Soluble N-Substituted Organosilane Polybenzimidazoles

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ABSTRACT: Six N-substituted polybenzimidazole organosilane derivatives ($-CH_2SiMe_2R$; R = methyl, vinyl, allyl, hexyl, phenyl, and decyl) were synthesized, and they are more soluble in common organic solvents (tetrahydrofuran and chloroform) than the parent polybenzimidazole. Our polymer modification pathway provides a straightforward synthesis that can be carried out at room temperature/pressure and give moderate yields. Solution ^{1}H NMR spectra of both the parent and deprotonated polybenzimidazoles are reported. On the basis of the NMR analysis in $CDCl_3$, nearly all of the benzimidazole N−H positions (two ligands per repeat unit) are substituted by the organosilane moieties. Some of the modified polymers have comparable thermal properties to the parent polymer, and the average molecular weights are higher for the substituted polybenzimidazoles than the parent PBI.

Introduction

Polybenzimidazole (PBI), also known as Celazole or poly-2,2′-(*m*-phenylene)-5,5′-bibenzimidazole) (Figure 1), is a polymer that is resistant to strong acids, bases, and high temperatures (up to 500 °C).[1,2] Because of these unique properties, PBI has been used to form membranes,[3] electrically conductive materials,[4] fire-resistant materials,[5] ultrafilters,[6] and other types of separatory media.[7] However, PBI has very poor solubility in common organic solvents. PBI is only soluble after heating in highly polar, aprotic organic solvents, such as dimethyl sulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylforamide (DMF), and *N*-methylpyrrilidone (NMP). These solvents have high boiling points and low vapor pressures and sometimes are not preferred for processing. In order for the polymer to be soluble in a wider range of organic solvents, PBI needs to be synthetically modified. This can be accomplished in two ways, either by polymer substitution (grafting) at the reactive benzimidazole N−H sites or by synthetically modifying the monomers prior to polymerization. Several groups[8−23] have tried modifying PBI with varying degrees of success. Synthetically altering the monomers to form the polymer can be difficult, and the resulting polymer molecular morphology can be considerably different from the parent PBI. Therefore, postpolymerization substitution of the polymer is a better choice since the parent polymer can be acquired by commercial means.

Even though PBI is resistant to harsh conditions, PBI has reactive imidazole nitrogens that can be used for modification by N-substitution (grafting) of the polymer. Throughout the literature, several synthetic methods have been investigated for PBI modification.[9−11] One approach isolates N-aryl-substituted PBI, but these polymers were not synthesized by deprotonation (i.e., using NaH) and significant heating was required.[12] In a separate article, PBI resin beads were N-substituted in an aqueous solution; however, the resulting substitution was simply a surface modification of the resin bead and not a fully substituted polymer backbone.[7]

Alternatively, the reactive benzimidazole N−H groups can be used to cross-link PBI or provide substitution points on the polymer chain.[2e,13] PBI was blended using aromatic polyamides or aromatic polyamide−hydrazides to yield heterocyclic linkages.[14] A clear way to use swelled PBI and form a matrix at room temperature was provided by Onorato et al.[15] Solubility of the PBI remains a problem in common organic solvents. For typical application(s) using unmodified PBI polymer, the common practice is to form a paste or gel ("dope") in strongly acidic conditions.[8]

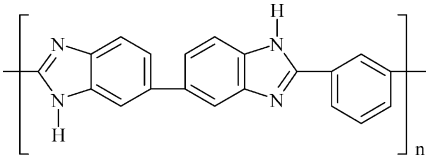
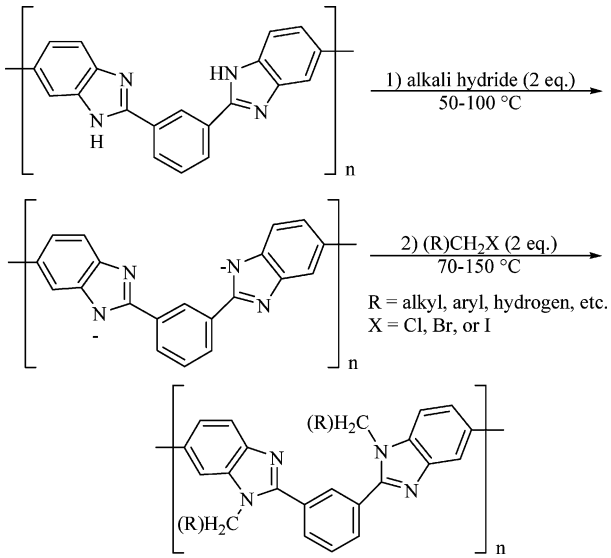


Figure 1. PBI (polybenzimidazole); traditionally drawn structure.

