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Synthesis of redispersible spherical cellulose II nanoparticles decorated with carboxylate groups

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Supplementary Information

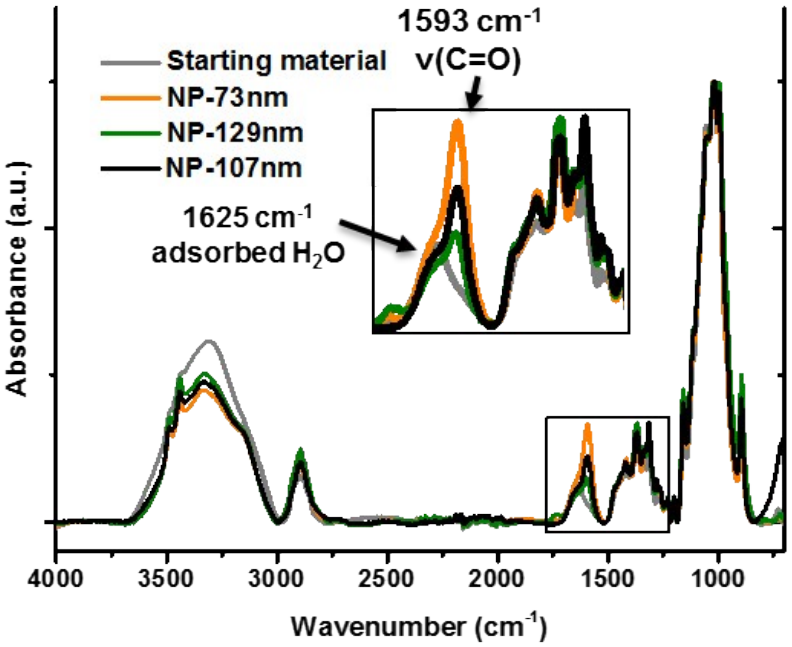

Figure S1 Infrared spectra of spherical nanoparticles in comparison to TENCEL® gel. The band at 1593 cm^{-1} corresponds to the carbonyl stretching of the carboxylate group.

Table S1 Analysis of the degree of substitution of NP-73nm, NP-107nm and NP-129nm by acidic hydrolysis in deuterated sulphuric acid.

Sample	DS (C2-OH)	DS (C3-OH)	DS (C6-OH)	DS(total)
NP-73nm	0.052	0.022	0.075	0.149
NP-107nm	0.035	0.011	0.045	0.091
NP-129nm	0.013	0.009	0.015	0.037

Table S2 Comparison of carboxymethylated nanoparticles to the precursor TENCEL® gel with regard to crystallinity (13C-MAS-NMR) and particle size.

Sample	Crystallinity	Particle size TEM / nm	Particle size DLS / nm
NP-73nm	46%	72.8	110.9
NP-107nm	47%	107.4	118.8
NP-129nm	47%	129.1	142.7
TENCEL® gel	47%	-	-

