

Nanocompartmentalization of Soft Materials with Three Mutually Immiscible Solvents: Synthesis and Self-Assembly of Three-Arm Star-Polyphiles

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Supporting Information

ABSTRACT: We report synthesis, thermotropic, and lyotropic mesomorphism of a family of novel "star-polyphiles": small star-shaped molecules bearing three mutually immiscible arms, hydrophilic (oligoethylene glycol), oleophilic (alkanes), and fluorophilic (perfluorinated alkanes), attached to a central 1,3,5-trihydroxybenzene core. A facile, flexible multistep synthesis giving high-purity yields of 14 distinct members of the family is described, with variable arm lengths, forming crystalline, or various mesostructured gel phases in their neat state at room temperature. Furthermore, we show that specific members of these star-polyphiles can be simultaneously loaded



with up to three mutually immiscible solvents, dodecane, perfluoro-nonane, and water, to form liquid crystals and microemulsions with multiple chemically distinct mesoscale compartments. The mesoscale chemical polyfunctionality of these polyphiles, coupled with thermotropic and lyotropic polymorphism, make them promising potential soft materials for a variety of applications, including host matrices for multiple mutually immiscible chemicals and drug delivery.

INTRODUCTION

Molecular self-assembly is a fascinating field of research. Amphiphilic molecules, such as lipids and surfactants, consisting of two covalently linked domains of opposing affinity (usually hydrophilic and hydrophobic), are well-known to exhibit rich phase diagrams and play an important role in nature,¹⁻³ as well as in a variety of nanotechnological applications in fields such as pharmaceutical,^{4,5} medical,⁶ and food sciences.⁷

As an extension, we have been developing small (oligomeric) molecules with three domains of opposing affinities in a starshaped geometry, so-called "star-polyphiles", consisting of a central core bearing a hydrocarbon, fluorocarbon, and hydrophilic chain;⁸ see Figure 1a. The star-shaped architecture of such molecules imposes strong constraints on their selfassembly behavior, leading to the formation of nanostructured materials with increased complexity. In particular, their selfassembly gives domains separated by three distinct interfaces (hydrocarbon-fluorocarbon, fluorocarbon-polar, and hydrocarbon-polar) necessarily merged along three-phase lines. They are therefore very different materials from the wealth of amphiphilic materials found in biological and synthetic systems, with potential to form far more structural and physical complexity.

This concept was first explored in the field of ABC miktoarm *star-copolymers*, 9^{-12} which like star-polyphiles have multiple arms linked to a common core. Miktoarm copolymers have polymeric arms; star-polyphiles have shorter oligomeric arms, ideally just long enough to ensure mutual immiscibility of the arms, yet short enough to accommodate lyotropic mesomorphism in the presence of liquid solvents. The exploration of self-assembly of miktoarm copolymeric materials continues to bloom. A large variety of nanostructures have been found in both experiments⁹⁻¹⁴ and simulations,¹⁵⁻¹⁷ including columns of different chemical species arranged in various 2D arrays (as in Figure 1b), zinc-blende type structures,18 quasi-crystalline materials,¹³ and decorated bicontinuous cubic gyroid structures.^{9,10} Polyphilicity in combination with branching has also been successfully employed in the field of thermotropic liquid crystals.¹⁹⁻²¹ In particular, polyphilic X-shaped and T-shaped mesogens have the capability to form structures of extra-

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Figure 1. (a) Star-polyphilic molecules bearing three mutually immiscible arms, (b) a hexagonal columnar liquid crystalline phase based on columns of different chemical species, whose cross section is 12.6.4. planar tiling, found experimentally for ABC miktoarm copolymers,^{9,37} X-shaped polyphilic thermotropic liquid crystals³⁸ and star-polyphiles,⁸ (c) a hypothetical tricontinuous structure consisting of three diamond networks composed of three distinct chemical species.



Figure 2. Molecular structure of the star-polyphiles synthesized, abbreviated as B- O_a - H_b - F_o where B denotes the aromatic molecular core and O/H/ F the methyl-capped oligo-ethylene glycol, hydrocarbon, and fluorocarbon chains of different lengths (a, b, and c), respectively (left). Various precursor chains used (right).

ordinary complexity such as axial bundle phases.^{22,23} Also, many hybrid hydrocarbon fluorocarbon surfactants²⁴⁻²⁷ share the feature of different chemical arms attached to a common center, and these molecules are most closely related to star-polyphiles. These surfactants have been largely explored with different applications in mind (e.g., suitable surfactants for supercritical CO₂ microemulsions or stabilizers for fluorocarbon oil emulsifiers as oxygen transporters). It seems that spatial nanosegregation into hydrophilic, oleophilic, and fluorophilic domains has not been reported in detail yet. For the purpose of exploring exotic self-assembled architectures, spatial segregation into three distinct nanodomains is of the highest importance. Though hydrocarbons and fluorocarbons are known to have nonideal mixing,²⁸ full hydrocarbon fluorocarbon segregation in triphilic systems cannot be assumed in general molecular systems, since the surface tension between hydrocarbon and fluorocarbon domains is much lower than the surface tension between either of them with water.²⁸ Using systematic SANS contrast variation experiments, we have shown previously that, for the star-polyphilic molecules discussed here, a fluorocarbon chain length of 8 units in combination with a hydrocarbon chain length of 14 units is sufficient to provide full segregation

in a hexagonal liquid crystal structure.⁸ Based on multiple experiments we proposed a columnar pattern whose cross section is a 12.6.4. tiling of the plane for a range of water contents in these systems (Figure 1b), although other hexagonal patterns are likely to form at low water contents, to be explored in detail elsewhere.