Scheme 1. General Approach to Polybenzimidazole Synthetic N-Substituent Modification



Sansone et al.[16−21] provided the first clear synthetic method for N-substituted PBI polymers (Scheme 1).[20] All of Sansone's synthetic methods required a PBI solution using *N*,*N*-dimethylacetimide (DMAc) or *N*-methylpyrrilidone (NMP). However, the polymer solutions were described as having polymer

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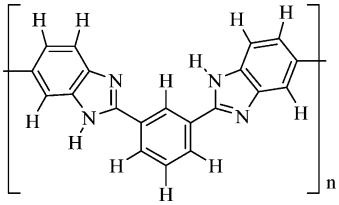


Figure 2. PBI (polybenzimidazole); symmetric structural representation of the parent polymer.

concentrations between 10 and 25 wt % in DMAc, and high temperatures (and pressure or stabilizers) were needed to fully dissolve the polymer. The literature shows that reaction solutions containing greater than 5 wt % polymer typically were not well substituted. These N-substitution reactions required heat (70−150 °C) to decrease the viscosity of the polymer solution enough that the substitution reactions would take place. The modified PBI with the greatest degree of N-substitution approached 82%; however, increasing concentrations of either base or electrophile ($R-CH_2X$) did not increase the degree of substitution on the PBI backbone. The polymers were purified by precipitation in a nonsolvent, such as water or acetone. This precipitation removed any excess solvent, but the percentage of DMAc or NMP that remained in the polymer was not described, and the solubility of the modified PBI in common organic solvents was not discussed.

Reynolds and Geiselman[22,23] improved Sansone's process[16] for producing PBI modified organo-sulfates. They used a 5−10 wt % solution of PBI in DMAc; however, the reaction mixture was a viscous liquid which required a mechanical stirrer due to ambient temperatures used for the reactions. Polymer precipitation was coupled with dialysis for polymer purification, and the isolated N-substituted PBI polymer was found to be water-soluble. An important aspect of their N-substituted PBI is that it retained the thermal stability of the original polymer.

In this paper we describe a synthetic route that gives N-substituted PBI derivatives that are soluble in tetrahydrofuran (THF), methylene chloride, and chloroform. Several different N-substituted organosilane PBI derivatives ($-CH_2SiMe_2R$; R = methyl, vinyl, allyl, hexyl, phenyl, and decyl) were synthesized and characterized, and all of the modified N-substituted polymers are significantly more soluble in organic solvents than the parent PBI.

Experimental Section

Materials and General Procedures. The following reagents were used without further purification: Me_3SiCH_2Cl (Petrarch), $PhMe_2SiCH_2Cl$ (Gelest), $(CH_2{=}CH)Me_2SiCH_2Cl$ (Avocado), $(CH_2{=}CHCH_2)Me_2SiCH_2Cl$ (Aldrich), $(Cl)Me_2SiCH_2Cl$ (Aldrich), *n*-hexylmagnesium bromide (2.0 M in diethyl ether) (Aldrich), *n*-decylmagnesium bromide (2.0 M in diethyl ether) (Aldrich), and polybenzimidazole (PBI; Celazole; poly-2,2′-(*m*-phenylene)-5,5′-bibenzimidazole) (PBI Performance Products, Inc.; previously Celanese Advanced Materials, Inc.). NaH (80% in oil dispersion) was obtained through Aldrich and used as received. Solvents employed were anhydrous *N*,*N*-dimethylacetamide (DMAc), tetrahydrofuran (THF), and hexanes, and they were used as received from the manufacturer (Aldrich). Water used for precipitations and washing was obtained as deionized water from in-house sources and further purified using a Millipore Nanopure filtration system producing water at ∼18 M ohm. Proton and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DMX 300WB spectrometer operating at 7.04 T: 300 MHz (^1H) and 75 MHz (^{13}C).

