

Supporting Information
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Confined crystallization of spin crossover nanoparticles in block copolymer micelles

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Abstract: Nanoparticles of the spin crossover coordination polymer $[\text{FeL}(\text{bipy})]_n$ were synthesized by confined crystallization within the core of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymer micelles ($D_{\text{core}} = 16 \pm 2$ nm, $D_h = 87 \pm 37$ nm), utilizing the 4VP units in the micellar core as coordination sites for the iron complex. In the bulk material, the spin crossover nanoparticles in the core are well isolated from each other allowing thermal treatment without disintegration of their structure, e.g. through agglomeration. During annealing above the glass transition temperature of the polystyrene block, the transition temperature is shifted gradually to higher temperatures from the as-synthesized product ($T_{1/2\downarrow} = 163$ K and $T_{1/2\uparrow} = 170$ K) to the annealed product ($T_{1/2\downarrow} = 203$ K and $T_{1/2\uparrow} = 217$ K) and goes along with an increase in hysteresis width from 6 K to 14 K. Thus, the spin crossover properties of the nanocomposite can be shifted towards the properties of the related bulk material by confined crystallization. The excellent stability of the nanocomposite allows further processing, demonstrated here using electrospinning from solution.

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General Procedures

Materials: All SCO CP-BCP syntheses were performed under inert conditions using argon 5.0 (purity $\geq 99,999\%$) using Schlenk tube technique. The synthesis of the sample was repeated at least twice. Tetrahydrofuran (THF, Fischer Scientific, $\geq 99.8\%$) for anionic polymerization was purified by successive distillation over calcium hydride (CaH₂, Merck) and potassium (K, Sigma-Aldrich) under N₂ atmosphere. Styrene (S, Sigma-Aldrich, $> 99\%$) was purified over dibutyl magnesium (Bu₂Mg, Sigma-Aldrich, 1M in heptane) and 4-vinylpyridine (4VP, Acros Organics, 95%) over triethyl aluminum (Et₃Al, Sigma-Aldrich, 1M in heptane), respectively, followed by condensing into storage ampoules. 1,1-Diphenylethylene (DPE, Acros Organics, 98%) was purified by addition of *sec*-butyl lithium (*sec*-BuLi, Acros Organics, 1.3M in cyclohexane/hexane 92/8) and subsequent distillation. 4,4'-bipyridine was obtained from Alfa Aesar and used as received. THF p.a. for the SCO synthesis was obtained from Bernd Kraft and degassed with argon for at least 30 min. [FeL(MeOH)₂] was synthesized as described before.^[1] THF for electrospinning (THF, $\geq 99.8\%$, Fisher Chemical, degassed with argon and consecutive freeze-pump-thaw cycles), polystyrene for electrospinning (PS, $M_n = 97\,000\text{ g}\cdot\text{mol}^{-1}$, $D = 1.02$, synthesized by anionic polymerization and reprecipitated from MeOH).

Transmission electron microscopy (TEM) was taken at a Zeiss CEM902 electron microscope (Zeiss, Oberkochen, Germany) and a JEOL 2200FS electron microscope. Samples were dissolved in THF. The solution was dropped on a carbon coated copper grid (mesh 200, Science Services, Munich). Electron acceleration voltage was set to 80 kV (CEM902) and 200 kV (JEOL 2200FS). Micrographs were taken with a MegaView III / iTEM image acquiring and processing system from Olympus Soft Imaging Systems (OSIS, Münster, Germany) and an Orius 830 SC200W / DigitalMicrograph system from Gatan (Munich, Germany). Particles size measurements were done with "ImageJ" image processing software developed by Wayne Rasband (National Institutes of Health, USA).

Dynamic light scattering (DLS) measurements were done at an AntonPaar Litesizer 500 in quartz glass cuvettes from Helma at 25 °C. One measurement consists of six consecutive runs.

Temperature-dependent **powder X-ray diffraction (T-PXRD)** pattern were recorded using a Bragg-Brentano type diffractometer (X'PERT-Pro, PANalytical with CuK α -radiation ($\lambda = 1.541\text{ \AA}$), equipped with a secondary monochromator to suppress fluorescence. The sample was placed on a flat surface in a flowing nitrogen atmosphere in a XRK chamber during the measurement.

Magnetic susceptibility measurements were performed at a Quantum Design MPMS-XL-5 SQUID magnetometer. Field strength of 3 T was applied and a temperature range of 50 – 400 K was used to determine the temperature dependency of the magnetism and the spin crossover behaviour. Sweep mode was used for the five cycles with a cooling and heating rate of 5 K min⁻¹. The final measurement was performed in settle mode with a cooling and heating rate of 5 K min⁻¹ between 50 K and 300 K. The samples were

prepared in gelatine capsules placed in a plastic straw. The measured values were corrected for the diamagnetism of the sample holder, the polymer matrix (measured values) and the ligand (tabulated Pascal constants).

The room temperature ^{57}Fe Mössbauer spectrum was recorded in transmission geometry with constant acceleration using a conventional Mössbauer spectrometer with a 50 mCi $^{57}\text{Co}(\text{Rh})$ source. The samples were sealed in the sample holder in an argon atmosphere. The spectra were fitted using Recoil 1.05 Mössbauer Analysis Software.^[2] The isomer shift values are given with respect to a $\alpha\text{-Fe}$ reference at room temperature.

