

# Shaping self-assembling small molecules into fibers by melt electrospinning

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## Experimental Methods

### *Materials*

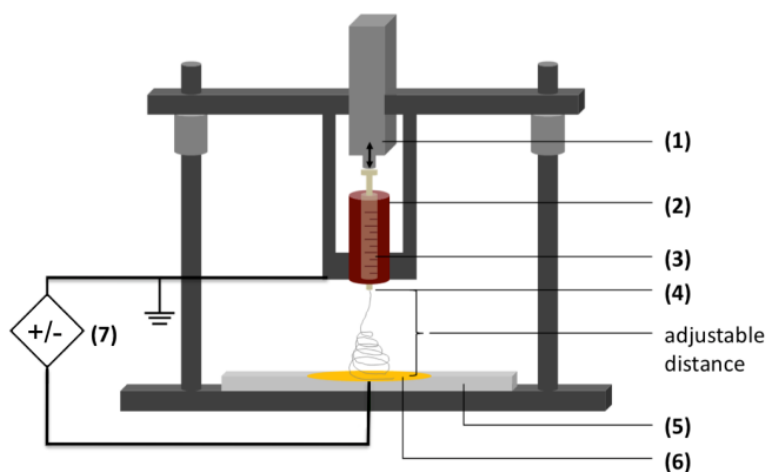
1,3,5-Cyclohexane- and 1,3,5-benzenetrisamides **1-3** were synthesized according to reference 16 and 17. The molecular weight of **1** is 634 g/mol, and of **2** and **3** 460 g/mol. The melting temperature of **3** was determined in a Perkin Elmer Diamond DSC (heating rate: 10 K/min, nitrogen flow: 20 mL/min). Temperature weight loss measurements of **1-3** were performed using a Mettler SDTA 851 TGA at 10 K/min (nitrogen flow: 60 mL/min). **1** shows a 10%-weight loss at 382°C, **2** at 390°C, and **3** at 379°C due to evaporation and not decomposition indicated by a 100% weight loss without any char yield.<sup>16</sup> In isothermal TGA runs at the spinning temperature under nitrogen atmosphere, **1-3** showed evaporation weight loss below 5 wt.% for at least 30 minutes which is much less than the typical time (15 min) for an electrospinning experiment. For each temperature a new sample and syringe was used.

### *Electrospinning and Characterization*

For melt electrospinning a custom designed equipment was utilized (**Figure S1**). An 1 mL glass syringe (3) (Poulsen & Graf, Fortuna Optima, luer glass tip) with a shortened (length: 1 mm) hypodermic 20G needle is placed in an electrically heated block (2) which temperature can be set up to 350°C with a fluctuation of  $\pm 0.5^\circ\text{C}$  at 250°C. The reported spinning temperature is the temperature of the heated cylinder around the syringe body. The temperature at the needle tip is max. 5 % lower. The plunger of the syringe is driven via a piston, equipped with a pressure transducer, by a precision motor and gear system (1). The entire drive unit can be tilted by 90° and thus the syringe can be easily replaced. Reversely to the most common design for electrospinning, in this setup the syringe needle and consequently all attached electronic components are earthed.<sup>3b,8</sup> The high voltage (HV) power supplies (7) (Schulz Electronic, high voltage units AK0175 and AK1026, +60 and -60 kV,

respectively) were connected to the collector plate (6) in the base plate (5) below the needle (4).