Thermal Analyses. Thermal degradation and transitions were analyzed by a TA Instruments model 2910 differential scanning calorimeter (DSC) and a model 2950 thermogravimetric analyzer (TGA). Typically, the samples were heated at 10 °C/min for both instruments while under nitrogen. The DSC was heated to 500 °C, and the TGA was heated to 550−600 °C.

Macromolecular Weight Determinations. The molecular weights for each polymer solution were achieved using a Wyatt Technologies DAWN-EOS laser light scattering detector using scintillation vials. Solution refractive index increments, d*n*/d*c* values, were determined using a Rainin Dynamax RI-1 refractive index detector. Because of the aggressive solvents (DMAc) needed for the parent PBI analysis, "batch mode" was used. Dilute solution techniques were used to characterize the macromolecular structure of the polymer. The scintillation vials were precleaned, and the solvents, tetrahydrofuran and DMAc, were filtered through a 0.02 μm filter. The polymer solutions were thoroughly mixed and filtered through a 0.45 μm PTFE filter prior to making dilute solutions in scintillation vials. All experiments were performed at 25 °C.

Dissolution of Polybenzimidazole. Typically, powdered PBI (5 g, −100 mesh resin) and placed directly into a 250 mL round-bottom flask. The flask was equipped with a water-jacketed condenser, gas inlet adapter, and magnetic stir bar. This system was placed under vacuum for 5−8 h, and the system was then purged with nitrogen. Anhydrous DMAc (200 mL) was transferred to the flask, and the solution was heated to a vigorous boil (∼165 °C) with stirring for about 24 h. The solution was allowed to cool to room temperature. Note: a small amount of the PBI polymer always precipitated out of solution as a fine dark brown powder. This amount was never directly measured because the fine powder can be easily suspended in the solution by the slightest agitation. This "stock" solution was used directly for the organosilane substitutions.

PBI Precipitate (for Analysis). The PBI/DMAc "stock" solution (see above) was used to make the PBI precipitate. Using a 1000 mL beaker, filled with 750 mL of deionized water, the PBI solution (31.0 mL, 0.775 g of PBI) was filtered through a 0.45 μm PTFE filter directly into vigorously stirred deionized water. The PBI immediately precipitated out of solution as it contacted the deionized water. A magnetic stir bar was used to vigorously stir the solution. The precipitated yellowish-brown PBI was filtered with fluted filter paper and air-dried, yielding a grainy, gray to brown solid. The amount of PBI collected after drying in an oven (120 °C) for 24 h was 0.758 g (roughly a 2% loss). This material was then dissolved in DMAc-d_9 for NMR analysis and in DMAc for molecular weight determination.

General Synthesis for Modified Polybenzimidazole.[24] The synthetic procedure provided by Lennon et al.[25] was followed to prepare the hexyl- and decyl(chloromethyl)dimethylsilanes.

In a typical postpolymerization modification reaction, the parent PBI/DMAc solution (38 mL, 0.0031 mol) was filtered through a 0.45 μm PTFE filter by syringe and transferred into a 100 mL round-bottom flask equipped with a gas inlet adapter and magnetic stir bar and purged with nitrogen. NaH (80% in oil dispersion, 190 mg, 0.0063 mol) was directly added to the PBI solution and stirred for about 6 h at room temperature. During this time, a deep red/violet color and increased viscosity of the solution were observed. After the NaH was consumed, the organosilane (Me_3SiCH_2Cl, 5 mL, 0.036 mol) was added via syringe to the flask. The reaction mixture changed color to a light reddish-purple after the organosilane addition. This solution was stirred for 48 h at room temperature. During this time, the solution color returned to a yellowish-brown. The reaction solution was transferred directly into a vigorously stirred 600 mL beaker filled with deionized, nanopure water (500 mL). The polymer immediately precipitated in water as a yellow-brown solid. The water−polymer slurry was mixed well and filtered through fluted filter paper. The collected polymer was transferred to a crystallizing dish to dry overnight. The next day, the dry polymer was dissolved in THF (200 mL); sonication was used to disperse the polymer in the solution. The THF solution was filtered through a 0.45 μm PTFE filter using a vacuum aspirator. The collected solids were set aside, and the yellow, polymer containing, THF solution was condensed to a minimal amount. This solution was added dropwise to a 600 mL beaker filled with hexanes (500

