Swelling of a cluster phase in Langmuir monolayers containing semi-fluorinated phosphonic acids

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Langmuir monolayers of semi-fluorinated nonadecylphosphonic acid (F8H11PO4), hexadecylphosphonic acid (H16PO4), and their mixtures were investigated by Brewster angle microscopy (BAM), atomic force microscopy (AFM) and surface-pressure measurements. Nanometre-scale two-dimensional clusters were observed by AFM in a spread monolayer of pure F8H11PO4 transferred to mica. Two different organized arrangements of clusters were observed. AFM and BAM observations showed that the mixture exhibits a solid phase over a large range of mole fraction and surface pressure, sometimes in coexistence with clusters. With increasing mole fraction of H16PO4, the lateral shape of these clusters remains the same while their organization and their height change.

Introduction

Perfluorinated alkanes are both hydrophobic and lipophobic. At the most fundamental level, this bifunctional behavior arises from molecular interactions, both long- and short-ranged, that stem from the high electronegativity, low polarizability, and large atomic radius of fluorine relative to hydrogen. Semi-fluorinated alkanes, or amphiphilic derivatives, are comprised of two chemically and structurally distinct blocks covalently bound to form a single molecule. This arrangement leads to unique self-assembly behavior that might be useful in cosmetics and in pharmaceutical applications such as pulmonary drug delivery.

Monolayer domains with finite lateral size generally originate from the competition between or incompatibility of molecular interactions. For example, the competition between line tension at domain boundaries and electrostatic dipole–dipole repulsion results in stable macroscopic domains in two-phase lipid monolayers. In practice, these domains have characteristic length scales \( \geq 1 \) \( \mu \)m; however, in principle they could be nanoscale for vanishingly small values of line tension.

The formation of nanoscale molecular clusters in thin films often arises from frustrated molecular packing and/or chemical dissimilarity. The research groups of Manne and Ducker have published extensive studies of surface micelles formed by wedge-shaped (i.e., micelle-forming) surfactants at the interface of aqueous solution and a solid surface. These clusters display a radius of curvature related to the molecular length, as observed with three-dimensional micelles. We have observed analogous behavior in reverse-micelle-forming surfactants at the interface between a solid and a solution with a non-polar solvent. In these cases, the tendency of the surfactant molecules to form curved aggregates was frustrated by the presence of a planar substrate, leading to periodic arrays of clusters (spherical or cylindrical surface micelles).

The chemical dissimilarity between hydrocarbons and fluorocarbons is known to induce phase separation in many situations. For example, binary mixtures of hydrocarbon and perfluorinated surfactants exhibit highly nonideal behavior (e.g., phase separation) at the air–water interface or in LB films. Such mixtures have also been reported to form two types of micelles simultaneously in solution – one rich in fluorocarbon and the other rich in hydrocarbon. The miscibility of fluorocarbon and hydrocarbon amphiphiles is highly sensitive to their chemical structure. The stronger the headgroup–headgroup interactions, the better mutual miscibility of the amphiphiles is observed. Lehmler et al. have reported some miscibility for mixtures of partially fluorinated carboxylic acids with dipalmitoylphosphatidylcholine (DPPC) at the air–water interface. Similar behavior has been observed for a mixture of partially fluorinated carboxylic acids and their respective hydrocarbon analogues.

When grafted together in the same molecule, the chemical dissimilarity between fluorocarbon and hydrocarbon can lead to unusual molecular and supermolecular structures. For monolayers of semi-fluorinated carboxylic acids in the temperature range of 4–30 \( ^\circ \)C, it has been shown that perfluorinated segments pack in a simple hexagonal array with their long axes nearly perpendicular to the surface, with a helical twist structure superimposed on the all-trans zigzag conformation of the hydrocarbon chain. Krafft and co-workers have observed that semi-fluorinated alkanes transferred onto silicon wafers form monodisperse surface micelles. They found that the hydrocarbon blocks were in contact with the silicon and the fluorinated blocks were pointing outward. In contrast with the observations of detergent surface micelles, the clusters of semi-fluorinated compounds displayed no organization or periodic behavior.

