Structure-property relationships of microphase-separated metallosupramolecular polymers

Electronic Supplementary Information

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1. Supplementary Figures S1–S36

1.1. Materials and Spectrophotometric Titrations S1–S6



Figure S1. Chemical structures of bis(1'-methylbenzimidazoyl)-4-(2-ethylhexyloxy)pyridine (**MC**) that was used as a model compound and of the macromonomers that were employed as macromonomer for the preparation of the investigated metallosupramolecular polymers, i.e., **BKB**₃₀₀₀ (with $M_n = 3800 \text{ g mol}^{-1}$; m ≈ 0.32 , n ≈ 0.68 , p ≈ 55) and **BKB**₂₀₀₀ (with $M_n = 3000 \text{ g mol}^{-1}$; m ≈ 0.30 , n ≈ 0.70 , p ≈ 41) consisting of the telechelic PEB core end-functionalized with 2,6-bis(1'-methylbenzimidazolyl)-pyridine (Mebip) ligands. The Mebip ligand, the low molecular weight model compound **MC**, and the **BKB** macromonomers were prepared following previously reported procedures.^{1,2,7}



Figure S2. Comparison of the size exclusion chromatography (SEC) traces of the telechelic, bis-hydroxyl terminated poly(ethylene-*co*-butylene) PEB₂₀₀₀ (M_n of 3100 g mol⁻¹) and PEB₂₀₀₀ (M_n of 2100 g mol⁻¹), as well as of the SEC traces of the macromonomers **BKB₃₀₀₀** (with an M_n = 3800 g mol⁻¹; m \approx 0.32, n \approx 0.68, p \approx 55) and **BKB₂₀₀₀** (with an M_n = 3000 g mol⁻¹; m \approx 0.30, n \approx 0.70, p \approx 41) consisting of the telechelic PEB core end-functionalized with 2,6-bis(1'-methylbenzimidazolyl)-pyridine (Mebip) ligands.



Figure S3. To demonstrate that the prepared macromonomers form complexes in the same manner as previously reported, UV-vis spectrophotometric titrations were carried out with $Zn(NTf_2)_2$. a) UV-vis absorption spectra of solutions of the BKB₃₀₀₀ macromonomer ($c = 10 \mu mol L^{-1}$ in CHCl₃/MeCN 9:1, black line). Upon titration with aliquots of $Zn(NTf_2)_2$ containing also the macromonomer in the same concentration ($c = 10 \mu mol L^{-1}$) to avoid dilution, the formation of the coordination complexes is observed. The spectrum obtained at a metal-to-ligand ratio of approximately 1:2 is highlighted (red line). b) Plot of the molar extinction coefficient at the absorption maximum of the metal-ligand complex at 340 nm as shown in (a) as a function of the 1:2 coordination complex occurs at a 1:2 metal-to-ligand ratio in the same way as previously reported.¹ c) UV-vis absorption spectra of solutions of the **BKB**₂₀₀₀ macromonomer ($c = 10 \mu mol L^{-1}$ in CHCl₃/MeCN 9:1, black line). The spectrum obtained at metal-to-ligand ratio of approximately 1:2 is highlighted (red line). d) Plot of the molar extinction coefficient at the absorption spectra at a 1:2 metal-to-ligand ratio in the same way as previously reported.¹ c) UV-vis absorption spectra of solutions of the **BKB**₂₀₀₀ macromonomer ($c = 10 \mu mol L^{-1}$ in CHCl₃/MeCN 9:1, black line). The spectrum obtained at metal-to-ligand ratio of approximately 1:2 is highlighted (red line). d) Plot of the molar extinction coefficient at the absorption maximum of the metal-ligand complex at 340 nm as shown in (c) as a function of the ratio between added $Zn(NTf_2)_2$ and the **BKB**₂₀₀₀ macromonomer.



Figure S4. UV-vis spectrophotometric titrations were carried out with **MC** and $Zn(OTf)_2$ to demonstrate that the complex formation occurs in the same manner as previously reported for $Zn(NTf_2)_2$.^{1,2} a) UV-vis absorption spectra of solutions of model compound **MC** ($c = 25 \mu mol L^{-1}$ in MeCN, blue line). Upon titration with aliquots of $Zn(OTf)_2$, containing also MC in the same concentration ($c = 25 \mu mol L^{-1}$) to avoid dilution, the formation of the coordination complexes is observed at a metal-to-ligand ratio of 1:2 (red line). b) Extinction of the free ligand (312 nm) and the metal-ligand complex (340 nm) as a function of the ratio of added $Zn(OTf_2)_2$ and the ligand.