Temperature dependent zero-field ^{57}Fe Mössbauer measurements on polycrystalline powders of SCO CP-BCP were performed on a commercial transmission spectrometer with sinusoidal velocity sweep. Temperature-dependent measurements at temperatures between $T = 80$ and 300 K were conducted on a CryoVac continuous-flow cryostat. After positioning the sample container, the sample chamber was evacuated, flushed five times with nitrogen gas, and kept at ca. $50 - 100$ mbar during the measurement. The temperature was measured with a calibrated silicon diode located close to the sample container, providing a temperature stability of better than 0.1 K. The nominal activity of the ^{57}Fe Mössbauer source used was 50 mCi of ^{57}Co in a rhodium matrix, stored at ambient temperatures during the measurement. Velocity calibration was done with an α -iron foil at ambient temperature and the minimum experimental line width (FWHM) was < 0.24 mm s^{-1} . Isomer shifts (δ) were specified relative to metallic iron at room temperature but were not corrected in terms of the second-order Doppler shift. The spectra were analysed by least-square fits using doublets of Lorentzian lines utilizing the software package NORMOS.^[3]

Carbon, nitrogen and hydrogen contents were collected at a Vario EL III with acetanilide as standard. The samples were placed in tin boats and measured at least twice. The average of the measurements was used.

Transmission **infrared (IR)** spectra were collected from a Perkin Elmer Spectrum 100 FT-IR (ATR). The samples were measured directly as solids.

Raman spectra were recorded with a confocal WITec Alpha 300 RA+ Raman microscope equipped with a UHTS 300 spectrometer and a back-illuminated Andor Newton 970 EMCCD camera. A frequency-doubled Nd-YAG laser with a wavelength of $\lambda = 532$ nm was used as the excitation source. All measurements were conducted using a $50 \times$ long working distance ($\text{NA} = 0.7$, lateral resolution ca. 500 nm) Zeiss objective. The laser power used was 0.1 mW for the neat SCO CP crystals as well as the SCO CP-BCP particles and 10 mW for the neat $\text{S}_{85}\text{V}_{15}^{154}$ diblock copolymer, respectively. The instrument was operated by the integrated Witec Control Five software (version 5.1). All spectra were subjected to a cosmic ray removal routine and baseline correction using Witec Project Five software (version 5.1).

Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209F1 Libra under nitrogen. The samples were heated from 25 - 600 °C at a heating rate of 10 K min^{-1} .

For **gel permeation chromatography (GPC)** in N,N -dimethylformamide (DMF) with lithium bromide (5 g L^{-1}), GRAM columns (300×8 mm, 10 μm particle size, PSS Mainz) with 100 and 3000 Å pore sizes were used. The sample was measured on a SEC 1260 Infinity system (Agilent Technologies) at a flow rate of 0.5 mL min^{-1} at 23 °C, using a refractive index detector (Agilent Technologies). The calibration was done with narrowly distributed polystyrene standards (PSS calibration kit) and toluene (HPLC grade) was used as internal standard.

MALDI-ToF MS (matrix-assisted laser desorption/ionization time-of-flight mass spectrometry) measurements were performed on a Reflex III (Bruker) equipped with a N_2 Laser ($\lambda = 337$ nm). An acceleration voltage of 20 kV was used in linear mode and the samples were prepared according to the dried droplet method. Therefore, matrix (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldiene]malononitrile (DCTB), 10 g L^{-1} in THF), analyte (10 g L^{-1} in THF) and salt (silver trifluoroacetate, 10 g L^{-1}) were dissolved and mixed in the ratio of $20 : 5 : 1$ and 0.5 μL of the mixture was placed and dried on the target plate.

$^1\text{H-NMR}$ spectra were acquired with a Bruker Ultrashield 300 spectrometer using CDCl_3 as solvent.

For **cryo transmission electron microscopy** studies, a sample droplet of 2 μL was put on a lacey carbon filmed copper grid (Science Services, Munich, Germany). Subsequently, most of the liquid was removed with blotting paper leaving a thin film stretched over the lace holes. The specimens were instantly shock frozen by rapid immersion into liquid nitrogen cooled to approximately 90 K in a temperature-controlled freezing unit (Zeiss Cryobox, Carl Zeiss Microscopy GmbH, Jena, Germany). The temperature was monitored and kept constant in the chamber during all the sample preparation steps. The specimen was inserted into a cryotransfer holder (CT3500, Gatan, Munich, Germany) and transferred to a Zeiss / LEO EM922 Omega EFTEM (Zeiss Microscopy GmbH, Jena, Germany). Examinations were carried out at temperatures around 90 K. The TEM was operated at an acceleration voltage of 200 kV. Zero-loss filtered images ($\text{DE} = 0$ eV) were taken under reduced dose conditions ($100 - 1000$ e/ nm^2). All images were registered digitally by a bottom mounted CCD camera system (Ultrascan 1000, Gatan, Munich, Germany) combined and processed with a digital imaging processing system (Digital Micrograph GMS 1.9, Gatan, Munich, Germany).

The **differential scanning calorimetry (DSC)** measurements were performed on a Phoenix 204 F1 (Netzsch) under nitrogen atmosphere, using aluminum crucibles (temperature range: $20 - 200$ °C, scanning rates: $10, 20$ and 30 K \cdot min^{-1}).

Scanning electron microscopy (SEM) micrographs were taken on a Zeiss LEO 1530 GEMINI. The acceleration voltage was set to 3 kV and the sample was sputter-coated with a 1.3 nm platinum layer. Scanning electron microscopy – energy dispersive X-Ray spectroscopy (SEM-EDX) were performed on the same device with an acceleration voltage of 15 kV.

Synthesis Procedures

Synthesis of the BCP S₈₅V₁₅¹⁵⁴

The PS-*b*-P4VP diblock copolymer (S₈₅V₁₅¹⁵⁴, ratio PS/P4VP = 85/15 (w/w), $M_n = 154\,000\text{ g mol}^{-1}$, $\bar{D} = 1.02$ (DMF-GPC)) was synthesized by sequential living anionic polymerization in THF using a laboratory autoclave (1 L, Büchi AG). Styrene was polymerized first for 30 min using *sec*-BuLi as initiator at -80 °C. After complete conversion of styrene a sample was taken for GPC and MALDI-ToF analyses. Subsequently, 1,1-diphenylethylene was added to the living polystyryllithium (equimolar amount to initiator), followed by the addition of 4-vinylpyridine (4-VP). After 4 h the polymerization was terminated with degassed methanol followed by precipitation in deionized water to isolate the diblock copolymer. The molecular weight of the PS-*b*-P4VP diblock copolymer was determined from ¹H-NMR (CDCl₃, Figure S10), employing the absolute molecular weight of the PS precursor obtained by MALDI-ToF MS (M_n (PS) = 131 000 g mol⁻¹) for signal calibration.

