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### Electroactive Linear–Hyperbranched Block Copolymers Based on Linear Poly(ferrocenylsilane)s and Hyperbranched Poly(carbosilane)s

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Abstract: A convenient two-step protocol is presented for synthesis of linearhyperbranched diblock copolymers consisting of a linear, organometallic poly(ferrocenylsilane) (PFS) block and poly(carbosilane) hyperbranched (hbPCS) segments. Linear PFS diblock copolymers were synthesized through photolytic ring-opening polymerization of dimethyl[1]silaferrocenophane as the first block and methylvinyl[1]silaferrocenophane as the second. These block copolymers served as polyfunctional cores in a subsequent hydrosilylation polyaddition of different silane-

#### Introduction

Metal-containing polymers have received increased attention during recent decades, owing to their unique properties arising from the presence of (transition) metals in the macromolecular structure.<sup>[1]</sup> In such materials, metals can be incorporated as side groups (for example, as in poly(vinylferrocene)<sup>[2]</sup>) or in the main chain. One of the most thoroughly investigated systems featuring a transition metal in the main chain is poly(ferrocenylsilane) (PFS).<sup>[3]</sup> Interesting properties of PFSs, such as redox activity, semiconductivity, and the ability to function as precursors to catalysts for the growth of carbon nanotubes, have been studied.<sup>[3,4]</sup> PFSs have also attracted attention as redox-active matrices for color-tunable photonic crystals,<sup>[5]</sup> etch resists,<sup>[6]</sup> charge-dissipation coatings,<sup>[7]</sup> photoconductive materials,<sup>[8]</sup> precursors to

based  $AB_2$  monomers. Three  $AB_2$ monomers (methyldiallylsilane; methyldiundecenylsilane, and ferrocenyldiallylsilane) were investigated; they introduced structural diversity to the hyperbranched block and showed variable reactivity for the hydrosilylation reaction. In the case with the additional ferrocene moiety in the ferrocenyldiallylsilane monomer, an electroactive hy-

**Keywords:** aggregation • block copolymers • electrochemistry • ferrocenes • hyperbranching perbranched block was generated. No slow monomer addition was necessary for molecular-weight control of the hyperbranching polyaddition, as the core had much higher functionality and reactivity than the carbosilane monomers. Different block ratios were targeted and hybrid block copolymers with narrow polydispersity (<1.2) were obtained. All the resulting polymers were investigated and characterized by size exclusion chromatography, NMR spectroscopy, cyclic voltammetry, and TEM, and exhibited strongly anisotropic aggregation.

magnetic<sup>[9]</sup> or catalytically active nanoparticles,<sup>[10]</sup> and materials with a high refractive index.<sup>[11]</sup> Since the discovery of thermal ring-opening polymerization of strained [1]silaferrocenophanes,<sup>[12]</sup> various other polymerization techniques such as transition-metal-catalyzed, living anionic, and photolytic ring-opening polymerization (PROP) have been developed.<sup>[3,13]</sup> Among these mechanisms, transition-metal-catalyzed polymerization and PROP are of special interest, owing to their tolerance to several functional groups that are present in the monomers; these would not endure, for example, the strongly basic conditions of a living anionic polymerization initiated with strong bases such as butyllithium (for *n*-butyllithium,  $pK_B \approx 42$ ). PROP of [1]silaferrocenophanes is initiated with weak bases such as sodium cyclopentadienide ( $pK_B \approx 16$ ) under irradiation, and thus tolerates functional groups such as alkenes, alkynes, and amines.<sup>[14]</sup> Furthermore, in contrast to transition-metal-catalyzed polymerization, PROP proceeds in a living manner and thus permits the synthesis of block copolymers or other macromolecular architectures. Such block copolymers (previously synthesized by living anionic ring-opening polymerization) have shown impressive self-assembly properties as a result of phase separation to give well-defined nanostructures.<sup>[3,15]</sup>

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Dendrimers are believed to be interesting candidates for incorporation in polymeric architectures because of their globular structure, low viscosity, and the high number of terminal (in many cases functional) end groups. However, owing to the demanding multistep synthesis and the need for high-conversion transformations, dendrimers are accessible only in limited quantities by time-consuming multistep processes, often followed by demanding purification steps.<sup>[16]</sup> In contrast, statistically branched (that is, hyperbranched) materials can usually be synthesized in a single polymerization step. By adjustment of the monomer/initiator (or core) ratio, even elevated molecular weights can be achieved in one step. Nevertheless, numerous studies on hyperbranched materials have revealed physical properties comparable with those of their perfect dendrimer analogues. A common drawback of hyperbranched polymers is their broad molecular weight distribution and imperfect structure, making further reactions or supramolecular assembly difficult. Furthermore, different functional end groups may be present, as a result of random branching, that is, formation of linear, dendritic, and terminal units. Thus, polymer chemists have found it a challenge to control molecular weight and branching during the synthesis of nonlinear macromolecules. Several studies describe the synthesis of dendrimer segments attached to a linear polymer chain;<sup>[17]</sup> in solution and in bulk the resulting hybrids show interesting properties that are currently under investigation. Only a few papers, however, have detailed the synthesis of linear-hyperbranched block copolymers with promising properties similar to those of perfect dendrimer blocks, but based on a feasible synthetic pathway.<sup>[18]</sup> Our group has developed the hypergrafting concept; an example is the formation of hyperbranched poly(carbosilane)s (hbPCSs) connected to a linear polymeric core by means of hydrosilylation polyaddition of a suitable AB<sub>2</sub> monomer. In this manner, poly(styrene)-bhb-poly(carbosilane)s<sup>[17a]</sup> and poly(ethylene oxide)-b-hb-poly(carbosilane)s<sup>[17d]</sup> have been realized. The basic idea guaranteeing molecular weight control is the use of a polyfunctional core, the incorporation of which is favored over homopolymerization of the AB<sub>2</sub> monomer, and which yields linear- hyperbranched block copolymers with narrowly distributed molecular weights.

