

SUPPORTING INFORMATION

Electrospun gamma-cyclodextrin (γ -CD) nanofibers for the entrapment of volatile organic compounds

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Experimental

Materials

The gamma cyclodextrin (γ -CD) was supplied from Wacker Chemie AG (Germany) commercially. Dimethyl sulfoxide (DMSO) (Sigma-Aldrich, 99.9%), aniline (Sigma-Aldrich, 99%), toluene (Sigma-Aldrich, $\geq 99.5\%$) and *d*6-DMSO (Merck) were purchased. The de-ionized water was used from the Millipore Milli-Q Ultrapure Water System. All the materials were used without any purification.

Electrospinning of γ -CD nanofibers

The highly concentrated solutions of γ -CD were prepared by using dimethyl sulfoxide (DMSO)/water (50/50, v/v) solvent mixture system. The electrospinning of these solutions were performed from 120% (w/v) to 140% (w/v) γ -CD concentrations and bead-free γ -CD nanofibers were obtained at 140% (w/v) concentration. The effect of urea on the fiber formation was investigated by adding 20% urea (w/w, with respect to γ -CD) into the optimized concentration (140% (w/v)) of γ -CD solution. Each time, the clear γ -CD solution was loaded into a syringe having metallic needle with 0.6 inner diameter and the syringe was horizontally positioned onto the syringe pump (Model: SP 101IZ, WPI). The high voltage power supply (Matsusada Precision, AU Series) was used for the electrospinning. The electrospinning parameters were determined as; applied voltage: 15 kV, tip-to-collector distance: 10 cm and the solution flow rate: 1 mL/h. The electrospinning was carried out in a closed Plexiglass box at 25 °C and 25% relative humidity conditions.

Measurements and characterizations

The rheometer (Anton Paar Physica MCR 301) equipped with cone-plate configuration (spindle type CP40-2) was used for the rheology study of γ -CD solutions. The shear rate

sweep and frequency sweep oscillatory tests were carried out at the range of 0-100 s⁻¹, 0-10 Hz, respectively. Moreover, the linear viscoelastic region was determined as 0.01 % strain value for the viscoelastic property measurements. For the solution conductivity measurements of γ -CD solutions, multiparameter meter InoLab-Multi 720 (WTW) was used at room temperature. The morphological characterization of nanofibers was performed by scanning electron microscope (SEM) (Quanta 200 FEG, FEI) and all samples were sputtered with 5 nm Au/Pd (PECS-682) for the imaging. The average fiber diameter (AFD) was calculated from the SEM images by analyzing at least 100 fibers. X-ray diffraction pattern of as-received γ -CD powder and γ -CD nanofibers were determined by X-ray diffractometer (XRD) (X'Pert powder diffractometer, PANalytical) with Cu K α radiation in the $2\Theta=5^\circ$ - 30° range. The γ -CD nanofibers were also investigated by transmission electron microscope (TEM) (FEI-Tecnai G2F30). For TEM imaging, HC200 TEM grids were attached on the aluminum foil and the samples were collected on the grids. Brunauer–Emmett–Teller (BET) surface area analyzer (Quantachrome, IQ-C model) was used to calculate the surface area of the γ -CD powder and γ -CD nanofibers. Nitrogen adsorption isotherm data were collected at 77 K in the range of 0.00–1.00 relative pressure. Prior to analysis, γ -CD powder and nanofibers were located into 9mm cell and degassed for 12 h at 373K.

Entrapment of organic vapours by γ -CD nanofibrous web

The molecular entrapment capability of γ -CD nanofibers was investigated by exposing them to the aniline and toluene vapours. For this experiment, 10 mL of aniline or toluene were put into glass Petri dishes and placed at the bottom of the desiccator (30 cm (diameter) and 30 cm (height)). Then, about 10 mg of γ -CD nanofiber mat and as-received γ -CD powder were placed into the sealed desiccator. The γ -CD nanofiber mat and γ -CD powder were kept in aniline or toluene vapour for 12 h, afterwards, they were taken out of the desiccators and

placed in suction hood for 2 h in order to remove the uncomplexed aniline or toluene which were only adsorbed onto the surface of the samples. The amount of entrapped aniline and toluene were examined by using proton nuclear magnetic resonance ($^1\text{H-NMR}$, Bruker D PX-400) system. The samples were dissolved in *d6*-DMSO for toluene and in D_2O for aniline experiments at the 20g/L concentration. The spectra were recorded at 400 MHz and at 16 total scan. The stoichiometries between γ -CD to toluene and aniline were determined by integrating the peak ratio of the characteristic chemical shifts (δ) corresponding to γ -CD, aniline and toluene by using NMR software. The particular peaks belong to aniline and toluene were observed at the aromatic region of NMR spectrum (6.7 and 7.1 ppm for aniline, 7.1 and 7.2 ppm for toluene). The stoichiometries were calculated by taking account the integration of aniline, toluene aromatic peaks and the γ -CD's characteristic peak at about 5.0 ppm for D_2O and 4.8 ppm for *d6*-DMSO system.