Synthesis of the SCO CP-BCP composite

50 mg S₈₅V₁₅¹⁵⁴ and 6.7 mg (15 μmol) [FeL(MeOH)₂] were dissolved in 20 mL THF in a 50 mL Schlenk flask. The solution was refluxed for 2 h. After cooling, 5.9 mg (37.5 μmol, 2.5 eq) 4,4'-bipyridine was added and the solution refluxed again for 1 h. After a short cool down to RT, 6.7 mg (15 μmol) [FeL(MeOH)₂] and 5.9 mg (37.5 μmol, 2.5 eq) 4,4'-bipyridine were added simultaneously and the solution was refluxed again for 1 h. The simultaneous addition of the reactants and the subsequent reflux of the solution were repeated three more times. In total, 33.5 mg [FeL(MeOH)₂] and 29.5 mg 4,4'-bipyridine were added to the 50 mg polymer. Consecutively, the solvent was removed by cold distillation and the resulting dark brown polymeric solid was dried *in vacuo*. Elemental anal. (%) found: C 67.06, H 6.59, N 5.85.

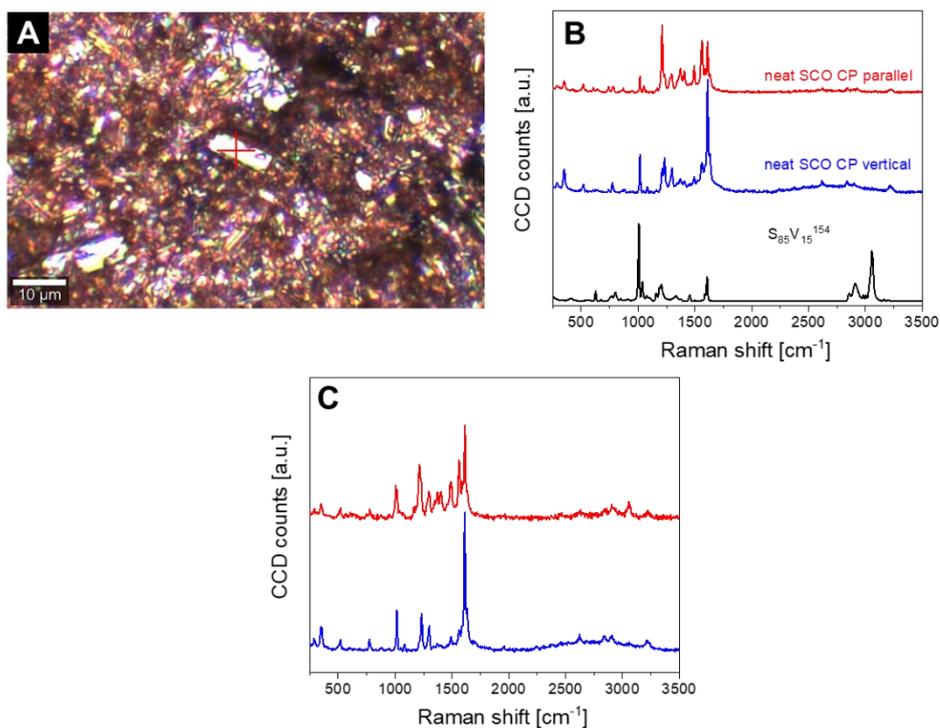
Electrospinning

For the preparation of PS/SCO CP composite fibers the SCO CP-BCP particles were dispersed in degassed THF (2.5 g·L⁻¹), followed by the addition of PS (19 wt%). The fibers were spun on a rotating disk collector ($D = 13\text{ cm}$, 60 rpm) placed at a distance of 11 cm from the stainless-steel needle ($d = 0.90\text{ mm}$) at a temperature of 21.7 °C and a relative humidity of ca. 30%. For electrospinning, a high voltage of 10.5 kV at the needle and -1.0 kV at the collector were applied. The feed rate of the solution was 1.2 mL·h⁻¹.

Characterization

Raman

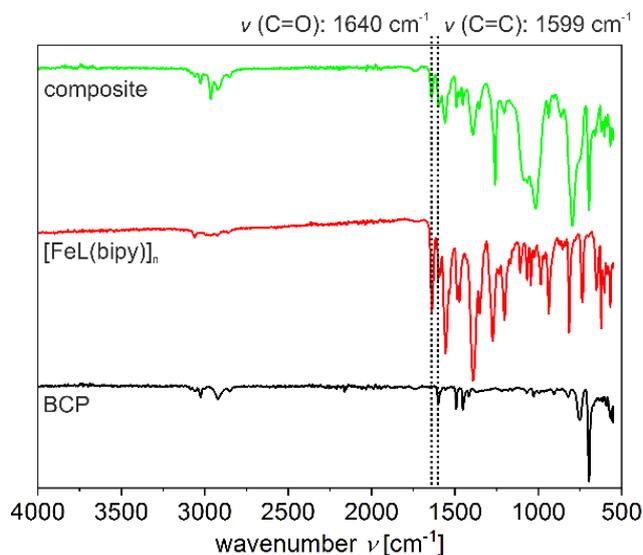
Figure S1. A) Digital photograph of neat SCO CP crystals, the position for Raman measurements is indicated by a red cross. B) Raman spectra of the neat $S_{85}V_{15}^{154}$ diblock copolymer and the neat SCO CP with polarization of the excitation laser parallel (red) and vertical (blue) to the long axis of the SCO CP crystal shown in A). C) Raman spectra of SCO CP-BCP particles taken at different positions, showing identical Raman spectra with respect to that observed for the neat SCO CP crystals. The spectra in B) and C) were shifted vertically for a better comparison. The neat SCO CP crystals are strong Raman scatterers, which allows measurements at very low laser intensities of 0.1 mW. Under these conditions the neat $S_{85}V_{15}^{154}$ diblock copolymer gives almost no Raman signals. Thus, for the



SCO CP-BCP particles only Raman bands attributable to the SCO CP are visible.

