Self-Assembly

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Small Molecule Modulation of Soft Matter Frank-Kasper Phases: A New Paradigm for Adding Function to Form

*Kätchen K. Lachmayr and Lawrence R. Sita**

Thermotropic 'one-component' soft matter Frank-Kasper (FK) phases are fascinating topologically-close-packed (TCP) periodic structures that arise in the condensed state through the reconfiguration and self-sorting of deformable sphere-shaped particles into two or more crystallographically distinct sets with different coordination number, size, or shape.[1-11] On the other hand, the small set of currently known thermotropic FK phases that have now been experimentally established over the past 20 years for a range of different soft materials are largely of structural interest, and with only a few rare examples that can be viewed as coupling form with function.[12] Very recently, we reported that the sugar-polyolefin conjugate, cellobiose-triazole-linked *atactic* poly(4-methyl-1-pentene) (CB-aPMP) (**1**), undergoes an irreversible thermotropic order-order transition from an initial hexagonal cylindrical (C) morphology to produce a cubic FK A15 ($Pm\bar{3}n$) phase with the unit cell shown in Fig. 1.[8] In addition to the unique exceptional stability displayed by this A15 nanostructure over long periods of time of, at least, several months and upon thermal cycling over a wide temperature range from 25 °C to 200 °C, sugar-polyolefin conjugates, such as **1**, can also be obtained in abundant quantities from readily available precursors and scalable synthetic processes, which include the living coordinative chain transfer polymerization (LCCTP) of α-olefins.[13,14] Given all of these favourable attributes of sugar-polyolefin FK phases, we have now embarked on a program to increase functional versatility. In this regard, soft matter FK phases appear to be well suited for mimicking the hierarchical spatial compartmentalization of orthogonally functional components and processes within cells.[15] Carrying this analogy further, the C → A15 phase transition of **1** can be seen as providing the basis for a rudimentary process by which the selective capture and sequestration of different components can occur simultaneously, and ideally, in response to an external triggering event. Herein, we now report experimental realization of the ability to modulate the thermotropic FK phase-forming behavior of **1** through incorporation of small quantities between 1% to 10% by weight of the small molecule, α-tocopherol (**2**) (also known as vitamin E). In addition to globally lowering phase transition temperatures, this small molecule modulation of the phase diagram of **1** provides access to not only stable FK A15 phases of increased functional complexity, but also, to the more structurally complex FK σ ($P4_2/mnm$) and the body-centered cubic (BCC, $Im\bar{3}m$) phases shown in Fig. 1 that appear under more moderate conditions with increasing **2** or temperature in the order: C < A15 < σ < BCC. Triple coexistence of these latter three phases is also shown to occur for certain blends at specific

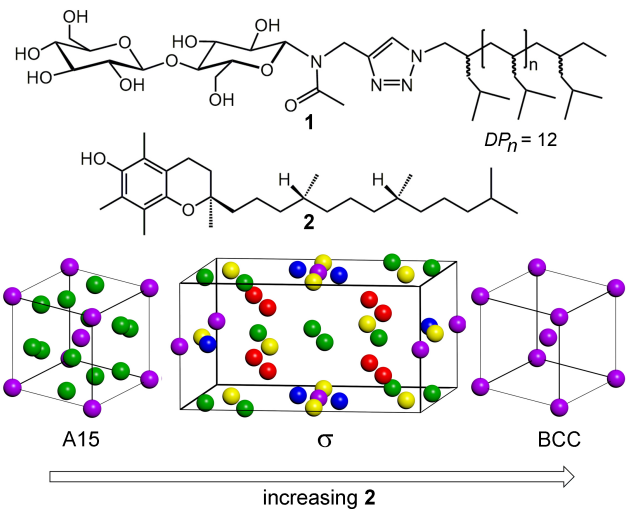

Fig. 1. Structures of CB-aPMP (**1**), vitamin E (**2**) and generic unit cells for A15, σ, and BCC phases. Colored spheres of arbitrary but equal size represent different sets of crystallographically equivalent positions with a total sphere count of 8, 30 and 2 for the unit cells of A15, σ, and BCC, respectively.

temperatures in what appears to be a first amongst all known FK phase-forming soft materials. Based on these results, it is highly probable that small molecule phase modulation can be used as a general strategy for the design, manufacture, and utilization of functionally competent soft matter FK phases.

