COMMUNICATION

Shaping self-assembling small molecules into fibres by melt electrospinning†

Julia C. Singer, Reiner Giesa and Hans-Werner Schmidt*

Self-assembling small molecules is considered a promising technology for fabricating micro- and nanosized features. Utilization of typical top-down approaches, such as electrospinning, is rare in combination with self-assembly. Here we report for the first time on melt electrospinning of 1,3,5-cyclohexane- and 1,3,5-benzenetrisamides into fibres. The fibre spinning conditions were investigated with respect to the type of mesophase and applied field strength. It is possible to electrospin fibres from the nematic liquid crystalline phase and, most surprisingly, also from the optical isotropic state slightly above the clearing temperature, but not from columnar LC phases. Under optimized conditions it is possible to prepare homogeneous fibres with diameters below 1 μm.

The formation of micro- and nanosized polymer fibres is realized commonly by typical top-down approaches including techniques such as melt blow spinning,[1] centrifugal spinning,[2] or electrospinning.[3] An alternative strategy yielding fibres in the same size range is self-assembly of small molecules as a typical bottom-up approach.[4] Here we report on the combination of both processes by employing electrospinning and self-assembly from the melt of small molecules.

Among top-down approaches, solution electrospinning became a straightforward and versatile fibre spinning technique for polymers.[3,5] In this process, charges are induced to a solution of a high molar weight polymer in the presence of a strong electric field. Due to polymer chain entanglements, breakup into droplets is not observed but a stable jet is formed when electrostatic repulsive forces on the fluid surface overcome the surface tension. For small low molecular weight molecules electrospraying into small spherical droplets is the result. As it was pointed out by Long *et al.*, a high molecular weight polymer is not actually essential for obtaining uniform electrospun fibres from solution. The primary criterion is the presence of sufficient intermolecular interactions which function similar to chain entanglements.[6] Only a few examples are reported where self-assembling small molecules have been electrospun from solution into fibres, for instance phospholipids,[6–8] surfactants,[9] cyclodextrins,[10] ureido-

pyrimidinone moieties,[11] diphenylalanine,[12] or heteroditopic monomers.[13] Long *et al.* reported also the first case where melt electrospinning at 200 °C of a low molecular weight amphiphilic phospholipid, forming long range aggregates, rendered fibres in the range of 6 μm.[8]

1,3,5-Cyclohexane- and 1,3,5-benzenetrisamides are an important class of self-assembling low molecular weight compounds. The mechanism of self-aggregation of this class of organic compounds into supramolecular structures is well established. Due to strong intermolecular interactions in the form of hydrogen bonds of three amide groups self-assembling takes place to form supramolecular structures such as fibres and networks, and can also induce solvent gelation.[14–16] Depending on the core structure and substituents, trisamides exhibit a complex mesophase phase behavior in the melt.[17–19] It was also shown that compounds of this class of organic molecules form macrodipoles due to columnar stacking.[17,20,21] This was utilized for electric-field assisted alignment of 1,3,5-cyclohexanetrisamides,[22] or remnant polarization studies of thermotropic 1,3,5-benzenetrisamides.[21] Furthermore, solution electrospinning of a liquid crystalline, α-helical poly(α-amino acid) with macroscopic dipoles prealigned in the direction of the helical axis resulted in materials with high thermally stable piezoelectric coefficients.[23] Trisamides were also employed in our group as supramolecular polymer additives to improve the charge storage capability of polypropylene as electret materials.[24] These results were our motivation to explore electrospinning of this class of compounds from the melt. Candidates presented in this communication were selected from a large pool of substances matching certain phase behavior and temperature criteria. Different mesophases and an isotropic melt should be in the experimentally accessible temperature range up to 330 °C, detailed experimental methods are included in the ESI.†

To demonstrate the general electrospinnability of this class of low molecular weight compounds, one 1,3,5-cyclohexane- (**1**) and two types of 1,3,5-benzenetrisamides (**2** and **3**) were selected differing in direction of the linkage of the amide groups to the core and core structure itself. Scheme 1 summarizes chemical structures, phase transition temperatures, type of mesophase, applied spinning temperatures and thermal stability of **1–3**. Compounds **1** and **2** exhibit liquid crystalline (LC) phases, denoted as $Cr_1 117 Cr_2 167 Col_{rp} 254 N_c 317 I$ and $Cr 72 Col_{hp} 172 Col_{ho} 218 I$, respectively.[17] Explicitly, **1** forms a columnar rectangular plastic mesophase (Col$_{rp}$) between 167 °C and 254 °C followed by a nematic phase (N$_c$) up to 317 °C.