Here we report on the first synthesis of linear-hyperbranched diblock copolymers based on PFS and hbPCS with narrow molecular weight distributions and different chemical compositions. The synthesis relies on a straightforward two-step method, combining PROP of [1]silaferrocenophanes for the generation of linear block copolymer cores with subsequent hydrosilylation polyaddition of suitable AB<sub>2</sub> monomers for the construction of the hyperbranched block. The molecular weights of both the linear precursors and the hyperbranched blocks were varied. The linear block copolymers were based on poly(dimethylferrocenylsilane) (PFDMS) and poly(methylvinylferrocenylsilane) (PFMVS). The polyfunctionality of the core with several Si–vinyl bonds was believed to favor the hypergrafting reaction over the homopolymerization of the AB<sub>2</sub> monomer. The activity of double bonds in PFSs in hydrosilylation reactions with monofunctional silanes had been investigated previously.<sup>[19]</sup> It was found that Si–vinyl bonds showed high reactivity in hydrosilylation reactions, higher than that of either allyls or oxyallyls.<sup>[20]</sup> Highly reactive core molecules have been employed in hyperbranching reactions in several other studies.<sup>[17d,21]</sup>

This paper presents the synthesis of several linear-hyperbranched ferrocene-based block copolymers (Figure 1) and their detailed characterization via NMR spectroscopy and size-exclusion chromatography (SEC). The electrochemistry



series 3 PFDMS-(PFMVS-hbPfcDAS)

Figure 1. Schematic representation of the linear-hyperbranched block copolymers based on poly(dimethylferrocenylsilane)-*b*-poly(methylvinylferrocenylsilane) (PFDMS-*b*-PFMVS) obtained after hypergrafting of the AB<sub>2</sub> monomers (series 1: methyldiallylsilane (MDAS) (1); series 2: methyldiundecenylsilane (MDUS) (2); series 3: ferrocenyldiallylsilane (fcDAS) (3)).

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was studied by cyclic voltammetry (CV) and supramolecular assembly was investigated by TEM.

#### **Results and Discussion**

**Synthesis**: Two different [1]silaferrocenophanes were synthesized according to literature methods: dimethyl[1]silaferrocenophane (4) and methylvinyl[1]silaferrocenophane (5).<sup>[13]</sup> Polymerization was conducted by consecutive PROP of 4 (as first block) and 5 (as second block) in THF as solvent at 5°C with sodium cyclopentadienide (NaCp) as the initiator (Scheme 1; molecular weights are listed in Table 1).



Scheme 1. Photolytic anionic ring-opening polymerization of dimethyl[1]silaferrocenylsilane and methylvinyl[1]silaferrocenylsilane.

Table 1. Molecular weight data and polydispersity indices for linear and linear-hyperbranched block copolymers.

Sample <sup>[a]</sup>		$M_n^{[b]}$	PDI <sup>[b]</sup>	$M_n^{[c]}$
6	PFDMS <sub>121</sub> -PFMVS <sub>22</sub>	35600 1	1.09	_
7	PFDMS <sub>165</sub> -PFMVS <sub>21</sub>	45400	1.09	-
8	PFDMS <sub>98</sub> -PFMVS <sub>29</sub>	31000	1.11	_
9	PFDMS <sub>121</sub> -(PFMVS <sub>22</sub> -hbPMDAS <sub>60</sub> )	38000	1.16	43200
10	PFDMS <sub>121</sub> -(PFMVS <sub>22</sub> -hbPMDAS <sub>88</sub> )	41400	1.06	46800
11	PFDMS <sub>121</sub> -(PFMVS <sub>22</sub> -hbPMDAS <sub>235</sub> )	44 500	1.07	65300
12	PFDMS <sub>165</sub> -(PFMVS <sub>21</sub> -hbPMDAS <sub>85</sub> )	49000	1.19	56200
13	PFDMS <sub>121</sub> -(PFMVS <sub>22</sub> -hbPMDUS <sub>25</sub> )	37300	1.09	44 200
14	PFDMS <sub>121</sub> -(PFMVS <sub>22</sub> -hbPMDUS <sub>30</sub> )	43400	1.08	46100
15	PFDMS <sub>121</sub> -(PFMVS <sub>22</sub> -hbPMDUS <sub>35</sub> )	47800	1.20	48900
16	PFDMS <sub>98</sub> -(PFMVS <sub>29</sub> -hbPfcDAS <sub>35</sub> )	34200	1.05	41 500
17	PFDMS <sub>98</sub> -(PFMVS <sub>29</sub> -hbPfcDAS <sub>60</sub> )	36600	1.15	48900
18	PFDMS <sub>98</sub> -(PFMVS <sub>29</sub> -hbPfcDAS <sub>76</sub> )	38700	1.07	53900
19	PFDMS <sub>08</sub> -(PFMVS <sub>20</sub> -hbPfcDAS <sub>110</sub> )	37500	1.06	66800

[a] Abbreviations: PFDMS: poly(dimethylferrocenylsilane); PFMVS: poly(methylvinylferrocenylsilane); PMDAS: poly(methyldiallylsilane); PMDUS: poly(methyldiundecenylsilane); PfcDAS: poly(ferrocenyldiallylsilane). [b] Determined by SEC in THF. [c] Determined by <sup>1</sup>H NMR spectroscopy.

After workup, these linear diblock copolymers served as macromolecular cores for the ensuing hyperbranching hydrosilylation polyaddition of 1, 2, and 3, respectively, to generate the linear-hyperbranched block copolymers. A higher reactivity of the core molecule than the monomers is desirable to achieve full incorporation of the core and to prevent homopolymerization of the carbosilane monomer without the core. By use of highly reactive double bonds in block copolymers containing poly(allyl glycidyl ether) (PAGE), the redundancy of the slow monomer addition technique in this special case has been proven.<sup>[17d]</sup> Usually this strategy is necessary to gain molecular weight control when a core with aliphatic double bonds is employed, for example, for poly-(butadiene).<sup>[17a]</sup> As is well known from the literature, vinylsilanes show even higher reactivity in hydrosilylation reactions than the aforementioned oxyallyl groups.<sup>[19]</sup> Therefore we believed that by using such highly reactive cores it was possible to avoid slow monomer addition. Indeed, detailed studies demonstrated that the highly reactive vinylsilane groups of the core permitted simultaneous copolymerization, so that slow monomer addition was avoided. Moreover, the vinylsilane groups are fully incorporated, even when the sterically demanding monomer 2 is polymerized. In the case of the PAGE core we found unreacted core double bonds, which we ascribed to steric reasons. Moreover, the Si-vinyl bonds cannot be isomerized, in contrast to allyl groups that can be rearranged to propenyl groups, which are unreactive in hydrosilylation.