We are most interested in the potential formation of structures in which the different chemical species form interpenetrating networks creating tri- and polycontinuous assemblies, as exemplified in Figure 1c. Such assemblies have emerged from theoretical considerations²⁹⁻³² based on hints from experimental data on miktoarm copolymers.¹⁴ These patterns can be regarded as an extension of the well-known amphiphilic bicontinuous cubic phases. Recently, an self consistent field theory study postulated that the tricontinuous so-called 3ths(5) phase is an equilibrium phase for triblock starcopolymers when an appropriate molecular core is introduced.³³ The first experimental tricontinuous structure, the 3etc(193) structure, has been discovered in mesoporous silica³⁴ and most recently in a Gemini surfactant phase.³⁵ In contrast to our aim of building interpenetrating networks of different chemical species, the three networks in these cases consist of the same material (air for mesoporous silica, and water for the Gemini surfactant), separated by a wall (silica wall and surfactant membrane, respectively). The formation of this and other tri- and polycontinuous assemblies in amphiphilic lipids has also been postulated on theoretical grounds.³⁶

In this article we focus on the synthesis, physicochemical characterization, and self-assembly of star-polyphiles containing a central 1,3,5-trihydroxybenzene core (Figure 1a and 2a). We developed a modular synthesis method for ease of chain variation, able to be scaled up readily to multigram levels. The final compounds are achiral and monodisperse, and possess high chemical stability, allowing for phase behavior studies and applications within a broad temperature range. The general synthesis scheme may also be useful for the asymmetric synthesis of discotic liquid crystals or dendritic molecules. Further, we demonstrate that star-polyphiles can be loaded simultaneously with up to three mutually immiscible solvents, namely dodecane, perfluoro-nonane, and water, to form thermodynamically stable lyotropic mesophases, including microemulsions and liquid crystals. This novel cosolubility, coupled with mesoscale compartmentalization into three distinct domains renders these star-polyphiles attractive for a range of applications, including multicomponent-molecular storage and drug delivery of mutually insoluble drugs and other chemical species, as well as a number of other applications that have been suggested for ABC miktoarm copolymeric materials.³⁹

RESULTS AND DISCUSSION

1. Synthesis. Our synthesis of triphilic star-polyphiles is based on sequential conjugation of three chemically different arms onto the three equivalent hydroxyl groups of 1,3,5trihydroxybenzene via O-alkylation (Williamson ether synthesis). Sequential etherification cannot be achieved using the nonprotected center, since the attachment of the first chain by O-alkylation is not selective to one hydroxyl group, and the attraction between chains of the same kind is expected to reduce the yield of molecules with three mutually repelling arms even further. Potential selective mono- and dialkylation using zinc as a catalyst has been reported,⁴⁰ but despite considerable efforts we were unable to successfully reproduce this reaction. Therefore, we developed an alternative method. as shown in Scheme 1. First, the three hydroxyl groups in the core module, 1,3,5-trihydroxybenzene, were protected with tosyl-groups, which were then selectively and consecutively deprotected in increasingly alkaline medium following a modified procedure developed by Kampouris.^{41,42} The three different chains were consecutively conjugated to the respective unprotected hydroxyl groups in a classical etherification reaction. A similar asymmetric synthesis approach but using two different types of protection has been developed by Lehmann and Jahr,43 designed for the sequential attachment of chains via ester bonds as opposed to the ether bonds used here.

A suite of star-polyphiles was synthesized with a range of chain lengths in the three arms listed in Figure 2. The resulting molecules are summarized in Table 1. Most of the functional hydrocarbon chains and fluorocarbon chains were commercially available, except for the tosyl-activated phytanol chain and monodisperse methyl-capped oligoethylene glycol chains with various lengths. The former compound was obtained by hydrogenation of phytol in the presence of Reney catalyst^{44,45} followed by the solid phase tosylation reaction developed by Kazemi et al.⁴⁶ The latter compounds were synthesized by an





^{*a*}Steps: (a) triple protection of 1,3,5-trihydroxybenzene with tosylchloride, (b) removal of the first (protecting) tosyl group, (c) attachment of the first chain (hydrocarbon chain H_b), (d) removal of the second tosyl group, (e) attachment of the second chain (methyl-capped oligoethyleneglycol chain O_a), (f) removal of the third tosyl group, and (g) attachment of the third chain (fluorocarbon chain F_c).

in-house method, which we developed to allow for large-scale synthesis and purification of monodisperse methyl-capped oligo-ethylene glycol without the use of column chromatog-raphy. This method is based on a classical etherification reaction, distillation, and the repeated application of the well established tosylation procedure by Ouchi et al.⁴⁷

Scheme 1 shows the seven steps of our modular synthetic method. Step (a) involves the triple tosylation of 1,3,5trihydroxybenzene (phloroglucinol) suspended in water with tosyl chloride in alkaline medium. High yields of pure triply protected product 1 can be achieved on a large scale following the procedure developed by Kampouris for the protection of polyhydric phenols such as benzenesulfonic esters.⁴¹ Methanolic KOH solution is used to hydrolyze the first protecting group in step (b), resulting in one free hydroxyl group and double-protected product 2. Step (c) is a standard mild Williamson ether synthesis reaction for phenols to introduce the hydrocarbon chain (H_h) ; we chose dimethylformamide (DMF) as the solvent rather than tetrahydrofuran (THF), as DMF reduces the possibility of C-alkylation.⁴⁸ Further, we used Cs₂CO₃ instead of K₂CO₃ as the base due to its higher efficiency in deprotonation of hydroxyl groups. Step (d) is a further pH-dependent reaction to remove the second protective group, followed by step (e), another standard Williamson reaction to attach the O_a -chain. The ultimate protecting tosyl group is removed at high pH (ca. 14) in step (f), using solid KOH and 18-Crown-6 to achieve such high pH in a THFsolution. In the final step (g), the fluorocarbon (F_c) chain was