We believe that mixtures of semi-fluorinated amphiphiles with hydrocarbon (or perfluorinated) amphiphiles might be
interesting because the latter component has the potential to “swell” the clusters formed by the semi-fluorinated component. This hypothesis motivated us to investigate whether the addition of a hydrocarbon component would influence the size, shape, and organization of these two-dimensional clusters. In the work reported here, Langmuir films of H16PO3 and F8H11PO3 and their mixture on a water subphase were investigated by BAM, while LB films on mica substrates were studied with AFM. Highly-organized two-dimensional clusters were observed for pure F8H11PO3 transferred to mica. We discuss the influence of the addition of a hydrocarbon component (H16PO3) on the size, height, and organization of these clusters.

Experimental

Materials

The strategy used to prepare 12,12,13,14,14,15,15,16,16,17,18,19,19-heptadecafluorononadecanol, (CF3(CF2)7(CH2)11OH; F8H11OH). This intermediate was synthesized via the radical addition of 1-bromoperfluorooctane to 10-undecen-1-ol. A 100 mL Schlenk flask equipped with a magnetic stirrer bar was charged with 2.00 g (11.7 mmol) of the alcohol, 200 mg of AIBN, and 6.40 g (12.0 mmol) of iodoperfluorooctane. The flask was sealed and submerged in liquid nitrogen to freeze the contents for degassing. After 10 minutes of submergence in the liquid nitrogen, the flask was evacuated and purged with argon 3 times. The flask was again sealed, evacuated, and heated at 100 °C for 3 more hours with stirring. The reaction was cooled to room temperature, and an additional 200 mg of AIBN was added to the flask, which was again sealed, evacuated, and heated at 100 °C for 12 hours with stirring. The flask was then cooled to room temperature and an additional 200 mg of AIBN was charged with 2.07 g (3.51 mmol) of F8H11OH and 3 molar equivalents of triethylamine (1.50 mL). The flask was purged with argon for 5 minutes, and then methanesulfonyl chloride (0.54 mL; 7.0 mmol) was slowly added via syringe. The reaction mixture was allowed to stir at room temperature for 12 hours with the septum vented with a needle. Deionized water (100 mL) was added and allowed to hydrolyze the reaction for 30 minutes. The organic phase was then separated and washed with water (2 × 100 mL) and with brine (1 × 100 mL). The organic phase was dried over magnesium sulfate, filtered, rotary evaporated, and dried further on a Schlenk line to give 2.23 g of F8H11OMs (3.34 mmol, 95% yield).1H NMR (300 MHz, CDCl3): δ = 3.64 (t, J = 6.6 Hz, 2H), 1.95–2.13 (m, 2H), 1.47–1.61 (m, 5H), 1.22–1.42 (m, 16H).

12,12,13,14,14,15,15,16,16,17,18,18,19,19,19-Heptadecafluorononadecyl-1-mesylate, (CF3(CF2)7(CH2)11OMs; F8H11OMs). A 250 mL round-bottomed flask containing 100 mL of reagent grade hexane and a magnetic stirrer bar was charged with 2.07 g (3.51 mmol) of F8H11OMs and 3 molar equivalents of triethylamine (1.50 mL). The flask was purged with argon for 5 minutes, and then methanesulfonyl chloride (0.54 mL; 7.0 mmol) was slowly added via syringe. The reaction mixture was allowed to stir at room temperature for 12 hours with the septum vented with a needle. Deionized water (100 mL) was added and allowed to hydrolyze the reaction for 30 minutes. The organic phase was then separated and washed with water (2 × 100 mL) and with brine (1 × 100 mL). The organic phase was dried over magnesium sulfate, filtered, rotary evaporated, and dried further on a Schlenk line to give 2.23 g of F8H11OMs (3.34 mmol, 95% yield).1H NMR (300 MHz, CDCl3): δ = 4.22 (t, J = 6.6 Hz, 2H), 3.00 (s, 3H), 1.70–1.77 (m, 2H), 1.51–1.62 (m, 2H), 1.22–1.42 (m, 14H).

