Articles

Synthesis, Characterization, and Properties of the Polyphosphinoboranes $[RPH-BH_2]_n$ (R = Ph, *i*Bu, *p*-*n*BuC₆H₄, *p*-dodecylC₆H₄): Inorganic Polymers with a Phosphorus–Boron Backbone

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ABSTRACT: The polyphosphinoboranes $[PhPH-BH_2]_n$ (1), $[iBuPH-BH_2]_n$ (2), $[(p-nBuC_6H_4)PH-BH_2]_n$ (3), and $[(p-dodecylC_6H_4)PH-BH_2]_n$ (4) were prepared from the corresponding phosphine-borane adducts $RPH_2 \cdot BH_3$ (R = Ph, *i*Bu, *p*-*n*BuC₆H₄, *p*-dodecylC₆H₄) via a rhodium-catalyzed dehydrocoupling procedure at elevated temperatures (ca. 90-130 °C). Samples of polymers 1 and 2 and the new materials 3 and 4 were characterized by multinuclear NMR spectroscopy, and the molecular weights were determined by light scattering methods in THF or CH₂Cl₂ solutions. The absolute weight-average molecular weight of **2** was determined by static light scattering and found to be $M_w = 13\,100$, and values of M_w of ca. 20 000 were estimated for the sample of polymers 1 and the new material 3 using dynamic light scattering (DLS). The molecular weights of polymers **3** and **4** were also analyzed by gel permeation chromatography using polystyrene standards, and values up to $M_{\rm w}$ = ca. 80 000, $M_{\rm n}$ = ca. 10 000 were determined for 3 and $M_w =$ ca. 168 000, $M_n =$ ca. 12 000 for **4**. The chemical stability of **1** in THF toward HNEt₂ or nBu_3P was demonstrated using NMR spectroscopy and DLS analysis, which indicated that no significant polymer degradation occurred. WAXS analysis of 1 and 3 showed that the polymers are amorphous. The glass transition temperatures (T_g) of polymers 2, 3, and 4 were analyzed by DSC and were detected at ca. 5, 8, and -1 °C, respectively. TGA analysis on 1-3 revealed $T_{5\%}$ values (temperature for which 5% or the weight is lost) of 240 °C for 1 and ca. 150–160 °C for 2 and 3. After heating to 1000 °C, ceramic yields in the range of 35–80% were obtained. The high ceramic yield for **1** (75–80%) indicates that this material is of interest as a pyrolytic precursor to boron phosphide-based solid-state materials.

Introduction

Macromolecules with backbones based on main group elements other than carbon are of considerable interest for accessing materials with unusual properties and significant applications.^{1–10} Compared to \dot{C} –C bonds, bonds between other main group elements can be stronger and more oxidatively and thermally stable or can provide additional conformational flexibility (e.g., Si-O bonds in polysiloxanes), interesting electronic effects (e.g., σ -conjugation in polysilanes and heavier group 14 analogues), versatile reactivity (e.g., the substitution of chlorine in polydichlorophosphazenes), or intriguing possibilities for the development of selfassembled, supramolecular materials.¹¹ However, the development of efficient synthetic procedures for the formation of bonds between main group elements is of critical importance for the construction of such inorganic polymer chains and also for the general development of macromolecular main group chemistry. In recent years, transition-metal-catalyzed dehydrocoupling routes have been established for the preparation of homo- and heteronuclear bonds between main group elements and polymers containing Si-Si,¹² Ge-Ge,¹³ Sn-Sn,⁶ and $\rm Si-O^{14}$ skeletons have been synthesized by this methodology. 15

The attempted synthesis of polymeric materials based on skeletons of alternating phosphorus and boron atoms, polyphosphinoboranes, received significant attention in the 1950s and 1960s, as valuable properties such as high-temperature stability and flame retardancy were anticipated.¹⁶ The main synthetic approach involved thermally induced dehydrocoupling of phosphine– borane adducts R₂PH·BH₃ and RPH₂·BH₃ at ca. 200 °C and above. Although in a few cases low yields of polymeric materials were claimed, none of the products were convincingly structurally characterized by present day standards and, when reported, the molecular weights were generally very low.^{17,18}

We have recently described the late transition metal (e.g., rhodium) catalyzed formation of phosphorus boron bonds and also the application of this process to the dehydropolymerization of the primary phosphine borane adducts PhPH₂·BH₃ and *i*BuPH₂·BH₃ to yield high molecular weight polyphosphinoboranes.^{19–21} In this paper we report further studies of the properties of these materials as well as those of two new polymers



 $[(p-nBuC_6H_4)PH-BH_2]_n$ (3) and $[(p-dodecylC_6H_4)PH-BH_2]_n$ (4).

Results and Discussion

Polymer Synthesis and Structural Characterization. We have previously shown that neat PhPH₂. BH₃ undergoes rhodium-catalyzed dehydrocoupling to give poly(phenylphosphinoborane) 1 (Scheme 1) after heating at 90 and 130 °C for 6 h, with concomitant evolution of hydrogen. The synthesis of high molecular weight 1 was achieved using either [{ $Rh(\mu-Cl)(1,5$ cod)]2], anhydrous RhCl3, or RhCl3 hydrate as dehydrocoupling catalyst (ca. $1-2 \mod \%$ Rh). For this work we performed the synthesis on a larger scale, using ca. 10 g of PhPH₂·BH₃. We also performed the rhodiumcatalyzed dehydropolymerization of *i*BuPH₂·BH₃ to give $[iBuPH-BH_2]_n$ (2). This required more forcing conditions than for the synthesis of 1 (heating at 120 °C for 15 h). The polymer structures of the samples of 1 and 2 were analyzed and confirmed by multinuclear (¹H, ¹¹B, ¹³C, ³¹P) solution NMR spectroscopy in CDCl₃. We have previously shown that both dehydrocoupling reactions are very sluggish in the absence of rhodium catalysts. The resulting products showed complex ¹H and ³¹P NMR spectra, indicating that mixtures of (perhaps branched) oligomers had been formed.