Figure S5. UV-vis spectrophotometric titrations were carried out with Tb(OTf)₃ and the model compound **MC** to demonstrate that the complex formation occurs in the same manner as previously reported for Tb(ClO₄)₃.^{1,3,4} a) UV-vis absorption spectra of solutions of model compound **MC** ($c = 25 \mu$ mol L⁻¹ in MeCN, blue line). Upon titration with aliquots of Tb(OTf)₃, containing also MC in the same concentration ($c = 25 \mu$ mol L⁻¹) to avoid dilution, the formation of the coordination complexes is observed. The spectra obtained at metal-to-ligand ratios of 1:3, 1:2, and 1:1 are highlighted (red, purple, and orange line, respectively). b) Extinction of the free ligand (312 nm) and the metal-ligand complex (352 nm) as a function of the ratio between added Tb(OTf)₃ and the ligand.



Figure S6. UV-vis spectrophotometric titrations were carried out with $Tb(OTf)_3$ and the model compound **MC** at higher concentrations ($c = 200 \mu mol L^{-1}$) to unambiguously demonstrate the formation of 1:3 metal-to-ligand complexes upon titration with $Tb(ClO_4)_3$.^{1,3,4} a) UV-vis absorption spectra of solutions of model compound **MC** ($c = 200 \mu mol L^{-1}$ in MeCN, blue line). Upon titration with aliquots of $Tb(OTf)_3$, containing also MC in the same concentration ($c = 25\mu mol L^{-1}$) to avoid dilution, the formation of the coordination complexes is observed. The spectra obtained at metal-to-ligand ratios of 1:3, and 1:1 are highlighted (red and orange line, respectively). b) Absorption intensity of the free ligand (312 nm) and the metal-ligand complex (352 nm) as a function of the ratio between added $Tb(OTf)_3$ and the ligand.

1.2. Thermal Properties S7–S15



Figure S7. Thermogravimetric analysis traces of the macromonomer **BKB**₃₀₀₀ (black), the MSP [Zn**BKB**₃₀₀₀](OTf)₂ (blue), and the MSP [Tb(**BKB**₃₀₀₀)_{1.5}](OTf)₃ (red) recorded in air. The traces reveal a 5% weight loss at temperatures of 351 °C for **BKB**₃₀₀₀, 386 °C for [Zn**BKB**₃₀₀₀](OTf)₂, and 263 °C in the case of [Tb(**BKB**₃₀₀₀)_{1.5}](OTf)₃.



Figure S8. Comparison of the ¹H NMR spectra (CDCl₃, 400 MHz) of the model compound **MC** (a) before and (b) after keeping a sample on a hot plate for 10 min at a temperature of 250 °C. The spectra appear identical, suggesting that no changes to the chemical structure occur when maintaining samples at this temperature.



Figure S9. Comparison of the ¹H NMR spectra (CDCl₃, 400 MHz) of the $[ZnMC_2](OTf)_2$ complex (a) before and after heating samples on a hot plate (b) for 10 min at 200 °C as well as (c) for 10 min at 250 °C. The spectra do not indicate changes, suggesting that the metal-ligand complexes retain their structural integrity when heating up to temperatures of 250 °C.



Figure S10. Differential scanning calorimetry (DSC) traces of the macromonomers BKB_{3000} ($M_n = 3800$ g mol⁻¹), BKB_{2000} ($M_n = 3000$ g mol⁻¹), and of the poly(ethylene-*co*-butylene) (PEB; Krasol[®], 2100 g mol⁻¹) core. a) First and second heating and cooling traces of compression molded samples of BKB_{3000} . b) First and second heating and cooling traces of samples of BKB_{2000} . c) First and second heating and cooling traces of samples of BKB_{2000} . c) First and second heating and cooling traces of samples of PKB_{2000} . c) First and second heating and cooling traces of samples of PKB_{2000} . c) First and second heating and cooling traces of samples of PKB_{2000} . c) First and second heating and cooling traces of samples of PKB_{2000} . c) First and second heating and cooling traces of samples of PKB_{2000} . c) First and second heating and cooling traces of samples of PKB_{2000} . C) First and second heating and cooling traces of samples of PKB_{2000} . C) First and second heating and cooling traces of samples of PKB_{2000} . C) First and second heating and cooling traces of samples of PKB_{2000} . C) First and second heating and cooling traces of samples of PKB_{2000} . C) First and second heating and cooling traces of samples of PKB_{2000} . C) First and second heating and cooling traces of samples of PKB_{2000} . C) First and second heating and cooling traces of samples of PKB_{2000} . C) First and PKB_{2000} . C) First and PKB_{2000} cooling traces of PKB_{2000} . C) First and PKB_{2000} cooling traces of PKB_{2000} . C) First and PKB_{2000} cooling traces of PKB_{2000} cooling traces of PKB_{2000} . C) First and PKB_{2000} cooling traces of PKB_{2000} cooling traces of $PKB_$