12,12,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Heptadecafluorononadecyl bromide, (CF3(CF2)7(CH2)11Br; F8H11Br). A 200 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with 2.23 g (3.34 mmol) of F8H11OMs and 3 molar equivalents of lithium bromide (0.87 g). Reagent grade acetone (100 mL) was added, and the reaction mixture was refluxed for 12 hours. The reaction was cooled to rt, and the acetone removed by rotary evaporation. The crude product was washed with 50 mL of deionized water then extracted into reagent grade diethyl ether (3 × 20 mL). The organic phase was dried over magnesium sulfate, filtered, rotary evaporated, and further dried on a Schlenk line to give 2.12 g of F8H11Br (3.25 mmol, 97% yield).1H NMR (300 MHz, CDCl3): δ = 3.41 (t, J = 7.1 Hz, 2H), 1.95–2.13 (m, 2H), 1.81–1.90 (quint, J = 7.2 Hz, 2H), 1.51–1.62 (m, 2H), 1.21–1.44 (m, 14H).

### Scheme 1

Synthesis of terminally perfluorinated phosphonic acid, F8H11PO3.
synergistic action, and the reaction mixture was heated at 200 °C for 1 hour, cooled to room temperature, and stirred for an additional 12 hours. The reaction was quenched with the addition of 30 mL of deionized water, and then allowed to stir for another 24 hours. The resulting mixture was extracted with carbon tetrachloride (2 × 50 mL). The organic phase was washed with deionized water (2 × 50 mL) and brine (1 × 50 mL), dried over magnesium sulfate, filtered, rotary evaporated, and dried on a Schlenk line to give 1.39 g of F8H11PO3Et2 (1.96 mmol, 60% yield). 1H NMR (300 MHz, CDCl3): δ = 4.02–4.15 (m, 4H), 1.95–2.13 (m, 2H), 1.54–1.79 (m, 4H), 1.34 (t, J = 6.9 Hz, 6H), 1.22–1.43 (m, 16H).

12,12,13,13,14,14,15,16,17,17,18,18,19,19-Heptadecafluoronadecyl phosphonic acid, (CF3(CF2)–(CH2)11PO(OH)2; F8H11PO3). A 200 mL Schlenk flask containing 1.39 g (1.96 mmol) of F8H11PO3Et2 was purged with argon for 10 minutes. Dry dichloromethane (50 mL) was then added via cannula, and trimethylsilyl bromide (TMSBr, 1.50 mL, 11.8 mmol) was added via syringe. The reaction mixture was stirred at room temperature for 12 hours. The solvent was then removed under vacuum on a Schlenk line, and 50 mL of deionized water was added. The mixture was allowed to stir at room temperature for another 12 hours. A large volume of ethyl acetate was required to extract the acid (3 × 500 mL). The organic phases were collected and dried over magnesium sulfate, filtered, rotary evaporated, and dried on a Schlenk line. The crude product was dissolved in a minimum amount of hot ethyl acetate, filtered hot, and then allowed to cool, giving 0.64 g (0.98 mmol, 50% yield) of recrystallized F8H11PO3. 1H NMR (300 MHz, TDF): δ = 2.10–2.23 (m, 2H), 1.51–1.61 (m, 6H), 1.30–1.50 (m, 14H), 1.34 (t, J = 6.9 Hz, 6H), 1.22–1.43 (m, 16H).

n-Hexadecyl phosphonic acid C16H33PO(OH)2 (denoted as H16PO3) was purchased from PolyCarbon Industries Inc. and used as received. Ultrapure water from a Millipore Milli-QUV system (resistivity 18.2 MΩ cm) and used as received. All measurements were made at room temperature (23 ± 1 °C).

Results

Phases and phase diagrams

Two distinct arrangements of clusters, denoted C1 and C2, were observed, as was a laterally-homogeneous phase that we denote the S1 phase. The structural details of these phases will be presented below. BAM and AFM images were used to determine the conditions under which the phases exist and coexist. Fig. 1 summarizes this information in the form of a monolayer phase diagram of H16PO3 and F8H11PO3. The collapse pressures (represented by squares in the phase diagram) were deduced from the surface-pressure measurements. For X_F8H11PO3 ≥ 0.8, two-dimensional clusters (C1 + C2) were observed at all surface pressures up to collapse. In the opposite limit, for X_H16PO3 ≲ 0.07, the mixed monolayer consisted of H16PO3-rich bright domains denoted S1 (solid phase) within a F8H11PO3-rich dark surrounding phase. At high surface pressures, the S1 domains came into close contact and sintered, but did not coalesce, consistent with the designation of this phase as solid. For intermediate mole...
fractions, $0.07 \leq X_{\text{F8H11PO3}} \leq 0.8$, the monolayer showed the coexistence of clusters (C1 + C2) and solid phase domains (S1).