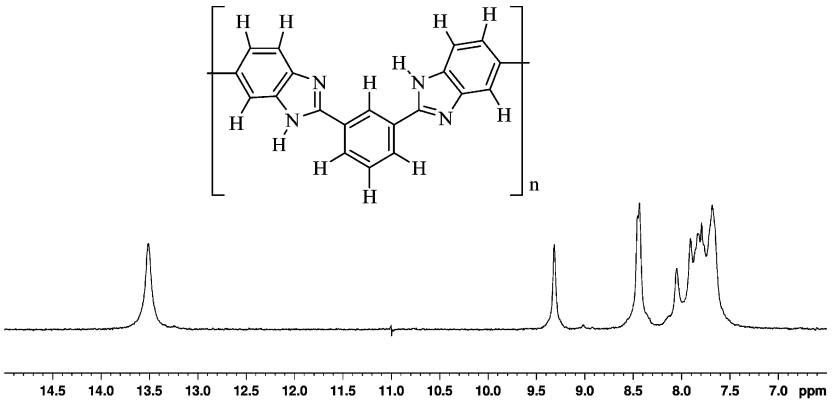


Figure 3. ^{1}H NMR spectrum of precipitated PBI in DMAc-d_9.

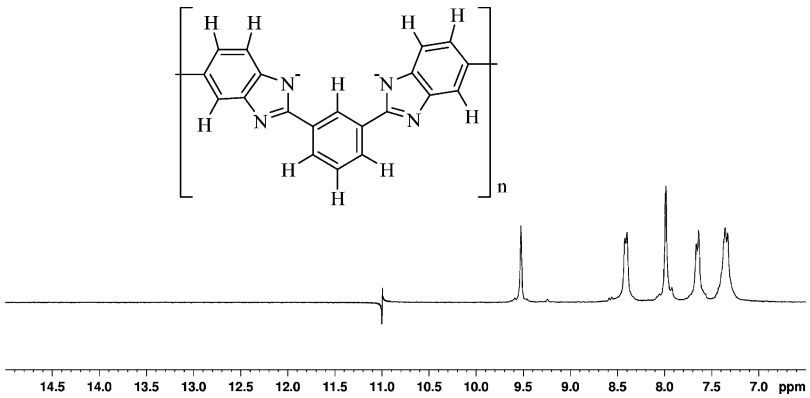


Figure 4. ^{1}H NMR spectrum of precipitated PBI and sodium hydride (80% in oil) in DMAc-d_9. Note the missing N−H resonance at 13.47 ppm.

mL). The polymer precipitated as light-yellow feathery solid or light-yellow flakes. The hexanes solution was mixed well and the solids were allowed to settle. The hexanes polymer solution was decanted through a paper filter. The polymer was collected from the filter paper and dried in a vacuum oven. NMR analysis was used to identify the products in $CDCl_3$, DMSO-d_6, and DMAc-d_9 (Figures 3−8).

Parent PBI (resin): T_d = 512 °C. ^{1}H NMR δ (DMSO-d_6) = 9.17 (s, 2H), 8.38−8.30 (2H), 8.06 (s, 2H), 7.90−7.75 (1H), 7.75−7.60 (1H).

Parent PBI (precipitated): av M_w = 8000−10 000 g/mol; T_d = 512 °C. ^{1}H NMR δ (DMAc-d_9) = 13.70−13.38 (2H), 9.45−9.22 (2H), 8.55−8.30 (2H), 8.05−7.85 (2H), 7.74 (s, 2H), 7.64 (s, 2H), 7.61 (s, 2H). ^{13}C {^{1}H} NMR δ (DMAc-d_9) = 150.2, 146.0−145.0, 144.8−143.7, 137.5−136.3, 135.5−135.0, 131.6, 129.5, 128.3−127.4, 125.8−125.1, 123.7−121.8, 120.2−119.0, 118.0−117.7, 112.5−111.3, 110.4−109.2.

