2CH_2(C}\mathit{H}_2)_9\mathrm{CH_3}$), 0.85 (t, $\mathrm{CH_3}$). ^{13}C NMR (62.9 Hz, $\mathrm{CDCl_3}$): $\delta = 159.7$ ($\mathit{C}\mathrm{O}$), 50.5 ($\mathrm{NH^+}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2NH^+}$, $\mathrm{NH^+}\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2NH^+}$), 49.5 ($\mathrm{NH^+}\mathit{C}\mathrm{H_2CH_2CH_2NHCONH}$), 42.3 ($\mathrm{NHCONH}\mathit{C}\mathrm{H_2CH_2}$), 37.8 ($\mathrm{NH^+CH_2CH_2}\mathit{C}\mathrm{H_2NHCONH}$), 31.9 ($\mathit{C}\mathrm{H_2CH_2CH_3}$), 30.6 ($\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 29.8−29.4 ($\mathrm{CH_2(}\mathit{C}\mathrm{H_2)_5CH_2}$), 24.4 ($\mathrm{NH^+CH_2}\mathit{C}\mathrm{H_2CH_2NHCONH}$), 27.2 ($\mathrm{NHCONHCH_2}\mathit{C}\mathrm{H_2CH_2}$), 23.7 ($\mathrm{NH^+CH_2}\mathit{C}\mathrm{H_2CH_2NH^+}$, $\mathrm{NH^+CH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2NH^+}$), 22.7 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_3}$), 14.1 ($\mathrm{CH_3}$). Elemental analysis: G4P, $\mathrm{C_{600}H_{1262}N_{94}O_{32}Br_{30}\ 4(H_2O)}$: Calcd: C, 56.37; H, 10.58; N, 10.30; Br 18.75. Found: C, 56.51; H, 10.48; N, 10.22; Br, 18.39. G5P, $\mathrm{C_{1208}H_{2542}N_{190}O_{64}Br_{62}\ 8(H_2O)}$: Calcd: C, 56.12; H, 9.97; N, 10.29; Br, 19.16. Found: C, 56.29; H, 10.31; N, 10.30; Br, 18.35.

Characterization. Liquid crystal textures were observed using a Leitz-Wetzlar polarizing microscope equipped with a Linkam hot stage. Thermotropic polymorphism was investigated by differential scanning calorimetry employing a DSC-10 calorimeter (TA instruments) with heating and cooling rates of 5 °C min^{-1}. The thermal stability of the functionalized dendrimers was assessed by thermogravimetry employing a TA TGA-2050 instrument. Liquid crystalline phases were investigated by X-ray diffraction using Cu Kα_1 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 Lindemann capillaries and heated employing an INSTEC hot stage.

Results and Discussion

The thermal stability of the amphiphilic dendrimers was assessed by dynamic and static thermogravimetry. The alkylated dendrimeric derivatives exhibited on heating under nitrogen satisfactory thermal stability up to 170 °C. Isothermal heating at 130 °C for 1 h resulted in a weight loss of about 0.4%. On the other hand, on heating the protonated dendrimers a rather abrupt weight loss was observed at temperatures below 100 °C due to absorbed water as already suggested by the elemental analyses. On further heating the materials remain stable up to about 160 °C. Isothermal heating for 1 h at 130 °C resulted in a weight loss of about 0.4%. The thermal stability of the compounds was duly taken into account especially during the X-ray experiments.

The nonprotonated derivatives melted at 92 °C into isotropic liquids as established by polarized optical microscopy and X-ray diffraction. The melting temperature, as determined by DSC, is not dependent on the generation being mainly associated with the melting of the aliphatic chains. The enthalpy associated with this transition, ΔH, is almost twice as large for the fifth generation compared to the fourth generation dendrimeric derivative (430 and 840 kJ mol^{-1} for G4 and G5, respectively), apparently due to the 2-fold increase of alkyl chains. The transition is fully reversible since on cooling both derivatives exhibited an exothermic peak at 70 and 67 °C for the G4 and G5, respectively, involving the same transition enthalpies. Accordingly, the second heating and cooling DSC runs are almost identical to the first ones.