As previously reported, the synthesis of **1** is easily achieved using copper-mediated 'click chemistry' between a cellobiose propargyl amide derivative and an azido-terminated *atactic* poly(4-methyl-1-pentene) (N_3-aPMP) building block.[8] For production of the N_3-aPMP component, LCCTP of a fixed amount of 4-methyl-1-pentene, followed by a reactive work-up with molecular iodine (I_2) and standard substitution chemistry with sodium azide (NaN_3), provides an amorphous, aPMP microstructure of tunable number-average degree of polymerization, (DP_n), and very narrow molecular weight distribution with a polydispersity index, $Đ$ (= M_w/M_n), of < 1.1, where M_n and M_w are the number-average and weight-average molecular weight indices, respectively.[13,14] Due to the targeted ultra-low molecular weight of **1**, values for DP_n, M_n and $Đ$ are best determined by matrix-assisted laser desorption ionization (MALDI) mass spectrometry of the sugar-polyolefin conjugate product, rather than through typical gel-permeation chromatography (GPC).

During extended investigations, it was quickly determined that the thermotropic phase behavior of a particular sample of **1** was highly dependent, and sometimes in dramatic fashion, upon the values of M_n and $Đ$ that are established using different batches of N_3-aPMP for the synthesis. As an important example, which is

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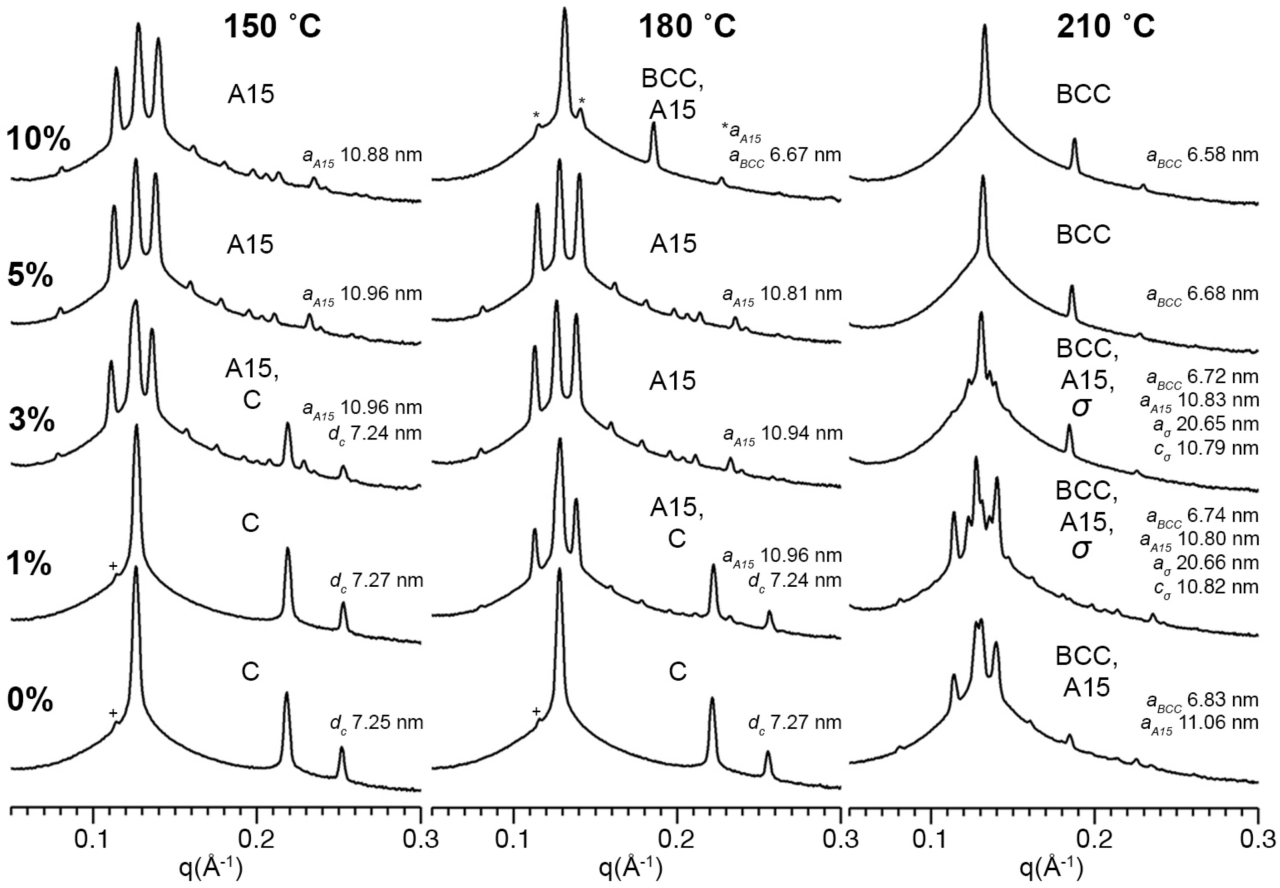