Table	1. P	hysicoc	hemical	Prop	perties	of	the	Synt	hesised	Star-Po	lyphil	es
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			DSC phase transition temp ^a									Structure at RT ^b				
		Heating	g	Cooling						d _{lam}	а	Ь	γ			
Samples		(°C)	(J/g)	(°C)	(J/g)	(°C)	(J/g)	(°C)	(J/g)	[nm]	[nm]	[nm]	[deg]			
B1	$B-O_5-H_{12}-F_8$	3.7	-36	-33.4	20					-	-	-	-	liquid		
B2	$B-O_5-H_{12}-F_{10}$	36.5	-11	34.5	11	-30.6	5			4.02	-	-	-	simple gel		
B3	$B-O_7-H_{14}-F_8$	10.5	-38	-15.9	28	-68.5	0.4			-	-	-	-	liquid		
B4	$B-O_7-H_{14}-F_{10}$	24.5 (d)	-40	9.6	8	-10.5	10	-49.1	0.1	4.65	4.72	2.27	99.5	oblique gel		
B5	$B-O_5-H_{14}-F_8$	30.7 (d)	-78	-16.7	22					3.91	3.91	1.17	93.6	oblique crystal		
B6	$B-O_5-H_{14}-F_{10}$	40.1 (d)	-73	20.4	11	4.0	0.5	-6.0	10	4.13	4.15	1.17	95.4	oblique crystal		
B 7	$B-O_3-H_{14}-F_{10}$	48.6 (d)	-66	33.5	12	-3.7 (d)	18			3.89	?	?	?	crystal		
B8	$B-O_7-H_{16}-F_8$	9.5	-24	-4.5	24					-	-	-	-	liquid		
B9	$B-O_7-H_{16}-F_{10}$	31.0	-48	10.4	8	5.8	11			4.58	4.64	2.40	99.5	oblique gel		
B10	$B-O_5-H_{16}-F_8$	36.4	-79	0.3 (d)	28					4.05	4.06	1.17	92.0	oblique crystal		
B11	$B-O_5-H_{16}-F_{10}$	45.0	-77	22.1	9	9.6	14			4.21	4.29	1.17	93.6	oblique crystal		
B12	$B-O_3-H_{16}-F_{10}$	59.1	-85	37.3	13	21.9 (d)	24			4.03	?	?	?	crystal		
B13	B-O ₈ -H ₂₀ -F ₁₀	-0.6	-8	-8.1	8					-	-	-	-	liquid		
B14	$B-O_7-H_{20}-F_{10}$	-12.0 (d)	-23	-15.0 (d)	5	-44.0	4			-	-	-	-	liquid		

^{*a*}DSC transition temperatures (peak positions) and associated enthalpies at a scan rate of 2.5 °C/min. The heating transitions listed correspond to melting or clearing points. The cooling transitions correspond to formation of (multiple monotropic) liquid crystalline phases until -70 °C. ^{*b*}Structural data at room temperature established from SAXS/WAXS spectra. The lamellar repeat was calculated as $d_{lam} = 2\pi/q$, and the unit cell parameters of the oblique unit cells are *a* and *b*, and γ is the angle between them.

attached. In the end, the crude final products were purified using column chromatography, and we achieved a purity of more than 99%. More experimental details are in the Experimental Section and Supporting Information sections S1 and S2.

2. Physico-chemical Characterization. Liquid Crystalline Textures of Neat and Hydrated Polyphiles: Polarized Optical Microscopy (POM). At room temperature the neat starpolyphiles are either liquid, waxy, or solid powders, as summarized in Table 1. The waxy materials are strongly birefringent, and typical textures as observed by POM for B2 $(B-O_5-H_{12}-F_{10})$ and B4 $(B-O_7-H_{14}-F_{10})$ are shown in Figure 3a,b. The waxy and liquid star-polyphiles with an O_7 - and O_8 -chain show lyotropic mesophormism at room temperature with addition of water. For example, the neat polyphile B3 $(B-O_7-H_{14}-F_8)$ is an isotropic liquid and develops a strongly birefringent fan-like texture at low water content, as well as a viscous isotropic phase at higher water content, as shown in Figure 3c.

Thermal Behavior: Thermogravimetric Analysis (TGA). Thermogravimetric data of two representative samples B5 (B- O_5 - H_{14} - F_8) and B6 (B- O_5 - H_{14} - F_{10}) are shown in the Supporting Information section S3. Weight loss occurs in a single step above 300 °C, indicating evaporation (with possible concomitant degradation) of the material. Below this temperature, the weight loss is negligible, which demonstrates that there is no degradation and suggests that these compounds are thermally stable.

Thermal Behavior: Differential Scanning Calorimetry (DSC). Most of these star-polyphiles show complex thermal behavior that is in part strongly history-dependent. DSC-scans reveal thermotropic mesomorphism (enantiotropic or mono-tropic) in all samples. This is exemplified by three examples.

Figure 4a shows the first heating, first cooling, and second heating DSC-scans of B2 $(B-O_5-H_{12}-F_{10})$. This star-polyphile has a waxy appearance at room temperature. In addition to some minor rearrangements at low temperature (below -20 °C), it shows one major reversible phase transition upon heating/cooling with minor hysteresis in the cooling scan (at



Figure 3. Polarizing microscopy images. (a) Simple gel phase (B2, *B*- O_5 - H_{12} - F_{10}), (b) Oblique gel phase (B4, B- O_7 - H_{14} - F_{10}), (c) lyotropic liquid crystalline textures in a water penetration scan of B3 (B- O_7 - H_{14} - F_8) at room temperature. The scale bars correspond to 100 μ m.

~35 °C). This transition is associated with a phase transition between a liquid crystal (lc) structure and the molten fluid isotropic state, with an associated enthalpy change of ~11 J/g. The lc-structure, that we call a "simple gel phase", is lamellar and similar to a surfactant gel or rotator phase in which the stiff fluorocarbon chains are packed in a hexagonal array. We discuss this phase in more detail in the SAXS section below.