The protonated amphiphilic derivatives melted to optically isotropic highly viscous fluids as observed under the polarizing optical microscope; however, upon exercising shear on the samples they become birefringent. The materials remain in this viscous state up to about 200 °C where degradation can be visually detected. The DSC thermograms of the protonated amphiphilic derivatives of the fourth and fifth generation exhibited endotherms at 86 and 80 °C, respectively, in agreement with optical microscopic observations. The transition enthalpy is doubled for the fifth generation derivative compared to the fourth generation, i.e., from 730 to 370 kJ mol^{-1}, respectively, reflecting again the alkyl chain contribution. On cooling from the optically isotropic phase the high generation dendrimer did not show any exothermic transition, whereas the low generation derivative showed only a small exothermic peak (with a transition enthalpy of about 20% of the enthalpy measured on heating), suggesting that the molecules and especially the aliphatic chains recover only partially their original arrangement.

The nature of the phases observed was established by X-ray diffraction experiments. The nonprotonated derivatives at room temperature display a number of rather broad and low-intensity reflections in the small-angle and medium-angle region that cannot be assigned to a known lattice. In the small-angle region the first reflections are located at 38.6 and 40.9 Å for G4 and G5, respectively, while in the wide-angle region a rather sharp peak at 4.20 Å indicates a hexagonal packing of the alkyl chains, usually observed in smectic B type liquid crystals.[11,12] Therefore, the amphiphilic dendrimers are not amorphous solids but have a tendency to organize at room temperature; a crystalline or even an ordered liquid crystalline phase was not however sufficiently developed. At temperatures exceeding their melting transitions, as already mentioned, both compounds melt into isotropic melts. Apparently, the forces leading to the segregation of the lipophilic from the hydrophilic segments are not strong enough to lead to microphase separation.[13,14]

The protonated derivatives on the other hand are significantly more organized. At room temperature the X-ray patterns show a sharp and intense diffraction peak at 45.9 and 46.6 Å for the fourth and fifth generation derivatives, respectively. Additionally, in the same region, another low-intensity reflection is observed, at 1:2 distance ratio, suggesting the existence of a lamellar

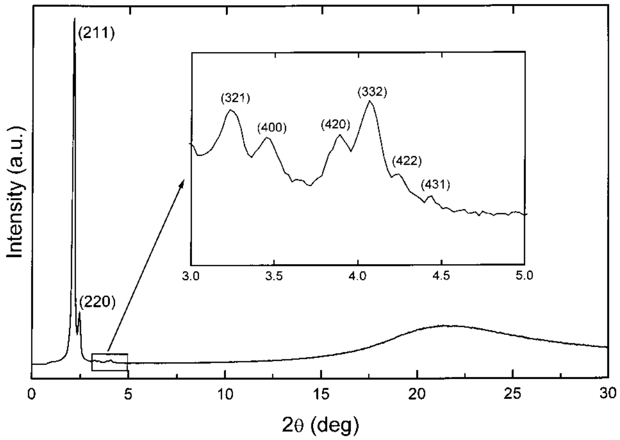

Figure 1. X-ray pattern of the *Ia*3*d* body-centered-cubic phase of G4P at 125 °C. Numerals represent the Miller indices of the observed Bragg reflections.

Table 1. X-ray Diffraction Data for the Protonated Derivatives and Structural Parameters (in Å) of the *Ia*3*d* Cubic Structure at 125 °C[a]

		G4P (α = 100.8)		G5P (α = 101.3)	
hkl	$(h^2 + k^2 + l^2)^{1/2}$	d_{calc}	d_{obs}	d_{calc}	d_{obs}
211	$\sqrt{6}$	41.1	41.1	41.4	41.4
220	$\sqrt{8}$	35.6	35.7	35.8	35.8
321	$\sqrt{14}$	26.9	26.9	27.1	27.1
400	$\sqrt{16}$	25.2	25.2	25.3	25.4
420	$\sqrt{20}$	22.5	22.5	22.7	22.7
332	$\sqrt{22}$	21.5	21.4	21.6	21.7
422	$\sqrt{24}$	20.6	20.6	20.7	20.8
431/510	$\sqrt{26}$	19.8	19.7	19.9	19.7

[a] d_{obs} and d_{calc} are the observed and calculated spacings of the (*hkl*) small-angle reflections, and α is the cubic cell parameter.

phase. In the wide-angle region a number of rather broad reflections were observed, indicating that crystalline chains are not fully crystallized. However, they seem to impose their lamellar arrangement in the polar dendrimeric regions which are therefore located in layers the thickness of which depend very little on the generation as already reported in the literature[7c,8c] for similar systems.