**Figure S1.** Drawing and details of the melt spinning equipment.

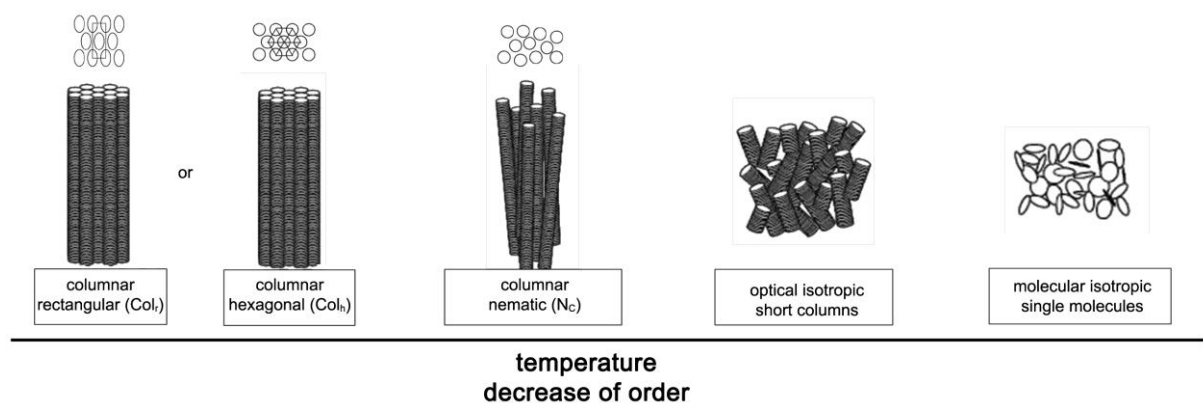


(1) drive unit: DC motor, gear, and pressure transducer, (2) band heater, (3) glass syringe with plunger, (4) metal hollow needle, (5) base plate (Teflon<sup>®</sup>), (6) collector plate/HV electrode, (7) HV supply max.  $\pm 60$  kV.

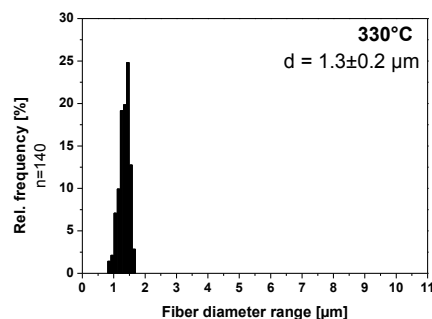
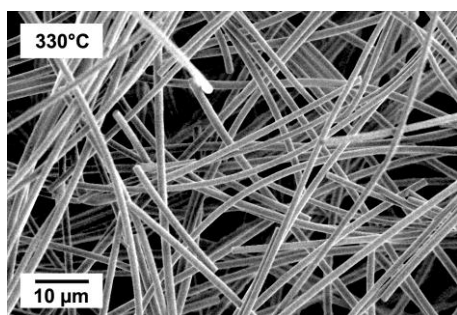
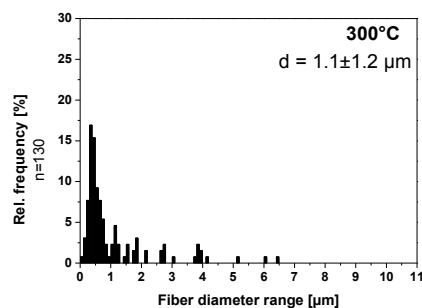
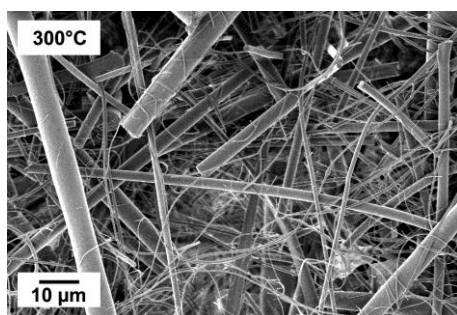
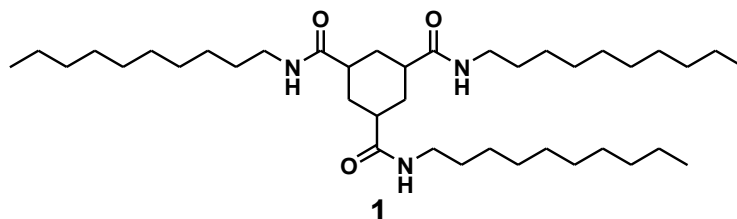
The maximal distance between needle tip and collector is 14 cm, and the feeding rate for a 1 mL syringe can be set from 20 to 1500  $\mu\text{L/h}$  by adjusting the plunger speed. In many preceding spinning experiments the influence of flow rate, needle ID, and distance needle tip-ground plate were optimized, and kept at 200  $\mu\text{L/h}$ , 0.6 mm, and 6 cm, respectively. Before applying HV, each sample was equilibrated for three minutes at the spinning temperature and flow rate. The electrospun material was collected on a single 12 mm diameter aluminum SEM stub which was mounted on the collector plate. To investigate the surface morphology, the stub was sputtered with platinum (2.0 nm) in a Cressington sputter coater 208HR and imaged in a SEM Zeiss LEO 1530 FESEM (Zeiss, Jena, Germany) at 1.5 to 3 keV. From SEM images the thickness distribution from at least 100 individual fibers or spheres was evaluated using AxioVision LE Software (Carl Zeiss AG, Germany). The histograms for all thickness distributions are listed in **Figure S3** to **S5**.