Upon increasing the H-chain length from 12 to 14 (B6 B- O_5 - H_{14} - F_{10}), the sample is crystalline at room temperature and melts upon heating at ~40 °C with a (split) melting enthalpy of 73 J/g, as shown in Figure 4b. Upon cooling, multiple metastable (so-called monotropic) liquid crystalline phases



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Figure 4. Typical DSC scans of neat polyphiles. Red: first heating, Blue: first cooling, and Orange: second heating scan. Samples were cooled to -75 °C at 10 °C/min and equilibrated for 10 min before the scans. Subsequent heating/cooling scans were performed at 2.5 °C/min. The scans are displayed with an offset for clarity. (a) B2 (B-O₅-H₁₂-F₁₀), (b) B6 (B-O₅-H₁₄-F₁₀), and (c) B4 (B-O₇-H₁₄-F₁₀).

occur, and only upon reheating, does the sample recrystallize back to its original thermodynamically stable crystalline state, as shown by the pronounced exothermic peak in the second heating scan.

Extending the O-chain from 5 to 7 units (B4 B- O_7 - H_{14} - F_{10}) results in a waxy material that is close to melting at room temperature. The DSC heating scan reveals a split clearing peak at ~25 °C, as shown in Figure 4c. Its associated enthalpy change of 40 J/g is between typical values obtained for the melting enthalpy of a crystal (as in Figure 4b) and a simple gel phase (as in Figure 4a). We call this phase a "complex gel phase" (see the SAXS section for more details). Upon cooling, this sample also forms multiple monotropic liquid crystalline structures, marked by multiple phase transitions. Two of these phase transitions are associated with significant enthalpies (-8)J/g at 9.5 °C and -10 J/g at -10.5 °C), and another very small rearrangement is observed at lower temperature. During cooling, the sample remains in a metastable state-similar to the previous sample, and only upon heating does a rearrangement to the thermodynamically stable phase take place, as shown by the combined melting/crystallization peak at ~ -5 °C that occurs in the second heating scan. For more details see Supporting Information section S4.

Table 1 gives a summary of the melting/clearing points as observed in the first heating scan, and the phase transition temperatures observed in the cooling scans together with the associated enthalpies for all star-polyphiles investigated here. In general, the melting/clearing points increase upon increasing the H-chain and/or F-chain length and decreasing the O-chain length. The only two samples with one single reversible clearing transition and little hysteresis are B2 and B13. All other samples show multiple monotropic liquid crystalline phases upon cooling.

Small- and Wide-Angle Scattering (SAXS/WAXS) of the Neat Star-Polyphiles. Figure 5 shows characteristic SAXS/ WAXS spectra of the neat star-polyphiles at room temperature, recorded at the SWAXS beamline of the Australian Synchrotron.⁴⁹ Star-polyphiles can form either structured fluids (red curve), thermotropic liquid crystals (simple and complex gels, black and green curve), or solid crystals (blue curve).

a. Liquid Star-Polyphiles. All liquid samples show a single correlation peak in the small-angle range $(q \sim 1.5 \text{ nm}^{-1})$, signifying the formation of structured fluids, and a broad peak in the wide-angle range $(q \sim 13 \text{ nm}^{-1})$, demonstrating that all chains are fully molten. A characteristic scattering pattern for



Figure 5. Characteristic SWAXS patterns of star-polyphiles in liquid form (red, B8 B- O_7 - H_{16} - F_8), simple gels (black, B2 B- O_5 - H_{12} - F_{10}), complex (oblique) gels (green, B9 B- O_7 - H_{16} - F_{10}), and crystalline forms (blue, B11 B- O_5 - H_{16} - F_{10}).

liquid samples, that for B8, is shown as a red curve in Figure 5. In general, the broad small-angle peak stems from a correlation between the H–H, F–F, and O–O domains, and its exact position depends on the size of each of the chain lengths.

b. Simple Gel Phase. The next simplest scattering pattern we observed stems from sample B2 $(B - O_5 - H_{12} - F_{10})$ and is shown as a black curve in Figure 5. It contains only one set of equidistant lamellar peaks in the small angle range resulting in a lamellar repeat of 4.02 nm, and one sharp peak in the wideangle range with a repeat distance of 0.498 nm. Measurement over an extended wide-angle range (Figure 6) reveals four wideangle peaks that can be indexed to a 2D hexagonal lattice, with lattice parameter 0.576 nm. This gives a 2D cell area of 28.7 ${\rm \AA}^2$ (0.287 nm^2) , in very good agreement with the value found for stiff hexagonally arranged fluorocarbon chains.²⁸ A broad halo around the first sharp wide-angle peak is consistent with disordered (molten) H-chains and O-chains. Although a little more complex, this scattering is similar to that of lipid or surfactant gel phases with molten hydrophilic groups and stiff hydrocarbon chains packed in a 2D hexagonal arrangement, free to rotate around their long axis (known as surfactant gel or rotator phases^{50,51}). Therefore, we call this phase, formed by star-polyphile B2 at room temperature, a simple gel phase.



Figure 6. Measured SWAXS (blue) and extended WAXS (black) pattern for star polyphile B2 in the simple gel phase. The inset shows the merged WAXS-range. The black arrows indicate the equidistant peaks in the small-angle region, corresponding to a lamellar structure as the molecular arrangement of the molecules. The red arrows indicate the peaks in the wide-angle range and can be indexed on a 2D hexagonal lattice ($\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$). The resulting hexagonal lattice parameter is in very good agreement with that typically found for stiff fluorocarbon chains arranged on a hexagonal lattice. (Note that the decreased intensity in the black extended spectrum at ~12 nm⁻¹ is due to a shadow in the experimental setup, and the broad peak at 27 nm⁻¹ is background scattering from the sample cell.) Right: Suggested structural model for this simple gel, made of stiff fluorocarbon chains (green) aligned normal to the vertices of a 2D hexagonal array, separated by interdigitated hydrocarbon (H) and oligo-ethylene glycol (O) chains (red and blue).