At higher temperatures the constraints imposed by the tendency of the aliphatic chains to assume a lamellar arrangement are released, and the dendrimeric part of the molecules can assume an almost spherical shape,[15] thus favoring their organization in a cubic lattice.[9] Indeed, the X-ray patterns contain (Figure 1) a broad band centered at 4.2 Å attributed to the alkyl chains in a disordered conformation and a number of sharp reflections in the small-angle region which can be indexed as reflections of a cubic structure (Table 1). The presence of the (321) and (420) Bragg reflections,[16,17] the systematic absence of the (110), (200), and (310) reflections, and the intensity distribution of the observed reflections, which is similar to that reported in the literature for a variety of thermotropic low molecular[16−18] and high molecular amphiphilic systems,[12] establish that the lattice is body-centered cubic of the *Ia*3*d* space group. The cubic cell parameters depend slightly on the generation (100.8 and 101.3 Å for G4P and G5P, respectively) and increase with temperature ($\partial a/\partial T \approx +2.5 \times 10^{-2}$ Å/°C). Taking into consideration that the density of G4P is 1.01 g cm^{-1} and that of G5P is 0.97 g cm^{-1},[19] the number of molecules per cubic unit cell can be estimated to be of about 49 for G4P and 24 for G5P. Furthermore, by considering the density of the lipophilic region as being equal to that of the dodecane at the same temperature, i.e., 0.669 g cm^{-1},[20] the volume fraction of the polar part can easily be calculated as being 36% for G4P and 39% for G5P.

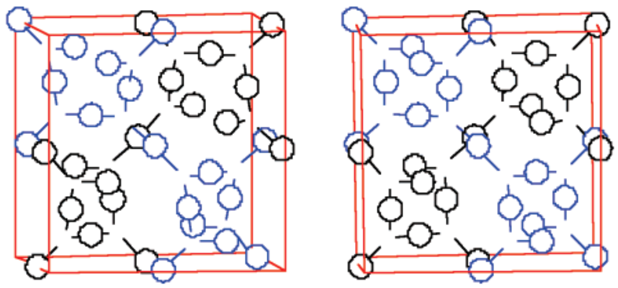

Figure 2. Stereoscopic view of one unit cubic cell containing 24 spheres positioned at the centers of the axes that constitute the skeletal graph of the gyroid. For clarity reasons, each sphere is drawn smaller than its actual size. The two different colors indicate the spheres positioned in the two distinct labyrinthine regions.

In amphiphilic thermotropic liquid crystals two models have been used so far to describe the *Ia*3*d* body-centered-cubic structure. In the first model, the Schoen's gyroid infinite periodic minimal surface[21] is used to describe these cubic phases of thermotropic low molecular weight[22] or polymeric[12] liquid crystals, block copolymers,[23] and lyotropic systems.[24] The gyroid surface divides three-dimensional space into two distinct and equivalent labyrinthine regions. The polar heads of the surfactant molecules can be located either on the gyroid surface with the disordered alkyl chains confined in the core of the labyrinths or in the center of the cores along the labyrinthine "axes", with the melted alkyl chains extending toward the minimal surface.[12,24] The "axes" of these regions constitute what is described as the skeletal graph of the gyroid and are in fact identical[22,25] with the rods used to describe the second, older, model.

In this second model, the structure consists of two interwoven unconnected networks consisting of 24 short columns (rods) crystallographically equivalent and "linked" three by three in a coplanar fashion.[17] The columns are not linked but are, usually, separated by a short gap (devoid of polar matter) at the ternary junctions as shown in Figure 2. The columns are formed by the polar headgroups of the molecules, which are surrounded by the melted alkyl chains. This model has successfully been used to describe a number of thermotropic low molecular weight amphiphilic compounds.[18,22]