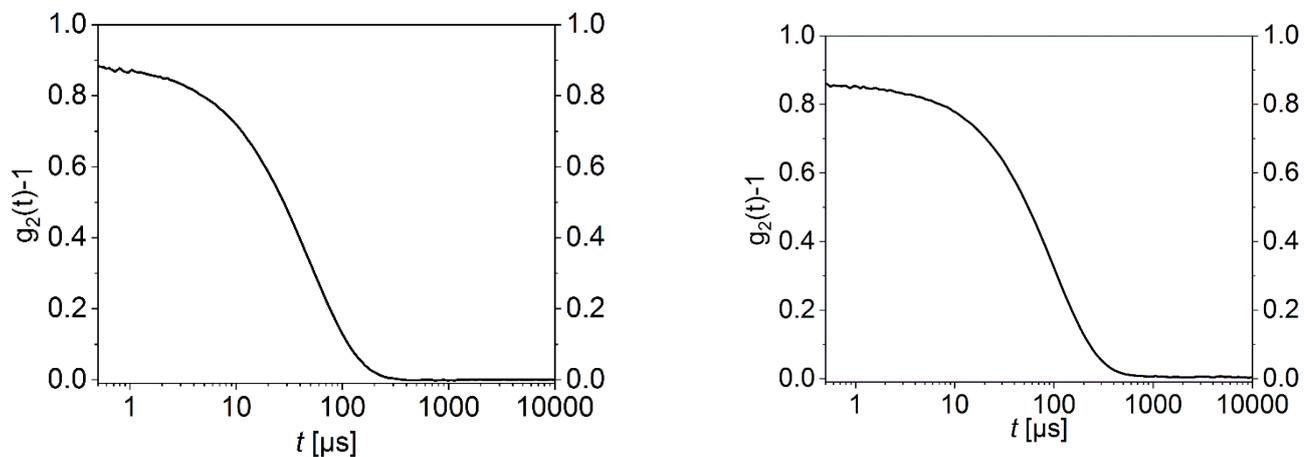
IR

Figure S2. IR spectrum of the SCO CP-BCP composite (green), the bulk $[\text{FeL}(\text{bipy})]_n$ (red) and the $S_{85}V_{15}^{154}$ diblock copolymer (BCP, black).



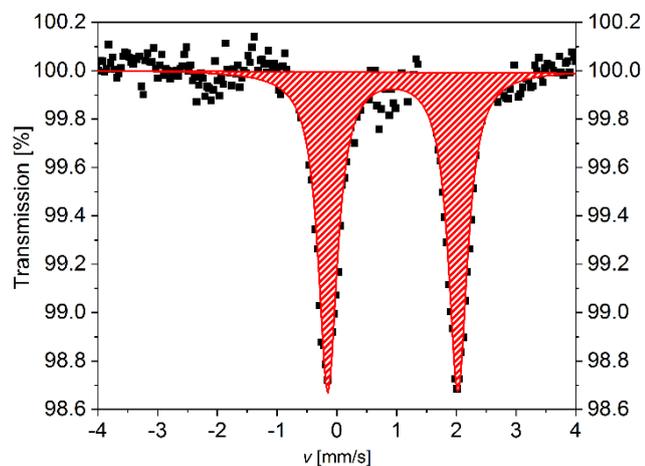
DLS autocorrelation functions of the empty BCP micelles and the SCO CP-BCP composite particles

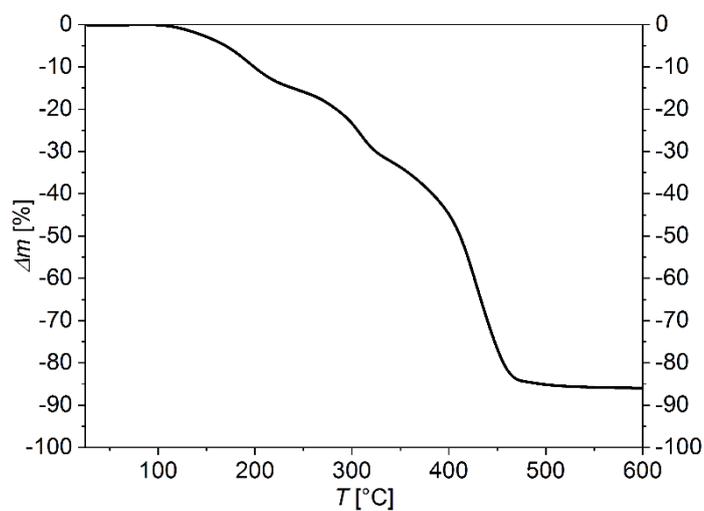
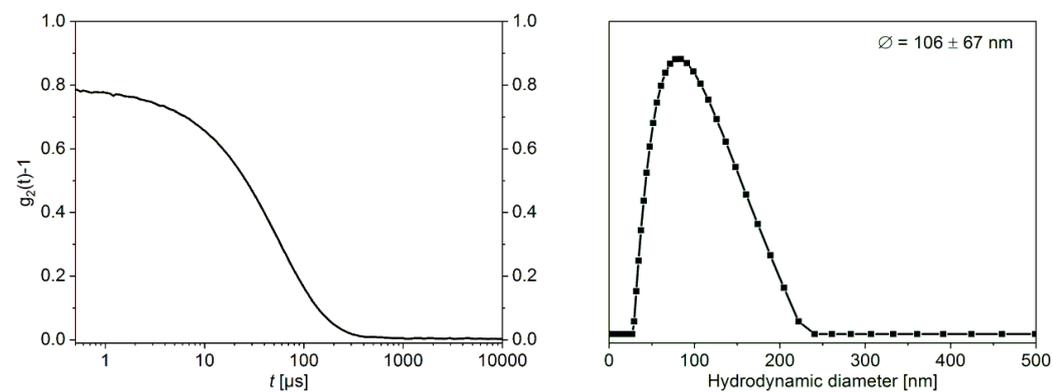
Figure S3. Autocorrelation function $g_2(t)-1$ of the empty BCP micelle (left) and the SCO CP-BCP particles (right) corresponding to the size distribution graphs of Figure 1B and 1E in the manuscript.