**Surface-pressure isotherms**

Fig. 2 shows isotherms of the surface pressure ($\Pi$) as a function of the molecular area ($A$) obtained for the pure components H16PO3 and F8H11PO3 and their mixtures. For pure H16PO3, $\Pi$ was negligible during compression until $A = 0.22$ nm$^2$. We will show below that this behavior corresponds to the coexistence of the S1 phase and a 2D vapor. At areas below $A = 0.22$ nm$^2$ per molecule, $\Pi$ increased steeply and monotonically until the monolayer collapsed at $\Pi = 57$ mN m$^{-1}$. The isotherm of pure F8H11PO3 began to rise at $\sim 0.28$ nm$^2$ and initially increased more gradually than the hydrocarbon monolayer. There were two noticeable kinks at $\Pi = 9$ mN m$^{-1}$ and $\Pi = 15$ mN m$^{-1}$. Presumably, these kinks represent some sort of phase transition; however, we did not observe any characteristic difference in the structure of the monolayer, with BAM or AFM, associated with the isotherm kinks. It is likely that the isotherm features indicate transitions associated with the details of molecular packing that do not result in changes to the mesoscale structure. Isotherms for mixed monolayers displayed intermediate behavior between the two pure components; in particular, the area at which $\Pi$ began to rise decreased with increasing mole fraction of H16PO3. Further, these isotherms of mixtures also displayed the same distinctive kinks as that of the fluorinated component.

**BAM images**

Representative BAM images of pure and mixed monolayers are shown in Fig. 3. Pure H16PO3 monolayers (Fig. 3a) displayed small, bright domains at low surface pressure ($\Pi = 0.01$ mN m$^{-1}$). We interpret these images to represent the coexistence of the S1 phase (bright domains) with a 2D vapor phase (dark surroundings). As the monolayer was compressed, the bright domains grew dramatically at the expense of the surrounding dark phase. Fig. 3b shows a representative BAM image at $\Pi = 0.14$ mN m$^{-1}$. Eventually, the dark phase disappeared completely ($\Pi \sim 0.3$ mN m$^{-1}$), and the BAM images appeared uniformly bright until the collapse pressure was reached.

Monolayers of pure F8H11PO3 showed little contrast in their BAM images (Fig. 3c), regardless of surface pressure, due to the fact that the refractive index of fluorocarbons is close to that of water. In fact, for $X_{\text{F8H11PO3}} \geq 0.8$, the BAM images were uniform and fairly dark; no bright domains were observed, suggesting that the monolayer was laterally-homogeneous on μm length scales. We will show below, however, that this phase has a distinctive nanostructure discernable with AFM.

For mixed monolayers in the large coexistence region of the phase diagram, the BAM images showed the presence of large, bright domains at all surface pressures up to collapse (Fig. 3d). As the mole fraction of F8H11PO3 was increased in the mixed monolayer, the amount of the bright solid phase decreased significantly, consistent with the phase diagram shown in Fig. 1. A careful analysis of these bright regions suggests that they are composed of small, circular islands that are more easily resolved in the AFM images below.

**AFM images**

Fig. 4 shows a representative AFM image of a pure H16PO3 monolayer transferred at 4 mN m$^{-1}$. The surface contained large, flat regions with lines of hole defects. The morphology of the image suggests that domains of the S1 phase failed to coalesce completely as they came together during compression. Analysis of the cross-section showed an average vertical distance of $\sim 1.47 \pm 0.1$ nm from the monolayer surface to the bottom of the holes, and phase-contrast images (from tapping mode AFM) indicated that the surface at the bottom of the holes had a mechanical response consistent with bare substrate.20 Thus, the film thickness is smaller than the extended molecular length of H16PO3 ($\sim 2$ nm) indicating a tilted molecular orientation of H16PO3 in the monolayer at this relatively low surface pressure. This hypothetical molecular tilt is also consistent with the relatively high compressibility of the monolayer and the fact that the molecular area at which the monolayer was deposited ($\sim 0.21$ nm$^2$) was significantly larger than the close-packed area of alkyl chains.
However, the evidence for molecular tilt in the S1 phase is not completely unambiguous. For example, in many tilted monolayer phases, distinctive textures (e.g. stars, boojums) can be observed within domains using BAM. No such textures are observed in S1-phase domains. Additionally, one might expect to see a kink in the isotherm associated with the untilted–tilted transition.