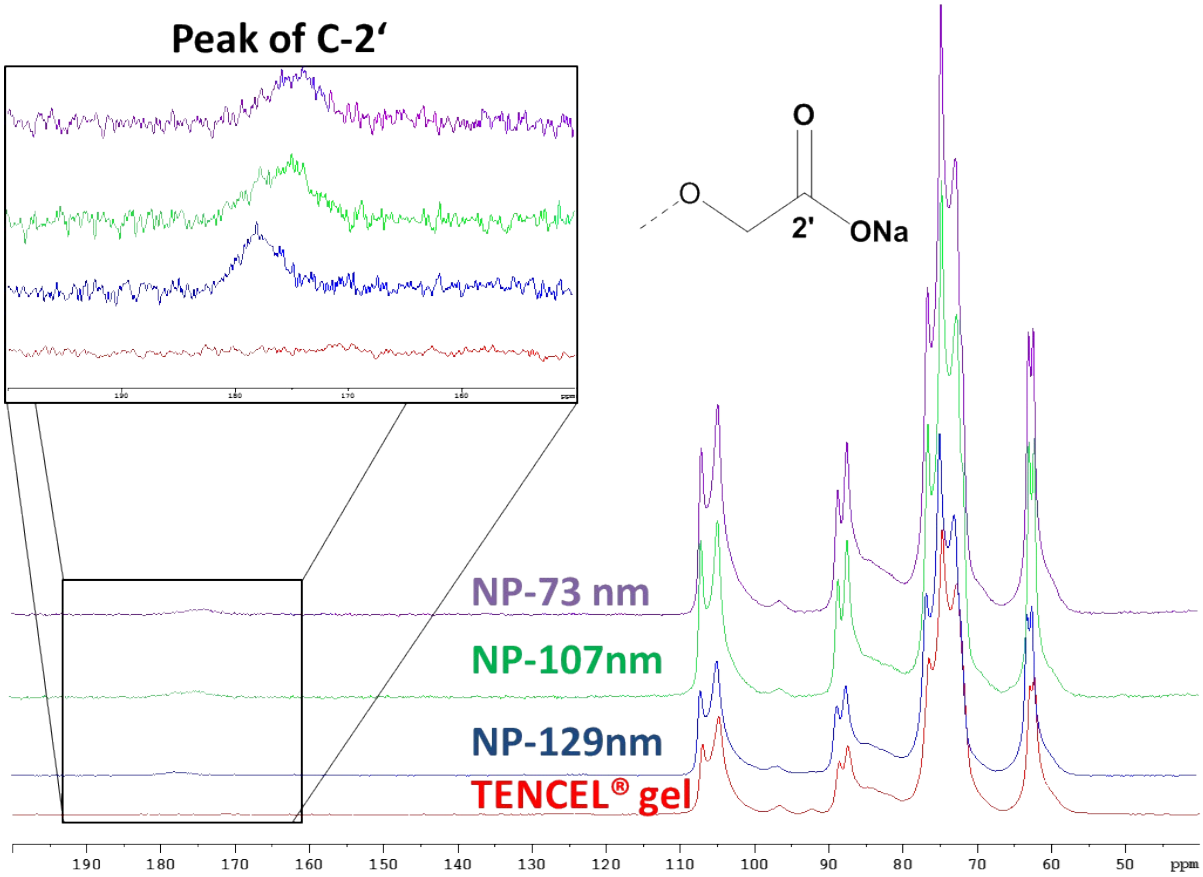

Figure S2 ^{13}C-NMR solid state spectra of NP-73nm, NP-107nm and NP-129nm compared to TENCEL® gel. Both samples feature very similar spectra compared to the starting material with exception of a slight broad peak at 175 ppm corresponding to the introduced carbonyl carbon. Fitting of the C4 peak between 79 and 91 ppm showed that the crystallinity is not affected (see Table S1).

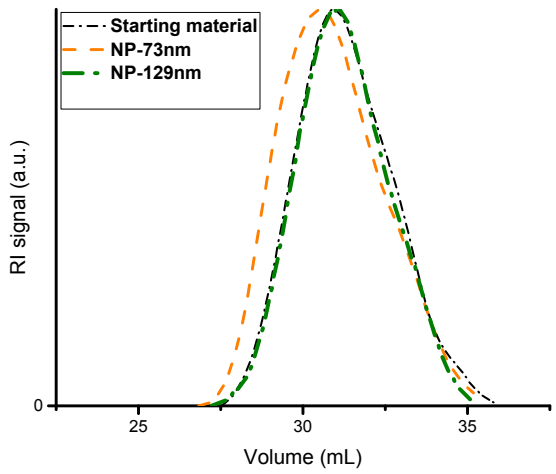

Figure S3 GPC chromatogram of NP-129nm and NP-73nm compared to the precursor TENCEL® gel. The chromatogram of NP-73nm is shifted to higher molar mass due to the introduction of carboxylate groups.