The  $AB_2$  monomer was added to the core in various numbers of equivalents, and polyaddition was started by addition of one droplet of Karstedt's catalyst (for polyaddition with monomer **1**, see Scheme 2). As a side reaction, homopoly-



Scheme 2. Hypergrafting of methyldiallylsilane (1) by hydrosilylation polyaddition to linear diblock copolymer precursors.

merization of the AB<sub>2</sub> monomer was observed, as reported previously.<sup>[17]</sup> However, the undesired low molecular weight homopolymer side product could be separated conveniently from the block copolymers in various ways: 1) preparative SEC in THF by cutting off the lower molecular weights (<10000 gmol<sup>-1</sup>); 2) dialysis in THF by using a dialysis tube with a molecular weight cutoff of around 8000 gmol<sup>-1</sup>; 3) repetitive precipitation of the crude reaction mixture from THF into hexanes/methanol (9:1). After separation of the broadly distributed homopolymer (PDI>3) the desired narrowly distributed linear-hyperbranched block copolymer was obtained in reasonable yields (50–80%). Different  $AB_2$  monomers have been employed: 1 and 2 were investigated previously in polyaddition reactions. A third novel  $AB_2$  monomer was synthesized, containing a ferrocenyl moiety to introduce electroactivity into the hyperbranched poly(carbosilane). Ferrocenyldiallylsilane (3) is synthesized in two steps (Scheme 3) from ferrocene, with dichloroferrocenylsilane (3a) as the intermediate product.



Scheme 3. Synthesis of diallylferrocenylsilane (3).

**Characterization**: SEC measurements and NMR spectroscopy were used to investigate the linear-hyperbranched block copolymers. Molecular weights determined by SEC are underestimated, as expected for branched polymers. Underestimation of molecular weight is more pronounced when the degree of polymerization of the hyperbranched block increases (see Table 1). Thus, absolute molecular weights of the block copolymers cannot be determined by SEC experiments.

Owing to the high molecular weights of the polymers and the absence of an easily detectable end group in the linear block copolymers, determination of the absolute molecular weights by NMR spectroscopy is not applicable or would cause a large error. Molecular weights were therefore determined as follows: 1) <sup>1</sup>H NMR of the linear block copolymers 6-8 provided the block ratio PFDMS/PFMVS, owing to distinct signals for the methyl group in PFMVS at  $\delta = 0.61$  ppm (methyl shifts in PFDMS are detected at  $\delta = 0.54$  ppm) and the signals for the vinyl group ( $\delta = 6.52-5.76$  ppm; compare the Supporting Information); 2) synthesis of PFDMS homopolymers with an end group<sup>[22]</sup> exhibiting distinct NMR resonances and comparison of the molecular weights determined by <sup>1</sup>H NMR and SEC showed that SEC values versus poly(styrene) standards gave reliable molecular weights with an estimated error of approximately 5%. We therefore used the molecular weights from the SEC experiments for 6-8 as a reference in the <sup>1</sup>H NMR spectra, and through knowledge of the block ratio the absolute molecular weight was determined. After hydrosilylation polyaddition the additional signals for the PCS block can be integrated separately in the <sup>1</sup>H NMR spectra and the  $DP_n$  of the AB<sub>2</sub> monomers can be calculated (see Table 1 and Figure 2).

**NMR analysis:** As mentioned previously, <sup>1</sup>H NMR spectroscopy was used to determine absolute molecular weights of the block copolymers. Figure 2 shows three representative



Figure 2. <sup>1</sup>H NMR ([D<sub>6</sub>]benzene) of different linear-hyperbranched block copolymers: a) PFDMS<sub>121</sub>-(PFMVS<sub>22</sub>-hbPMDAS<sub>88</sub>) (**10**); b) PFDMS<sub>121</sub>-(PFMVS<sub>22</sub>-hbPMDUS<sub>25</sub>) (**13**); c) PFDMS<sub>98</sub>-(PFMVS<sub>29</sub>-hbPfcDAS<sub>76</sub>) (**18**).

hbPCS

 $\delta$ /ppm

 $\delta/ppm$ 

6 5 4 3 2

<sup>1</sup>H NMR spectra for linear-hyperbranched block copolymers based on all three AB<sub>2</sub> monomers. The <sup>1</sup>H NMR spectra for the linear precursors can be found in the Supporting Information. In the case of **2** as the respective monomer, the DP<sub>n</sub> can be determined by integration of the distinct methyl signals of the hbPCS block ( $\delta$ =0-0.2 ppm). Additionally, one can distinguish between monomers that are directly linked to the core ( $\delta \approx 0.1$  ppm) and monomers in the periphery ( $\delta \approx 0.18$  ppm). The double bonds of hbPCS can be detected at lower field ( $\delta$ =5–6 ppm); partial isomerization of the double bonds during hydrosilylation is also detected (Figure 2b).

For polymers with **3** as the branching monomer, additional broad ferrocenyl signals can be detected between  $\delta = 4.0$ 

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and 4.4 ppm overlapping with the signals representing the PFS backbone, which are much sharper (Figure 2c). Polymers with **1** as the AB<sub>2</sub> monomer show several signals in the silane region ( $\delta = 0$ –1 ppm) of the <sup>1</sup>H NMR spectrum for the methyl group, indicating the branched structure of the PCS segment. An analysis by <sup>13</sup>C NMR and <sup>29</sup>Si NMR spectroscopy (Figure 3) supports the complete reaction of the core



Figure 3. a) <sup>29</sup>Si NMR spectra of **6** (top) and **10** (bottom). b) <sup>13</sup>C NMR spectra of **6** (top) and **10** (bottom). N.B.:  $[D_6]$ benzene = 128 ppm.