Figure 7. Measured SAXS pattern for sample B9 with 2D oblique indexing. Right: Proposed schematic model of complex gel phases. Note the colocation of hydrocarbon (H, red) and fluorocarbon (F, green) chains, segregated from the hydrophilic (oligo-ethylene, O) chains (blue), in contrast to the simple gel phase.

A likely model structure for this simple gel can be inferred from the molecule's architecture combined with the scattering data. The lamellar repeat distance of 4.02 nm obtained from the scattering is at the upper limit of a fully stretched crystalline molecule (i.e., chains in all-trans configurations, see Supporting Information section S5), which suggests an interdigitated bilayer arrangement. The 2D hexagonal (close-packed) array is strongly suggestive of stiff extended fluorocarbon chains stacked along the long axis. A structure consistent with the scattering, containing mixed O and H chains segregated from the F chains, is shown on the right in Figure 6. This gel structure is built of flat bilayers, containing extended fluorocarbon chains normal to the layers, interdigitated in an antiparallel fashion to form stiff layers, sandwiched between molten, mixed hydrocarbon and Ochains, with a single star-polyphile molecule per unit cell. We note that the proposed structure resembles the smectic B phase found for branched and unbranched perfluoroalkyl-alkanes.52 Unlike all other observed liquid crystalline phases formed by

these star polyphiles, it is reasonable to assume that the Hchains and O-chains are able to mix in the structure of this neat polyphile, since the short dry O-chains (O_5) are not very polar in the absence of free OH-groups. This assumption is strongly supported by the observation that this structure cannot be swollen with water. We note, however, that the paucity of scattering peaks makes unequivocal structural assignment difficult, and we cannot rule out more complex disordered structures. This structural model, with a 3D unit cell defined by the lattice vectors of the 2D hexagonal lattice (giving the *a* and b lattice vectors of the 3D cell) and the c axis equal to the lamellar repeat distance, has a volume of 1.15 nm³. Our estimate of the molecular volume based on bulk densities of the constituent parts is between 1.3 and 1.4 nm³. As a consequence, our proposed structure would be unusually tightly packed, though this increased density can be ascribed to very closely packed chains, consistent with the gel character of the phase (see Supporting Information section S6).



Figure 8. Scattering pattern of (a) dry star-polyphile B13 ($B-O_8-H_{20}-F_{10}$) with either H-oil, F-oil, combined H/F-oil, or water; (b) a hexagonal liquid crystal with 5% water with added H-oil, F-oil, or both at 22 °C; (c) same samples as in (b) at 50 °C. All percentages are given in V/wt % (volume of added solvent/weight of star-polyphile*100).

c. Complex Gel Phases. Simultaneous extension of the Hchains (from H_{12} to H_{14} or H_{16}) and the O-chains (from O_5 to O_7) results in the more complex gel phases at room temperature (sample B4 and B9). In common with the simple gels, these waxy samples also display a small-angle signal consistent with a 1D lattice. However, the occurrence of additional peaks in the small- and wide-angle range signifies a more complex arrangement (Figure 5). Given the multitude of (broadened) wide-angle peaks, these samples form phases between more common gel and crystalline phases, which is also in agreement with their DSC thermograms. They display characteristics of disordered crystalline phases, though their waxy appearance, as well as their capability to significantly swell with water, is consistent with macroscopic gel phases. We therefore call samples with these features "complex gels".

All small-angle peaks can be indexed on a 2D oblique lattice, as shown in Figure 7 for sample B9. The resulting lattice parameters and angles are summarized in Table 1. A large number of overlapping peaks of variable widths are observed in the wide-angle range, arising from chain packing, as well as the higher-order lattice peaks. Resolution of the individual chainchain structural contributions to the wide-angle scattering is currently impossible, leaving an open question as to which of the molecular moieties are molten and which are frozen or even crystalline. Some information can nevertheless be inferred from the swelling of these complex gels. In contrast to the simple gel above, these liquid crystals can be swollen with water, retaining a swollen oblique lattice (from SAXS). Clearly, this feature is incompatible with the mixed H and O chains of the simple gel, suggesting that they are segregated in the complex gel phase, consistent with the formation of this phase on lengthening H and O chains in the star polyphiles. The scattering and swelling data suggest the presence of lamellae made up of layers of molten O-chains, interleaved with layers of alternating patches of H- and F-chains that cause in plane ordering as illustrated in the right picture of Figure 7, resulting in the second repeat distance. The formation of an oblique-and not rectangularunit cell is likely caused by a tilt between the O-chains with H-/ F-chains mismatch in order to match cross-sectional areas (see Figure 7).

d. Crystals. Crystals are obtained if the O-chains are small $(O_5 \text{ or } O_3)$, and their crystalline character is retained when the F-chain is shortened from F_{10} to F_8 . The observed scattering peaks are much sharper for these samples, and once again the lamellar spacing is retained. The samples with O_5 chain can again be indexed on a 2D oblique lattice, as summarized in Table 1. The first peak that cannot be accounted for is already in the wide-angle range; see Supporting Information section S6 for more details. The indexing of crystals with an O_3 -chain remains ambiguous at this stage due to the formation of coexisting metastable structures.