Figure S11. Comparison of the differential scanning calorimetry (DSC) traces of the macromonomers and metallosupramolecular polymers. a) First heating and (b) first cooling scans of compression molded samples of [ZnBKB₃₀₀₀](OTf)₂, [ZnBKB₂₀₀₀](OTf)₂, [ZnBKB₃₀₀₀](NTf₂)₂, [ZnBKB₃₀₀₀](OTf)₂, [Tb(BKB₃₀₀₀)_{1.5}](OTf)₃, [Tb(BKB₂₀₀₀)_{1.5}](OTf)₃, and [La(BKB₃₀₀₀)_{1.5}](NTf₂)₃. The experiments were conducted at a heating rate of 10 °C min⁻¹ in a N₂ atmosphere and the traces are vertically shifted for clarity. Measurements with lanthanoid MSPs were carried out up to 200 °C since sample failure and loss of ordering occurs at lower temperatures in DMA and SAXS measurements.



Figure S12. Comparison of the differential scanning calorimetry (DSC) traces of the model compound (**MC**) and its complexes with different metal salts. a) First heating, b) first cooling, and (c) second heating scans of the model compound **MC**, $[ZnMC_2](OTf)_2$, $[ZnMC_2](NTf_2)_2$, $[TbMC_3](OTf)_3$, $[LaMC_3](NTf_2)_3$, and $[TbMC_3](ClO_4)_3$. The experiments were conducted at a heating rate of 10 °C min⁻¹ in a N₂ atmosphere and the traces are vertically shifted for clarity.



Figure S13. Optical microscopy (left) and polarized optical microscopy (right) images recorded during heating of (a) solid samples of $[ZnMC_2](OTf)_2$ and (b) of solid samples of $[ZnMC_2](NTf_2)_2$ during heating and cooling. The scale bars represent 100 μ m.



Figure S14. Optical microscopy (left) and polarized optical microscopy (right) images of solid samples of (a) $[TbMC_3](OTf)_3$ during heating as well as (b) $[LaMC_3](NTf_2)_3$ during heating and cooling. The scale bars represent 100 µm.

[TbMC₃](ClO₄)₃



Figure S15. Optical microscopy (left) and polarized optical microscopy (right) images of solid samples of $[TbMC_3](ClO_4)_3$ during heating. The scale bars represent 100 μ m.

1.3. Small- and Wide-Angle X-ray Scattering S16–S19



Figure S16. a) Comparison of the small- and wide-angle X-ray scattering (SAXS/WAXS) profiles of samples of the macromonomers **BKB**₃₀₀₀ and **BKB**₂₀₀₀. A main Bragg peak (q^*) and integer higher-order reflections are observed that imply a lamellar morphology. b) Comparison of SAXS/WAXS profiles of a sample of **BKB**₃₀₀₀ upon heating to different temperatures between 20 and 50 °C. A shoulder at a smaller scattering vectors is discernible. The heating and cooling rate for these temperature-dependent scattering experiments was 10 °C min⁻¹ and samples were equilibrated at each temperature for 10 min before data collection was started. Scattering profiles are shifted vertically for clarity.



Figure S17. Comparison of the small- and wide-angle X-ray scattering (SAXS/WAXS) profiles of samples of the MSP [Zn**BKB**₃₀₀₀](OTf)₂ upon heating to different temperatures between 20 and 240 °C. The heating and cooling rate for these temperature-dependent scattering experiments was 10 °C min⁻¹ and samples were equilibrated at each temperature for 10 min before data collection was started. Scattering profiles are shifted vertically for clarity.



Figure S18. Comparison of the small- and wide-angle X-ray scattering (SAXS/WAXS) profiles of samples of the MSP [Zn**BKB₃₀₀₀**](NTf₂)₂ upon heating to different temperatures between 20 and 240 °C. The heating and cooling rate for these temperature-dependent scattering experiments was 10 °C min⁻¹ and samples were equilibrated at each temperature for 10 min before data collection was started. Scattering profiles are shifted vertically for clarity.



