Poly(ferrocenylsilane-*b*-polyphosphazene) (PFS-*b*-PP): A New Class of Organometallic−Inorganic Block Copolymers

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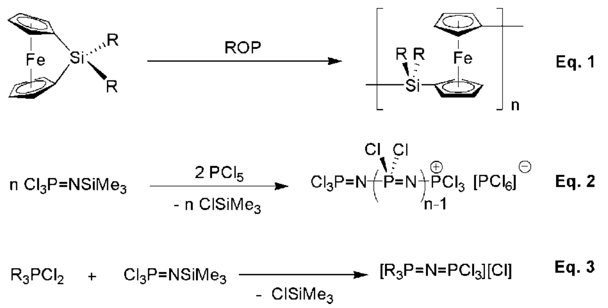
Received July 23, 2008
Revised Manuscript Received October 27, 2008

The self-assembly of block copolymers with immiscible segments is known to generate a variety of different morphologies because of phase separation in the solid state and selective solvation in block selective solvents and provides an attractive route to different nanostructures.[1] The incorporation of transition metals and main group elements into one of the blocks provides an attractive method for expanding the range of properties present in the resulting self-assembled materials.[2−5] In this context, poly(ferrocenylsilane) (PFS) block copolymers[6] represent an interesting class of new materials, and recent studies have taken advantage of their properties such as redox activity,[7] etch resistance,[5c,8] the ability to form magnetic[9] and catalytically active ceramics,[10] and the electron density contrast[11] arising from the presence of the metalloblock. PFS materials are prepared by ring-opening polymerization (ROP) of silicon-bridged[1]ferrocenophanes (eq 1 in Chart 1). PFS block copolymers can be prepared by means of the living anionic and photocontrolled living anionic protocols.[12] The possibility of combining the properties of a PFS block with a second readily tuned block could allow the rational design of different nanostructures, especially novel materials such as block comicelles, which are available via crystallization-directed living supramolecular polymerization processes.[13] In this communication, we report the synthesis of PFS-*b*-PP (PP = polyphosphazene), a rare example of an organometallic−inorganic block copolymer. Polyorganophosphazenes, $[N{=}PR_2]_n$, represent one of the most versatile classes of macromolecules with facile side-group tunability that allows properties such as hydrophobicity and hydrophilicity to be introduced.[14] These materials should be ideal for micellization studies and may possess many intrinsically interesting properties as well.

Polyphosphazene block copolymers have been accessible comparatively recently using the living cationic chain growth polycondensation of the phosphoranimine $Cl_3P{=}NSiMe_3$ (**4**) (eq 2 in Chart 1).[15] The latter species is readily available in a one-pot synthesis from PCl_3.[16] Recently, we showed that dichlorophosphoranes R_3PCl_2 (R = *n*-Bu, Ph) stoichiometrically react with **4** to yield the salts $[R_3P{=}N{=}PCl_3][Cl]$ (eq 3 in Chart 1) that function as initiators in the polymerization of **4**.[17] For the preparation of PFS-*b*-PP block copolymers, our strategy was to generate a PFS macroinitiator with a phosphorane end group and to use this species to initiate the living cationic polymerization of **4** (Scheme 1).

First, dimethylsila[1]ferrocenophane (**1**) was polymerized by living anionic ROP in THF at room temperature using *n*-BuLi as an initiator. The resulting living polymer was then quenched with an excess of $ClPPh_2$, and the reaction was stirred for 6 h to ensure the complete end-capping of the polymer with phosphine groups. The resulting PPh_2-end-functionalized polymer (**2**) was isolated by several precipitations in hexanes as an orange solid in quantitative yield. The ^{31}P NMR spectrum of **2** in CH_2Cl_2 showed a sharp peak at −16 ppm, and integration of the PPh_2 end-group resonances (7.33 ppm, in CD_2Cl_2) in the ^1H NMR spectrum gave an absolute molecular weight similar to that obtained by GPC relative to polystyrene standards (^1H NMR: $M_n = 14\,050$; number-average degree of polymerization $DP_n = 58$. GPC in THF: $M_n = 13\,390$; PDI = 1.03; $DP_n = 54$).

Chart 1. Routes to PFSs and Polyphosphazenes



Telechelic **2** was then dissolved in CH_2Cl_2, and the mild chlorinating agent C_2Cl_6 was added (1.1 equiv per PPh_2 unit). After 1.5 h, the ^{31}P NMR showed a single peak at 74 ppm consistent with the formation of the desired end-functionalized PFS (**3**).[18,19] The solution of **3** in CH_2Cl_2 was then separately reacted with different amounts of the phosphoranimine monomer **4** in the same solvent to obtain PFS-*b*-PP diblock copolymers (**5a**−**d**) with a representative range of block ratios. The ^{31}P NMR spectra of these new block copolymers showed a sharp peak at −17 ppm corresponding to the $[NPCl_2]$ units and the total consumption of the monomer **4** ($\delta_{31P} = -54$). In the ^{31}P NMR spectrum of **5a**, the lowest molecular weight material, we also detected a signal for the [Cp*P*Ph$_2$N] switching group unit ($\delta_{31P} = 25$) and the PCl_3^+ end group ($\delta_{31P} = 8.7$).[20] After the removal of the solvent and the $ClSiMe_3$ byproduct under vacuum, the resulting pale-orange polymer was dissolved in THF and treated with an excess of $NaOCH_2CF_3$ in the same solvent to obtain the desired PFS-*b*-PP block copolymers **6a**−**d** as air- and moisture-stable pale-orange materials.