The electronic character of the organic group on the phosphorus was expected to play a major role in the dehydrocoupling and should have interesting effects on the polymerization rate as well as on the polymer properties. The observation that the catalytic dehydrocoupling of PhPH₂·BH₃ is more facile and leads to higher molecular weights compared to *i*BuPH₂·BH₃ may be associated with differences in the polarity of the P–H bonds. The strong (+)-inductive effect of the alkyl group attached to phosphorus likely decreases the polarity of the P–H functionality which, in turn, renders the bond less reactive for dehydrocoupling events.²²

To investigate whether aryl-substituted phosphineborane adducts are indeed more reactive, we have synthesized and investigated the para-substituted phosphine-borane adducts (p-nBuC₆H₄)PH₂·BH₃ and (pdodecylC₆H₄)PH₂·BH₃. These monomers were prepared in four steps from PCl₃ using a protection-deprotection sequence (Scheme 2). An additional step involving Pd catalysis was required in the case of (p-dodecylC₆H₄)-PH₂·BH₃ as the p-dodecylC₆H₄Br was not commercially available. Characterization of the adducts was achieved by ¹H, ³¹P, ¹³C, and ¹¹B NMR which afforded spectra completely consistent with the assigned structures.

We found that the optimum conditions for the dehydrocoupling of neat $(p \cdot n BuC_6H_4)PH_2 \cdot BH_3$ to give polymeric $[(p \cdot n BuC_6H_4)PH - BH_2]_n$ (3) required heating at 100 °C for 5 h in the presence of ca. 1–2 mol % rhodium in the form of $[{Rh(\mu-Cl)(1,5-cod)}_2]$. Subsequent precipitation into 2-propanol and drying under

Scheme 2
i) nBuLi, Et₂O, 0 °C
ii) PCI(NEt₂)₂, Et₂O, -78 °C
R-Br

$$R-P(NEt_2)_2 + 4$$
 HCI
 $Et_2O, -78 °C$
 $R-PCI_2 + 2 [H_2NEt_2]CI$

R-PCl₂ + 2 Li[BH₄] ______ R-PH₂-BH₃ + 2 LiCl + 0.5 B₂H₆

$R = p - nBuC_6H_4$ or p-dodecylC₆H₄

vacuum afforded spectroscopically pure polymer 3 in 61% yield. The polymer was analyzed by multinuclear solution NMR spectroscopy in CDCl₃. Most notably, the ¹H-coupled ³¹P NMR spectrum showed a broad doublet at δ –49.7, with a coupling constant $J_{\rm PH}$ of 356 Hz which was also observed in the P-H region of the corresponding ¹H NMR spectrum. Polymer end groups such as (p $nBuC_6H_4)PH_2$ or BH_3 could not be detected by NMR spectroscopy. When heated for longer periods of time (>5 h) or at higher temperatures (>100 °C), the final product was found to be insoluble in all common organic solvents. This was attributed to cross-linking or very high molecular weights. In the absence of any rhodium catalyst, the dehydrocoupling reaction of (p-nBuC₆H₄)-PH₂·BH₃ was extremely slow (only ca. 50% conversion after 5 h at 100 °C) and produced only oligomers. The rather complex ³¹P and ¹H NMR spectra suggest that these materials are also branched, but the structure was not investigated in any detail.

The dehydrocoupling of neat (*p*-dodecylC₆H₄)PH₂·BH₃ to give polymeric $[(p-dodecylC_6H_4)PH-BH_2]_n$ (4) required heating at 120 °C for 9.5 h in the presence of ca. $1-2 \mod \%$ rhodium in the form of $[{Rh(\mu-Cl)(1,5-cod)}_2]$. Subsequent precipitation into 2-propanol and drying under vacuum afforded spectroscopically pure 4 as a brown gum in 67% yield. Polymer 4 showed similar spectroscopic data to 3; for example, the ¹H-coupled ³¹P NMR spectrum shows a broad doublet at δ –49.4, with a coupling constant of $J_{\rm PH}$ = ca. 330 Hz which was also observed in the corresponding proton spectrum. The absence of rhodium catalyst in the polymerization of (pdodecylC₆H₄)PH₂·BH₃ has a similar effect as in the case of $(p-nBuC_6H_4)PH_2 \cdot BH_3$: conversions are extremely slow, and reactions yield rather complicated ³¹P and ¹H spectra, which suggest branched structures.