vinyl bonds and gives evidence of the hyperbranched nature of the PCS block. Separate signals for dendritic ( $\delta =$ 1.2 ppm), linear ( $\delta = 0.8$  ppm), and terminal ( $\delta = 0.23$  ppm) silanes in the <sup>29</sup>Si spectra of the polymers for polymers with 1 as the  $AB_2$  monomer are observed. In addition, the signal for the core Si–vinyl bonds ( $\delta = -13$  ppm) vanishes after hydrosilylation and is shifted to lower field ( $\delta = -3.8 \text{ ppm}$ ), owing to the presence of the attached carbosilane moiety. Interestingly, the <sup>29</sup>Si shifts for copolymers with **3** as a monomer differ significantly from the abovementioned spectra: the dendritic Si centers can be detected at  $\delta = 2.6$  ppm, the linear centers at  $\delta = -3.6$  ppm, and the terminal <sup>29</sup>Si centers at  $\delta = -4.7$  ppm. Furthermore, the signal for the reacted core vinyl bonds is shifted to higher field ( $\delta = -21$  ppm). In the <sup>13</sup>C NMR spectrum of polymers **16–19** additional broad signals for ferrocenes in the hbPCS compartment (at  $\delta =$ 68.2 and 70.7 ppm) can be assigned separately from the signals for ferrocene carbons of the PFDMS backbone ( $\delta =$  73.2 and 71.3 ppm) and the reacted PFMVS core ( $\delta$ =73.4 and 71.4 ppm). (For the spectra, see the Supporting Information.)

Figure 3b shows a zoom-in to the <sup>13</sup>C NMR spectrum of **10** in the  $\delta = 145$ –105 ppm region. Here again, as mentioned earlier for the Si centers, the signals for the carbon atoms of the vinyl bonds at  $\delta = 138$  ppm and 132 ppm are not detected after hypergrafting of **1**. The spectrum shows the terminal and linear allyl groups, and only a small amount of isomerization to the respective propenyl signals ( $\delta = 142.4$  and 144.3 ppm) is observed. This isomerization can be prevented when the reaction time is reduced and complete conversion can be maintained in this case (samples taken for IR control: disappearance of Si–H vibration at approximately 2100 cm<sup>-1</sup>; see the Supporting Information).

SEC analysis: A crucial aspect of the preparation of complex macromolecular architectures is control over molecular weights and polydispersity of the resulting materials. In hyperbranched polymers, not only is there molecular-weight polydispersity (as in any other synthetic polymer), but in addition, as a result of the randomly branched architecture, structural polydispersity has to be considered because of the large number of configurational isomers for one distinct molecular weight. SEC experiments, however, usually give an apparent molecular weight distribution. Samples that were analyzed by SEC directly after the hypergrafting step showed a multimodal SEC elugram (see the Supporting Information). In addition to the desired linear-hyperbranched block copolymer, low molecular weight hbPCS was present in the mixture. After separation from the broadly distributed homopolymer by preparative SEC, dialysis in THF, or repetitive precipitation, all materials exhibit a monomodal, narrow, apparent molecular weight distribution in SEC (compare Figure 4 and the Supporting Information) with low polydispersities below 1.15 in most cases. We observed undesired coupling only after a prolonged reaction time with Karstedt's catalyst, resulting in a second mode in SEC elugrams (sample 18, Table 1). These high molecular weight shoulders were removed by preparative SEC, but was avoided if the catalyst was removed from the crude reaction mixture by addition of charcoal followed by filtration over Celite (see the Experimental Section) directly after disappearance of the Si-H functionality in the IR spectrum.

**Electrochemistry**: A significant issue related to the synthesis of the linear-hyperbranched block copolymers was their electroactivity. Specifically, there were some intriguing questions: 1) does the electroactivity change after polyaddition of an electrochemically inactive species? 2) is it possible to tailor the electroactivity of the polymers by polyaddition of a novel electroactive monomer (3)? This is a crucial aspect for the future application of such materials in, for example, tunable (bio)sensors.

It is well known from the literature<sup>[1]</sup> that PFSs exhibit two single oxidation waves in a CV experiment, resulting from stepwise oxidation (or reduction) of the iron centers



Figure 4. SEC elugrams in THF: a) series 1, b) series 3.

along the backbone. The first oxidation wave arises from oxidation of every second ferrocenyl moiety (Fe<sup>2+</sup>) into the respective ferrocenium (Fe<sup>3+</sup>) ion. The second oxidation wave at higher voltage indicates oxidation of the remaining ferrocenes ("communicating ferrocenes"). When the voltage is reduced, the opposite devolution can be observed. The block copolymers were dissolved in dichloromethane  $(\approx 2 \text{ gL}^{-1})$  containing Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) as the conducting salt, and degassed before measurements were taken. Figure 5 shows four different CVs at scan rates from 0.1 to  $0.9 \text{ Vs}^{-1}$ : the CVs resulting from two different linear-hyperbranched block copolymers based on the electro-inactive monomers 1 (Figure 5a; Table 1, sample 11) and 2 (Figure 5b; Table 1, sample 14) do not differ from each other, and therefore their electrochemical properties are determined only by the PFS backbone and no change in their behavior is observed after hypergrafting. The additional functional groups still offer potential for further application of these materials for electrochemical devices.

If **3** is used as the respective  $AB_2$  monomer (Figure 5c; Table 1, sample **18**), the electrochemical properties of the linear block are clearly affected: the first oxidation wave is shifted to higher voltages and is more pronounced than those in Figure 5a,b; this indicates oxidation of every second ferrocenyl moiety in the PFS chain and oxidation of the fer-



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Figure 5. Cyclic voltammograms of different linear-hyperbranched block copolymers: a)  $PFDMS_{121}$ -( $PFMVS_{22}$ -hb $PMDAS_{235}$ ) (11); b)  $PFDMS_{121}$ -( $PFMVS_{22}$ -hb $PMDUS_{30}$ ) (14); c)  $PFDMS_{98}$ -( $PFMVS_{29}$ -hb $PfcDAS_{76}$ ) (18); d) oligomers separated from the crude reaction mixture for 18.

rocene moieties in the hyperbranched periphery (which are not communicating with each other, owing to a lack of conjugation between them). The second oxidation wave remains unchanged. For comparison, Figure 5d shows the CV of a

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homopolymer of **3** ( $M_{n(\text{SEC})} = 1200 \text{ gmol}^{-1}$ ,  $M_{n(\text{MALLS})} = 4500$ , PDI = 1.5) (separated from the crude reaction mixture from **18**), exhibiting only a single oxidation wave and no communicating ferrocenes. Polymers based on **3** might therefore be of considerable interest when oxidative or reductive activity is required at different potentials and with different intensities.

