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Solvent induced supramolecular anisotropy in molecular gels

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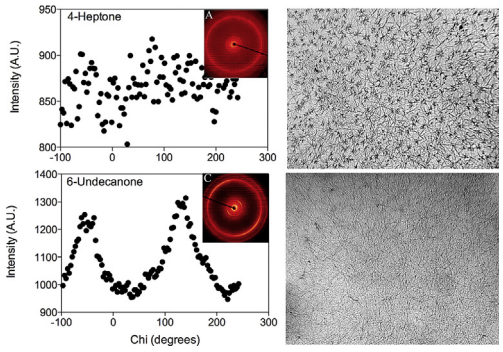
HIGHLIGHTS

- 12-HSA self-assembles into crystalline supramolecular morphologies depending on the solvent.
- Alkanes, short chain nitriles and ketones led to 12-HSA displaying supramolecular isotropy.
- In long chain nitriles and ketones, 12-HSA displays supramolecular anisotropy.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein is the first report of solvent induced anisotropy in 12-hydroxystearic acid self-assembled fibrillar networks. Increasing the chain length of polar solvent, such as nitriles and ketones, tailored the anisotropy of the fibrillar aggregates. 12HSA molecular gels, comprised of alkanes, exhibited an isotropic fibrillar network irrespective of the alkane chain length. In polar solvents, anisotropy, observed using 2D powder x-ray diffraction profiles, is correlated to a fibrillar supramolecular morphologies in long chain nitriles and ketones while sphereulitic crystals are correlated to x-ray diffraction patterns with an isotropic scatter intensity in short chain ketones and nitriles. These changes directly modify the final physical properties of the gels.

1. Introduction

Molecular self-assembly, a form of 'bottom-up' nanofabrication, constructs materials with precision to construct supramolecular structures assembled molecule-by-molecule, where the coding for assembly is embedded in the structural motifs of the molecule [1]. The coding is based on chemical complementarity and structural compatibility, facilitating weak non-covalent interactions to stabilize the hierarchical resultant structures [1]. Low molecular weight organogelators (LMOGs) self-assemble into fibrillar networks (SAFiNs) via non-covalent interactions including: hydrogen bonding [2], π-π stacking [3], dipole-dipole interactions [2], and van der Waals interactions [4]. In SAFiNs, a meticulous balance between divergent parameters that govern solubility and intermolecular interactions drive epitaxial growth, is required [5,6]. Structural aspects of the gelator [7,8] and solvent [6,9,10] have been

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exhaustively studied to understand the molecular controls that regulate self-assembly into molecular gels.

During the self-assembly of LMOGs, changing the solvent induces polymorphic nanoscale modifications to the SAFiN [6], and alters the supramolecular structure [5,9,10]. Solvent polarity effects numerous properties of the SAFiN including but not limited too: the branching rate [11–15], fiber thickness [10], sense of helical twist [16–18] and fiber-fiber interactions [12]. The microscopic changes alter the macrostructures of these gels (i.e., crystallinity, hardness and opacity). Herein, a previously unknown phenomenon, that certain solvents induce a supramolecular anisotropy, resulting in the alignment of crystalline 12 hydroxystearic (12HSA) fibers in molecular gels, is reported.

Crystal and polymer physics have long been concerned with the ability of supramolecular aggregates to align in the presence of external shear and electrostatic fields [19–24]. The anisotropic alignment of fibers is desirable in cell scaffolds [25,26], solar cells [27,28], and tissue engineering [29]. The transition from an anisotropic to an isotropic SAFiN allows the mechanical [29], and electrical [30] properties to be engineered. Specifically, aligned fibers tend to have modified mechanical properties when employed as a biodegradable nanofibrous scaffolds for the tissue engineering [29]. Modifying solvent chemistry is a simple tool that could be used to aligned self-assembled fibers in molecular gels.

2. Methods

2.1. Materials and sample preparation

Alkanes (hexane, octane and dodecane), ketones (4-heptone, 5-nonanone, and 6-undecanone) and nitriles (propanenitrile, hexanenitrile, heptanenitrile, and nonanenitrile) were used to disperse R-12-hydroxystearic acid (12HSA). Solvents and 12HSA were obtained from Sigma-Aldrich (Cherry Hill, NJ, USA) with purity greater than 0.95%. 4 ml glass vials capped with PTFE lined lids (VWR, Randor, PA) were used to produce 2 wt% 12HSA dispersed in each solvent. The dispersions were placed in a hot water bath set at 95 °C for 20 min until dissolution occurred. After the sol appeared clear, it was removed from the water bath and stored for 24 h at 20 °C until further analysis. The critical gelator concentration was determined by combining 12HSA and solvent at 0.1 wt% intervals and inverting the vial for 1 h to observe flow. If no flow was detected, it was classified as a gel. Advanced rheological techniques could not be performed due to the volatility of the solvent which prevented the formation of the organogels in the mould, used to transfer the gel onto the rheometer, without significant solvent evaporation.