FIGURES:

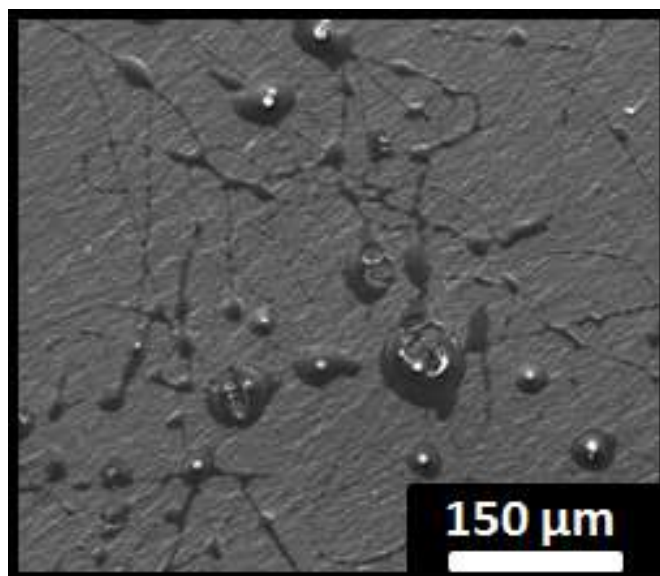


Fig S1. The representative SEM image of splashed area as a results of adding 20% (w/w) urea to the 140% (w/v) γ -CD solution.

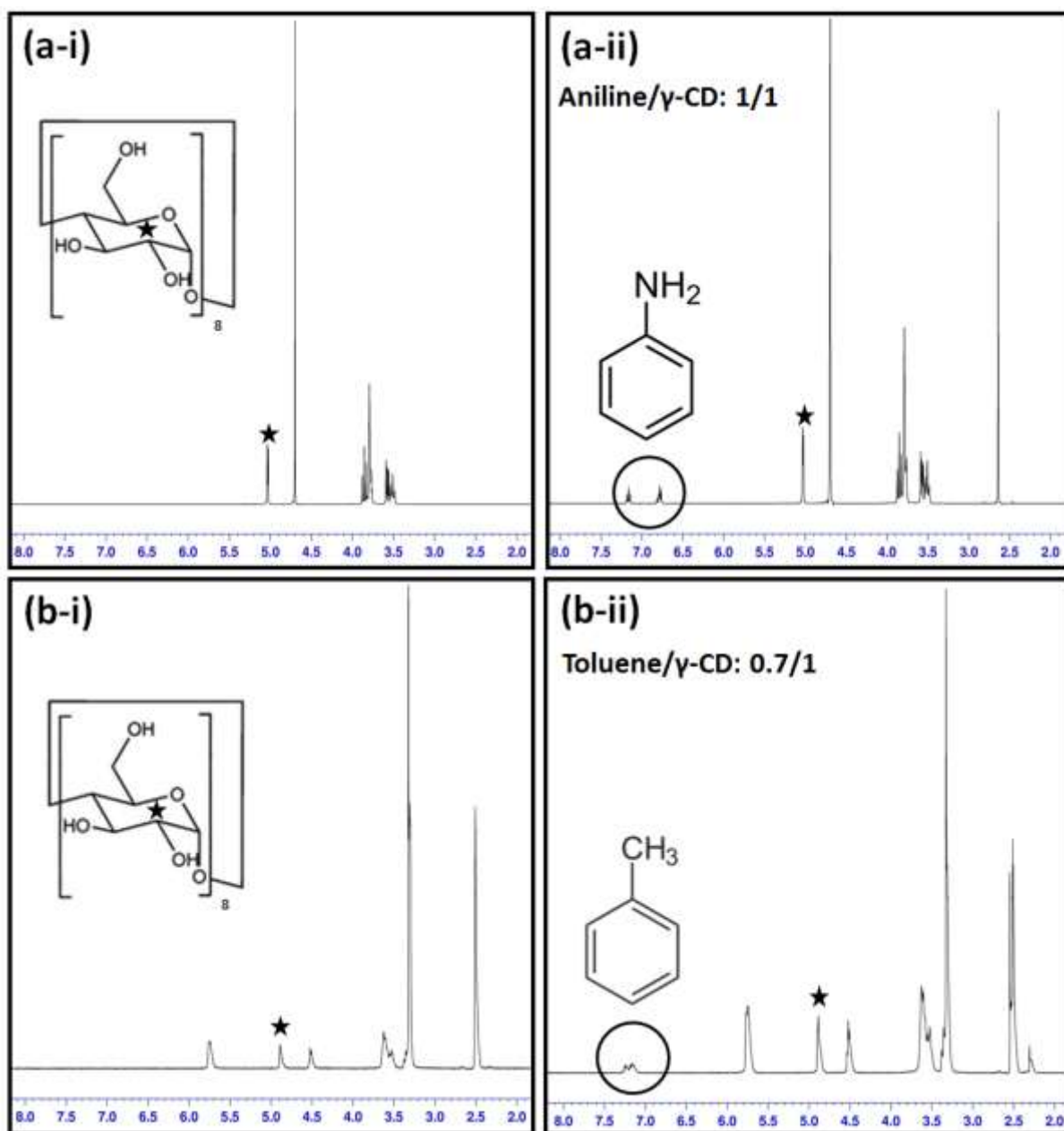


Fig. S2. ¹H-NMR spectra of (a-i) aniline exposed γ -CD powder and (ii) aniline exposed γ -CD nanofibers in D₂O; (b-i) toluene exposed γ -CD powder and (ii) toluene exposed γ -CD nanofibers in d₆-DMSO. From the NMR software, the molar ratio of γ -CD to aniline and toluene was calculated about 1:1 and 1:0.7, respectively. On the other hand, the γ -CD powder form could not entrap these organic molecules so we could not observe the characteristic shifts of aniline and toluene at the aromatic region for this sample.