Mössbauer spectroscopy of the SCO CP-BCP composite particles

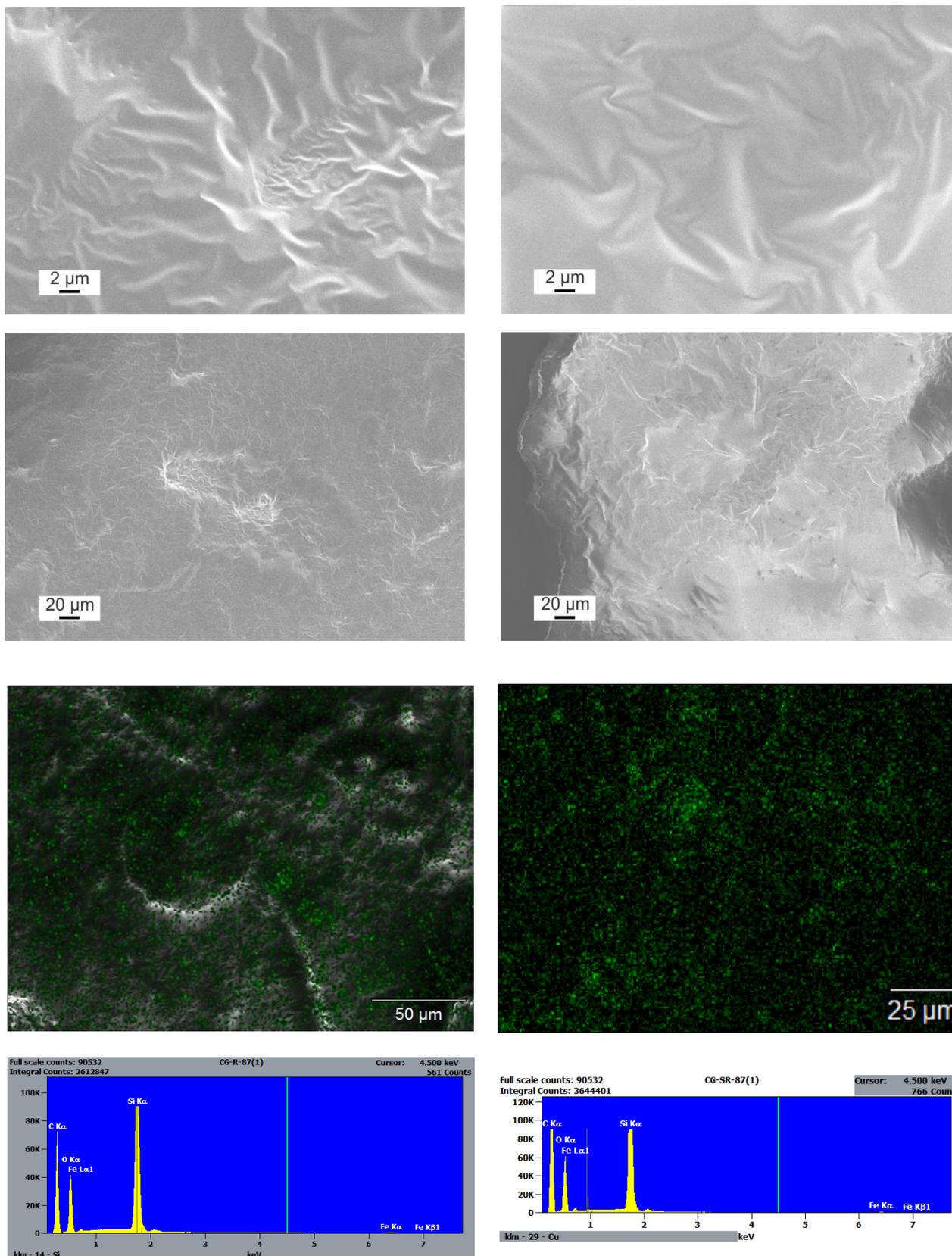
Figure S4. Room-temperature ^{57}Fe Mössbauer spectrum of the SCO CP-BCP composite showing only one doublet for the CP. The spectrum is displayed in respect to $\alpha\text{-Fe}$ as reference.



TGA of the SCO CP-BCP composite particles**Figure S5.** TGA measurement of the SCO CP-BCP showing no significant mass loss until 100 °C indicating that no residual solvent is present in the composite.**DLS of the SCO CP-BCP composite particles after annealing****Figure S6.** Autocorrelation function $g_2(t)-1$ vs. t (left) and the size distribution of the particles (right) of redissolved sample after the thermal annealing process.