**Figure S2.** Illustration of loosing order with increasing temperature in a discotic mesophase and optical isotropic melt of trisamides.

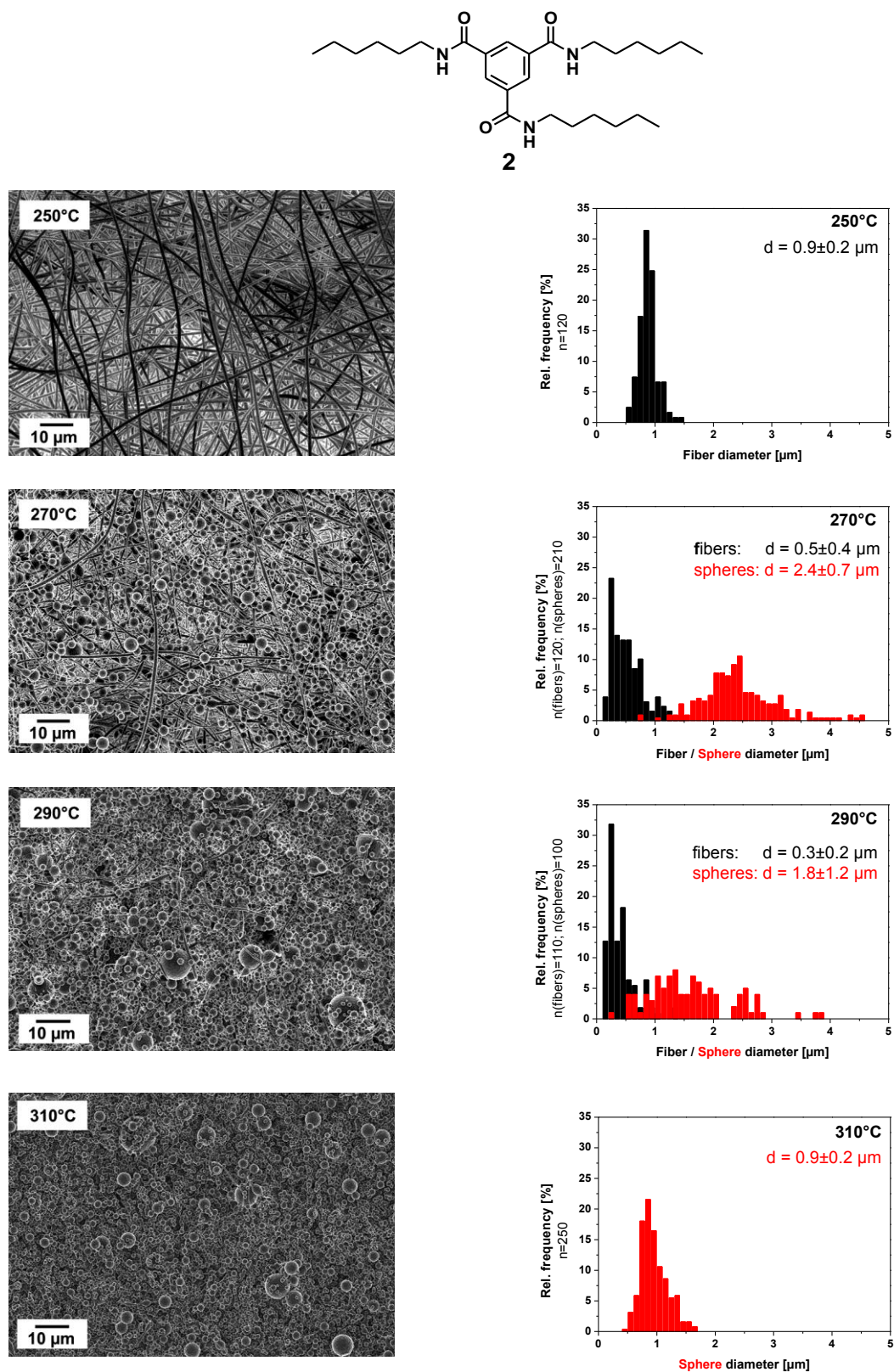
In general for discotic mesophases, the order of the liquid crystalline phases decreases with temperature.[see reference 17, and for instance, S. Laschat et al., *Angew. Chem. Int. Ed.*, 2007, **46**, 4832.] Please note that typical and characteristic for trisamides, the isotropic phase still consists of shorter columns but without birefringence, thus called optical isotropic. At higher temperatures the interaction between individual molecules in form of hydrogen bonds is lost resulting in molecular isotropic, single molecules.