The catalytic P–B dehydrocoupling mechanism is unknown at present but probably involves a sequence of oxidative addition/reductive elimination and/or σ -bond metathesis reactions involving P–H, B–H, Rh–P, Rh–B, and Rh–H bonds.²³

Molecular Weight Characterization. The molecular weight of the sample of $[PhPH-BH_2]_n$ (1) in THF was analyzed by dynamic light scattering (DLS) on a solution of 1 that had been left undisturbed for 24 h. The mean hydrodynamic diameter (D_h) of ca. 7 nm suggested an absolute molecular weight M_w of ca. 20 000, which is slightly lower compared to samples of 1 prepared previously²⁰ under similar conditions but on a smaller scale. For example, $[PhPH-BH_2]_n$ with M_w = 33 300 (as determined by static light scattering, SLS) displayed a hydrodynamic diameter of $D_h \approx 9-10$ nm.²⁰ The absolute molecular weight of the sample of $[IBuPH-BH_2]_n$ (2) was analyzed for the first time by SLS on dilute solutions of 2 in THF. The refractive index



Figure 1. Low-angle laser light scattering plot for [*i*BuPH–BH₂]_{*n*} (**2**) in THF at 22 °C (K = optical constant, c = concentration, R_{θ} = Rayleigh ratio). The absolute molecular weight $M_{\rm w}$ is determined as the inverse of the intercept on the *y* axis ($M_{\rm w}$ = 13 100).

increment dn/dc was found to be 0.17 mL/g. Figure 1 shows the low-angle laser light scattering plot for $[iBuPH-BH_2]_n$ at five different concentrations in the range 1.1–5.5 mg/mL. The absolute weight-average molecular weight was determined as the inverse of the intercept on the *y* axis and found to be $M_{\rm w} = 13\ 100$, corresponding to a weight-average degree of polymerization (DP_w) of 128. Note that the second virial coefficient A_2 , which describes the polymer-solvent interactions and is obtained from the slope of the line in Figure 1, equals zero. This was also observed²⁰ for all SLS experiments carried out on $[PhPH-BH_2]_n$ and indicates that THF is a Θ solvent at 22 °C and that the polyphosphinoboranes are on the verge of precipitation. The size distribution of 2 obtained by DLS showed a single broad peak, with a peak value of $D_{\rm h} \approx 4$ nm.

The solution behavior of the polyphosphinoboranes 1 and **2** is complicated by facile aggregate formation in THF, which is not unexpected as this is a Θ solvent for these materials. For example, a DLS analysis of a freshly prepared THF solution of polymer 1 consisted of two distinct species, presumably polymer aggregates $(D_h \text{ ca. } 30 \text{ nm})$ and single chains $(D_h \text{ ca. } 10 \text{ nm})$, as was indicated by the bimodality of the size distribution. Over a period of 1-2 days, however, the amount of aggregates decreased, and a single broad size distribution with $D_{\rm h}$ ca. 9–10 nm was then observed. The facile aggregation of the polyphosphinoboranes may arise from charge alternations along the polymer backbone, since phosphorus and boron possess +1 and -1 formal charges, respectively. In turn, the P-H and B-H bonds would retain some acidic and hydridic character, respectively, which could lead to attractive interactions between single polymer chains and thus cause aggregation. Indeed, nonclassical hydrogen bonding²⁴ was observed in the solid-state structure of PhPH₂·BH₃, where two molecules showed weak intermolecular contacts of the type $P-H(\delta^+)\cdots H(\delta^-)-B$ to form a centrosymmetric dimer.20

The mean hydrodynamic diameter of $[(p-nBuC_6H_4)-PH-BH_2]_n$ (3), measured by DLS in THF at a concentration of 4 mg/mL, was found to be 7 nm, with a broad size distribution. The D_h value of 3 was not affected by a change in polymer concentration, which was confirmed by DLS experiments using concentrations of 2 or 8 mg/mL. Furthermore, the hydrodynamic diameter of 7 nm was observed immediately after the sample preparation as well as after a period of 2 days, at polymer concent



Figure 2. GPC trace (THF, vs polystyrene standards) of $[(p \cdot nBuC_6H_4)PH-BH_2]_n$ (**3**); [**3**] = 4.15 mg/mL, $M_w = 19500$, $M_n = 2820$, $M_w/M_n = 6.92$.

trations of 2, 4, and 8 mg/mL. Thus, polymer **3** does not seem to form any larger aggregates in THF solution, in contrast to the situation for freshly prepared solutions of polymers **1** and **2**. This suggests the *n*-Bu substituent on the phenyl group imparts improved solubility in this solvent. On the basis of comparable solution behavior of the poly(phenylphosphinoborane) **1**, a molecular weight of M_w ca. 20 000 was estimated for polymer **3**. Only low molecular weight materials ($D_h < 1$ nm) were observed in the case of the uncatalyzed thermal dehydrocoupling of of (*p*-*n*BuC₆H₄)PH₂·BH₃.

Previous studies on solutions of high molecular weight polymers **1** and **2** in THF using gel permeation chromatography (GPC) for molecular weight characterization were found to be problematic due to facile aggregation and/or adsorption of the polymer chains to the GPC columns. Once again, this behavior is not surprising as THF is a Θ solvent under these conditions. However, in contrast, GPC analysis of polymer **3** in THF revealed M_w values were in fairly good agreement with the light scattering data. A value of $M_w = 19$ 430 (based on polystyrene references) was determined by GPC, and a value of M_w ca. 20 000 was estimated from the DLS experiments ($D_h = 7$ nm) on the sample. A GPC trace for this sample of polymer **3**, which shows a very broad distribution, is shown in Figure 2.

An average value of $M_w = 168\ 000$ (based on polystyrene references) was determined by GPC analysis of polymer **4**. As in the case of polymer **3**, the GPC trace for this sample of polymer **4** shows a very broad distribution of molecular weights ($M_w = 168\ 000/M_n =$ 12 000).