3. Lyotropic Phase Behavior: Formation of Multicompartments. The star-polyphiles with an O-chain length of 7 or 8 exhibit lyotropic mesomorphism, as already demonstrated by the water penetration scan shown in Figure 3c. A detailed study of their lyotropic phase behavior will be published in the near future. Here we report only preliminary data establishing that some polyphiles can be loaded simultaneously with the three mutually immiscible solvents dodecane, perfluoro-nonane, and water, to form single, thermodynamically stable mesophases. The resulting materials contain four distinct chemical species, intimately mixed at the supramolecular level to form microemulsions and liquid crystals with multiple chemically distinct compartments, as outlined next.

At room temperature, the neat star-polyphile B13 ($B-O_8-H_{20}$ - F_{10}) forms an isotropic, slightly viscous liquid phase. The liquid is miscible with H-oil (dodecane) in any ratio, while the maximum amount of incorporated F-oil (perfluoro-nonane) is limited to 7.5 V/wt % at this temperature. This star-polyphile can also be swollen with water, whereby only a small amount of water (about 3 V/wt %) can be added at room temperature before a transition from a liquid to a birefringent liquid crystal takes place, which persists in excess water (at above 25 V/wt %). These solubilities suggest that, in this particular liquid star-polyphile phase, the H-chains can form a continuous matrix, embedding the F- and O-domains.

Figure 8a shows the evolution of the SAXS pattern upon addition of the various solvents. The neat polyphile is a structured liquid phase, characterized by a single broad correlation peak in the SAXS region (black curve). The addition of 5 V/wt % H-oil dampens the peak and moves it to slightly higher *q*-values (red curve), indicating decreased order in the system at a slightly reduced correlation length. The addition of 5 V/wt % F-oil, on the other hand, enhances the correlation peak and moves it to lower *q*-values (green curve), denoting swelling and increased order in this sample. Addition of 5 V/wt % H-oil to this F-oil loaded sample (orange curve) demonstrates a combination of both these effects. Water also swells the structure (blue curve), in a similar fashion to the addition of F-oil for small water fractions. Water dilution of 5 V/wt % and beyond is sufficient to induce a phase transition from the molten phase to a hexagonal liquid crystalline mesophase (cyan curve). We have shown elsewhere that the star-polyphilic hexagonal phase consists of hexagonally arranged aqueous domains, embedded in a hydrophobic matrix that is segregated into hydrocarbon and fluorocarbon regions.⁸ Oil dilution necessarily enlarges the size of the hydrocarbon and fluorocarbon domains, and further promotes nanophase segregation. Note that an F10-chain is required to allow for the incorporation of F-oil, whereas an F₈-chain is too short, despite the fact that an F₈-chain was shown to be sufficiently long to induce full segregation between the fluorocarbon and hydrocarbon nanodomains in the hexagonal phase.⁸

Figure 8b demonstrates the effect of oil addition to this binary polyphile-water hexagonal liquid crystal at 22 °C. Once again, H-oil and F-oil have different effects: 5 V/wt % H-oil dampens the peaks and shrinks the hexagonal unit cell slightly (red curve), while 5 V/wt % F-oil significantly swells this structure (green curve). The addition of both oils at the same time results in a structure that gives rise to the orange scattering curve. The resulting structure shows the combined effect of both oils: the material remains a well-ordered hexagonal liquid crystal, indicating that the melting effect of the H-oil is annulled by the addition of F-oil. Its lattice parameter is only slightly larger than that of the starting binary sample, due to competing swelling and shrinkage effects of the F- and H-oil, respectively. At 50 °C, these hexagonal liquid crystals melt to form microemulsions, whose scattering data are plotted in Figure 8c. The effects of the H- and F-oils are very similar to those at lower temperature, namely shrinkage of characteristic distances and reduced order in the presence of H-oil, and enhanced ordering on addition of F-oil.

These phenomena are consistent with swelling of conventional amphiphiles in the presence of oils. As a general rule, Hoils whose chain lengths are less than those of the host amphiphile intercalate between chains toward the hydrophilic end of the host, splaying and shortening the chains, analogous to the effect of increasing temperature. For example, Siegel et al.⁵³ report that addition of diglycerides and short-chain alkanes to a type II hexagonal mesophase in excess water (curved toward water) increases the curvature of the cylindrical micelles within the phase, leading to reduced lattice parameters. In contrast, large hydrophobic molecules, such as long-chain hydrocarbons and squalene, intercalate between the hydrophobic chain ends and swell the structure.

The orange curves in Figure 8b and c denote single-phase liquid crystals and microemulsions containing star-polyphile and all three mutually immiscible solvents simultaneously, demonstrating the formation of separate hydrophilic, hydrophobic, and fluorocarbon domains. A schematic illustration of this three-phase miscibility in the presence of the polyphiles at room temperature is shown in Figure 9. The neat star-polyphile



Figure 9. Sketch of quaternary phase tetrahedron at room temperature in wt/wt. While the solvents dodecane (H-oil), perfluoro-nonane (Foil), and water are mutually immiscible, star-polyphile B can incorporate a significant amount of them simultaneously, forming macroscopic single phases of multicompartment microemulsions (yellow) and liquid crystals (red). The remaining part of the phase tetrahedron is multiphasic and shown as empty.

can incorporate significant amounts of H-oil, F-oil, and water either separately or simultaneously to form multicompartment microemulsions (yellow body) at lower water contents or liquid crystals at higher water contents (red body). Generally, increasing the amount of incorporated H-oil reduces the maximum solubilization capacity of water. Preliminary tests suggest that the solubilization capacity of FC-oil is around 7.5 V/wt % irrespective of the presence of water and/or H-oil.