**Transmission electron microscopy (TEM)**: Transmission electron microscopy (TEM) measurements were used to investigate the self-assembly of the novel linear-hyperbranched block copolymers in solution. In a previous report on poly(ethylene oxide)-*b*-hbPCS copolymers,<sup>[17d]</sup> unusual, rodlike micelles were detected in various solvents. The rod-like structures observed are believed to be a consequence of the crystallization of the linear PEO chains and the constraints resulting from the hyperbranched structure at the junction point between the two blocks. Motivated by such findings, we investigated self-assembly for the novel series of block copolymers in decane, which is a nonsolvent for the crystalline PFDMS block but a good solvent for the highly apolar hbPCS segment.

The TEM images in Figure 6 show block copolymer solutions (approximately  $1 \text{ mgmL}^{-1}$ ) in decane/THF (9:1) mixtures, drop-cast onto a carbon-coated copper grid. General-



 $\begin{array}{l} \label{eq:spinor} Figure 6. TEM images of a decane/THF (9:1) solution (1 mgmL^{-1}), drop- \\ cast onto copper grids, of: a) PFDMS_{121}-(PFMVS_{22}-hbPMDAS_{60}) (9); \\ b) PFDMS_{165}-(PFMVS_{21}-hbPMDAS_{85}) (12); c) PFDMS_{121}-(PFMVS_{22}-hbPMDUS_{25}) (13); d) PFDMS_{121}-(PFMVS_{22}-hbPMDUS_{35}) (15). \end{array}$ 

ly, large, bundled aggregates with a high aspect ratio are detected for block copolymers with different hbPCS blocks. The density of these bundles varies with the DP<sub>n</sub> of the hbPCS: as shown in Figure 6a,c, block copolymers based on **1** or **2** as the AB<sub>2</sub> monomer form highly bundled structures, molecular weight  $\approx 8000 \text{ gmol}^{-1}$ , for both hbPCS structures. As the molecular weight of hbPCS increases, the solubility of the block copolymers rises and less bundled aggregates are detected (Figure 6b,  $M_{\rm w}$ (hbPCS) = 10500 gmol<sup>-1</sup>) or even almost distinct, single rods several micrometers (5-10  $\mu$ m) in length, are obtained (Figure 6d,  $M_w$ (hbPCS) =  $12500 \text{ gmol}^{-1}$ ). A key mechanism for the formation of these impressive aggregates is most probably epitaxial growth. When a solution of 15 was investigated 30 min after addition of decane, shorter rods (between 250 nm and few micrometers long) were detected. Solutions that had been allowed to equilibrate over a period of several hours showed cylindrical aggregates with lengths exceeding several micrometers. To gain further insight into the aggregation behavior of the materials, we sonicated a micellar solution of 15 for 30 min to destroy the long aggregates and to obtain small rods (see Figure 7a). Figure 7b demonstrates the presence of rodlike



Figure 7. TEM images of a decane/THF (9:1) solution  $(1 \text{ mgmL}^{-1})$ , drop cast-onto copper grids, of PFDMS<sub>121</sub>-(PFMVS<sub>22</sub>-hbPMDUS<sub>35</sub>) (**15**): a) micellar solution after sonification for 30 min; b) micellar solution after 1 h of equilibration; c) micellar solution after sonication for 30 min and addition of an unimer solution of PFDMS<sub>165</sub>-(PFMVS<sub>21</sub>-hbPMDAS<sub>85</sub>) (**12**); d) Micellar solution of **15** sonicated for 30 min and addition of extra unimer solution of **15**.

aggregates with a uniform diameter but a broad length distribution in the micellar solution after 1 h of equilibration. After addition of a unimer solution of **15** or of **12** in THF to the shortened cylindrical micelles, the aspect ratio of the resulting aggregates rises strongly, and very long entangled rods can be detected by TEM investigations (Figure 7c,d) that display several bends and crossovers. This indicates epitaxial growth of the unimer block copolymers onto the previously formed short rods that act as nuclei for a supramolecular aggregation in the nonsolvent decane (>10  $\mu$ m). Interestingly, the micellar solutions of these highly entagled

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aggregates stay clear for days without any precipitation, indicating that they are very stable.

#### **Conclusion and Outlook**

A straightforward two-step approach for the synthesis of linear-hyperbranched block copolymers with an organometallic linear poly(ferrocenylsilane) block has been described. The molecular weights of the polymers can be tailored in two ways: 1) the molecular weight of the linear block can be adjusted very accurately by living anionic polymerization of ferrocenophanes; 2) the molecular weight of the hyperbranched block can be controlled by the amount of AB<sub>2</sub> monomer employed. Narrowly distributed block copolymers are obtained in reasonable yields. It was demonstrated that different AB<sub>2</sub> monomer structures can be used for the synthesis of structurally different and functional materials. Three different AB<sub>2</sub> monomers have been investigated: methyldiallylsilane (MDAS) (1); methyldi(undecenyl)silane (MDUS) (2); and ferrocenyldiallylsilane (fcDAS) (3). By application of these monomers in the hypergrafting step, the architecture of the hyperbranched block was varied from a high-density branched segment with 1 as the respective AB<sub>2</sub> monomer to a low-density branched block when monomer 2 was polymerized. The highly flexible hyperbranched segments based on 2 can be viewed as analogous to low-density poly(ethylene). By introduction of an additional ferrocene moiety into the hyperbranched block using 3 as a novel AB<sub>2</sub> monomer, the electroactivity of the resulting block copolymers can be tailored.

The electrochemical properties of the block copolymers have also been studied. Clearly, by the use of an electrochemically active  $AB_2$  monomer one can adjust the electrochemical response of the polymers, for example, for application in sensors. Furthermore, aggregation of the block copolymers in solution has been investigated. A nonsolvent (decane) for the linear crystalline poly(dimethylferrocenylsilane) block was added slowly to the block copolymer solution in THF to induce micellization. Anisotropic rodlike aggregates with varying structures and sizes depending on the molecular weight of the hyperbranched block were visualized by TEM.