A general problem associated with the preparation of the polyphosphinoboranes was the increasing viscosity of the neat reaction mixture at the end of the reaction, at which point stirring (using magnetic stir bars) was often no longer possible. However, the production of high molecular weight polyphosphinoboranes requires extremely high conversion (>99%) of the phosphine-borane adducts due to the step-growth nature of this polycondensation reaction. Thus, insufficient stirring and inefficient removal of hydrogen gas could significantly limit the formation of long, linear phosphinoborane chains. This led to poor reproducibility of the molecular weights. For example, over a series of experiments, samples of 3 were found to possess molecular weights in the range $M_{\rm w} = \text{ca. } 5000-80\ 000$ and $M_{\rm n}$ = ca. 3000–10 000. High molecular weights were





Figure 3. WAXS curves of $[PhPH-BH_2]_n$ (1) and $[(p-nBuC_6H_4)-PH-BH_2]_n$ (3).

generally formed with higher catalyst loadings and longer reaction times and at higher temperatures. However, the use of catalyst loading of 5 mol % or greater led to rapid solidification of the reaction mixture and completely insoluble products.

Polymer Stability. With a view to understanding the chemical stability and reactivity of the polyphosphinoboranes, we investigated the reaction of [PhPH-BH₂]_n with diethylamine and tributylphosphine. Amines are often used for the decomplexation of phosphineborane adducts to give the corresponding amine-borane adduct and free phosphine.²⁵ Polymer 1 and an excess of diethylamine were stirred in THF for 24 h. After removing the volatiles under vacuum and precipitation into hexanes, the off-white solid was analyzed by NMR spectroscopy and DLS. The ³¹P NMR spectrum showed only one broad signal at $\delta = -48.9$ ppm, assignable to unreacted [PhPH-BH₂]_n. Furthermore, no trace of free phosphine (PhPH₂) was detected. DLS measurements in THF showed a hydrodynamic diameter of $D_{\rm h} \approx 7$ nm, which was comparable to the initial $D_{\rm h}$ value of polymer 1, and indicated that no significant degradation of the polymer backbone had occurred. Tributylphosphine, which is a strongly coordinating phosphine, was also added to a THF solution of polymer **1** and stirred at room temperature. After precipitation into hexanes and drying under vacuum, the ¹H and ³¹P NMR spectra did not display any significant changes. DLS analysis of the reprecipitated material revealed a hydrodynamic diameter of $D_{\rm h} \approx 5$ nm, which was only slightly lower than the value of the starting polymer ($D_h \approx 7$ nm). Overall, these experimental observations show that coordinating reagents such as amines or phosphines do not significantly affect the stability of poly(phenylphosphinoborane) 1.

WAXS. Wide-angle X-ray scattering (WAXS) diffractograms on solution-cast films of polymers **1** and **3** are shown in Figure 3. The films were obtained from concentrated solutions of **1** and **3** in dichloromethane and solvent evaporation at room temperature. The WAXS experiments showed that both polymers **1** and **3** were amorphous, although halos arising from some short-range order were detected at diffraction angles $2\theta = 20^{\circ}$ and $2\theta = 18^{\circ}$, respectively.

The predominantly amorphous character of the polymers²⁶ is not unexpected and may be ascribed to the presumed stereochemical irregularities (atactic place-

Figure 4. TGA thermograms of $[PhPH-BH_2]_n$ (1) and $[iBuPH-BH_2]_n$ (2).

ment) of the side groups arranged along the polymer chain.

Thermal Behavior. The thermal behavior of the polyphosphinoboranes **1**–**4** was analyzed by differential scanning calorimetry (DSC) and/or thermogravimetric analysis (TGA).

The glass transition temperatures (T_g) of [*i*BuPH- $BH_2]_n$ (2), $[(p-nBuC_6H_4)PH-BH_2]_n$ (3), and $[(p-dodecyl-BH_2)]_n$ (3), and [(p-dodecyl-BH_2)]_n (3), and [(p-dodecyh C_6H_4)PH-BH₂]_n (4) determined by DSC were found to be below room temperature in all cases.²⁷ Polymer 2 has a T_g of ca. 5 °C, polymer **3** has a T_g of ca. 8 °C, and polymer **4** has a T_g of ca. -1 °C. For comparison, the analogous organic polymer poly(4-methylpent-1-ene) has a T_g in the range 45-50 °C,²⁸ and a T_g of 33 °C has been reported for syndiotactic poly(4-butylstyrene).²⁹ The relatively low T_{σ} values of the polyphosphinoboranes may be attributed to the high degree of torsional flexibility in the polymer main chain. Given that P–B bonds in phosphinoboranes (1.9–2.0 Å) are long compared to C–C bonds (ca. 1.54 Å), this would reduce steric interference between the side groups and thus generate free volume that facilitates polymer motion and lowers the $T_{\rm g}$.

The thermal stability of $[PhPH-BH_2]_n$ (1) and $[iBuPH-BH_2]_n$ (2) (Figure 4) and of $[(p-nBuC_6H_4)PH-BH_2]_n$ (3) was further investigated by TGA under an argon atmosphere and a heating rate of 10 °C/min.

The onset of weight loss for **1** occurred at 160 °C, and this material showed a $T_{5\%}$ (temperature at which the polymer has lost 5% of its original weight) at ca. 240 °C. Polymer **2** began to exhibit slight weight loss at 120 °C and had a significantly lower $T_{5\%}$ at ca. 150 °C. For polymer **3**, the onset temperature was found to be similar to that for **2** with a $T_{5\%}$ at ca. 160 °C. However, polymers **2** and **3** showed the major weight loss between 200 and 400 °C.