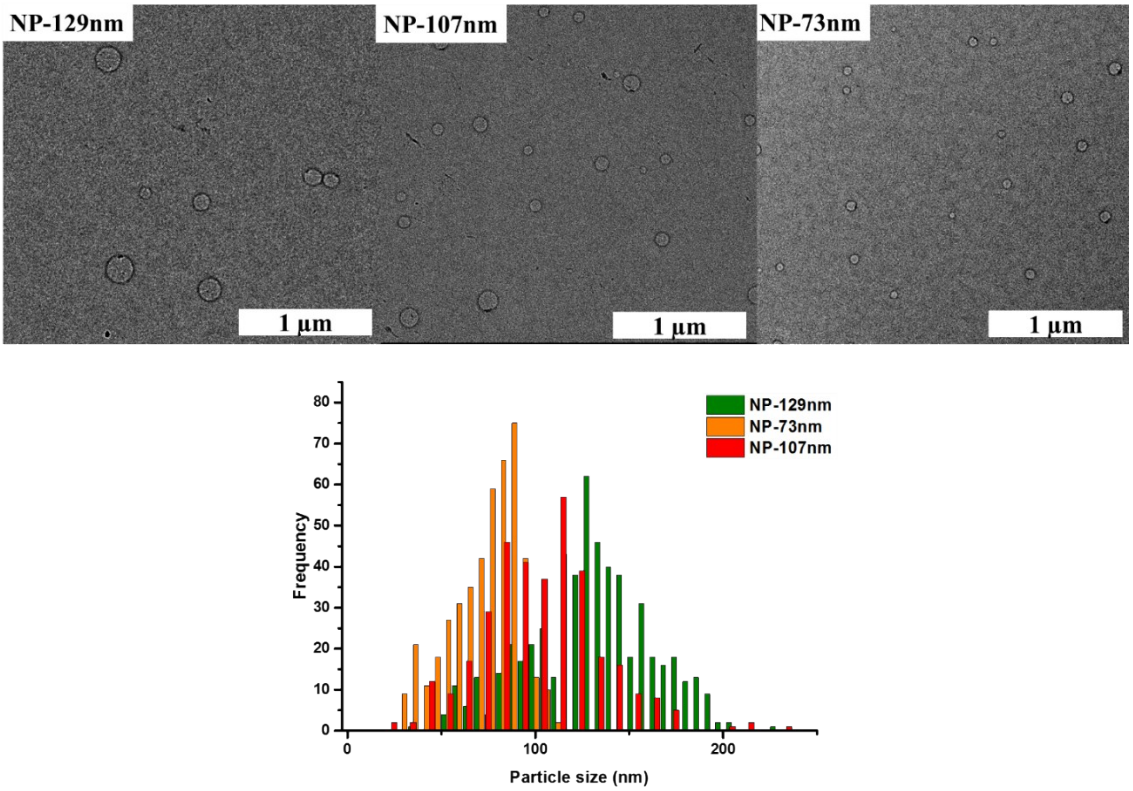

Figure S4 TEM micrographs of NP-129nm, NP-107nm and NP-73nm and particle size analysis of the TEM micrograhs to show number-weighted particle-size distribution.

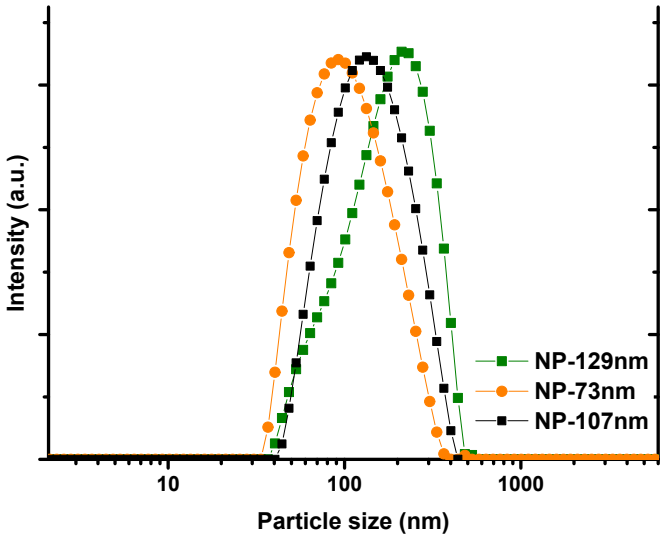

Figure S5 Intensity-weighted size distribution of the hydrodynamic radius from DLS measurement. The mean hydrodynamic radii are shown in Table S2.