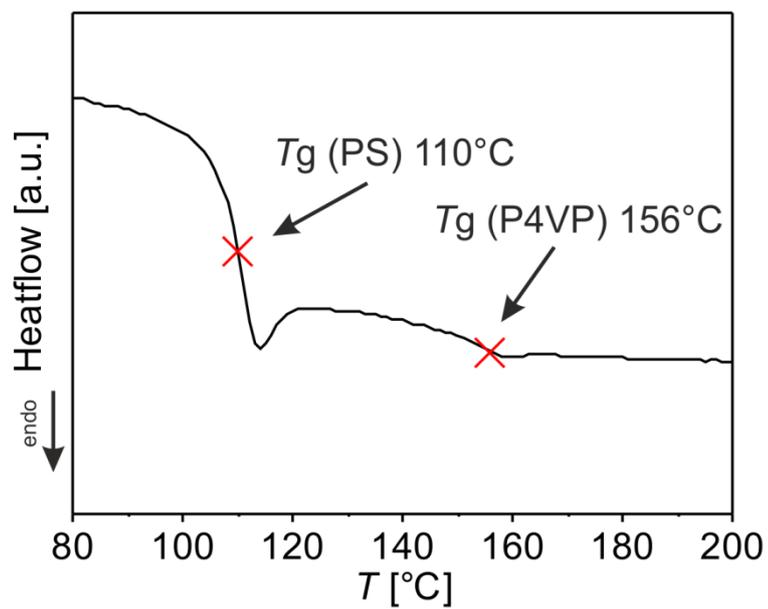
SEM and SEM-EDX of the SCO CP-BCP composite particles before and after annealing

Figure S7. SEM images and SEM-EDX measurements of the sample before (left) and after thermal annealing (right). SEM-EDX measurements showing homogeneously distributed iron indicated by the green color. No indication for the formation of agglomerates or larger crystallites is observed.



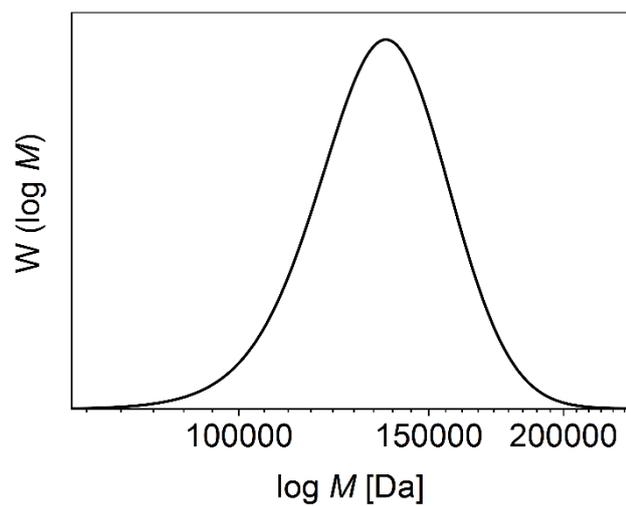
DSC of the BCP

Figure S8. DSC measurement of the pure PS-*b*-P4VP showing the glass transition temperature T_g for PS at 110 °C and P4VP at 156 °C.



GPC of the BCP

Figure S9. Size distribution of the pure S₈₅V₁₅¹⁵⁴ measured by DMF-GPC.



NMR of the BCP

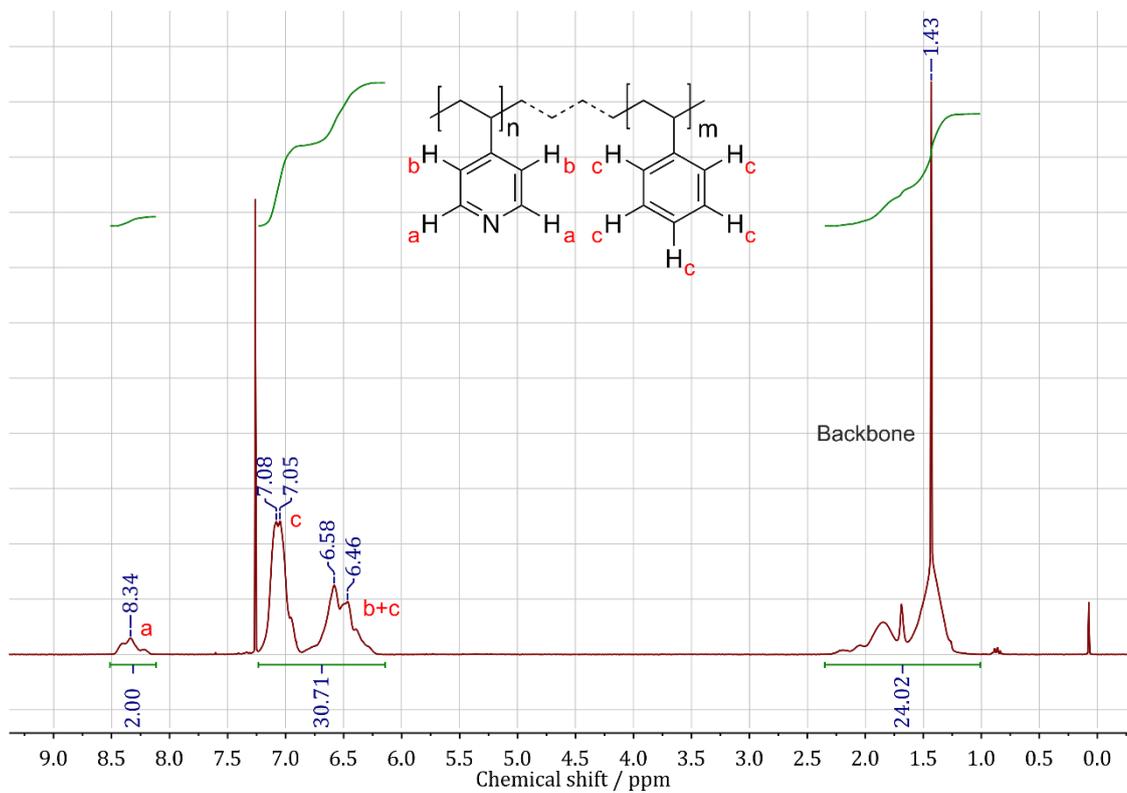
Figure S10. ^1H -NMR spectrum of $\text{S}_{85}\text{V}_{15}^{154}$ diblock copolymer showing signals for the pyridine, styrene and aliphatic hydrogen atoms.