Fig. 2. Selected VT SAXS data for blends of CB-aPMP (**1**) with (from bottom to top) increasing weight percentage of vitamin E (**2**) and (from left to right) increasing temperature (see SI for complete data). The cylinder-to-cylinder distance, d_C for the C phase and the unit cell parameters for the A15, σ, and BCC phases are provided for each temperature and level of vitamin E incorporation. An anomalous scattering peak that appears alongside those for the C phase is marked with a plus (+) sign.

also the focus of the present study, the originally reported sample of **1**, with M_n = 1.4 kDa and $Đ$ = 1.05, was shown by variable temperature small angle x-ray scattering (VT SAXS) data to undergo the thermotropic C → A15 phase transition starting at 145 °C and providing a pure A15 phase upon reaching the upper temperature limit of 200 °C. Isothermal annealing of a bulk sample at 180 °C for 15 h was also sufficient to provide a pure A15 phase of **1** that remained unchanged upon cooling to room temperature and after extended storage under ambient conditions. In contrast, a new sample of **1**, which was produced with nearly the same molecular weight index, but a slightly narrower polydispersity (*cf.* M_n = 1.5 kDa and $Đ$ = 1.02), now failed to provide a pure A15 phase even after reaching the upper temperature limit according to the VT SAXS data provided in Fig. 2. More specifically, with no additive of any kind, a thermotropic C phase for **1** was observed for most of the temperature range sampled between 25 °C to 210 °C, and only at the highest temperature reached was an A15 phase obtained, but now as a mixture with a previously unencountered second phase.[16] Through indexing of the Bragg scattering peaks, the identity of this second phase of **1** was determined to be either simple cubic or BCC, with the latter being chosen based on precedent with block copolymers.[17]

Recognizing that extremely tight control over M_n and $Đ$ values at such a low DP_n value for N_3-aPMP would be challenging, if not impossible, to secure for reliably reproducing the phase behavior of different synthetic samples of **1**, we sought to develop an alternative strategy for this purpose. In this regard, it has been proposed, and computationally and experimentally verified, that blends comprised of an AB diblock copolymer and either a complimentary lower molecular weight homopolymer or an isostructural AB block copolymer with a shorter A block domain can be used to increase polydispersity of the composite material, and thereby, provide access to a wider range of FK phases that are formally based on different sized sets of spherical particles.[10b-f, 11a,f] On the other hand, this polymer blending strategy now requires solving the potentially even greater challenge of having to optimize synergistic interactions between multiple polymer components that are each still subject to the whims of synthetic variance in M_n and $Đ$ values.[18] Accordingly, we decided to explore the use of a *monomolecular weight* small molecule as a FK phase diagram modulator that could be reliably sourced in pure form and in commercially scalable volumes as required. Here, the bioactive lipophilic antioxidant **2** (see Fig. 1) appeared to be a good choice given the rich scientific literature available regarding its impact on the stability and phase behavior of lipid bilayers and self-assembling amphiphiles, including those developed for drug delivery systems.[19]

Fig. 2 presents a subset of results obtained from a VT SAXS investigation of the thermotropic phase behavior of blends of **1** prepared with 0%, 1%, 3%, 5%, and 10% by weight of **2**.[16] As can be clearly seen from these data, one of the most significant outcomes of blending **1** with increasing amounts of vitamin E was to lower all phase transitions for the system to the extent that a pure A15 phase could now be accessed at a temperature as low as 120 °C for a 10% blend (see Fig. S4D), and a pure BCC phase could be obtained at 210 °C for both 5% and 10% blends. Surprisingly, a significant effect on thermotropic phase behavior

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was achieved at even the lowest 1% level of incorporation of **2** in a blend with **1**. Most notably, at 210 °C, triple coexistence occurs for A15, BCC, and yet another new phase, which was identified as being the FK σ phase through a successful indexing of the associated Bragg scattering peaks for this structure (see Fig. 1 and Fig. S5). As Fig. 2 further reveals, a similar triple coexistence of these three phases persists at 210 °C for a 3% blend, but now with an increase in BCC relative to both the A15 and σ components. To the best of our knowledge, these results provide the first example of the triple coexistence of thermotropic phases based on different formal spherical particle packing schemes for a soft matter FK system.