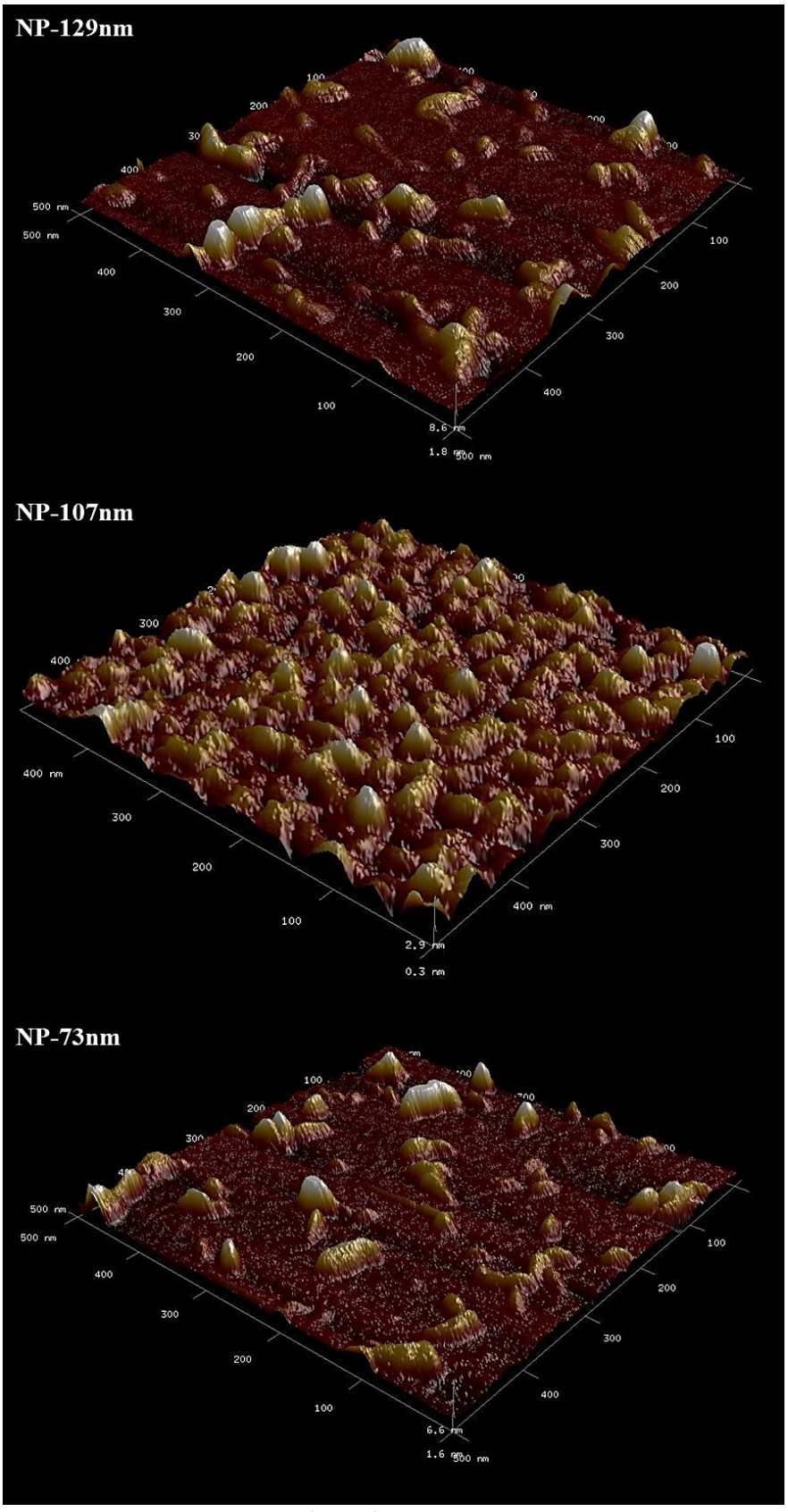

Figure S6 AFM 3D height profiles of the spherical nanoparticles.

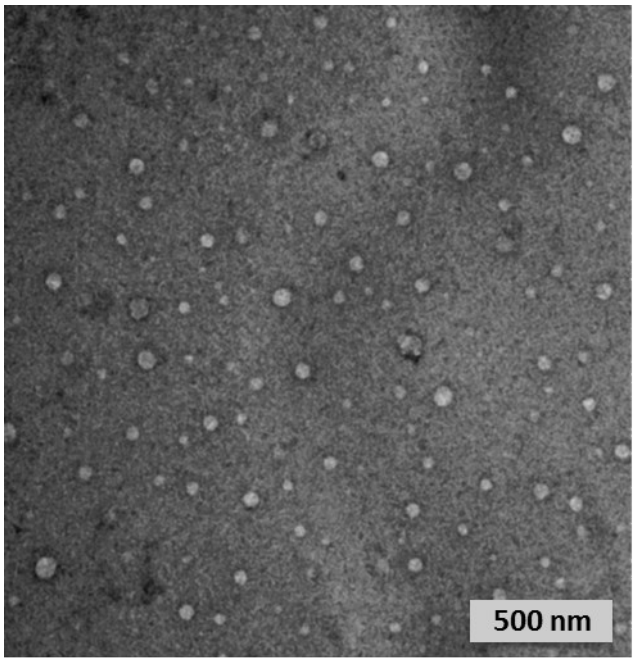

Figure S7 TEM micrograph of redispersed NP-73nm by stirring for 4 min.