CONCLUSION AND OUTLOOK

We hope that this report on the synthesis and rudiments of selfassembly in the presence of up to three mutually immiscible solvents demonstrates the extraordinary versatility of starpolyphiles. The key feature of these star-polyphilic assemblies is the spatial segregation into three distinct hydrophilic, oleophilic, and fluorophilic nanodomains, enabling them to simultaneously incorporate three mutually immiscible solvents (dodecane/perfluoro-nonane/water). It is clear that they can form crystals, structured melts, and at least two distinct thermodynamically stable gel phases as neat chemicals (thermotropic liquid crystals), dependent on chain lengths and temperature. In addition, a variety of metastable (monotropic) liquid crystals can form upon cooling neat polyphiles from the melt. Star-polyphiles whose hydrophilic methyl-capped oligo-ethylene glycol chain is sufficiently long (more than 5 monomers) are able to incorporate water and self-assemble to form reverse microemulsions and a variety of lyotropic liquid crystals. Detailed exploration of those phases will be reported in the near future. Their capability to incorporate multiple immiscible solvents enriches their capacity to form exotic nanostructures and also makes them very attractive for a range of applications. The most obvious applications lie in simultaneous segregated loading, storage, and release of multiple immiscible cargos. Segregated loading has previously been achieved in miktoarm polymeric micelles,⁵⁴ and in particular applications in fields such as simultaneous storage, delivery and release of multiple incompatible cargos are being explored.39

EXPERIMENTAL SECTION

Polarizing Light Microscopy (POM). Textures were observed with an Olympus BX53F microscope using crossed polarizers and a quarter wavelength retarder ($\lambda = 530$ nm), and images were taken with a digital MicroPublisher 3.3 RTV camera.

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Phase transition temperatures and associated enthalpies were measured with a Mettler Toledo DSC 822 system with a Mettler TSO 801RO sample robot (Mettler Toledo; Melbourne, Australia). Temperature and enthalpy calibrations were performed using indium as the standard. The samples were run in aluminum crucibles in a sealed furnace and were cooled to -75 °C at 10 °C/min, before subsequent heating/cooling cycles at a rate of 2.5 °C/min between -75 and 75 °C. All samples were thoroughly freeze-dried using *tert*-butyl alcohol before the first DSC scan. Thermogravimetry analyses were performed using a Mettler Toledo TGA SDTA851 with a Mettler TSO801RO sample robot (Mettler Toledo; Melbourne, Australia). Samples were run in aluminum crucibles in a sealed furnace and in a stream of air at a scan rate of 10 °C/min from RT to 500 °C.

Synchrotron SAXS/WAXS. SAXS/WAXS measurements were performed at the Australian synchrotron.⁴⁷ Most samples were measured in 0.7 mm borosilicate capillaries, using the temperature controlled multicapillary sample holder designed and built at the synchrotron. The measurements shown in Figure 7b were done in homemade solvent tight temperature controlled paste cells. Measurements were performed at a maximally offset detector to cover a wide *q*-range, with the energy of 8 or 20 keV. For the measurement in Figure 6, an additional wide-angle detector was installed. The 2D spectra were converted to 1D scattering curves, transmission and background corrected using the software Scatterbrain.

Mass Spectroscopy (LC-MS). LC-MS spectra of all reaction mixtures and compounds were monitored on a Thermo Fisher Scientific LCQ Advantage MAX ion trap mass spectrometer (Thermo Scientific, San Jose, CA, USA) equipped with an APCI interface. The LC was equipped with a Phenomenex column Gemini-NX 5 μ m C18-110 Å (150 × 2.0 mm). For the final products, the mobile phases consisted of (A) 100% water and (B) 100% methanol. The samples were analyzed on a linear mobile phase gradient from 60% solvent A to 100% solvent B within 5 min and then 100% buffer B within the next 10 min. For analysis of the reaction mixtures, the mobile phase was methanol at a constant rate of 0.5 mL/min.

High Performance Liquid Chromatography (HPLC). Analytical HPLC was performed on Waters HPLC equipment (Waters Corporation, Milford, MA, USA), comprising a 600 solvent delivery system with a 600 automated gradient controller using a Phenomenex Gemini C18 column (5 μ M, 4.6 X150 mm) and a UV detector and Altech 2000 evaporative light scattering detector (ELSD). The mobile phases consisted of (A) 100% H₂O, 0.05% (v/v) trifluoroacetic acid (TFA) and (B) 60% THF, 40% AcCN with 0.05% TFA. The samples were analyzed on a linear mobile phase gradient from 80% solvent A to 100% solvent B within 5 min followed by 100% solvent B within the next 15 min. Flow rate was set to 1 mL/min. The ELSD detector nebulizer temperature and nitrogen gas flow were set to 103 °C and 2.9 L/min, respectively.

Starting Materials. Most of the starting materials were purchased from Sigma-Aldrich (Castle Hill, Sydney-Australia), unless otherwise mentioned. All solvents were of analytical grade and purchased from MERCK (Australia) and were used without further processing. Cs_2CO_3 and DMF were anhydrous. The fluorocarbon-iodides and FluoroFlash cartridges were obtained from Fluourous (Pittsburgh, USA).

Synthesis. The synthesis details are exemplified for B8 $(B-O_7-H_{16}-F_8)$ in the following; all other syntheses were performed analogously. It should be noted that there was no purification performed for intermediate compounds, which means that the given yields after each step are not a direct measure of pure sample, but include all byproducts formed.