Signal a has been normalized to 2 protons from the 4-vinylpyridine. Signal c from the 5 styrene protons and signal b from 2 remaining 4-vinylpyridine overlap.

$$30.71 - 2 = 28.71 \text{ (styrene protons)}$$

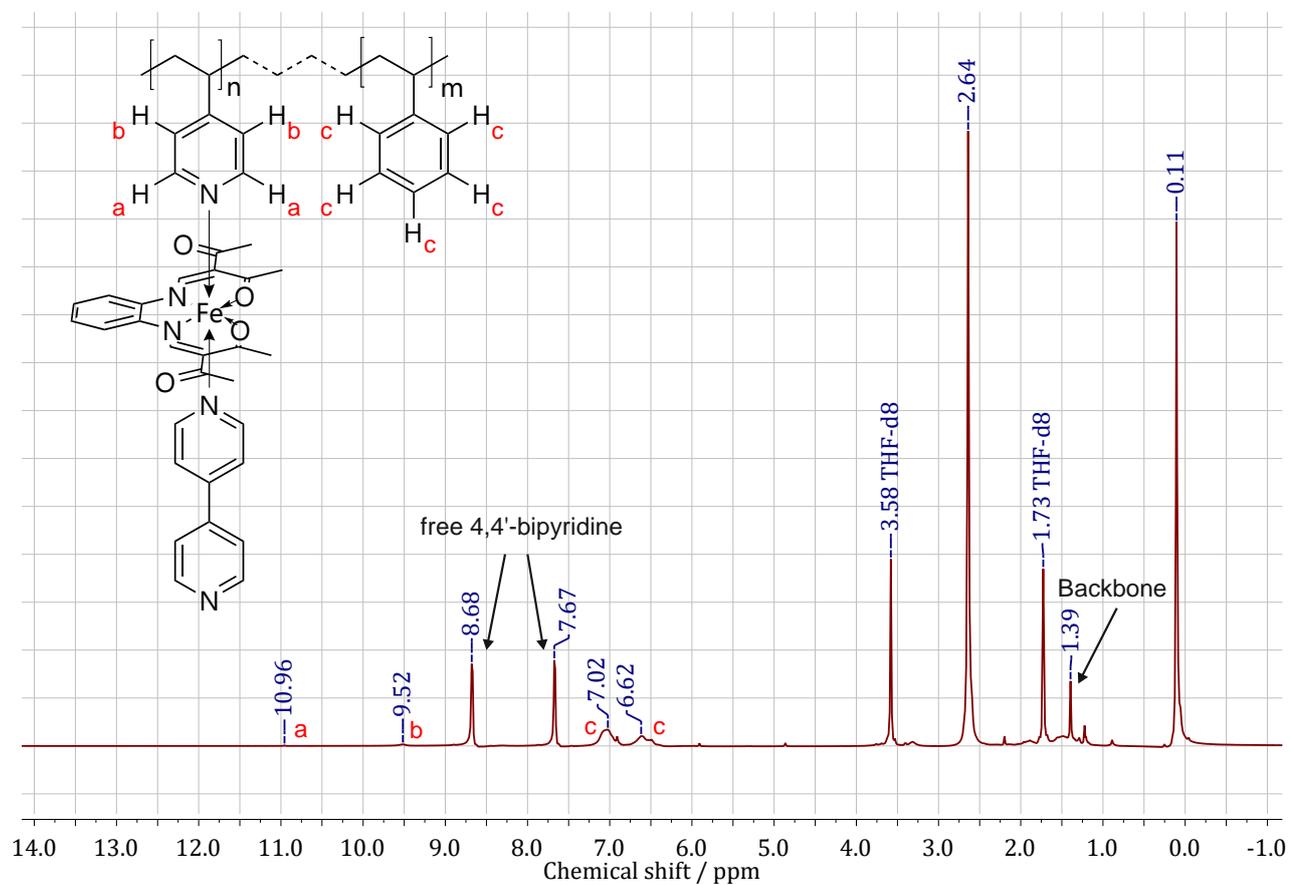
$$28.71 / 5 = 5.742$$

$$\rightarrow \text{P4VP} : \text{PS} = 1 : 5.742 \rightarrow \text{S}_{85}\text{V}_{15}$$



NMR of the SCO CP-BCP

Figure S11. $^1\text{H-NMR}$ spectrum of SCO CP- $\text{S}_{85}\text{V}_{15}^{154}$ diblock copolymer showing signals for the pyridine, styrene and aliphatic hydrogen atoms. The signals of the pyridine protons a and b are shifted to 10.96 ppm and 9.52 ppm (compared to 8.34 ppm and 6.5 ppm for the pure polymer, see figure S10) due to the coordination of the paramagnetic iron center while the signal of the styrene protons c do not change.



Temperature dependent Mössbauer spectra of the SCO CP-BCP

Figure S12. Zero-field ^{57}Fe Mössbauer spectra of SCO CP-BCP recorded at temperatures between $T = 300$ and 80 K before (A) and after (B) annealing at $T = 393$ K for 1 h under nitrogen atmosphere. The measurements on both compounds were carried out starting at $T = 300$ K and then at $T = 175, 80, 175$ and 300 K. Symbols: Experimental data. Lines: Fit with one or two doublets of Lorentzian lines, respectively. The parameters of the fit are summarized in Table S1. The colored lines represent the corresponding sub-spectra of the fit, which are attributed to the Fe(II) low-spin (green) and Fe(II) high-spin sites (red), respectively.