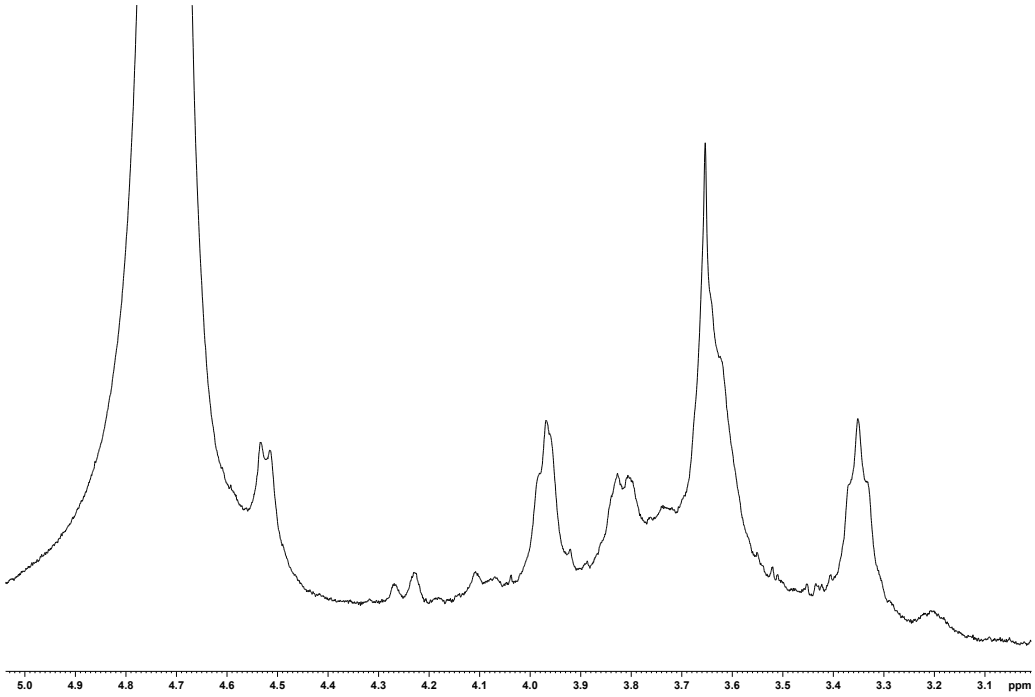

Figure S8 ^{1}H-NMR spectrum of redispersed NP-73 nm in D_2O. The resolved signals correspond to the flexible, amorphous nanoparticle surface, whereas the broad background peak corresponds to crystalline, non-flexible regions.

Materials and Methods

Materials

All chemical reagents were purchased in puriss. p.a. grade at Sigma-Aldrich. Technical 2-PrOH was supplied from VWR. D_2SO_4 and D_2O were obtained from Euriso-top.

Carboxymethylated nanoparticles (NP-73nm, NP-107nm, NP-129nm) can be obtained starting from TENCEL® gel or from its gel-like precursor using the same protocol. TENCEL® gel and its gel precursor were provided by Lenzing AG and used as received. A detailed characterization of TENCEL® gel and its production process was reported by Beaumont et al..[1]

Synthesis of NP-129 nm

To a stirred aqueous suspension of 100 mL TENCEL® gel with a solid content of 4.0 wt% (4 g, 24.7 mmol) was added drop wise a 12.5M aqueous solution of sodium hydroxide (2.5 g, 62.5 mmol, 2.5 Eq) and the mixture was stirred for 30 min at room temperature. Subsequently, sodium chloroacetate (5.8 g, 50 mmol, 2 Eq) was added portion wise and the reaction mixture was stirred overnight at 55°C. The yellowish raw product was filtrated and transferred into a centrifugation tube. The suspension was washed intensively with deionized water by a set of washing and centrifugation (5 min@4000 rcf) steps to neutral pH. After two washing steps, the centrifugation time was increased to 30 min. After washing the opaque aqueous suspension was diluted to a solid content of 1.4 wt% and homogenized in a high-pressure homogenizer (APV-1000, SPX FLOW) at 800 bar in 4 cycles to obtain a translucent suspension of NP-129nm, which was centrifugated for 5 min at 4000 rcf to remove a small amount of remaining bigger particles.