Macromolecular Chemistry I, Bayreuth Institute of Macromolecular Research (BIMF), and Bayreuth Center for Colloids and Interfaces (BZKG), University of Bayreuth, 95440 Bayreuth, Germany. E-mail: hans-werner.schmidt@uni-bayreuth.de; Fax: +49 (0)921 553206; Tel: +49 (0)921 553200
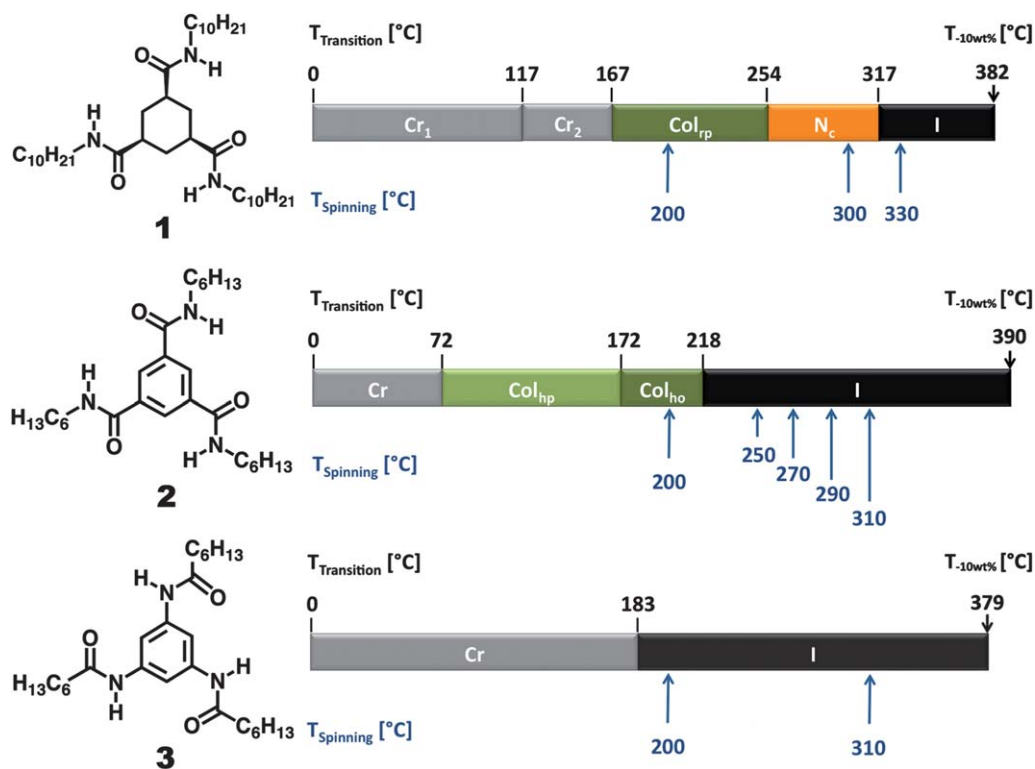
Scheme 1 Representative trisamides subjected to melt electrospinning with phase transition temperatures, type of mesophase, temperature of 10 wt% loss, and the investigated spinning temperatures (vertical arrows) (Cr: crystalline, Col: columnar mesophase, h: hexagonal, r: rectangular, p: plastic crystalline, o: ordered liquid crystalline, N_c: columnar nematic).

Compound **2** forms a columnar hexagonal plastic phase (Col_{hp}) starting at 72 °C, transforming into a columnar hexagonal ordered phase (Col_{ho}) at 172 °C, and changes at 218 °C into an isotropic melt. An exhaustive identification and characterization of all mesophases are reported elsewhere,[17] and the sequence of losing order in discotic mesophases and isotropic phases of trisamides with increasing temperature, which has a direct impact on the melt electrospinning results, is illustrated in Fig. S2 (ESI†). Finally, compound **3** exhibits no mesophase and melts at 183 °C.