Interestingly, the onset temperatures for polymers **2** and **3** are likely to correspond to loss of H_2 and occur at approximately the same temperature as that used for the polymer synthesis. This suggests that additional intermolecular P–B coupling (with loss of H_2) occurs between polymer chains to presumably give branched structures. This also correlates with our findings that prolonged heating of the polyphosphinoboranes during the synthesis resulted in the formation of insoluble, cross-linked materials.³⁰

The ceramic yields that remained after heating to 1000 °C, defined in terms of the percentage of the

original weight, were found to be in the range 75-80% for polymer **1**, 40-45% for polymer **2**, and 35-40% for polymer **3**. Previously, polymers based on borazine units or borane cages have been shown to function as high yield precursors to boron-based ceramics at elevated temperatures.⁷ The high ceramic yield for **1** suggests that this material and analogues are potentially of interest as preceramic polymers.³¹

Summary

The results reported here show that polyphosphinoboranes of high molecular weights are available via rhodium-catalyzed dehydrocoupling reactions. Light scattering methods such as SLS and DLS are very useful for the molecular weight characterization of these materials; however, the new polymers $[(p-nBuC_6H_4) PH-BH_2]_n$ (3) and $[(p-dodecylC_6H_4)PH-BH_2]_n$ (4) could also be analyzed using GPC and showed very broad molecular weight distributions. The irreproducibility of the molecular weights, which is a function of the high molecular conversion necessary for step growth processes, the high viscosity, and facile solidification of the bulk reaction mixture, underlines the need for the development of improved catalysts that are sufficiently active to allow high molecular weight products to be formed in solution. Further understanding of the dehydrocoupling mechanism would represent a key step in this direction, and we have already initiated studies in this area.^{23c,e} All of the polymers exhibited relatively low-thermal stability; however, the ceramic yields were high, especially for $[PhPH-BH_2]_n$ (1), which makes it an interesting precursor for boron phosphide-based materials.32

In contrast to the materials investigated here, cyclic phosphinoboranes of the formula $[R_2P-BH_2]_x$ (x=3,4), which are derivatives of secondary phosphine-borane adducts, are thermally stable up to ca. 300 °C.^{17a} This suggests that the P–H functionality of polymers **1–4** is relatively reactive, and for example, additional dehydrocoupling (with BH₂ groups) upon heating or chain fragmentation processes may occur at moderate temperatures. Future work will therefore focus on the preparation of high polymers $[R^1R^2P-BH_2]_n$ which are potentially accessible³³ via the functionalization of the P–H bonds in polymers **1–4**.

Experimental Section

General Methods. All reactions were performed under an atmosphere of dinitrogen using dry solvents. Workup of all phosphinoborane compounds was carried out in air. RhCl₃, RhCl₃ hydrate (Pressure Chemical Co.), PCl₃, HNEt₂ (BDH), p-nBuC₆H₄Br, nBuLi (1.6 M solution in hexanes), HCl (2.0 M solution in diethyl ether), dodecylmagnesium bromide (1.0 M solution in diethyl ether), $PdCl_2(dppf)$ where dppf = diphenylphosphinoferrocene, Li[BH₄], and nBu₃P (Aldrich) were purchased and used as received. PhPH₂·BH₃,³⁴ *i*BuPH₂·BH₃,²⁰ and $[{Rh(\mu-Cl)(1,5-cod)}_2]^{35}$ were prepared following literature procedures. NMR spectra were recorded on a Varian Gemini or Mercury 300 MHz spectrometer. Chemical shifts are referenced to solvent peaks (1H, 13C) or external BF₃·Et₂O (11B) or $H_3PO_4\ (^{31}\text{P}).$ SLS and DLS experiments were carried out as described in detail elsewhere.²⁰ The absolute molecular weight of polymer 2 in THF at 22 °C was determined by lowangle laser light scattering at a wavelength of 632.8 nm and a scattering angle of $6-7^{\circ}$. The refractive index increment, dn/dc, of the solutions of polymer 2 in THF was determined to be 0.17 mL/g. DLS experiments were performed on polymer solutions in THF with a concentration of 4 mg/mL (unless otherwise noted) at a scattering angle of 90°. Molecular

weights determined by GPC were run on a Waters Associates 2690 separation module which was equipped with a Waters 410 differential refractometer as the concentration detector. Software from Viscotek was used to analyze the data. Columns from Polymer Laboratories were used with THF as eluent at a flow rate of 1.0 mL/min. Polystyrene standards purchased from Aldrich and Viscotek were used for calibration.

Synthesis of [PhPH–BH₂]_{*n*} (1) and [*i*BuPH–BH₂]_{*n*} (2). Both polymers were synthesized according to procedures described earlier, and NMR and IR spectroscopic data have been reported previously.²⁰

[PhPH–BH₂]_n (1). PhPH₂·BH₃ (9.25 g, 74.6 mmol) and anhydrous RhCl₃ (ca. 160 mg, 1.0 mol % Rh) were heated at 90 °C for 3 h and then at 130 °C for 3 h. The resulting material was dissolved in THF (15 mL), precipitated into hexanes (750 mL), washed with hexanes, decanted, and dried under vacuum to give 6.80 g (75%) of **1** as an off-white solid. DLS (THF): $D_h \approx 7$ nm.

[*i*BuPH-BH₂]_{*n*} (2). *i*BuPH₂·BH₃ (1.49 g, 14.3 mmol) and [{Rh(μ -Cl)(1,5-cod)₂] (ca. 65 mg, 1.8 mol % Rh) were heated at 120 °C for 15 h. The resulting material was dissolved in THF (8 mL), precipitated into 2-propanol/water (100 mL/100 mL), decanted, dissolved in CH₂Cl₂ (10 mL), and filtered. Removal of the solvent under vacuum yielded 1.20 g (82%) of spectroscopically pure **2** as a gumlike material. SLS (THF): $M_{\rm w} = 13\ 100$, DP_w = 128, $A_2 = 0$; DLS (THF): $D_{\rm h} \approx 4$ nm.