Transferred films of the pure semi-fluorinated monolayers, F8H11PO3, at 4 mN m⁻¹, showed the coexistence of two distinctive nanostructures (Fig. 5). In both structures, small features representing molecular clusters were observed, with characteristic dimensions of ~30 nm; however, the shape and arrangement of the clusters was distinctly different in the two cases. Most regions of the film surface were represented by the structure we denote as the C1 phase. C1 clusters are elongated and arranged in regular rows (stripes). The major axis of each cluster is tilted with respect to the row normal. In the minority C2 phase, the clusters are approximately round, and either randomly-ordered or in a local hexagonal arrangement. In both phases, the clusters are extremely monodisperse. We were not able to discern any systematic trend in the appearance of the C2 phase, as a function either of composition or surface pressure. Since, however, this structure was relatively uncommon under all conditions, we focus the remaining discussion on the more prevalent C1 phase.

Representative AFM images corresponding to various regions of an equimolar-mixed monolayer of H16PO3 and F8H11PO3 are shown in Fig. 6. The images in these different regions are consistent with the coexistence of the phases described above. Fig. 6a shows a region consisting of clusters, C1 in this case. Fig. 6b shows a different region of the film that...
displays large circular islands of varying size, suggesting a similarity with the S1-phase domains described above. On rare occasions, a region of the surface was encountered (Fig. 6c) that appears to show explicitly the coexistence of a laterally-homogeneous S1 phase and clusters. In this particular image, the S1 regions are relatively small with distinctive faceted shapes.

As described above, one of the major objectives of this research was to understand how the incorporation of a hydrocarbon component might alter the structure of molecular clusters composed of a semi-fluorinated component. The region of the phase diagram for $X_{\text{F8H11PO3}} \geq 0.8$ is particularly interesting in this regard, because only the cluster phase is present, but the average composition varies significantly. The most noticeable effect of composition on the cluster phase involved the apparent height of clusters. For example, at $X_{\text{F8H11PO3}} = 0.85$, the height of the clusters was $\sim 0.7$ nm. As the mole fraction of F8H11PO3 was decreased to 0.79, however, the cluster height systematically increased to $\sim 1.5$ nm. We note that this dimension is the same as the thickness of the S1-phase domains, suggesting that the hydrocarbon component might control the cluster height. Further addition of H16PO3 failed to increase the height of the clusters beyond this value. If we accept the premise of mixed clusters containing both H16PO3 and F8H11PO3, this result suggests that incorporation of H16PO3 into the clusters swelled them in the vertical direction. Presumably, the clusters could accommodate only a certain amount of hydrocarbon, and at mole fractions above $X_{\text{H16PO3}} = 0.2$, the height of the clusters saturated at a constant value. We presume that additional H16PO3 was partitioned into a coexisting phase.

With increasing mole fraction of H16PO3, we also observed an increase in the degree of organization of the clusters. For $X_{\text{F8H11PO3}} > 0.80$, rows or stripes of clusters were clearly visible in AFM images, and a 2D Fourier transform showed distinct spots that are characteristic of these rows (see Fig. 7a). This organization has a liquid-crystalline appearance reminiscent of a smectic phase in 2D. However, for $X_{\text{F8H11PO3}} < 0.80$, the organization of the clusters in the C1 phase improved significantly to the point where crystalline order was readily apparent. Fig. 7b shows a Fourier transform of an AFM image from this regime. Sharp spots in a rectangular arrangement are clearly visible and have been assigned to reciprocal lattice vectors $a_1$ and $a_2$. This reciprocal lattice and the real-space images themselves are consistent with the arrangement of clusters shown in Fig. 7c. In this structure, the oblong clusters are arranged in rows that are separated by 50.5 ± 0.5 nm.

Within a row, the clusters are separated by $41.5 \pm 1.5$ nm. The major axis of each cluster is tilted with respect to the row normal; the tilt angle varied from domain to domain within the range 34–64°.