(Methyl)Me_2SiCH_2-(PBI**) (1)**: ∼50% yield; M_w = 10 000−15 000 g/mol; T_d = 449 °C. ^{1}H NMR δ ($CDCl_3$) = 8.17−8.00, 8.00−7.80, 7.80−7.70, 7.70−7.57, 7.50−7.40, 4.10−3.90 (2H), −0.09 (s, 9H). ^{13}C NMR δ ($CDCl_3$) = 153.1, 143.8, 142.5, 137.0, 135.8, 131.9, 131.0, 130.3, 129.6, 122.9, 120.1, 118.5, 111.1, 109.7, 36.6, −1.4.

(Phenyl)Me_2SiCH_2-(PBI) **(2)**: ∼15% yield. ^{1}H NMR δ ($CDCl_3$) = 8.75−8.45, 8.45−8.20, 8.20−7.95, 7.95−7.75, 7.75−7.50, 4.80−4.50 (*CH_2*), 4.50−4.25 (*CH_2*), 0.68 (s, Si(CH_3)$_2$) 0.68. ^{13}C NMR δ ($CDCl_3$) = 153.1, 143.8, 142.5, 137.0, 135.8, 131.9, 131.0, 130.3, 129.6, 122.9, 120.1, 118.5, 111.1, 109.7, 36.6, −1.4.

(CH_2═CH)Me_2SiCH_2-(PBI) **(3)**: ∼50% yield; M_w = 10 000−15 000 g/mol; T_d = 464 °C. ^{1}H NMR δ ($CDCl_3$) = 8.40−8.05, 8.05−7.70, 7.70−7.10, 7.10−6.90, 6.05−5.80 (CH_2═*CH*), 5.50−5.05 (*CH_2*═CH), 4.40−3.95 (*CH_2*), 0.00 (s, Si(*CH_3*)$_2$). ^{13}C NMR δ ($CDCl_3$) = 153.0, 143.6, 142.2, 136.8, 135.7, 134.3, 131.5, 131.0, 129.3, 129.6, 122.7, 119.9, 118.3, 111.0, 109.6, 35.7, −3.5.

(CH_2═CHCH_2)Me_2SiCH_2-(PBI) **(4)**: ∼50% yield; M_w = 45 000−55 000 g/mol; T_d = 451 °C. ^{1}H NMR δ ($CDCl_3$) = 8.27−8.10, 8.10−7.85, 7.85−7.55, 7.55−7.40, 5.70−5.40 (CH_2═*CH*), 4.95−4.45 (*CH_2*═CH), 4.20−3.85 (*CH_2*), 1.55−1.30 (*CH_2*), −0.09 (s, Si(*CH_3*)$_2$). ^{13}C NMR δ ($CDCl_3$) = 153.7, 144.2, 142.8, 137.4, 137.3, 136.1, 133.4, 132.2, 131.4, 130.7, 123.3, 120.5, 119.0, 115.1, 111.3, 109.9, 109.7, 35.5, 23.0, −3.0.

(Hexyl)Me_2SiCH_2-(PBI) **(5)**: ∼50% yield; M_w = 45 000−55 000 g/mol; T_d = 390 °C. ^{1}H NMR δ ($CDCl_3$) = 8.22−8.10, 8.07−7.83, 7.83−7.60, 7.60−7.43, 4.05 (*CH_2*), 3.98 (*CH_2*), 1.40−0.95 (*CH_2*), 0.95−0.73 (*CH_2*), 0.53−0.35 (*CH_3*), −0.10 (s, Si(*CH_3*)$_2$). ^{13}C NMR δ ($CDCl_3$) = 153.6, 153.2, 143.8, 142.4, 136.5−138.0, 136.0, 135.8, 131.9, 131.1, 130.4, 129.5, 123.5, 123.2, 122.9, 120.2, 118.7, 111.0, 110.2, 109.7, 108.7, 35.7, 33.3, 32.2, 31.6, 23.6, 22.7, 15.0, 14.3, −3.1.