Synthesis of (*p*-*n***BuC**₆**H**₄)**PCl**₂. The (Et₂N)₂PCl required for this experiment was prepared by reaction of PCl₃ with diethylamine in a 1:4 molar ratio in diethyl ether, followed by filtration and distillation of the filtrate (bp 50-55 °C, ca. 0.05 mmHg).

1-Bromo-4-butylbenzene (23.70 g, 111.2 mmol) in diethyl ether (30 mL) was added dropwise to a solution of butyllithium (76.5 mL of a 1.6 M solution in hexanes, 122.4 mmol) in diethyl ether (300 mL) at 0 °C. After stirring for 1 h at room temperature, the clear yellow solution was added to (Et₂N)₂PCl (23.40 g, 111.1 mmol) in diethyl ether (150 mL) at -78 °C. The reaction mixture was allowed to warm to room temperature, stirred overnight, and filtered. The resulting solution of $(p-nBuC_6H_4)P(NEt_2)_2$ in diethyl ether $({}^{31}P{}^{1}H{}NMR$ (121 MHz, D₂O): $\delta = 100.3$ (s)) was used without further purification. Hydrogen chloride (250 mL of a 2.0 M solution in diethyl ether, 500 mmol) was then added at -78 °C, and the reaction mixture was stirred overnight at room temperature. The white precipitate of [H₂NEt₂]Cl was filtered off and washed with diethyl ether (150 mL). The solvent was removed by distillation under atmospheric pressure. Distillation of the liquid residue at 85–90 °C (ca. 0.05 mmHg) gave pure $(p-n\text{BuC}_6\text{H}_4)\text{PCl}_2$ (19.55 g, 75%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.84 - 7.72$ (m, 2H, Ar-H), 7.38-7.26 (m, 2H, Ar-H), 2.66 (t, J_{HH} = 7.69 Hz, 2H, CH₂CH₂CH₂CH₃), 1.60 (m, 2H, CH₂CH₂- CH_2CH_3), 1.35 (m, 2H, $CH_2CH_2CH_2CH_3$), 0.92 (t, $J_{HH} = 7.14$ Hz, 3H, $CH_2CH_2CH_2CH_3$). ³¹P{¹H}NMR (121 MHz, $CDCl_3$): δ = 163.0 (s).

Synthesis of p-dodecylC₆H₄Br. Dodecylmagnesium bromide (86.6 mL of a 1.0 M solution in Et₂O, 86.6 mmol) was added dropwise to a red mixture of 1,4-dibromobenzene (20.43 g, 86.6 mmol) and PdCl₂(dppf) (0.15 g, 0.18 mmol) in diethyl ether (50 mL) at 0 °C. After stirring at room temperature for 2 days, the mixture was refluxed for 2.5 h, exposed to the atmosphere, and then poured into water (200 mL) to give a biphasic mixture. This mixture was extracted $(3 \times 50 \text{ mL})$ with diethyl ether, then dried over MgSO₄, and filtered. All volatiles were removed under reduced pressure. Short path vacuum distillation (200 °C, ca. 0.1 mmHg) of the yellow residue gave *p*-dodecylC₆H₄Br as a colorless solid (23.07 g, 82%). ¹H NMR (300 MHz, CDCl₃): $\delta = 7.37$ (d, $J_{\text{HH}} = 8.4$ Hz, 2H, Ar–H), 7.03 (d, $J_{HH} = 4.2$ Hz, 2H, Ar-H), 2.55 (t, $J_{HH} = 7.8$ Hz; 2H, $C_6H_4CH_2C_{11}H_{23}$), 1.58 (m, 2H, $C_6H_4CH_2C_{10}H_{21}$), 1.26 (m, 18H, $C_6H_4(CH_2)_2(CH_2)_9CH_3$, 0.89 (t, $J_{HH} = 6.6$ Hz, 3H, $-CH_3$). ¹³C NMR (75 MHz, CDCl₃): δ = 141.7, 131.1, 130.0, 119.1 (aromatic), 35.4, 32.0, 31.4, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 22.8 (CH2), 14.2 (CH3). MS (EI, 70 eV) m/z (%): 324 (80, M⁺), 169 (100, CH₃(CH₂)₁₁).

Synthesis of (p-dodecylC₆H₄)PCl₂. Butyllithium (7.7 mL of a 1.6 M solution in hexanes, 12.32 mmol) was added to a solution of 1-bromo-4-dodecylbenzene (3.66 g, 11.25 mmol) in diethyl ether (100 mL) at 0 °C. After stirring for 1 h at room temperature (Et₂N)₂PCl (2.37 g, 11.25 mmol) was added to the clear yellow solution at -78 °C to give a cloudy white mixture, which was then stirred at room temperature for 2 days. The LiCl was allowed to settle for 5 h, and the clear supernatant was then decanted. $(p-dodecylC_6H_4)P(NEt_2)_2$ (³¹P{¹H}NMR (121 MHz, C₆D₆): δ = 99.5 (s)) was used without further purification. Hydrogen chloride (22.3 mL of a 2.0 M solution in diethyl ether, 44.6 mmol) was added at -78 °C, and the reaction mixture was stirred overnight at room temperature. The white precipitate of [H₂NEt₂]Cl was filtered off, and the volatiles were removed under reduced pressure to yield (pdodecylC₆H₄)PCl₂ (3.28 g, 84%) as a yellow oil. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.82$ (t, $J_{\text{HH}} = 8.6$ Hz, 2H, Ar–H), 7.34 (m, $J_{\rm HH} =$ 7.8 Hz, 2H, Ar-H), 2.70 (t, $J_{\rm HH} =$ 7.8 Hz; 2H, $C_6H_4CH_2C_{11}H_{23}$, 1.66 (m, 2H, $C_6H_4CH_2CH_2C_{10}H_{21}$), 1.29 (m, 18H, $C_6H_4(CH_2)_2(CH_2)_9CH_3)$, 0.92 (t, $J_{HH} = 6.9$ Hz, 3H, $(CH_2)_{11}CH_3$). ¹³C NMR (75 MHz, CDCl₃): $\delta = 130.4$, 130.0, 129.0, 128.9 (aromatic), 36.4, 32.3, 31.5, 30.0, 29.9, 29.8, 29.7, 29.6, 23.1 (*C*H₂), 14.5 (*C*H₃); ³¹P NMR (121.5 MHz, CDCl₃): δ