In the following, we will discuss fibre morphologies obtained as a function of core structure, spinning temperature, and applied electric field strength. Compound **1**, a derivative of cyclohexane-*cis,cis*-1,3,5-tricarboxylic acid, exhibits a columnar rectangular (Col_{rp}) and a columnar nematic (N_c) phase (Scheme 1), but our efforts to electrospin **1** at 200 °C from its Col_{rp} phase failed due to the high viscosity of this mesophase impeding the elongation and deformation of the droplet at the tip. Instead, a translucent soft strand was extruded at high pressure. In general, nematic phases are less viscous than columnar phases because of reduced secondary interactions.[25] Due to the lower viscosity of the N_c phase, compound **1** was successfully electrospun at 300 °C and, most surprisingly, also from the optical isotropic melt at 330 °C, as illustrated in Fig. 1. Very homogeneous and long fibres with a narrow size distribution of 1.3 ± 0.2 μm were collected at 330 °C. A larger variety of diameters (histograms are included in Fig. S3–S5†) were observed for fibres electrospun from the nematic phase at 300 °C, indicating a more heterogeneous spinning process.

Compound **2**, based on trimesic acid with *n*-hexyl substituents, exhibits a columnar hexagonal plastic (Col_{hp}) and a hexagonal
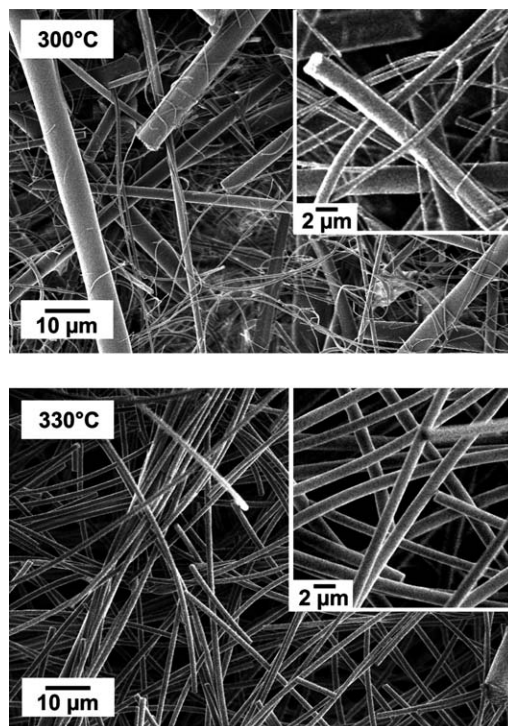

Fig. 1 Comparison of SEM images of melt electrospun fibres of **1** from the nematic phase at 300 °C and optical isotropic phase at 330 °C. In both cases fibre formation is observed, fibres from the isotropic melt are thinner and more homogeneous (spinning conditions: voltage: −40 kV, flow rate: 200 μL h^{-1}, distance needle tip–ground plate: 6 cm, needle ID: 0.6 mm).
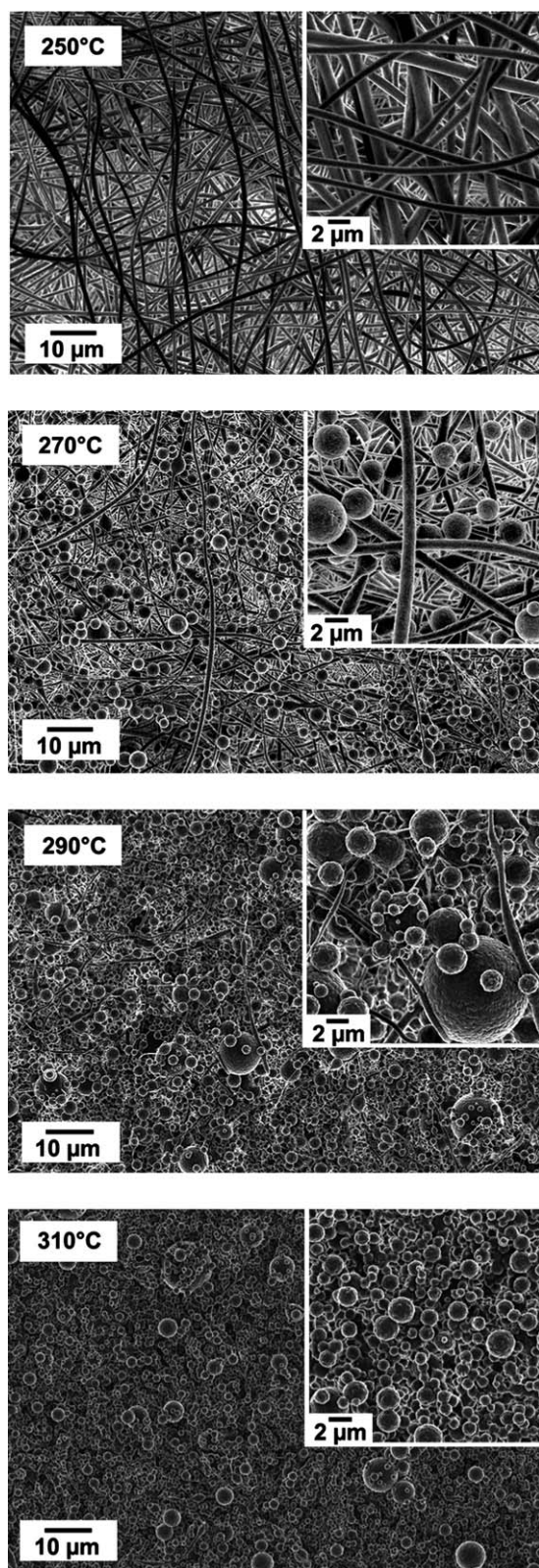
Fig. 2 SEM images of melt electrospun fibres and spheres of **2** as a function of the spinning temperature in the optical isotropic melt. Progressing sphere formation is observed with increasing spinning temperature due to the decreasing H-bond interactions between the molecules (spinning parameters: voltage: −30 kV, flow rate: 200 μL h^{-1}, distance needle tip–ground plate: 6 cm, needle ID: 0.6 mm).