Further studies are currently in progress, such as variation of the core polymer to an amorphous structure and the generation of different functional groups at the polymer backbone, and more detailed investigation (including light scattering techniques) on the aggregation behavior. The complex materials introduced here may find applications as electrode material or precursors for nanostructured ferromagnetic ceramics.

#### **Experimental Section**

Instrumentation and general procedures: Most reactions and manipulations were performed under an atmosphere of pre-purified nitrogen or argon using Schlenk techniques, or in a nitrogen-filled glovebox. The airand moisture-stable polymers were handled in air with p.a. grade solvents after workup. <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were recorded by using a Bruker AC-300 or a Bruker AMX-400 spectrometer, operated at 400 MHz for <sup>1</sup>H, employing deuterated chloroform as a solvent. <sup>13</sup>C NMR spectra (referenced internally to solvent signals) were recorded at 100.15 MHz and <sup>29</sup>Si NMR spectra (referenced externally to TMS) at 79.49 MHz. FTIR spectra were recorded by using a Nicolet SDXC FTIR spectrometer equipped with an ATR unit. SEC was performed with an instrument consisting of a Waters 717 plus autosampler, a TSP Spectra Series P 100 pump, and a set of three PSS-SDV 5 Å columns with 100, 1000, and 100000 Å porosity. THF was used as an eluent at 30 °C and at a flow rate of 1 mLmin<sup>-1</sup>. UV absorptions were detected by a Spectra-SYSTEM UV2000. An Optilab DSP was used as the RI detector, calibration was carried out with poly(styrene) standards provided by Polymer Standards Service and performing a third-order polynomial fit. Photocontrolled ring-opening polymerization reactions were performed by using a Philips 125 W high-pressure mercury arc lamp. A Pyrex filter was placed inside the quartz immersion well to filter out wavelengths below 310 nm. and a thermostated water bath was used to maintain the reaction temperature at 5°C. CV was performed using a BAS CV-50W potentiostat with dichloromethane as solvent under an inert atmosphere (N2). The supporting electrolyte was tetra-n-butylammonium hexafluorophosphate (TBAH, 0.1 M). All experiments were performed at 25 °C, in a conventional three-electrode cell using a platinum working electrode (A =0.02 cm<sup>2</sup>). All potentials are referred to a saturated calomel reference electrode (SCE). A coiled platinum wire was used as counter electrode. A Philips EM420 transmission electron microscope (TEM) using a LaB<sub>6</sub> cathode at an acceleration voltage of 120 kV was used to obtain TEM images. TEM grids (carbon film on copper, 300 mesh) were obtained from Electron Microscopy Sciences, Hatfield, PA, USA.

**Materials**: Allyl bromide, 11-bromoundec-1-ene, dichloromethylsilane, chlorodimethylsilane, ferrocene, trichlorosilane, and *tert*-butyllithium (1.5 m in pentane) were purchased from Aldrich and used as received. Pentane and diethyl ether were dried at reflux over sodium/benzophenone and were distilled before use. Platinum divinyltetramethyldisiloxane complex (Karstedt catalyst, 2.1–2.4 % Pt) in xylene was purchased from Gelest. Deuterated chloroform and benzene were purchased from Deutero GmbH, dried and stored over molecular sieves. 1,1'-Dilithioferrocene (fcLi<sub>2</sub>.<sup>2</sup>/<sub>3</sub> TMEDA; TMEDA= *N*,*N*,*N*,*N*'-tetramethyl-1,2-ethane) was prepared by a literature method.<sup>[23]</sup>

**DiallyImethylsilane (1)**: The monomer was synthesized according to literature procedures,<sup>[23]</sup> from allyl bromide (68.96 g, 0.57 mol), magnesium (69.28 g, 2.85 mol), and dichloromethylsilane (21.86 g, 0.19 mol). Yield: 13.82 g (57%); b.p. 123 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.78 (m, 2 H, -CH=CH<sub>2</sub>), 4.95–4.83 (m, 4 H, -CH=CH<sub>2</sub>), 3.79 (m, 1 H, Si-H), 1.68–1.52 (m, 4 H, -CH<sub>2</sub>-CH=CH<sub>2</sub>), 0.09 ppm (d, *J*=3.67 Hz, 3 H, Si-CH<sub>3</sub>).

**Methyldi(undec-10-enyl)silane (2):** The monomer was synthesized according to literature procedures,<sup>[24]</sup> from 11-bromoundec-1-ene (50 g, 21.4 mmol), magnesium (26.1 g, 1.1 mol), and dichloromethylsilane (8.21 g, 7.1 mmol). Yield: 17.4 g (75%); b.p. 144–149°C, 0.2 mbar; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 5.83$  (m, 2H, –CH=CH<sub>2</sub>), 4.97 (dd, 4H, –CH=CH<sub>2</sub>), 3.77 (m, 1H, Si–H), 2.05 (m, 4H, –CH<sub>2</sub>–CH=CH<sub>2</sub>), 1.47–1.14 (m, 28H, CH<sub>2</sub>), 0.58 (m, 4H, Si–CH<sub>2</sub>), 0.05 ppm (d, J=3.68 Hz, 3H, Si–CH<sub>3</sub>).

**Dichloroferrocenylsilane (3a)**: Ferrocene (13.02 g, 70 mmol) was suspended in freshly distilled pentane/THF (75 mL, 1:1) under a N<sub>2</sub> atmosphere, cooled to 0 °C, and stirred for 15 min. A solution (50 mL, 1.5 M) of *tert*-butyllithium in pentane (75 mmol) was added over 60 min. The mixture was stirred for an additional 30 min at 0 °C and was then cooled to -78 °C. The mixture was treated with HSiCl<sub>3</sub> (11.38 g, 84 mmol) through a syringe, allowed to warm to room temperature, and stirred overnight. The precipitate was filtered off and the filtrate was concentrated by evaporation of the solvent. The residue was diluted with pentane (30 mL) and filtered once again. Pentane was removed and the product was purified by vacuum distillation (b.p. 77–80 °C/4×10<sup>-3</sup> mbar). Yield: 6.14 g (31%) of a viscous red oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 6.03$  (s, 1H, Si–H),

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4.56 (t, J=1.47 Hz, 2H,  $\eta$ -C<sub>5</sub>H<sub>4</sub>), 4.39 (t, J=1.47 Hz, 2H,  $\eta$ -C<sub>5</sub>H<sub>4</sub>), 4.28 ppm (s, 5H,  $\eta$ -C<sub>5</sub>H<sub>5</sub>).