Synthesis of NP-73nm

In order to obtain NP-73nm with a higher degree of substitution TENCEL® gel was solvent-exchanged to 2-PrOH prior to carboxymethylation. 100 mL of TENCEL® gel (4.0 wt%, 4 g, 24.7

mmol) was concentrated by centrifugation at 4000 rcf for 5 min. The concentrated slurry was diluted with 100 mL of technical 2-PrOH, filtrated and washed with technical 2-PrOH (3 x 100 mL). The solid content of the alocoholic suspension was adjusted to 4 wt%. An aqueous solution of sodium hydroxide (1.3 M, 1.1 g, 27.2 mmol, 1.1 Eq) was added drop wise and after equilibration at 30 min, sodium chloroacetate (2.9 g, 24.7 mmol, 1.0 Eq) was added. The reaction mixture was stirred at 55°C for 4.5 h and purified as described above. After homogenization and centrifugation a translucent suspension of NP-73nm was yielded.

Synthesis of NP-107nm

NP-107nm was obtained using a similar protocol as NP-73nm. 100 mL of TENCEL® gel (4.0 wt%, 4 g, 24.7 mmol) was first solvent exchanged as described above. After the solvent-exchange an aqueuous NaOH was added drop wise (0.8 M, 0.6 g, 14.8 mmol, 0.6 Eq) and the mixture was stirred for 30 min at room temperature. Sodium chloroacetate (2.9 g, 24.7 mmol, 1.0 Eq) was added and the reaction mixture was stirred at 55°C for 4.5h and subsequently worked up as described in synthesis of NP-129nm. After homogenization and centrifugation a turbid suspension of NP-107nm was yielded.

Methods

Drying and redispersion of NP-73nm

30 mL of NP-73nm(1 wt%) were mixed with approximately 4 mg of rhodamine B to dye the suspension. The suspension was concentrated to a solid content of 3 wt% by heating and stirring at 60°C. The suspension was dried at room temperature in a polypropylene mold to obtain a film. 20 mg of the resulting xerogel was added to 2 mL of water and redispersed with a mechanical stirrer by gentle stirring (250 rpm) for 4 min to obtain a clear translucent suspension. The redispersed nanoparticles were analyzed by DLS and TEM.

^{1}H-NMR analysis

The degree of substitution was determined by acidic hydrolysis of 15 mg of each freeze-dried sample in D_2SO_4 according to Bose et al.[2]. 0.2 mL of 72 wt% D_2SO_4 was added to each sample (10-20 mg of freeze-dried material) and the slurry was stirred for 2h at room temperature. The transparent solution was diluted with 0.3 mL of D_2O and stirred at 80°C in a water bath. Subsequently, 0.2 mL of D_2O was added and the samples were stored at −20°C until ^{1}H-NMR spectra were measured. Liquid ^{1}H-NMR experiments of samples were performed on a Bruker Avance II 400 instrument (Rheinstetten, Germany). The spectra were analyzed according to Heinze and Pfeiffer.[3]

Solid-state NMR and crystallinity

Solid state NMR experiments were performed on a Bruker Avance III HD 400 spectrometer with a 4 mm dual broadband CP-MAS probe, as described previously.[1] Peak fitting was performed with the Dmfit program.[4] All materials for solid-state NMR were freeze-dried before measurement.

GPC

The GPC chromatograms were acquired as described previously.[5]

Dynamic Light Scattering

Autocorrelation functions were acquired using DynaPro Nanostar (Wyatt) system. The auto-correlation function were generated by 20 measurements for 10 s each and Dynamics V7 software was used to process these data in order to calculate the intensity-weighted particle size distribution. The intensity-weighted distribution were acquired at least 8 times for each sample to ensure reproducibility. The mean hydrodynamic radii were calculated as average from the diffusion coefficients of eight measurement for each sample.

TEM

3 µl of the dispersions/solutions was dropped onto the TEM-grid (3.05 mm HR-TEM-grid, copper 300 mesh, carbon film, EMS, Hatfield PA 19440, USA). All pictures were taken using a FEI TECNAI G2 20 (FEI) at 160 kV. The size of the particles was calculated by manual measurement of >200 particles per sample.

AFM

AFM imaging was performed using a Veeco Dimension Icon AFM (Bruker) and OTESPA silicon tips (Bruker). The AFM images were collected in air using scanning rates of ca. 1 Hz.

Zeta Potential

Nanoparticles were diluted with a 10 mM $NaHCO_3$ buffer (pH = 9) to a solid content of approximately 0.3 wt%. Zeta potential of these suspension was determined using Zetasizer Nano ZS (Malvern).

References

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