Synthesis of (p-nBuC₆H₄)PH₂·BH₃. To a suspension of $Li[BH_4]$ (1.69 g, 77.6 mmol) in diethyl ether (150 mL) was added dropwise (p-nBuC₆H₄)PCl₂ (9.06 g, 38.5 mmol) at 0 °C. The reaction mixture was stirred overnight at room temperature and filtered, and the solvent was removed under vacuum. Hexanes (20 mL) were added, and some insoluble material was filtered off. Evaporation of the volatiles under vacuum yielded pure 3 (6.70 g, 97%) as a colorless liquid. ¹H NMR (300 MHz, $CDCl_3$): $\delta = 7.64 - 7.53$ (m, 2H, Ar-H), 7.30-7.25 (m, 2H, Ar–H), 5.48 (dq, $J_{PH} = 371$ Hz, $J_{HH} = 7.69$ Hz, 2H, PH₂), 2.63 (t, $J_{\rm HH} = 7.42$ Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.58 (qn, $J_{\rm HH} = 7.69$ Hz, 2H, $CH_2CH_2CH_3$), 1.33 (m, $J_{\rm HH} = 8.24$ Hz, 2H, CH₂CH₂CH₂CH₃), 0.91 (t, J_{HH} = 7.28 Hz, 3H, CH₂CH₂- CH_2CH_3), 0.86 (br q, $J_{BH} = 108$ Hz, 3H, BH₃). ¹³C NMR (75 MHz, CDCl₃): $\delta = 147.5$ (d, $J_{CP} = 2.9$ Hz, C_{para}), 133.7 (d, J_{CP} = 9.2 Hz, C_{ortho}), 129.3 (d, J_{CP} = 10.9 Hz, C_{meta}), 116.2 (d, J_{CP} = 59.3 Hz, C_{ipso}), 35.5, 33.2, 22.2 (*C*H₂), 13.9 (*C*H₃). ³¹P NMR (121 MHz, CDCl₃): $\delta = -47.5$ (br t, J_{PH} ca. = 370 Hz). ¹¹B{¹H} NMR (96 MHz, $CDCl_3$): $\delta = -42.4$ (d, $J_{BP} = 38.2$ Hz).

Synthesis of (p-dodecylC₆H₄)PH₂·BH₃. To a suspension of Li[BH₄] (435 mg, 20 mmol) in diethyl ether (50 mL) was added dropwise (p-dodecylC₆H₄)PCl₂ (3.28 g, 9.4 mmol) at 0 °C. The reaction mixture was stirred overnight at room temperature, and the volatiles were removed under reduced pressure. The residue was dissolved in hexanes (30 mL) and centrifuged. The supernatant was decanted, and the solvent was removed under reduced pressure. The remaining residue was crystallized from hexanes (-30 °C, 5 h) to yield (pdodecylC₆H₄)PH₂·BH₃ (2.33 g, 85%) as a colorless material; mp 48.5–49.5 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.63-7.56$ (m, 2H, Ar-H), 7.30-7.25 (m, 2H, Ar-H), 5.49 (dq, ${}^{1}J_{PH} = 369.9$ Hz, ${}^{4}J_{\text{HH}} = 7.8$ Hz, 2H, PH₂), 2.65 (t, $J_{\text{HH}} = 7.8$ Hz; 2H, $C_6H_4CH_2C_{11}H_{23}$), 1.62 (m, 2H, $C_6H_4CH_2CH_2C_{10}H_{21}$), 1.27 (m, 18H, C₆H₄(CH₂)₂(CH₂)₉CH₃), 1.5–0.3 (q (very broad), ${}^{1}J_{BH}$ ~ 99 Hz, 3H, BH₃), 0.89 (t, $J_{\rm HH} = 6.6$ Hz, 3H, (CH₂)₁₁CH₃). ¹³C NMR (75 MHz, CDCl₃): $\delta = 133.7$, 133.6, 129.4, 129.3 (aromatic), 36.2, 32.2, 31.5, 30.0, 29.9, 29.8, 29.7, 29.5, 23.1 (*C*H₂) 14.5 (*C*H₃). ³¹P NMR (121.5 MHz, CDCl₃): $\delta = -47.6$ (t, ${}^{1}J_{\rm PH} = 372.5$ Hz). ${}^{11}B$ NMR (96 MHz, CDCl₃): $\delta = -42.6$ (dq, ${}^{1}J_{BP} = 35.3$ Hz, ${}^{1}J_{BH} = 99.9$ Hz). MS (EI, 70 eV) m/z (%): $27\hat{8}$ (100, M⁺ - BH₃), 165 (11, C₁₂H₂₁), 137 (18, M⁺ - C₁₀H₂₁ BH₃), 124 (37, $M^+ - C_{11}H_{22} - BH_3$).