2.2. Optical brightfield microscopy

2 wt% 12HSA organogels were placed on 25 × 75 mm x 1 mm glass slides (Fisher Scientific, Pittsburgh, PA, USA) and were compressed with 22 × 22 mm x 0.15 mm glass cover slips (Fisher Scientific, Pittsburgh, PA, USA). The slides was transferred into a peltier temperature control stage (LTS120, Linkham, Surrey, England), heated to 90 °C and then were slowly cooled to 20 °C at 2 °C/min to observe the supramolecular structure using non-polarized light. Images were acquired using a Linkham imaging station (Linkham, Surrey, England) equipped with a Q imagining 2560 × 1920 pixel CCD camera (Micropublisher, Surrey, Canada) and a 10× Olympus lens (0.25 N.A.) (Olympus, Tokyo, Japan).

2.3. X-ray diffraction

2 wt% 12HSA organogels were loaded into 1 mm silica capillaries and flame sealed. The capillaries were placed into an Enraf-Nonius

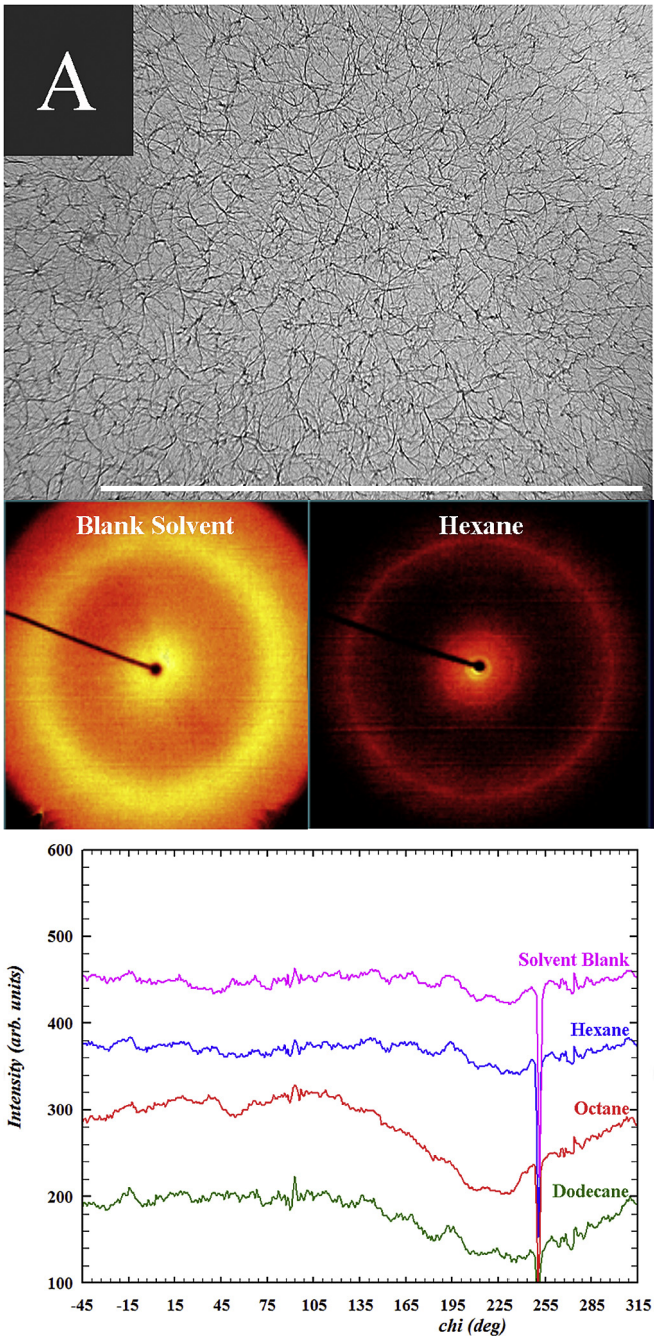

Fig. 1. Polarized light micrographs and intensity profiles versus orientation angle of 2 wt% gels of 12HSA in A) hexane. The scale bar is 100 μm 2-D XRD patterns for a solvent blank and 2 wt% HSA in hexane gel in which intensity vs. chi plots were obtained.

FR571 rotating anode x-ray generator equipped with Rigaku Osmic mirror optic system (~0.06 deg 2q nominal dispersion for Cu Ka; l = 1.5418 Å) and a Bruker HiStar area detector operating at 40 kV and 40 mA. The x-ray diffraction (XRD) or wide-angle x-ray scattering (WAXS) patterns of 12HSA gels were collected at room temperature over a period of 300 s. The sample to detector distance was 10.0 cm and the standard spatial calibration was performed at that distance. Scans were 4 deg wide in omega (w) with fixed detector, or Bragg, angle (2q) of 0 deg, and fixed platform (f and c) angles of 0 and 45 deg, respectively. The beam diameter for the 1 mm capillary and transmission geometry used, was