Diallylferrocenylsilane (3): A solution of dichloroferrocenylsilane (3a) (6.00 g, 21 mmol) in dry diethyl ether (10 mL) was added slowly to a freshly prepared solution (90 mL) of allylmagnesium bromide (0.9 M; 81 mmol) in diethyl ether. To complete the reaction the mixture was stirred for 12 h at reflux. At 0 °C a saturated solution (10 mL) of NH<sub>4</sub>Cl was added, followed by H<sub>2</sub>O (15 mL). The organic layer was separated and washed twice with a saturated Na2CO3 solution. The diethyl ether layer was washed with water until the aqueous layer gave a neutral reaction. The organic layer was dried with MgSO<sub>4</sub>. The crude product (5.9 g) obtained by removal of the solvent was purified by column chromatography (silica, petroleum ether,  $R_f = 0.22$ ). Yield: 4.6 g (74%) of a red oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 5.92$  (m, 2H, -CH=CH<sub>2</sub>), 5.09-4.85 (m, 4H, -CH=CH<sub>2</sub>), 4.38 (m, 2H, η-C<sub>5</sub>H<sub>4</sub>), 4.32 (m, 1H, Si-H), 4.19 (m, 2H,  $\eta\text{-}C_5H_4),\;4.17\;\;(s,\;5H,\;\eta\text{-}C_5H_5),\;1.91\text{--}1.81\;ppm\;\;(m,\;4H,\;CH_2);\;{}^{13}C\;NMR$ (75 MHz, CDCl<sub>3</sub>): δ=134.56 (-CH=CH<sub>2</sub>), 114.05 (-CH=CH<sub>2</sub>), 73.75 (η- $C_5H_4(CH)$ ), 71.13 ( $\eta$ - $C_5H_4(CH)$ ), 68.51 ( $\eta$ - $C_5H_5$ ), 64.57 ( $\eta$ - $C_5H_4(C)$ ), 19.84 ppm (CH<sub>2</sub>); <sup>29</sup>Si-NMR (60 MHz, CDCl<sub>3</sub>):  $\delta = -4.20$  ppm; IR  $\tilde{\nu} =$ 3075 (stretching C-H), 2954, 2922, 2853 (stretching C-H), 2117 (stretching Si-H), 1630 cm<sup>-1</sup> (stretching C=C); FDMS: m/z: calcd (%) for C16H20FeSi: 296.3; found: 295.9. elemental analysis: calcd (%) for C<sub>16</sub>H<sub>20</sub>FeSi: C 64.87, H 6.80; found: C 64.85, H 6.80.

**Dimethyl[1]silaferrocenophane (4)**: Over a 5 min period, Me<sub>2</sub>SiCl<sub>2</sub> (4.6 mL, 38 mmol) was added dropwise to a suspension of fcLi<sub>2</sub>·<sup>2</sup>/<sub>3</sub>TMEDA (10.0 g, 36.4 mmol) in diethyl ether (500 mL) at -60 °C. The reaction mixture was then allowed to warm slowly to 20 °C over 4 h, during which the reaction mixture changed from orange-yellow to red. The solvent and excess Me<sub>2</sub>SiCl<sub>2</sub> were removed in vacuo. The crude product was redissolved in dry hexane, filtered, and concentrated in vacuo. Crystallization of the crude product from hexanes (-20 °C) and repetitive sublimation (×3, 0.005 mmHg) at room temperature onto a cold probe afforded red crystalline [1]ferrocenophane 4 (6.98 g, 79%). <sup>1</sup>H NMR (300 MHz,C<sub>6</sub>D<sub>6</sub>):  $\delta$ =0.51 (s, 6H, Me), 4.08 (t,  $J_{H-H}$ =1.7 Hz, 4H, Cp), 4.48 ppm (t,  $J_{H-H}$ =1.7 Hz, 4H, Cp).

**Methylvinyl[1]silaferrocenophane (5)**: Synthesis and purification were analogous to the methods used for **4**, but with (CH<sub>2</sub>=CH)MeSiCl<sub>2</sub> (4.97 mL, 38 mmol) as the respective silane instead of Me<sub>2</sub>Cl<sub>2</sub>, Yield: 6.5 g (70%); <sup>1</sup>H NMR (300 MHz,C<sub>6</sub>D<sub>6</sub>):  $\delta$ =0.61 (s, 3H, Me), 4.08 (t,  $J_{\rm H-H}$ =1.7 Hz, 4H, Cp), 4.48 (t,  $J_{\rm H-H}$ =1.7 Hz, 4H, Cp), 5.98 (dd, 2H, J= 20 Hz, J=80 Hz), 6.54 ppm (t, 1H, J=16 Hz).

General procedure for photocontrolled polymerization of 4 and 5: In an inert atmosphere glove box a Schlenk tube was charged with 4 (500 mg, 2.06 mmol) dissolved in THF (ca. 4 mL) and a THF solution (21 µL) of Na[C5H5] (1 M, 0.021 mmol) was added to the dark red solution in the absence of light. The mixture was photolyzed for 4 h at 5°C. The reaction vessel containing an orange solution was introduced into the glove box and the calculated amount of 5 (160 mg, 0.63 mmol for sample 8, Table 1) was added in the absence of light. Photolysis was continued for 2 h and the reaction was quenched with 10 drops of freshly distilled Me<sub>3</sub>SiCl. The solvents were removed in vacuo to give an orange film, which was redissolved in THF and precipitated into MeOH to give an orange powder that was dried in vacuo at 40 °C for 48 h and stored under argon at 5 °C. For molecular weight data for 6-8, see Table 1; <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta = 6.54$  (t, J = 16 Hz), 5.98 (dd, J = 20 Hz, J = 80 Hz), 4.31–4.00 (br, m, Cp), 0.62 (s), 0.54 ppm (s);  ${}^{13}$ C NMR (100.15 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta =$ 137.9 (Si-CH=CH<sub>2</sub>), 132.2 (Si-CH=CH<sub>2</sub>), 73.5-71.3 (Cp), -1.0 (SiMe<sub>2</sub>), -3.3 ppm (SiMeVi); <sup>29</sup>Si NMR (79.49 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -6.5$  (SiMe<sub>2</sub>), -13.0 ppm (SiMeVi).