GPC analysis (in THF with 0.1% *n*-Bu_4NBr) showed the presence of small quantities of PFS homopolymer, probably due to the loss of small amounts of the highly reactive initiating group in **3** due to hydrolysis. The block copolymers **6a**−**6d** were purified from small amounts of PFS homopolymer by selective precipitation of the block copolymer using mixtures of 1,2-dichloroethane/hexane or by preparative SEC column chromatography. The resulting pure polymers **6a**−**6d** were isolated in 40−55% yield and showed dramatically higher relative M_n values by GPC relative to polystyrene standards compared with ^1H NMR integration, which determined the absolute value (Table 1). We account for this by the very different hydrodynamic behavior of the PP block copolymers and the polystyrene standards used for the GPC calibration. Very narrow PDIs (PDI < 1.15) were obtained compared with those generally found for PP block copolymers (PDI ≈ 1.3 to 2). This indicates that the materials are well defined and ideal for self-assembly studies.[9,13] This points to a very efficient initiation of

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10.1021/ma8016713 CCC: $40.75

Scheme 1. Synthesis of End-Functionalized PFS Homopolymer (2) and PFS-*b*-PP Diblock Copolymers (6a−d)

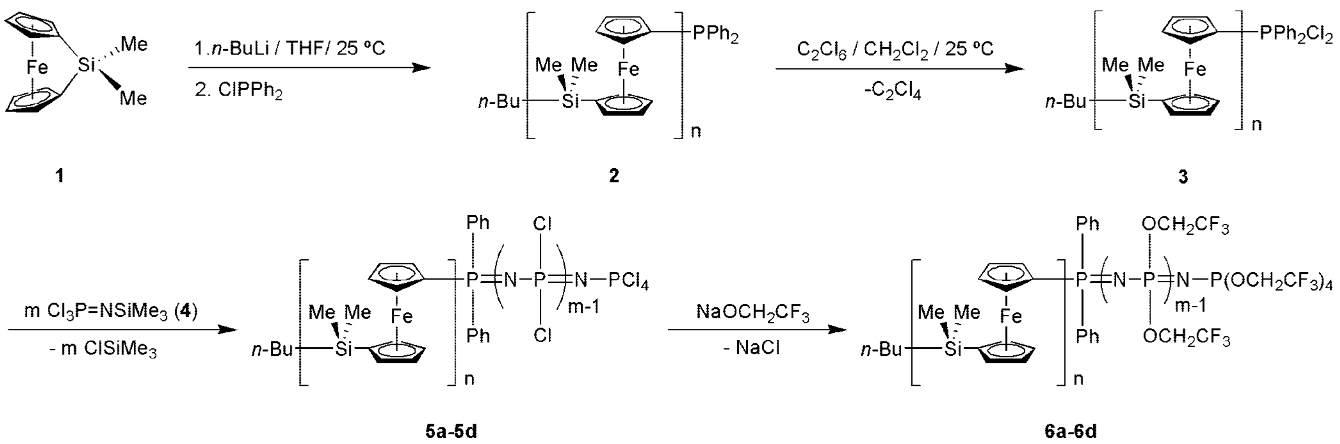

Table 1. Characterization of End-Functionalized PFS Homopolymer 2 and PFS-*b*-PP Block Copolymers 6a−d

polymer	DP$_n$ (PFS)[a]	DP$_n$ (PP)[b]	M_n	PDI (M_w/M_n)	block ratio (*n*/*m*)[e]	φ_{PFS}[f]
2	58 (54)		14 290[c] (13 390)[d]	1.03		
6a	58 (54)	54	27 170[c] (125 320)[d]	1.19	1:1	0.60
6b	58 (54)	77	32 480[c] (206 270)[d]	1.09	1:1.5	0.51
6c	58 (54)	116	42 220[c] (373 470)[d]	1.15	1:2	0.40
6d	58 (54)	290	84 490[c] (401 740)[d]	1.16	1:5	0.21

[a] Degree of polymerization (DP$_n$) of PFS obtained by ^{1}H NMR integration and by GPC with tetrahydrofuran (THF) and polystyrene standards in brackets. [b] DP$_n$ of polyphosphazene obtained by ^{1}H NMR integration. [c] Molecular weight obtained by ^{1}H NMR integration. [d] Molecular weight obtained by GPC with 0.1% *n*-Bu$_4$NBr THF solution. [e] Number-average block ratio between the PFS block and the polyphosphazene calculated by ^{1}H NMR. [f] Volume fraction of PFS block calculated using the following density values (g/cm^{-3}) for both blocks: 1.26 (PFS) and 1.665 (PP).

the living cationic polymerization of **4** by **3** to generate the PP block.