A simple first-order analysis based on the experimentally derived unit cell parameters provided in Fig. 2 for the 1% blend at 210 °C was used to establish the volume-occupied-per-spherical-particle for each of the coexisting phases to be 157 nm^3 for A15 (8 particles), 154 nm^3 for σ (30 particles) and 153 nm^3 for BCC (2 particles). This apparent shrinkage in spherical micelle volume in the order A15 < σ < BCC is in keeping with an increase in conformational disorder of the aPMP chains that results in a longitudinal contraction and lateral expansion in the average shape of the hydrophobic domain.[20] It is also possible that the more complex FK σ phase observed for the 1% and 3% blends of **1** and **2** at 210 °C is either an intermediate state involved in a discrete A15 → [σ]→ BCC order-order transition, or it is simply a manifestation of thermal equilibration of molecular and spherical particles that occurs between nearly degenerate states at this temperature. A definitive answer to this question of relative stability awaits production and investigation of a pure FK σ phase for a blend of **1** and **2** that can likely be secured through further optimization of blend ratio, temperature, and M_n and $Đ$ values. However, it is already apparent that each of the three phases, A15, σ, and BCC, arise through order-order transitions that occur at temperatures well below the order-disorder transition temperature of the system, which is, in fact, never reached due to high temperature constraints imposed by decomposition of **1** that occurs above 210 °C. In this respect, the thermotropic phase behavior displayed by blends of **1** and **2** is reminiscent of that reported for one-component dendritic liquid crystals in which the occurrence of reversible C ↔ A15 and A15 ↔ BCC order-order transitions have been established.[3c,h] On the other hand, the present strategy of using programmed small molecule modulation as a means by which to access unique thermotropic soft matter FK phases under moderate conditions and within short timeframes is without precedent. Successful extension of this paradigm to other FK phase-forming soft materials is highly likely, and here it could provide an attractive alternative to methods being employed with block copolymers and blends of block copolymers that rely on empirically-driven thermal processes that involve long isothermal annealing times and mass transfer of polymeric components within the melt or disordered state to secure various soft matter FK and dodecagonal quasi-crystal (DDQC) phases.[2,4,11] As a final consideration, for the full utility of small molecule modulation as a strategy for obtaining soft matter FK phases to be realized, the specific role(s) played by **2** in the present system must be unequivocally determined. At this stage, it is reasonable to assume that **2** resides within the aPMP domain of **1**, and potentially, with the methylated phenol moiety preferentially located near the sugar-polyolefin interface. Surprisingly, however, the unit cell parameters shown in Fig. 2 for the various phases of the blends of **1** and **2** remain essentially invariant to the level of incorporation of the small molecule modulator. To account for this observation, we currently favor a model in which **2** serves to swell the aPMP domain through an increase in density that, on average, formally stabilizes what would be higher energy conformational polymer chain configurations at lower temperatures. It nonetheless remains remarkable that such a small level of incorporation of **2** at 1% can have such a major impact on the phase behavior of **1**, and that such a relatively high level of incorporation at 10% can still be accommodated without completely disrupting order at the highest temperatures sampled.

In summary, the results of this preliminary study demonstrate that small molecule modulation can be an effective strategy for accessing novel and non-canonical FK phases of sugar-polyolefin conjugates of increased structural and functional complexity. Extension of this paradigm to provide control over the phase behavior of other FK-phase-forming classes of materials should be possible, and it avoids some of the complications that arise with other current strategies. Finally, proof that **2** and other functionally competent small molecule modulators can be incorporated at high levels of loading without disrupting periodic order under various conditions presents a new opportunity to use this strategy to purposefully add function to form in soft matter FK phases. Additional research along these lines in currently in progress.

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Experimental Section

Complete experimental details are provided in the Supporting Information.

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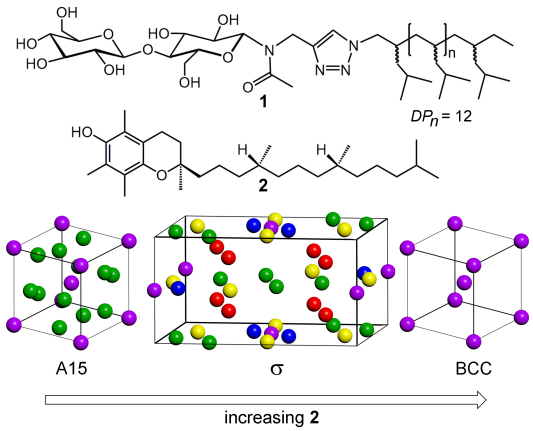

Incorporation of small amounts of α-tocopherol (vitamin E) (**2**) in blends with the cellobiose-triazole-linked *atactic* poly(4-methyl-1-pentene) (CB-aPMP) sugar-polyolefin conjugate (**1**) can be used to exert external control over thermotropic phase behavior and provide access to non-canonical soft matter Frank-Kasper A15 and σ phases, as well as a novel BCC phase. These results establish a new paradigm that can be used for the further design and development of scalable quantities of soft matter FK phases of increased structural complexity and functional capability.