Synthesis of $[(p-nBuC_6H_4)PH-BH_2]_n$ (3). Neat $(p-nBuC_6H_4)PH_2 \cdot BH_3$ (1.02 g, 5.67 mmol) and $[{Rh}(\mu-Cl)(1,5-cod)_2]$ (ca. 20 mg, 1.5 mol % Rh) were stirred for 5 h at 100 °C. After cooling to room temperature, the material was dissolved in THF (4 mL) and precipitated into 2-propanol (180 mL). The solution was decanted, and the product washed with 2-propanol (30 mL) and dried under vacuum (45 °C/16 h) to give $[(p-nBuC_6H_4)PH-BH_2]_n$ as a sticky, off-white solid (620 mg, 61%). ¹H NMR (300 MHz, CDCl₃): $\delta = 7.20-6.40$ (br, 4H,

Ar-*H*), 4.21 (br d, $J_{\rm PH} = 356$ Hz, 1H, P*H*), 2.45 (br, 2H, C H_2 C H_2 C H_2 C H_3), 1.48 (br, 2H, C H_2 C H_2 C H_2 C H_3), 1.29 (br, 2H, C H_2 C H_2 C H_2 C H_3 C H_3), 0.88 (br, 3H, C H_2 C H_2 C H_2 C H_3), B H_2 not observed. ¹³C NMR (75 MHz, CDCl₃): $\delta = 143.9$, 132.4, 128.1, 124.8 (aromatic), 35.5, 33.4, 22.5 (CH₂), 14.1 (CH₃). ³¹P{¹H}-NMR (121 MHz, CDCl₃): $\delta = -49.7$ (br, $\nu_{1/2} = 135$ Hz). ³¹P NMR (121 MHz, CDCl₃): $\delta = -49.7$ (br, $J_{PH} = 356$ Hz). ¹¹B{¹H} NMR (96 MHz, CDCl₃): $\delta = -35.7$ (br). GPC (THF, polystyrene calibration): [**3**] = 1.50 mg/mL: $M_w = 20$ 800, $M_n = 2830$, $M_w/M_n = 6.72$; [**3**] = 4.15 mg/mL: $M_w = 19$ 500, $M_n = 2820$, $M_w/M_n = 6.92$. DSC: $T_g \approx 8$ °C.

Synthesis of [(p-dodecylC₆H₄)PH-BH₂]_n (4). Neat (pdodecylC₆H₄)PH₂·BH₃ (350 mg, 1.20 mmol) and [{Rh(µ-Cl)(1,5cod)₂] (ca. 16 mg, 1 mol % Rh) were mixed and placed into a preheated oil bath at 80 °C, the temperature was rapidly raised to 120 °C, and the contents were stirred for 9.5 h. After cooling to room temperature the material was dissolved in CHCl₃ (5 mL) and precipitated into 2-propanol (75 mL). The product was filtered and dried under vacuum to give [(p-dodecylC₆H₄)PH- $BH_2]_n$ as a sticky, brown solid (235 mg, 67%). ¹H NMR (300 MHz, CDCl₃): $\delta = 8.2-6.4$ (br, 4H, Ar-H), 4.21 (br d, $J_{PH} =$ 350 Hz, PH), 2.53 (br, 2H, C₆H₄CH₂C₁₁H₂₃), 1.8-1.2 (br, 20H, $C_6H_4CH_2(CH_2)_{10}CH_3)$, 0.94 (br, 3H, (CH₂)₁₁CH₃), BH₂ not observed. ¹³C NMR (75 MHz, CDCl₃): δ = 132.5, 128.1 (br aromatic), 36.3, 32.4, 31.9, 30.2, 23.2 (CH2), 14.6 (CH3). 31P NMR (121.5 MHz, CDCl₃): $\delta = -49.4$ (d, $J_{PH} = 332.4$ Hz). ¹¹B NMR (96 MHz, CDCl₃): $\delta = -37.5$. GPC (THF, polystyrene calibration): [4] = 3.0 mg/mL: $M_w = 168\ 000$, $M_n = 12\ 300$, $M_{\rm w}/M_{\rm n} = 13.7$. DLS (CHCl₃): $D_{\rm h} \approx 14$ nm. DSC: $T_{\rm g} \approx -1$ °C.

Stability of [PhPH–BH₂]_{*n*} (1) to HNEt₂. Sample of 1 was prepared as above ($D_h \approx 7$ nm in THF). Polymer 1 (190 mg, 1.6 mmol) and HNEt₂ (230 mg, 3.1 mmol) were dissolved in THF (3 mL) and stirred for 24 h at room temperature. All volatiles were removed under vacuum, THF (2 mL) was added, and the polymer solution precipitated into hexanes (100 mL). After decanting the solution, the off-white material was dried under vacuum at 45 °C overnight. Yield: 125 mg (66%). ³¹P{¹H} NMR (121 MHz, CDCl₃): $\delta = -48.9$ (br, [PhPH–BH₂]_{*n*}); DLS (THF): $D_h \approx 7$ nm.

Stability of [PhPH–BH₂]_{*n*} (1) to *n***Bu**₃**P**. Sample of 1 was prepared as above ($D_h \approx 7$ nm in THF). Polymer 1 (480 mg, 4.0 mmol) was dissolved in THF (7 mL), and *n*Bu₃P (1.0 mL, 4.0 mmol) was then added at room temperature. After stirring for 16 h, the reaction mixture was precipitated into hexanes (200 mL), decanted, washed with hexanes, and dried under vacuum at 45 °C overnight. Yield: 450 mg (93%). ³¹P{¹H} NMR (121 MHz, CDCl₃): $\delta = -48.9$ (br, [PhPH–BH₂]_{*n*}); DLS (THF): $D_h \approx 5$ nm.

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