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Liquid-Crystalline Polymers from Cationic Dendronized Polymer−Anionic Lipid Complexes

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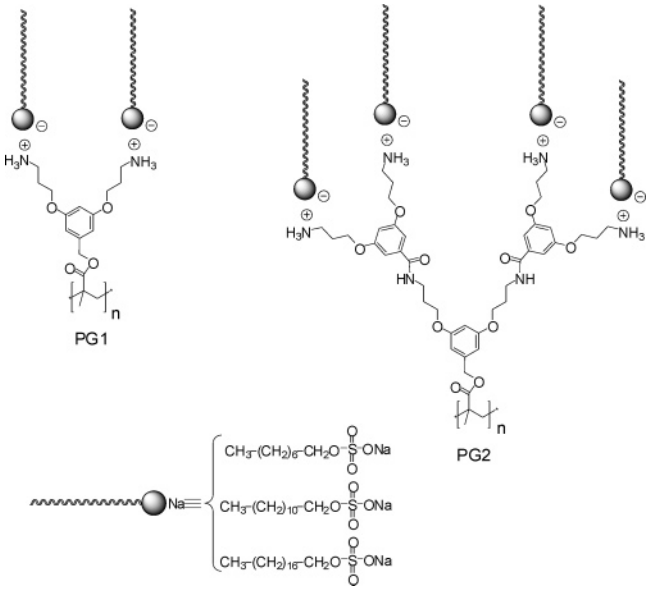
During the past decade, ionic complexation of polyelectrolytes and oppositely charged low molecular mesogenic units has been gaining increasing attention as a viable route to design liquid-crystalline (LC) polymers with long-range order.[1,2] The main advantage of this strategy over other self-assembly methods is the simplicity with which complex architectures can be accessed by putting together simple constituents from a "toolbox". At the same time, the liquid-crystalline phases obtained for the ionic supramolecular complexes are comparable to those obtained in systems where mesogenic units are covalently attached to macromolecules.[3−5]

Various molecular architectures have been investigated for cationic and anionic polymers, including linear,[6] dendritic,[7] and hyperbranched polyelectrolytes.[8] Hydrocarbon-based cationic and anionic surfactants, which have been the most widely investigated class of mesogenic units, have also been shown to directly control the period and the structure of the complex mesophases.[9]

Here we report for the first time the use of cationic dendronized polymers[10] and anionic lipids as a model system in which the molecular architecture can be rationally controlled by two factors, the generation of the dendrons attached to the polymer backbone and the length of the lipid tail. Scheme 1 shows the molecular structures of the first (**PG1**) and second (**PG2**) generation dendronized polymers used in this study. They have two and four ammonium triflate end groups, respectively. The syntheses (see Supporting Information) follow closely the lines given for a similar **PG2** polymer.[11] The polymers were isolated on the multigram scale in their *tert*-butyloxycarbonyl (Boc)-protected form. The molar masses were determined by gel permeation chromatography (in DMF, 1% LiCl, 80 °C, referenced to PMMA standards using two-angle light scattering, refractive index, and viscometry detectors): **PG1** ($M_w = 1.5 \times 10^6$), **PG2** = ($M_w = 2.5 \times 10^6$).[12] The deprotection was achieved quantitatively by treatment with neat trifluoroacetic acid.

Complexation with the lipids was carried out by mixing polymers and lipids at a stoichiometric ratio in water at pH = 3, so that the dendrons' primary amines and the lipids' sulfonic groups are positively and negatively charged, respectively. Upon complexation, the comb-like supramolecule precipitates in water. After its re-precipitation into water from an ethanol/butanol mixture as solvent, drying, and annealing at 50 °C under ultrahigh vacuum (10^{-8} mBar), the complete complexation of NH_3^+/SO_4^- in the solid polymer/lipid complex was demonstrated by the appearance of the FTIR band at 1074 cm^{-1} corresponding to the bound sulfonic groups. All the comb-like complexes obtained as described above showed liquid-crystalline behavior as indicated by birefringency in cross-polarized optical microscopy.

Scheme 1. Complexes of Dendronized Polymers and Surfactants Used



Small-angle X-ray scattering allowed us to determine the specific group space of the LC complexes as a function of the lipid tail length and dendron generation. The effect of the alkyl chains can be understood by comparing, in Figure 1, SAXS diffractograms of the same **PG1** complexed with C8, C12, and C18 sulfonated lipids (lowest three curves). The C8 lipid is too short to induce segregation of the backbone and alkyl chain, and the corresponding spectrum shows a single broad peak indicative of an amorphous structure. By increasing the alkyl chain length, however, segregation of the polymer backbone and lipid chains takes place. This is reflected in the SAXS spectrum of the **PG1**−C12 complex, where a first sharp peak centered at $q_1 = 1.9$ nm^{-1} appears together with a second reflection at $q_2 = 3.8$ nm^{-1}. The spacing ratio of 2 for q_2/q_1indicates a lamellar structure with periodicity $d = 2\pi/q_1 = 3.3$ nm. By further increasing the length of the alkyl chain to C18, increased segregation drives the system into a lamellar phase with very long range order, as revealed by the respective SAXS diffractogram showing as much as four consecutive reflections, q_1:q_2:q_3:q_4 spaced as 1:2:3:4. The first peak, centered at $q_1 = 1.52$ nm^{-1}, reveals a period of 4.13 nm for the C18-dendronized polymer complex lamellar phase, which is 0.8 nm larger compared to the lamellar phase obtained for the C12-dendronized polymer complex, consistent with the larger size of the alkyl chain.