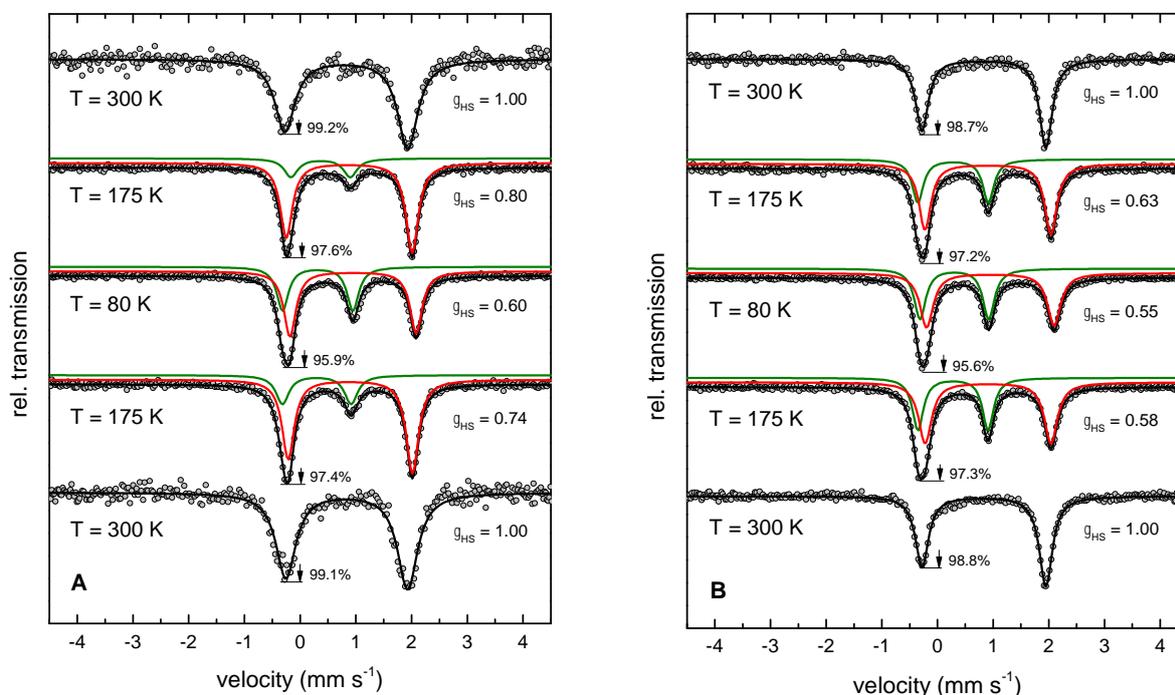


Table S1. Summary of Mössbauer parameters determined for SCO CP-BCP **before** and **after annealing** at $T = 393$ K for 1 h (under nitrogen atmosphere) by a fit with one or two doublets of Lorentzian lines, respectively, with isomer shift δ , quadrupole splitting ΔE_Q and Lorentzian line width Γ_{FWHM} (full width at half maximum). A_2/A_1 describes the relative intensities of the two corresponding lines of a given doublet, while AREA quotes the relative (integral) intensities of the individual doublets, attributed to the molar fraction of the high-spin and low-spin Fe species in SCO CP-BCP, respectively. The measurements on both compounds were carried out starting at $T = 300$ K and then at $T = 175, 80, 175$ and 300 K.

Before annealing

T (K)	δ [a] (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ_{FWHM} (mm s^{-1})	A_2/A_1 [b]	AREA (%)
300	0.951(5)	2.200(9)	0.44(1)	1.23(4)	100
175	1.020(2)	2.224(5)	0.264(4)	1.20(2)	79.7
	0.412(7)	1.22(1)	0.28(2)	1*	20.3
80	1.071(1)	2.265(2)	0.262(4)	0.94(1)	60.1
	0.437(1)	1.263(3)	0.254(5)	1*	39.9
175	1.022(2)	2.230(3)	0.268(5)	1.17(3)	74.0
	0.420(6)	1.232(9)	0.28(1)	1*	26.0
300	0.959(4)	2.184(7)	0.44(1)	1.13(4)	100

After annealing

T (K)	δ [a] (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ_{FWHM} (mm s^{-1})	A_2/A_1 [b]	AREA (%)
300	0.955(2)	2.225(4)	0.277(5)	1.24(2)	100
175	1.027(2)	2.263(3)	0.264(5)	1.07(2)	63.2
	0.402(3)	1.268(6)	0.243(8)	1*	36.8
80	1.071(1)	2.292(3)	0.287(4)	0.97(2)	54.7
	0.424(2)	1.236(3)	0.252(4)	1*	45.3
175	1.020(1)	2.260(3)	0.283(5)	1.00(2)	58.0
	0.400(2)	1.260(3)	0.239(5)	1*	42.0
300	0.955(2)	2.224(4)	0.285(7)	1.27(3)	100

Values marked with an asterisk (*) were fixed in the fit. [a] The isomer shifts (δ) were specified relative to metallic iron at room temperature but were not corrected in terms of the second-order Doppler shift. [b] In case of a polycrystalline powder with random orientations of the crystallites, the expectation value of this parameter is $A_2/A_1 = 1$.^[4] Deviations from this value, which are clearly observed at $T = 300$ K, are attributed to the presence of texture effects due to partial orientations of crystallites on compacting the powder in the sample containment.

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Author Contributions

C. Göbel synthesized the SCO CP BCP nanoparticles, did most of the formal analysis (SQUID, TEM, DLS, IR Mössbauer, elemental analysis, ...) and did write the original draft.

C. Hils synthesized and characterized the electrospun fibers of the composite nanoparticles in PS.

M. Drechsler did the cryo-TEM measurements and helped with the TEM measurements in general.

D. Baabe measured and interpreted the temperature-dependent Mössbauer spectra.

A. Greiner helped with the project administration and the funding acquisition.

H. Schmalz synthesized and characterized the BCP and supervised the electrospinning and the Raman measurements and was involved in the writing of the manuscript.

B. Weber was responsible for the funding acquisition and project administration and involved in the writing of the manuscript.