Figure S19. Comparison of the small- and wide-angle X-ray scattering (SAXS/WAXS) profiles of samples of the MSPs (a) [Tb(**BKB**₃₀₀₀)_{1.5}](OTf)₃, b) [La(**BKB**₃₀₀₀)_{1.5}](NTf₂)₃, and (c) [Tb(**BKB**₂₀₀₀)_{1.5}](OTf)₃ upon heating to different temperatures between 20 and 160, 240, and 200 °C, respectively. The heating and cooling rate for these temperature-dependent scattering experiments was 10 °C min⁻¹ and samples were equilibrated at each temperature for 10 min before data collection was started. Scattering profiles are shifted vertically for clarity.

1.4. Thermomechanical Characterization S20



Figure S20. Comparison of the storage moduli, loss moduli, and tan δ traces determined by dynamic mechanical analysis (DMA). a) Storage moduli, b) loss moduli, and (c) tan δ traces of MSPs with different transition metal ions and varying counter ions and polymer cores. d) Storage moduli, e) loss moduli, (f) tan δ traces of MSPs with different lanthanide metal ions with varying counter ions and polymer cores.

1.5. Rheological Investigations S21–S36



Figure S21. Plots of the modulus against the oscillation strain as determined by strain sweep experiments with poly(ethylene-*co*-butylene)s at a fixed angular frequency of 10%. The measurements were employed to determine the limit of the linear response behavior of a) PEB₃₀₀₀ and b) PEB₂₀₀₀.



Figure S22. Linear shear rheology of poly(ethylene-*co*-butylene)s. Storage and loss moduli of (a,b) PEB₃₀₀₀ and (c,d) PEB₂₀₀₀ as a function of angular frequency at different temperatures in the range of –80 to 20 °C (γ = 0.02% (–80 to –40 °C), 0.1% (–30 °C), 1% (–20 to –10 °C), and 10% (0 to 20 °C)). The power laws ω^2 and ω^1 are indicative of terminal flow (black lines).



Figure S23. Plots of the modulus against the oscillation strain as determined by strain sweep experiments with poly(ethylene-*co*-butylene) macromonomer end-functionalized with Mebip-ligands (**BKB**₃₀₀₀) at a fixed angular frequency of 10%. The measurements were employed to find the limit of the linear response behavior.



Figure S24. Linear shear rheology of the poly(ethylene-*co*-butylene) macromonomer end-functionalized with Mebip-ligands (**BKB**₃₀₀₀). a) Storage and b) loss modulus as a function of angular frequency at different temperatures in the range of –30 to 50 °C (γ = 0.1%). At 50 °C, the storage and loss moduli scale according to the power laws ω^2 and ω^1 respectively (black lines), indicative for terminal flow.



Figure S25. Horizontal shift factors a_T versus the inverse temperature of poly(ethylene-*co*-butylene) PEB₃₀₀₀ (black squares) and PEB₂₀₀₀ (blue circles), as well as the VFT-fit at temperatures above the T_g with an extrapolation towards higher temperatures (red line).



Figure S26. Linear shear rheology of the poly(ethylene-*co*-butylene) macromonomer **BKB**₃₀₀₀ end-functionalized with Mebip-ligands. Master curve of **BKB**₃₀₀₀ at 0 °C using extrapolated PEB₃₀₀₀ shift factors as shown in Figure S25.



Figure S27. Plots of the modulus against the oscillation strain as determined by strain sweep experiments with the MSPs (a) $[ZnBKB_{3000}](OTf)_2$ and (b) $[ZnBKB_{3000}](NTf_2)_2$ at a fixed angular frequency of 10%. The measurements were employed to determine the limit of the linear response behavior.



Figure S28. Linear shear rheology of $[ZnBKB_{3000}](NTf_2)_2$ ($\gamma = 0.1\%$ (-20 to 210 °C), 1.0% (220 to 240 °C)). Master curves of (a) *G*' and *G*'', and (b) tan δ at $T_{ref} = 0$ °C constructed using the extrapolated PEB₃₀₀₀ shift factors as shown in Figure S25. The curves do not scale according to the power laws (black lines), indicating the absence of terminal flow in the material.



Figure S29. Strain sweep experiments at a fixed angular frequency of 10% to find the limit of the linear response behavior of (a) [Tb(**BKB**₃₀₀₀)_{1.5}](OTf)₃, b) [La(**BKB**₃₀₀₀)_{1.5}](OTf)₃, and (c) [Gd(**BKB**₃₀₀₀)_{1.5}](OTf)₃.



Figure S30. Linear shear rheology of the MSP [Tb(**BKB**₃₀₀₀)_{1.5}](OTf)₃. a) Storage and (b) loss moduli as a function of angular frequency at different temperatures in the range of –20 to 140 °C ($\gamma = 1.0\%$, $\omega = 0.01-100$ rad s⁻¹).