Block copolymers **6a−d** were structurally characterized by NMR. The peak detected at −7.2 ppm by ^{31}P NMR (in THF-*d*$_8$) and a broad signal at 4.5 ppm found by ^{1}H NMR (in THF-*d*$_8$) confirmed the presence of the PP block with OCH$_2$CF$_3$ groups at phosphorus.[14b,c] Resonances assigned to cyclopentadienyl and SiMe$_2$ groups in the ^{1}H NMR spectrum confirmed the presence of the PFS block.[12a] Thermogravimetric analysis (TGA, at 10 °C/min under N$_2$) showed that all block copolymers **6a−d** exhibit very similar thermal stability profiles and are stable to weight loss until ca. 250 °C.

The anticipated phase separation in the new PFS-*b*-PP block copolymers was confirmed by differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). The DSC thermograms of **6a−d** showed transitions associated with the individual blocks. Thus, an endothermic transition at 49 °C was assigned to the *T*(1) transition for the PP block,[14b,c] and a melting endotherm (T_m) for the PFS block was detected at 130 °C.[12a] The glass-transition temperatures (T_g) for each block were also detected in some of the cycles (T_g = −56 °C, PP block; T_g = 35 °C, PFS block, detected as a shoulder on the more intense *T*(1) at 49 °C).

Bright field TEM studies of drop-cast thin films of the PFS-*b*-PP block copolymers **6a−d** provided clear evidence of the formation of well-defined phase-separated nanodomains. Representative TEMs for **6c**,**d** are shown in Figure 1. The dark regions are indicative of the electron-rich PFS nanodomains and, as expected for the relative volume fractions of PFS, φ_{PFS} (Table 1), consist of apparent PFS cylinders (Figure 1A) and PFS spheres (Figure 1B) in a PP matrix for **6c** and **6d**, respectively.

In summary, we report the synthesis and characterization of a series of well-defined organometallic−inorganic PFS-*b*-PP block copolymers by using a sequential anionic and cationic polymerization strategy. The materials are well defined with narrow PDIs. We and our collaborators are currently performing in depth studies of the self-assembly of these materials in the solid state and in solution.[21] We anticipate that the combination of the crystallinity of the PFS block and tunability of the PP block arising from the versatility of the macromolecular substitution step from the chlorinated precursor block in **5a−c** should facilitate the development of a variety of uses in, for example, crystallization-directed living supramolecular polymerizations. This would allow us to prepare self-assembled

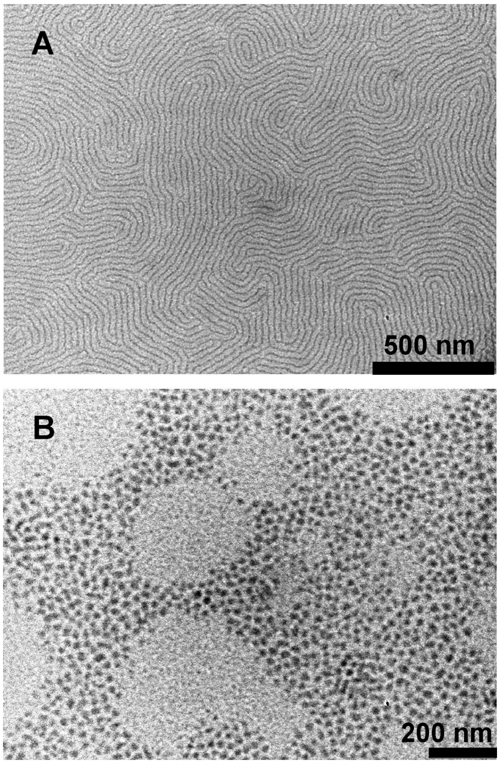

Figure 1. TEM micrographs of drop-cast thin films PFS-*b*-PP block copolymers (A) **6c** and (B) **6d**. A drop of a 10 mg/mL solution of the polymers in THF was cast directly on copper grid, and the solvent was allowed to evaporate at 25 °C over 12 h.

materials with spatially defined and readily tunable coronal chemistry.[13]

Acknowledgment. A.P. thanks the European Union for a Marie Curie Fellowship. I.M. thanks the European Union for a Marie Curie Chair and the Royal Society for a Wolfson Research Merit Award.

Supporting Information Available: Experimental procedures and characterization details. This information is available free of charge via the Internet at http://pubs.acs.org.

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MA8016713