Step (a): 1,3,5-p-Toluenesulfonylbenzene B-Ts₃ (1). To a stirred dispersion of 1,3,5-trihydroxybenzene $\cdot 2H_2O$ (32.2 g, 0.2 mol) in 500 mL of water was added 0.63 mol of tosyl chloride TsCl (120.1 g). The dispersion was heated to 35 °C and stirred vigorously while concentrated KOH was continuously added. The addition was continued until the pH remained permanently basic and no more KOH was required to keep the solution basic. A sticky, white precipitate formed that was crushed into a powder using a mortar and

pestle. The precipitate was washed with copious amounts of water to remove all nonreacted TsCl and TsOH. Yield: 92% (108.2 g). Mw: 588.67. $R_{\rm f}$ values in 70/30 hexane/ethyl acetate on silica gel TLC plates with fluorescent indicator 254 nm: TsCl: 0.76, B-Ts₃ 0.46, B-Ts₂ 0.32, B-Ts₁ 0.18

Step (b) B-Ts₂ (2). B-Ts₃ (41.1 g, 0.07 mol) was dispersed in 100 mL of methanol at 35 °C. Twenty-nine mL of an aqueous solution containing water/methanol/KOH = 40/40/20 solution was added dropwise within about 10 min. The dispersed material dissolved, resulting in a brown solution accompanied by some salt. The solution was heated to 45 °C for 5 min, diluted to 1.5 L with water (brown solution), acidified with 1/2 conc HCl to ~pH = 5 (thick emulsion), and continued to stir for 1 h. A sticky, viscous precipitate formed (B-Ts₂ and some B-Ts₁), which was separated from the aqueous phase. We could not find a suitable solvent to recrystallize B-Ts₂, and proceeded with the crude sample that was redissolved in DCM, washed with water, and dried over MgSO₄. Yield: 85% (25.8 g). Mw: 434.48. LC-MS m/z: 434.48/452.02 at t = 1.22 min, HPLC: t = 9.2 min.

Step (c) $B-Ts_2-H_{16}$ (3). Crude product 2 (25.8 g, 0.06 mol) and C₁₆Br (16.8 g, 0.055 mol) were dissolved in 200 mL of anhydrous DMF at ~30 °C. Cs₂CO₃ (58 g, 0.18 mol) was added, and the suspension was stirred overnight. DMF was evaporated under reduced pressure. The residue was dissolved in ether and washed 3 times with 10% NaCl solution. Yield: 92.7% (36.4 g). Mw: 658.91. LC-MS m/z: 659.42/676.37 at t = 2.86 min, HPLC: t = 11.5 min.

Step (d) B-Ts-H₁₆ (4). Crude product 3 (36.4 g, ~0.055 mol) was dispersed in 100 mL of methanol at 40 °C. 65 mL of a 20% KOH solution was added dropwise, and the dispersion was stirred well until all the material was dissolved and no more B-Ts₂-H₁₆ was left (~45 min). The solution was diluted with water to 1.5 L (turbid solution), acidified with 1/2 conc HCl to about pH = 5, and stirred for 1 h. The residual oily material on top of the solution was separated from the rest, dissolved in DCM, and washed with copious amounts of water. The DCM phase was dried over Mg₂SO₄ and evaporated to dryness to obtain the title compound. Yield: 85% (23.1 g). Mw: 504.72. LC-MS m/z: 505.35 at t = 1.94 min, HPLC: t = 11.1 min.

Step (e) B-Ts- O_7 - H_{16} (5). Crude product 4 (23.1 g, 0.047 mol) was reacted with O_7 -Ts (23.3 g, 0.047 mol) similar to step (c) to obtain the title compound. Yield: 88% (34.3 g). Mw: 827.12. LC-MS m/z: 828.32 at t = 2.1 min.

Step (f) B- O_7 - H_{16} (6). 34.3 g (~0.041 mol) of crude product S and 1 g of 18 Crown 6 (=0.0038 mol) were dissolved in 150 mL of THF, followed by addition of an excess amount of crushed KOH flakes (7 g). The dispersion was heated to 50 °C and stirred overnight while covered with parafilm. 150 mL of water was added, forming a dark brown solution, followed by neutralization with 1/4 conc HCl. The reaction mixture was extracted with ether, and the ether phase washed repeatedly with water. Yield: 90% (25.1 g). Mw: 672.93. LC-MS m/z: 673.58 at t = 1.81 min, HPLC: t = 10.4 min.

Step (g) B-O₇-H₁₆-F₈ (7). Analogous to step (c), but react crude product **6** (10.0 g, 0.015 mol) with C₈F₁₇C₃H₆I (6.1 g, 0.01 mol). Yield: 89% (15g). Mw: 1133.06. LC-MS *m/z*: 1133.58 at *t* = 3.12 min, HPLC: *t* = 11.5 min. ¹H NMR in CDCl₃: δ: 0.89 (t, 3H, *J* = 6.59 Hz, H_b (CH3)), 1.19–1.39 (m, 20H, H_b (CH2)), 1.43 (quin, 2H, *J* = 7.20 Hz, H_b (γ-CH2)), 1.70–1.84 (quin, 2H, *J* = 8.10 Hz, H_b (β-CH2)), 2.08 (m, 2H, F_c (CF2-CH2-CH2)), 2.19–2.41 (m, 2H, F_c (CF2-CH2-CH2)), 3.38 (s, 3H, O_a (CH3-O)), 3.52–3.59 (m, 2H, O_a (CH2-O– CH3)), 3.60–3.77 (m, 22H, O_a (CH2-O)), 3.84 (t, 2H, *J* = 4.76 Hz, O_a (β-CH2)), 3.90 (t, 2H, *J* = 6.59 Hz, H_b (α-CH2)), 3.99 (t, 2H, *J* = 5.85 Hz, F_c (α-CH2)), 4.09 (t, 2H, *J* = 4.94 Hz, O_a (α-CH2)), 6.00– 6.16 (m, 3H, b (CH=C)).

The total yield of the 7 steps combined after purification (using column chromatography and Fluoroflash cartridges) is between 10 and 15% with respect to the starting 1,3,5-trihydroxybenzene. More details on the purification procedure and sample purity of the final compounds by NMR, HPLC, and LC-MS are included in Supporting Information sections S1 and S2.

ASSOCIATED CONTENT

S Supporting Information

More details on sample purification, final sample purity, thermogravimetric analysis data (TGA), differential scanning calorimetry data (DSC), and indexing and interpretation of the SAXS/WAXS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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