Figure S31. Linear shear rheology of the lanthanoid-based MSPs. Master curves of (a) $[Tb(BKB_{3000})_{1.5}](OTf)_3$ ($\gamma = 1.0\%$), b) $[La(BKB_{3000})_{1.5}](OTf)_3$ ($\gamma = 0.5\%$), and (c) $[Gd(BKB_{3000})_{1.5}](OTf)_3$ ($\gamma = 0.5\%$) at 0 °C constructed using the PEB₃₀₀₀ shift factors as shown in Figure S25. The power laws ω^1 and ω^2 are plotted as well (black lines) to determine the region of terminal flow in the materials.



Figure S32. Plots of the modulus against the oscillation strain as determined by strain sweep experiments with the MSPs (a) $[Tb(BKB_{2000})_{1.5}](OTf)_3$ and (b) $[La(BKB_{3000})_{1.5}](NTf_2)_3$ at a fixed angular frequency of 10%. The measurements were employed to determine the limit of the linear response behavior.



Figure S33. Linear shear rheology of the lanthanoid-based MSPs. Master curves of (a) $[Tb(BKB_{2000})_{1.5}](OTf)_3$ and (b) $[La(BKB_{3000})_{1.5}](NTf_2)_3$ at 0 °C constructed using the PEB₃₀₀₀ shift factors as shown in Figure S25. The power laws ω^1 and ω^2 are plotted as well (black lines) to determine the region of terminal flow in the materials.



Figure S34. Linear shear rheology of lanthanoid-based MSPs. a-b) Master curves of $[La(BKB_{3000})_{1.5}](OTf)_3$ for (a) *G'* and *G''*, and (b) tan δ at $T_{ref} = 0$ °C constructed using manual horizontal and vertical shift factors a_T and b_T , respectively. c-d) Master curves of $Gd(BKB_{3000})_{1.5}](OTf)_3$ for (c) *G'* and *G''*, and (d) tan δ at $T_{ref} = 0$ °C constructed using manual horizontal and vertical shift factors a_T and b_T , respectively. c-d) Master curves of $Gd(BKB_{3000})_{1.5}](OTf)_3$ for (c) *G'* and *G''*, and (d) tan δ at $T_{ref} = 0$ °C constructed using manual horizontal and vertical shift factors a_T and b_T , respectively. The power laws ω^1 and ω^2 are plotted as well (black lines) to determine the region of terminal flow in the materials.



Figure S35. Linear shear rheology of lanthanoid-based MSPs. a-b) Master curves of $[Tb(BKB_{2000})_{1.5}](OTf)_3$ for (a) *G'* and *G''*, and (b) tan δ at $T_{ref} = 0$ °C constructed using manual horizontal and vertical shift factors a_T and b_T , respectively. c-d) Master curves of $[La(BKB_{3000})_{1.5}](NTf_2)_3$ for (c) *G'* and *G''*, and (d) tan δ at $T_{ref} = 0$ °C constructed using manual horizontal and vertical shift factors a_T and b_T , respectively. The power laws ω^1 and ω^2 are plotted as well (black lines) to determine the region of terminal flow in the materials.



Figure S36. Plot of the manual horizontal shift factors (a_T) as a function of inverse temperature of the MSPs [Tb(**BKB**₃₀₀₀)_{1.5}](OTf)₃ (black squares), [La(**BKB**₃₀₀₀)_{1.5}](OTf)₃ (orange triangles), [Gd(**BKB**₃₀₀₀)_{1.5}](OTf)₃ (green diamonds), [Tb(**BKB**₂₀₀₀)_{1.5}](OTf)₃ (blue triangles), and [La(**BKB**₃₀₀₀)_{1.5}](NTf₂)₃ (red stars).

2. Supplementary Tables S1–S2

Table S1. Overview of the thermal transitions as observed by differential scanning calorimetry (DSC) for selected metal-ligand complexes with the model compound bis(1'-methylbenzimidazoyl)-4-(2-ethylhexyloxy)pyridine (**MC**).

Compound	Τ _g (°C)	τ _m (°C)	T _c (°C)
МС		152–156	109
[Zn(MC) ₂](OTf) ₂		314	141
$[Zn(MC)_2](NTf_2)_2$		241	126
[Tb(MC) ₃](OTf) ₃	137	171	
$[La(\mathbf{MC})_3](NTf_2)_3$	100	150	

All values as observed in the first heating and cooling cycle (10 °C min⁻¹).

Table S2. Volume of the hard- and soft phase of the different MSPs as estimated via computational analysis. The values were used to calculate the volume fraction of the hard- and soft phase.