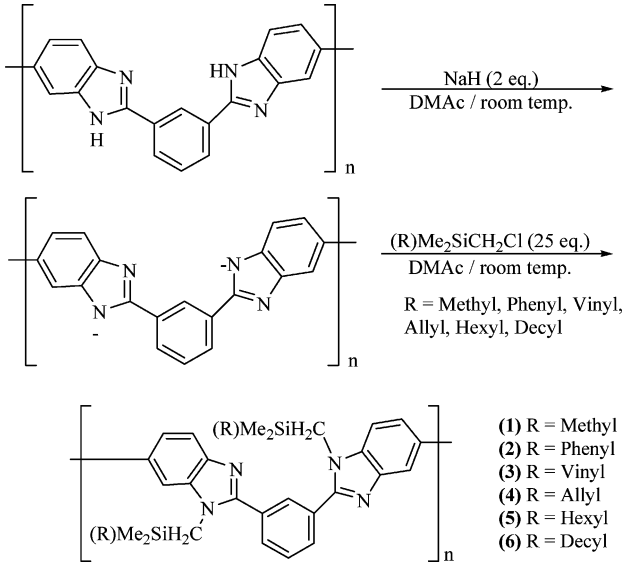
(Decyl)Me_2SiCH_2-(PBI) **(6)**: ∼50% yield; M_w = 65 000−90 000 g/mol; T_d = 382 °C. ^{1}H NMR δ ($CDCl_3$) = 8.25−8.10, 8.10−7.85, 7.85−7.57, 7.57−7.40, 4.15−3.80 (*CH_2*), 1.45−0.95 (*CH_2*), 0.95−0.71 (*CH_2*), 0.53−0.35 (CH_2), 0.07 (t, J_{HH} = 9 Hz, *CH_3*), −0.11 (Si(*CH_3*)$_2$). ^{13}C NMR δ ($CDCl_3$) = 153.6, 153.2, 143.8, 142.4, 137.5, 137.1, 131.9, 131.1, 130.4, 129.5, 123.5, 123.2, 122.9, 120.2, 118.7, 111.0, 110.1, 108.7, 35.7, 33.6, 32.1, 28.9−29.4, 23.6, 22.8, 15.0, 14.3, −3.1.

Results and Discussion

Because of the difficult solubility characteristics of PBI, the parent PBI (resin) is refluxed with DMAc. However, the parent PBI resin when dissolved in DMAc can easily be precipitated into deionized water and air-dried. The precipitated PBI is much easier to redissolve back into DMAc or NMP than the original parent PBI resin. This suggests that the original parent PBI resin is more crystalline or densely packed which causes it to be much more difficult to dissolve into solution. Therefore, it is necessary to breakup the packing of the parent PBI.

Traditionally, PBI is drawn as a linear polymer (Figure 1); however, a symmetrical representation of the polymer (Figure 2) helps with interpretation of the NMR spectra. From the ^{1}H NMR, the precipitated PBI benzimidazole N−H protons are

Scheme 2. Synthetic Route for N-Substituent Modification of Polybenzimidazole with Organosilane Groups



deshielded (13.47 ppm, Figure 3), and this downfield shift is consistent with the benzimidazole N−H being hydrogen bonded, with either another benzimidazole or the solvent. Similar results have been observed previously with PBI using FT-IR and proton NMR spectroscopy.[26] The symmetry of the aromatic protons of the parent PBI becomes more apparent in the ^{1}H NMR spectrum when the precipitated PBI is deprotonated (Figure 4). The changes in spectral shifts seen in the ^{1}H NMR spectrum on the deprotonated PBI are probably due to the anionic charges and/or loss of hydrogen bonding on the backbone.