**Discussion**

Supermolecular organization into discrete assemblies is a general phenomenon associated with bifunctional molecules that consist of dissimilar blocks. Micelles (spherical or cylindrical) of small molecule surfactants and diblock copolymers are classic examples. These are equilibrium structures associated with equilibrium conditions, and the characteristic dimension of the assembly is monodisperse and generally associated with a molecular dimension. Thus, as the concentration of the assemblies is increased, there is a tendency for them to pack regularly – long-range order often results, as in lyotropic liquid crystals. The characteristic dimension can often be modified by the addition of a third component that “swells” the surfactant assemblies. Some of these principles have also been demonstrated at interfaces. For example, regular arrays of micelles or reverse micelles form readily at the interface between surfactant solution and a solid surface of the appropriate polarity. The interfacial analog of the “swelling” behavior has not been observed previously.

While the clusters observed in the current work have many characteristics that are similar to the micelles and surface micelles described above, there are also some discrepancies. The lateral dimension of the clusters observed here are significantly larger than any molecular dimension, and they have no discernable curvature, although a subtle molecular splay cannot be ruled out. In these regards, they are reminiscent of equilibrium domains that form in phase-separated monolayers composed of cholesterol and the lipid DPPC. These domains are flat in shape, and the lateral size is much larger than molecular dimensions. The domain shapes and sizes in these lipid mixtures have been interpreted in terms of a competition between line tension at the domain boundaries and dipole–dipole electrostatic repulsion between molecules within and between domains. Similar arguments have been used to explain domains in perfluorinated monolayers. In principle, extremely low values of line tension could lead to nanoscale domains. However, experimentally-observed lipid domains are $\geq 1$ μm in size, even in the vicinity of the critical point, where the line tension should vanish.

The purely two-dimensional analogue of the aforementioned micellar structures requires a trifunctional molecule in general. For example, a hydrophobic moiety may be used to anchor a molecule at the air–water interface, and two dissimilar hydrophobic blocks (e.g., fluorocarbon and hydrocarbon) may be attached to this headgroup. There are also examples of situations in which a hydrophilic headgroup is not actually required for stable monolayer formation, as in the case of perfluorinated (or partially-perfluorinated) alkanes. Clusters are often observed in this class of monolayer. Kato et al. observed nanoscale molecular clusters in monolayers of a series of semi-fluorinated long-chain acids. Although the clusters had a characteristic range of sizes, they were not truly monodisperse. Perhaps due to this lack of monodispersity, the
clusters displayed no long-range order. The authors speculated that the clusters were not equilibrium structures, but formed as a result of a spreading instability. However, the characteristic cluster size and shape in these systems have generally been observed to depend systematically on the hydrocarbon and fluorocarbon block lengths, suggesting that the clusters are indeed equilibrium structures. Our observation in the current work – that clusters (of the same size and shape) continue to exist in concert with the excess of another phase – is also consistent with the equilibrium interpretation. We also note that clusters of most amphiphiles fuse upon compression, forming a uniform monolayer. However, the clusters reported here are quite stable and do not fuse even at high surface pressure.

In previous observations of molecular clusters in Langmuir monolayers, long-range organization of the clusters was generally absent, or at least quite rare. We attribute this behavior to the fact that the clusters themselves displayed significant variability of size and shape. In contrast, in the current system, the clusters are extremely uniform, which promotes efficient packing and long-range order, even the complex rectangular C1 phase.

Conclusions

AFM images of a semi-fluorinated phosphonic acid transferred to mica reveal the presence of two-dimensional nanoscale molecular clusters. Two types of clusters are observed: C1 clusters are elongated and arranged in regular rows, and C2 clusters are circular and randomly ordered. We found that the height and organization of the C1 clusters changed systematically upon the addition of a purely hydrocarbon component (H16PO3). In particular, the addition of H16PO3, up to a concentration of ~20%, increased the height of the clusters and converted the long-range order from liquid-crystalline to crystalline. Upon further addition of H16PO3, the height of the clusters saturated, and the additional H16PO3 phase separated.

This work demonstrated that the height and the organization of semi-fluorinated clusters changes upon the addition of a purely hydrocarbon component. We suggest that this behavior can be interpreted as the 2D analog of micelle swelling. Further work is necessary to clarify the influence of the length of the hydrocarbon and the semi-fluorinated segments on the shape, size, and organization of the clusters and to investigate the influence of adding a hydrocarbon component to a series of semi-fluorinated components.

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