**Figure S3.** SEM images and fiber histograms of **1**, electrospun as function of the spinning temperature. At 300°C the compound exhibits a nematic mesophase, at 330°C, above the clearing temperature at 317°C, an isotropic melt is formed. Spinning parameters: voltage: -40 kV, flow rate: 200  $\mu\text{L/h}$ ; distance needle tip – ground plate: 6 cm; needle ID: 0.6 mm.

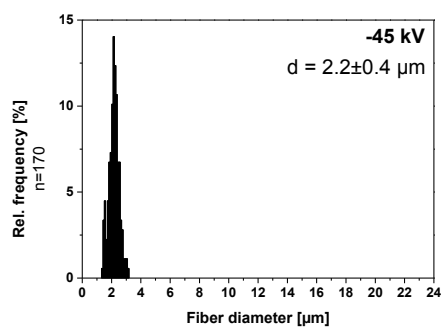
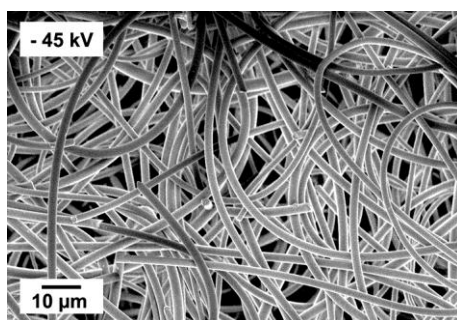
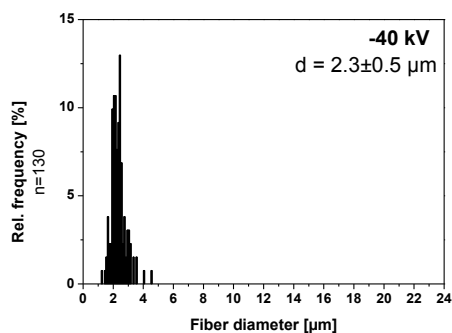
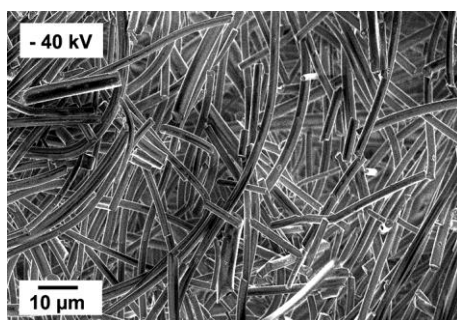
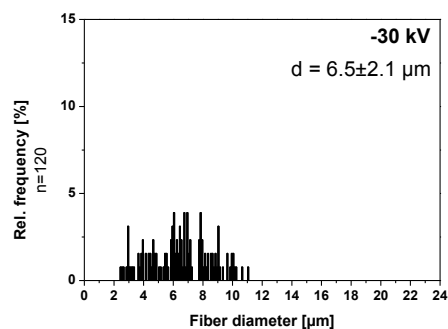
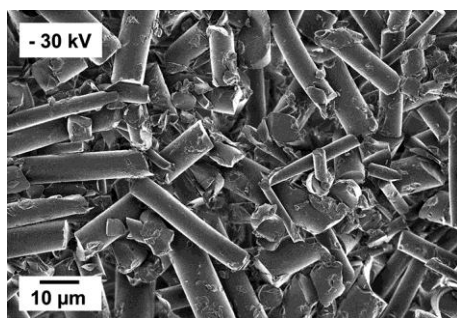
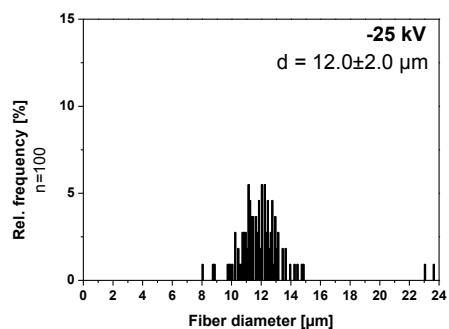
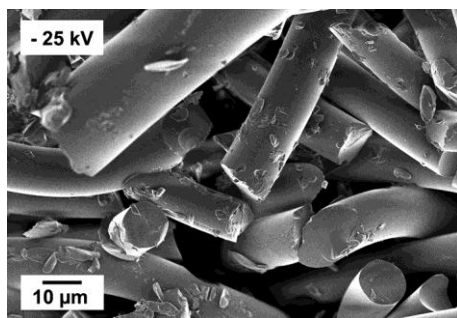
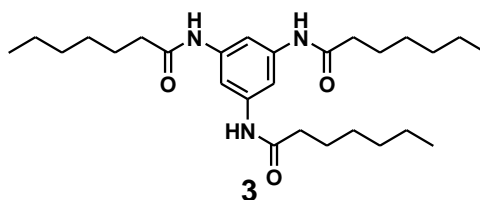


**Figure S4.** SEM images and fiber/sphere diameter histograms of **2**, electrospun as function of the spinning temperature in the optical isotropic melt. Spinning parameters: voltage: -30 kV; flow rate: 200  $\mu\text{L/h}$ ; distance needle tip – ground plate: 6 cm; needle ID: 0.6 mm.





**Figure S5.** SEM images and fiber diameter histograms of **3** as function of the electric field strength at 200°C in the optical isotropic melt. Spinning parameters: temperature: 200°C; flow rate: 200  $\mu\text{L/h}$ ; distance needle tip – ground plate: 6 cm; needle ID: 0.6 mm.



**Figure S6.** Melt viscosity as function of the temperature of compound **2** for the first cooling run at 2K/min. During cooling, at 207°C the viscosity of the melt dramatically soars during 10 K. Note, that the transition temperatures determined with DSC (Scheme 1) and melt rheology of compound **2** differ by approx. 10 K. (Measured in a CVO150 rheometer (Malvern, Germany) using an oscillating (1 Hz) cone-plate geometry (2.5°/25 mm) at a cooling rate of 2K/min)