ordered (Col$_{ho}$) mesophase. Our efforts to electrospin **2** at 200 °C from the Col$_{ho}$ phase also failed due its high viscosity. The melt viscosity of **2** as a function of temperature is plotted in Fig. S6† and the viscosity of the Col$_h$ mesophases (10 Pa s) is two magnitudes higher compared to the very fluid optical isotropic phase. The unexpected result that occurred during melt electrospinning of **1**, fibres are also formed from the optical isotropic melt, motivated us to study the influence of spinning temperature on fibre morphology in this phase. Compound **2** is most suitable, since it possesses a broad isotropic phase of around 170 K permitting electrospinning even at 310 °C (Scheme 1). At 250 °C, approx. 30 K above the clearing temperature of 218 °C, **2** was melt electrospun into homogeneous, continuous fibres with a narrow diameter size distribution of 0.9 ± 0.2 μm (Fig. 2). At 270 °C, the fibre diameter decreases to 0.5 ± 0.4 μm and concurrently spheres with a diameter of 2.4 ± 0.7 μm appear. At 290 °C, spheres with an average diameter of 1.8 ± 1.2 μm dominate, whereas the diameter of the few visible fibres reduces to 0.3 ± 0.2 μm. Finally at 310 °C, no fibres and only spheres with a diameter of 0.9 ± 0.2 μm are observed.

The fibre formation even from the optical isotropic melt is very extraordinary and a unique consequence of the supramolecular structure of trisamides. In a temperature range above the transition from the mesophase into the optical isotropic phase, columnar aggregates are still present. This was confirmed by temperature-dependent X-ray diffraction and FTIR investigations.[17] Due to these supramolecular columns, fibre formation is still observed slightly above the clearing temperature. It is feasible that these individual columns of 1,3,5-cyclohexane- and 1,3,5-benzenetrisamides build up a macrodipole,[17,20,21] which in return interacts with the applied electric field. At higher temperatures (for instance at 310 °C) the columnar pre-aggregates, which we consider essential for fibre formation, are reduced in length or completely absent, and only sphere formation is observed.

Compound **3**, based on 1,3,5-triaminobenzene, does not exhibit any LC mesophases and only a melting point at 183 °C. In Fig. 3 the results for electrospinning experiments at 200 °C at different electric field strengths are depicted. The fibre morphologies observed for **3** prove that the existence of a mesophase at lower temperatures is not a prerequisite for fibre formation from the optical isotropic melt. At a low electric voltage (−25 kV), short and thick fibre fragments with an average diameter of 12.0 ± 2.0 μm were collected. At increasing voltage, the diameter of the fragments decreases from 6.5 ± 2.1 μm (−30 kV) to 2.3 ± 0.5 μm (−40 kV) by elongating the fragments to fibres. At −45 kV homogeneous and thin fibres (2.2 ± 0.4 μm) were observed.