The lamellar phases are made up of two segregated domains: the dendronized polymer and the lipid tails. Yet, the alkyl chains can form both a bilayer of facing lipid chains or a monolayer of intercalated lipid chains. Because the three lowest diffractograms

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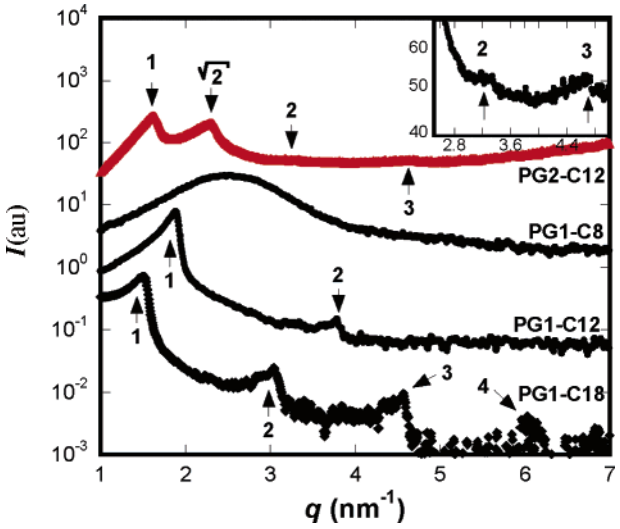

Figure 1. SAXS diffractograms for **PG1** (three lowest curves) and **PG2** (upper and inset curves) dendronized polymers complexed with C8, C12, and C18. Multiple reflections are indexed by arrows. The **PG2**−C12 spectrum (zoomed in the inset in the 2.5−5 nm^{-1} region) is given in $I \times q^2$.

in Figure 1 refer to complexes with the same **PG1** polymer but different alkyl tails, the difference in period of the lamellar phase can only arise from the difference in lengths of sulfonated C12 and C18 lipids. By considering fully stretched lipid chains, the difference in length between C18 and C12 chains is 0.65 nm. Because a bilayer model for lipids would then lead to an increase of 1.3 nm when going from C12 to C18, calculations are consistent with an intercalated alkyl tails model or a bilayer of tilted alkyl tails. Moreover, a fully stretched intercalated lipid chain model combined with SAXS period also yields the thickness of the dendron phase, calculated at 1.63 nm for **PG1**, indicating high space filling efficiency of dendronized polymers.[13]

Figure 1 also highlights the effect of generation of dendronized polymer when the surfactant is kept at fixed length, if one considers the **PG1**−C12 and **PG2**−C12 SAXS spectra. As discussed previously, when C12 is complexed to a **PG1**-dendronized polymer, the liquid-crystalline phase is lamellar with 3.3 nm period. When a **PG2** polymer is complexed with the same C12 alkyl chain, however, the diffractogram changes into four q_1:q_2:q_3:q_4 reflections spaced as 1:$\sqrt{2}$:2:3 (top curve and inset), which is the signature of a rarely observed and well-organized columnar tetragonal phase, with period 3.93 nm. The larger period of the tetragonal phase, whose existence has been reported in the literature for phthalocyanine derivatives[14−16] and dendrimer−lipid complexes,[9] is consistent with the increase of generation of the dendronized polymer. The change in structure is, however, more interesting. Presumably, in **PG1** polymers, the dendrons are still small enough to accept alkyl chains in a lamellar arrangement, similarly as linear polymer−lipid complexes.[1] With increasing generation, however, steric hindrance between dendrons starts to play an important role, further enhanced by the volume occupancy of alkyl chains. Thus, to optimize space-filling requirements and reduce lipid crowding, the dendron−lipid bulky moieties will have to twist each other with respect to the polymer backbone, leading to a columnar rather than a lamellar phase, thus undergoing a transition similar to that reported in dendrimer-based LC.[17]

On the basis of SAXS data and molecular calculations on the size of alkyl tails, we propose the molecular organization model sketched in Figure 2 for the LC polymers based on **PG1** and **PG2** complexed with sulfonated C8, C12, C18 lipids.

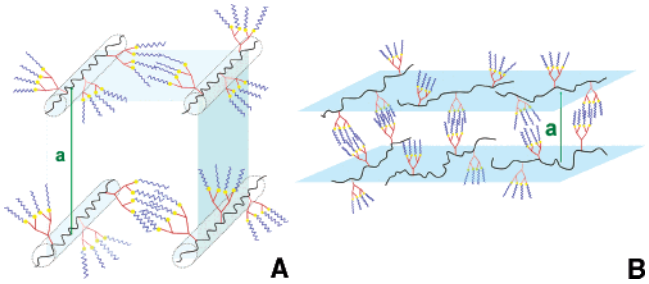

Figure 2. Schematic representation of (A) tetragonal columnar phase and (B) lamellar phase obtained for **PG2**−C12 and **PG1**−C12 dendronized polymer−surfactant complexes, respectively (see Supporting Information).

The present results demonstrate that self-assembly of dendronized polymers decorated by alkyl chains ionically attached onto the dendrons' "surfaces" is a viable route to design liquid-crystalline mesophases where both structure and period can be rationally tuned by either the dendron generation (and thus the cross-section of the polymers) or by the length of the alkyl chains. Owing to the reversible nature of the ionic complexation, this process proves high relevance for nanoporous channels, biomimetic, transport, and nanotemplating applications.

Note Added after ASAP Publication. After this paper was published ASAP on October 6, 2006, production errors in Scheme 1 were corrected on the same day.

Supporting Information Available: Synthesis and molecular packing data. This material is available free of charge via the Internet at http://pubs.acs.org.

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