General procedure for hypergrafting of AB<sub>2</sub> monomers (1, 2, 3) to linear PFS block copolymers (6, 7, 8): The polymer core (100 mg) was placed in a Schlenk tube under argon. The polymer was dissolved in dry chlorobenzene (ca. 200  $\mu$ L) and the calculated amount of AB<sub>2</sub> monomer was added. The mixture was heated to 60 °C and Karstedt's catalyst (2.4% in xylene, 2  $\mu$ L (0.25  $\mu$ mol Pt)) was added to start the reaction. The tube was closed by means of a Teflon tap and hydrosilylation was continued for ca. 10 h (until the Si–H vibration (at ca. 2100 cm<sup>-1</sup>) was absent from the IR spectrum). The sludge was diluted with THF (5 mL) and MeOH

(1 mL), and stirred in the presence of an excess of active charcoal to bind most of the platinum. The solution was filtered over Celite to remove charcoal, concentrated in vacuo, and precipitated into MeOH. After drying in vacuo the mixture of hyperbranched homopolymer and the desired block copolymer was purified by 1) dialysis in THF using a dialysis tube with a molecular weight cutoff of ca. 8 kgmol<sup>-1</sup> to remove the hbPCS; or by 2) repetitive precipitation into hexanes to remove the hexane-soluble hbPCS (only applicable for block copolymers with a low DP<sub>n</sub> of the hypergrafted hbPCS); or by 3) preparative SEC in THF to remove all low molecular weight material. Yields varied between 40 and 90%. For molecular weight data for **9–19**, see Table 1.

NMR characterization for block copolymers based on 1: <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): 5.85 (m, CH=CH<sub>2</sub>), 4.98 (m, CH=CH<sub>2</sub>), 4.31–4.00 (br, m, Cp), 1.83–1.31 (br, m, SiCH<sub>2</sub>), 1.10–0.62 (br, m, SiCH<sub>2</sub>), 0.54 (s, SiMe (PFS)), 0.24–0.01 ppm (br, m, SiMe (PCS)); <sup>13</sup>C NMR (100.15 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =134.9 (linear), 134.5 (terminal) (CH=CH<sub>2</sub>), 113.1 (linear), 112.8 (terminal) (CH=CH<sub>2</sub>), 73.5–71.0 (Cp), 21.9–18.0 (different CH<sub>2</sub>), -1.0 (SiMe<sub>2</sub> (PFS)), -4 to -6.4 ppm (different SiMe); <sup>29</sup>Si NMR (79.49 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =1.2 (dendritic PCS), 0.8 (linear PCS), 0.2 (terminal PCS), -3.5 (SiMe (PFS)), -6.5 ppm (SiMe<sub>2</sub> (PFS)).

NMR characterization for block copolymers based on 2: <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta = 5.85$  (br, m, CH=CH<sub>2</sub>), 5.10 (br, m, CH=CH<sub>2</sub>), 4.31–4.00 (br, m, Cp), 2.06 (br, CH<sub>2</sub>), 1.83–1.31 (br, m, SiCH<sub>2</sub>), 1.40 (br, CH<sub>2</sub>), 0.70–0.56 (br, SiMe (PFS)), 0.18 (br, SiMe (PCS directly bound to PFS)), 0.10 ppm (br, SiMe (PCS periphery)); <sup>13</sup>C NMR (100.15 MHz,  $C_6D_6$ ):  $\delta = 134.9$ , 134.5 (CH=CH<sub>2</sub>), 113.1, 112.8 (CH=CH<sub>2</sub>), 73.5–71.0 (Cp), 21.9–18.0 (different CH<sub>2</sub>), -1.0 (SiMe<sub>2</sub> (PFS)), -4.2 ppm (different SiMe).

NMR characterization for block copolymers based on 3: <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta = 6.04$  (m,  $CH=CH_2$ ), 5.14 (m,  $CH=CH_2$ ), 4.35–4.01 (br, m, Cp), 1.96–0.92 (br, m, SiCH<sub>2</sub>), 0.55 (s, SiMe<sub>2</sub> (PFS)), 0.28 ppm (s, SiMe (PFS)); <sup>13</sup>C NMR (100.15 MHz,  $C_6D_6$ )  $\delta = 135.3$  (linear), 134.9 (terminal) (CH=CH<sub>2</sub>), 113.5 (linear), 113.2 (terminal) (CH=CH<sub>2</sub>), 73.5–71.0 (Cp (PFS)), 70.7, 68.2 (br, *Cp* (PCS)), 21.9–18.0 (different *CH*<sub>2</sub>), 0.9 (SiMe (PFS), -1.0 ppm (SiMe<sub>2</sub> (PFS)); <sup>29</sup>Si NMR (79.49 MHz,  $C_6D_6$ ):  $\delta = -2.6$  (dendritic PCS), -3.6 (linear PCS), -4.6 (terminal PCS), -6.5 (*Si*Me<sub>2</sub> (PFS)), -21.5 ppm (*Si*Me (PFS)).

**Preparation of TEM samples**: Block copolymer (1 mg) was dissolved in THF (50  $\mu$ L). Then decane was added dropwise to the mixture to give a decane/THF (9:1) mixture . The opaque solutions were allowed to stabilize for 12 h, then drop-cast onto copper TEM grids and dried overnight to remove the solvents.

Sonification was conducted over a period of 30 min at room temperature, then a solution (50  $\mu$ L) of a unimer (ca. 1 gL<sup>-1</sup> in THF) was added to the mixture and allowed to equilibrate over a period of 5 h. The sample was drop-cast onto a copper grid and dried in vacuo overnight.

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