Hard phase	Volume (ų)	
[M ²⁺ Mebip ₂](OTf) ₂	887	
[M ²⁺ Mebip ₂](NTf ₂) ₂	1027	
[M ²⁺ Mebip ₂](ClO ₄) ₂	827	
[M ³⁺ Mebip ₃](OTf) ₃	1313	
[M ³⁺ Mebip ₃](NTf ₂) ₃	1527	
[M ³⁺ Mebip ₃](ClO ₄) ₃	1223	
Soft Phase	Volume (ų)	
PEB ₃₀₀₀	4016	
PEB ₂₀₀₀	2721	

3. Experimental Details

3.1. Instrumentation

NMR Spectroscopy. NMR spectra were recorded at 297.2 K on a Bruker Avance DPX 400 spectrometer at frequencies of 400.19 MHz for ¹H nuclei and 100.63 MHz for ¹³C nuclei. Spectra were calibrated to the residual solvent peak of CDCl₃ (7.26 ppm ¹H NMR; 77.16 ppm ¹³C NMR) or DMSO-d₆ (2.50 ppm ¹H NMR; 39.52 ppm ¹³C NMR). Data were treated with MestReNova (12.0.2) software suite and all chemical shifts δ are reported in parts per million (ppm) relative to tetramethyl silane.

Size exclusion chromatography (SEC). SEC analysis was conducted on an Agilent 1200 series HPLC system equipped with two Agilent PLgel mixed-D columns (ID = 7.5 mm, L = 300 mm, particle size = 5 μ m) and an Agilent PLgel mixed guard column (particle size = 5 μ m) at 30 °C and a flow rate of 1.0 mL min⁻¹ using THF as the eluent. Signals were acquired by an Optilab REX interferometric refractometer and data was processed using the Astra software (Wyatt Technology Corp.).

UV-vis spectroscopy. Solution phase UV-vis spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer using quartz cuvettes of 1 cm path length.

Thermogravimetric analysis (TGA). Measurements were conducted in air using a Mettler-Toledo STAR thermogravimetric analyzer in the range of 25 °C to 500 °C with a heating rate of 10 °C min⁻¹.

Differential scanning calorimetry (DSC). Measurements were performed under N₂ using a Mettler-Toledo STAR system operating at a heating/cooling rate of 10 °C min⁻¹ in the range of –80 to 200 °C, unless indicated otherwise. The midpoint of the step change in the heat capacity is reported as the glass transition temperature (T_g), the melting temperature (T_m) is reported based on the minimum of the major endothermic melting peak, and the crystallization temperature (T_c) is reported based on the maximum of the major temperature crystallization peak.

Dynamic mechanical analyses (DMA). Measurements were conducted under N_2 on a TA Instruments DMA Q800 with a heating rate of 3 °C min⁻¹, a frequency of 1 Hz, and an amplitude of 15 μ m in the range of -80 to 300 °C, using tensile clamps and rectangular shaped samples. The reported mechanical data are averages of 3 independent experiments, and all errors are standard deviations.

Small-angle and wide-angle X-ray scattering (SAXS/WAXS). Experiments were performed on a Rigaku NanoMax camera (Rigaku Innovative Technologies, Auburn Hills, MI). The camera was equipped with a Cu target sealed tube source (MicroMax 003 microfocus, Rigaku), and the scattering data were recorded by a Pilatus100 K detector (Dectris). The sample-to-detector distance was calibrated using silver behenate. For the temperature-dependent experiments a Linkam HFS-X350-GI heating stage module with a T95

controller was used. Stainless-steel discs with a thickness of 2 mm and a central cylindrical hole (diameter of 2 mm) were employed as samples holders that were mounted onto the heating stage. Samples were cut into pieces of appropriate size and pressed into the sample holder. The heating and cooling rate for temperature-dependent scattering experiments was 10 °C min⁻¹, and samples were equilibrated at each temperature for 10 min before data collection was started. Raw data were processed according to standard procedures. Scattering spectra are presented as a function of the momentum transfer $q = 4\pi\lambda^{-1} \sin(\theta/2)$, where θ is the scattering angle and $\lambda = 0.1524$ nm is the photon wavelength.

Scanning transmission electron microscopy (STEM). Imaging was performed on a Thermo Scientific Titan Themis 60-300 transmission electron microscope operated at 200 kV in scanning mode and using highangle annular dark-field conditions (STEM-HAADF). The microscope is equipped with a high brightness X-FEG gun and silicon drift Super-X EDX detectors and Velox acquisition software. Samples for STEM analysis were prepared by cryo-ultramicrotomy. Sample were ultramicrotomed at –50 °C with a Leica EM FC7 machine (equipped with a Diatome cryo-knife 35° angle) at a cutting speed of 0.2 mm s⁻¹. Ultramicrotomed slices were deposited on an ultra-thin carbon support grid.