For the protonated dendrimers under investigation the polar part constituting the core of the molecule apparently due to structural reasons cannot outline the gyroid surface as it was the case, for instance, with alkylammonium poly(vinylsulfonate)s[12] where the protonated polymeric chains were located on the minimal surface. Although it has been proposed, for similar molecules, that the polar region can take the form of very thin (5−6 Å) layers,[7c,g] in this case however due to the molecular topology the alkyl chains, being attached at the periphery of the polar region, cannot extend to the core of the labyrinth without, at least partially, perturb the continuity of the polar layer. Furthermore, since the volume fraction of the polar part is about 37%, it is more appropriate to be located in the narrow space around the axis of the rods.[12] Moreover, the number of molecules calculated is surprisingly close to the number of columns of the second model (24 for the G5P and close to twice that number, 49, for the G4P). Additionally, the thermal expansion coefficient determined is positive in contrast to previously reported data where, "paradoxically", thermal contraction of the cubic cell with temperature was reported.[12,16,18,26] Since the molar volume can only expand upon heating, it is evident that in those cases the number of molecules per unit cell decreases steadily with temperature. In the case under investigation however this is not observed since the same number of molecules (24 or 48) forms each cell irrespective of temperature. For the above reasons the possibility of the polar heads to form a continuous phase along the labyrinthine axes must be ruled out. In this last case the number of molecules per unit cell would not have to be related to the number of rods and should also change with temperature.

It seems therefore reasonable to assume that this cubic structure is similar to that described by the second model in which however each column is replaced by the polar part of the amphiphilic dendrimers (Figure 2). According to this model, the length of the "columns" is slightly shorter than the distance between the ternary junctions ($\alpha/\sqrt{8}$) due to the presence of the gap, ϵ, at both ends. Assuming that the polar region of the fifth generation dendrimeric amphiphile, due to its chemical structure, has a spherical shape, its diameter can easily be calculated from the known polar volume and found to be 31.5 Å, which is actually the distance between the junctions (35.8 Å) assuming an acceptable[17,18] short gap length, ϵ, of about 2.2 Å. Also, for the fourth generation dendrimer one is led to assume that two dendrimeric polar groups constitute each spherical entity as suggested by the twice as many molecules present in the cell. In this case the diameter is slightly smaller (31.1 Å) than that of the next generation derivative while the gap length is almost the same (~2.2 Å). In this context it must be pointed out that if it is assumed that the polar region has the shape of a rod with a length of $\leq\alpha/\sqrt{8}$, then the resulting diameter of the rod will be almost equal to its length, indicating that the shape of the cylinder is again roughly spherical. Finally, it should be noted that the structure factor and intensities calculated for lyotropic *Ia*3*d* phases with rods having lengths almost equal to their diameters[17] are consistent with the present experimental data.

As already mentioned, the broad band in the wide-angle region of the diffractogram of these compounds is located at 4.2 Å, a value rather unusual for alkyl chains in a disordered conformation which normally show a lateral distance between the aliphatic chains on the order of 4.5−4.6 Å. Such values are usually observed for alkyl chains arranged in a hexagonal fashion.[11,12] By assuming a "hexagonal" packing of the aliphatic chain, the (mean) molecular area of each aliphatic chain can be estimated: $2 \times (4.2)^2/\sqrt{3} = 20.4$ Å^2. Alternatively, this molecular area can be verified from the number of aliphatic chains inside one cubic unit cell (64×24 or 32×48) and the total extension of the gyroid surface[25] ($3.091\alpha^2$). The calculated area, 20.5 Å^2, is in very good agreement with the value obtained above from the X-ray diffraction pattern. The close packing of the aliphatic chains observed in this case is not surprising since the polar spheres are almost in contact in some directions (Figure 2), while the melted lipophilic chains extend to fill up the remaining space toward the direction of the minimal gyroid surface (see also Figure 6 in ref 12).

Concluding Remarks

Protonated *n*-dodecylurea functionalized poly(propylene imine) dendrimers exhibit thermotropic cubic phases of *Ia*3*d* space group symmetry. This is attributed to the enhancement of the amphiphilic character and the subsequent "nanophase" segregation of the two incompatible parts. The proposed structure consists of 24 nearly spherical, multicationic dendrimeric entities located in the axes constituting the skeletal graph of the gyroid, while the aliphatic chains are located on each side of the minimal surface. This model satisfactorily explains the fact that although two consecutive generations are employed, the cubic cell dimensions remain almost the same and that the unit cell increases with temperature, which, to our knowledge, has not been reported so far.

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