Hence, a stronger electrical field is necessary to form long and homogeneous fibres from the melt droplets by inducing additional charges. This phenomenon is also known for several polymers in melt or solution electrospinning.[26]

Additional spinning experiments with **3** at 310 °C and −45 kV revealed besides fibers (0.5 ± 0.3 μm) sphere formation (2.1 ± 1.5 μm, not shown) similar to compound **2** in Fig. 2.

Conclusions

In this communication we demonstrated for the first time that columnar supramolecular structures of self-assembling 1,3,5-cyclohexane- and 1,3,5-benzenetrisamides can be melt electrospun from the nematic LC phase and, most surprisingly, even from the optical
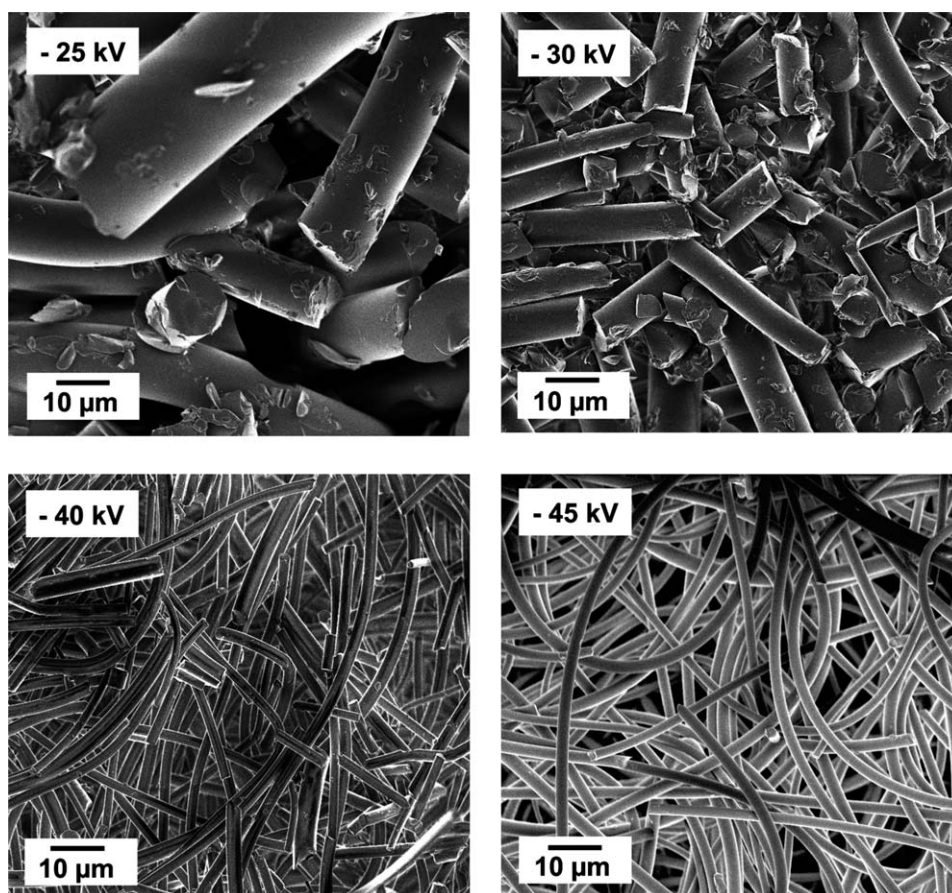
Fig. 3 SEM images of melt electrospun fibres of **3** spun at 200 °C as a function of the electric field strength. Thick fragments are obtained at low field strengths, elongation with increasing field strength to homogeneous long and much thinner fibres is observed (spinning conditions: temperature: 200 °C, flow-rate: 200 μL h^{-1}, distance needle tip–ground plate: 6 cm, needle ID: 0.6 mm).

isotropic melt. Other liquid crystalline phases were too viscous to be electrospun. In future work we will evaluate the nano-mechanical properties[27] of melt electrospun fibres and assess their potential for instance in filters and piezoelectric applications.

Acknowledgements

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