Optical microscopy (OM) and polarized optical microscopy (POM). Images were acquired with an Olympus BX51 microscope equipped with a DP72 digital camera and polarized optical microscopy images were collected with crossed polarizers. For temperature-dependent experiments, a Linkam LTS 350 heating stage module was used. Heating and cooling rates of 10 °C min⁻¹ were used in the temperature regime where thermal transitions were observed in the DSC traces, and heating and cooling rates of 30 °C min⁻¹ were used outside these regimes.

Rheological measurements. The measurements were performed using either an Anton Paar MCR 501 rheometer connected to a Peltier controlled measurement system in parallel plate geometry and a dry N_2 stream for temperature control, or an ARES-G2 from TA-Instruments with a constant N_2 gas stream for temperature control. A geometry with parallel plates with a diameter of 25 mm or 8 mm was used. All lanthanide films were equilibrated in the melt at 160 °C ([Tb(BKB₃₀₀₀)_{1.5}](OTf)₃, [Tb(BKB₂₀₀₀)_{1.5}](OTf)₃, and [Gd(BKB₃₀₀₀)_{1.5}](OTf)₃) or 180 °C ([La(BKB₃₀₀₀)_{1.5}](NTf₂)₃) before the start of the measurement to remove any thermal history from the compression-molding step. For MSP films containing Zn²⁺ ions, samples were employed as obtained by compression-molding as an annealing in the melt was not possible because the melting temperature is around the onset of thermal degradation in the materials. The sample thickness was between 0.4 and 1.0 mm. The limit for linear response behavior was checked first. Afterwards, rheological measurements at each temperature were performed after an equilibration time of at least 5 min at an angular frequency range of 100–0.1 rad s⁻¹ unless otherwise indicated. Time-temperature superposition was performed by shifting the frequency-dependent

oscillatory G' or G'' shear moduli or the loss tangent (tan δ) horizontally along the frequency axis to a reference temperature (T_{ref}) of 0 °C until good overlap was achieved. If necessary, for a good overlap of G' and G'', the data was subsequently shifted along the horizontal axis by a vertical shift factor b_T .

The scaling of the horizontal shift factors a_T was fitted to the VFT-model:⁵

$$a_T = a_{T,0} \ 10^{(A + \frac{B}{T - T_0})}$$
 Equation S1

where A and B represent fitting constants, $a_{T,0}$ represents the horizontal shift factor at the reference temperature, T is the temperature in K, and T_0 is the Vogel temperature that is typically 50 °C below T_g .

The apparent activation energies were fitted according to the following equations:⁶

$$Ln(a_T) = B_0 + \frac{E_a}{RT}$$
 Equation S2
$$Ln(\tau_b) = A_0 + \frac{E_a}{RT}$$
 Equation S3

where τ_b represents the supramolecular bond lifetime determined as the crossover point of G' and G'', a_T are the manual horizontal shift factors, E_a is the apparent activation energy in J mol⁻¹, R is the gas constant 8.3145 J K⁻¹ mol⁻¹, and T is the temperature in K.

3.2. Materials and Methods

UV-vis spectrophotometric titrations. To demonstrate that the prepared macromonomer forms complexes in the same manner as previously reported UV-vis absorption spectra were acquired upon titration of solutions of the macromonomers **BKB**₃₀₀₀ and **BKB**₂₀₀₀ ($c = 10 \mu \text{mol L}^{-1}$ in CHCl₃/MeCN 9:1) with aliquots of Zn(NTf₂)₂ ($c = 230 \mu \text{mol L}^{-1}$ in CHCl₃/MeCN 9:1, containing also the respective BKB ($c = 10 \mu \text{mol L}^{-1}$ to avoid dilution). Moreover, UV-vis absorption spectra were acquired upon titrations of the low molecular weight model compound **MC** ($c = 25 \mu \text{mol L}^{-1}$) in anhydrous MeCN with Zn(OTf)₂ ($c = 303 \mu \text{mol L}^{-1}$) or Tb(OTf)₃ ($c = 208 \mu \text{mol L}^{-1}$) in anhydrous MeCN, unless otherwise indicated. In this case, the solutions contained **MC** ($c = 25 \mu \text{mol L}^{-1}$) to avoid dilution effects. The characteristic absorbance band for the ligand and the formed Zn²⁺⁻ or Tb³⁺-complexes were plotted as a function of the metal-to-ligand ratio.

Metallosupramolecular polymerization and film formation. To a stirred solution of the BKB macromonomer in CHCl₃, the proper amount of a solution of the metal salt in anhydrous MeCN was added to ensure a stoichiometric metal-to-ligand ratio. The solution was stirred for 10 minutes, the solvent was removed *in vacuo* and the sample was redissolved in CHCl₃. The solution was dried *in vacuo*, and placed in a vacuum oven overnight at 40 °C. Subsequently, the samples of the metallosupramolecular polymers

were compression molded at different temperatures with a pressure of 3 tons for 4 min. The compressionmolding was carried out at 200 °C for ($[ZnBKB_{3000}](OTf)_2$, $[ZnBKB_{2000}](OTf)_2$, $[FeBKB_{3000}](OTf)_2$, and $[FeBKB_{2000}](OTf)_2$), at 140 °C for samples of ($[ZnBKB_{3000}](ClO_4)_2$, $[FeBKB_{3000}](ClO_4)_2$, $[FeBKB_{2000}](ClO_4)_2$, $[ZnBKB_{3000}](NTf_2)_2$, $[ZnBKB_{2000}](NTf_2)_2$, and $[La(BKB_{3000})_{1.5}](NTf_2)_3$, or at temperatures of 100 °C for samples of ($[Tb(BKB_{3000})_{1.5}](OTf)_3$, $[Tb(BKB_{2000})_{1.5}](OTf)_3$, $[La(BKB_{3000})_{1.5}](OTf)_3$, $[Tb(BKB_{3000})_{1.5}](ClO_4)_3$.

Formation of metal-ligand complexes with model ligand. To a stirred solution of the ligand **MC** in CHCl₃, a proper amount of a solution of the metal salt in anhydrous MeCN was added to ensure a stoichiometric metal-to-ligand ratio. The solution was stirred for 10 min, and subsequently dried under an N₂ stream and then in a vacuum oven overnight at 40 °C.

Computational analysis of the volume fraction. A geometry optimization was performed with the semiempirical PM3 model as implemented in the Spartan 16 software suite. All thresholds were left to the default settings and the provided values for the CPK volume of the different complexes are those obtained after structure optimization.

3.3. Synthetic Procedures and Analytical Data

General Procedures. Poly(ethylene-*co*-butylene) (Krasol[®]) of a number-average molecular weight of 3100 and 2100 g mol⁻¹ was obtained from Cray Valley HSC and dried *in vacuo* at 40 °C overnight prior to use. Spectroscopy grade chloroform (Acros organics) was passed over dry, activated (Brockman I) basic alumina prior to use to remove acidic impurities. Zinc(II) trifluoromethanesulfonate (Zn(OTf)₂) (Aldrich), Zinc(II) perchlorate hexahydrate (Zn(ClO₄)₂ · 6H₂O) (Strem), Zinc bis(trifluoromethylsulfonyl)imide (Zn(NTf₂)₂) (Aldrich), Iron(II) trifluoromethanesulfonate (Fe(OTf)₂) (Aldrich), Iron(II) perchlorate hexahydrate (Fe(ClO₄)₂ · 6H₂O) (Aldrich), Terbium trifluoromethanesulfonate (Tb(OTf)₃) (Aldrich), Terbium perchlorate (Tb(ClO₄)₃; 50% aqueous solution) (Strem), Gadolinium trifluoromethanesulfonate (Gd(OTf)₃) (Aldrich), Gadolinium perchlorate (Gd(ClO₄)₃) (50% aqueous solution) (Strem), Lanthanum bis(trifluoromethanesulfonyl)imide (La(NTf₂)₃) (TCI), anhydrous MeCN (Acros organics), and all other reagents were commercially obtained and used without further purification.

The 2,6-bis(1'-methylbenzimidazolyl)pyridine (Mebip) ligand, the bis(1'-methylbenzimidazoyl)-4-(2-ethylhexyloxy)pyridine **MC** as a low molecular weight model compound, and the bis(Mebip)-functionalized telechelic poly(ethylene-*co*-butylene) (BKB) macromonomers BKB₃₀₀₀ and BKB₂₀₀₀ were prepared following previously reported procedures.^{1,2,7}

3.4. NMR and MALDI spectra

 ^1H and ^{13}C NMR Spectra (CDCl_3, 400 MHz) of $\text{BKB}_{3000}.$



MALDI of BKB₃₀₀₀.



 ^1H and ^{13}C NMR Spectra (CDCl_3, 400 MHz) of $\text{BKB}_{2000}.$



MALDI of BKB₂₀₀₀.



4. References

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