The nature of the benzimidazole N−H proton on the parent PBI was investigated by titration experiments using concentrated sulfuric and phosphoric (85%) acids. The ^{1}H NMR spectra show that the acidic proton resonance for concentrated sulfuric acid and phosphoric acid (85% in water) are 12.26 and 8.62 ppm, respectively, in DMAc-d_9, well upfield of the observed N−H resonance (13.47 ppm) in the parent PBI precipitate. The addition of 10 μL concentrated sulfuric acid to the PBI DMAc-d_9 solution (~0.05 g/mL) caused the PBI to yield a pale-yellow, insoluble, swelled polymer gel. Addition of more DMAc-d_9 did not dissolve any more of the polymer. However, heating to reflux conditions forced the acidified PBI to dissolve into solution. This suggests that strong acids such as sulfuric acid will promote cross-linking between polymer strands through hydrogen bonding and ionic interactions. These observations provide insight into the nature of the parent and provide a rationale for the vigorous techniques that are needed to dissolve the polymer.[8] However, when NaH is added to the PBI/DMAc-d_9 solution, PBI remains in solution (Figure 4) and the ^{1}H NMR spectra show PBI's benzimidazole N−H resonance (13.70−13.38 ppm) disappears, but the other polymer resonances remain, indicating that the resonance at 13.47 ppm is due to the acidic benzimidazole protons. These limited data provide a hint that the parent polymer has strong interactions with itself by hydrogen bonding and/or ionic cross-linking. It is clear that these interactions must be disrupted before the polymer will dissolve.

Understanding the interpolymer molecular interactions of the parent PBI resin makes possible reaction condition modification and provides a synthetic route for PBI derivatization reactions that require less vigorous reaction conditions than those developed by Sansone.[20] All of the new reactions proceed with a ~2.5 wt % PBI/DMAc solution (Scheme 2). Because of the reduced amount of PBI needed, it is possible to dissolve the parent PBI resin at reflux in DMAc in about 24 h. After cooling to room temperature, small quantities of dark-brown, finely divided PBI are observed at the bottom of the flask after standing for several weeks. We were concerned that the insoluble PBI in our solutions could affect our reactions; therefore, all of the solutions were filtered using a 0.45 μm filter prior to use of the solutions in reactions. Typically, the overall loss of polymer from the stock PBI solution due to filtration was small (2% or less). Using the filtered ~2.5 wt % PBI/DMAc solution, the deprotonation reaction was found to proceed at room temperature. At room temperature, a deep red/violet viscous solution is observed after the sodium hydride is consumed (3−6 h), which is consistent with Reynolds and Geiselman's[21] reports. A crucial point within this new synthesis is the amount of organosilane used to effect the substitution reactions. It was found that the amount of organosilane added makes a significant difference between soluble and slightly soluble modified polymer products in THF. The slightly soluble polymer products are the result of an incomplete substitution reaction on the PBI framework. Approximately 20 equiv of organosilane (based upon polymer concentration) was needed to give the fully substituted, soluble products. In fact, another color change (light reddish-purple) can be observed after the addition of organosilane, and the solution viscosity suddenly decreases dramatically. Over time the reddish-purple color returns to a yellow-brown solution, similar to the parent PBI/DMAc solution. These reactions take roughly 48 h to complete at room temperature. The modified PBI polymers can be isolated by simple precipitation in nonsolvents, water, and hexanes to give yellow to brownish-yellow powders. The reaction yields among the methyl-, vinyl-, and allyl-substituted derivatives were ~50%. The reaction that provided the phenyl derivative resulted in a very low yield. The lower yield was probably due to the phenyl group's steric size and/or its inability to access the deprotonated amine site on the PBI backbone.

From the literature, there are a very limited number of citations that describe N-substituted PBI materials that are soluble in common solvents. We found that even small quantities (2−3 drops) of polar aprotic solvents, such as DMAc, changed the solubility of the modified PBI materials. However, the purified modified polymers dissolve in THF and chloroform without the aid of a cosolvent, such as DMAc (Table 1). When using dichloromethane, the modified polymers swelled, and (methyl)Me_2SiCH_2−PBI (**1**) was the only one that showed any appreciable solubility at room temperature.

From the NMR analysis, the integration ratios of the ^{1}H NMR spectra show that nearly all of the PBI N−H sites (two per repeat unit) are substituted with the organosilane. This is further corroborated by the absence of the unsubstituted imidazole (N−H) proton resonance at 13.47 ppm for the parent PBI (vide supra) of polymers **1**−**6**. The difference in spectral resolution (peak sharpness) is especially pronounced in the ^{13}C{^{1}H} NMR spectra from the precipitated PBI (Figure 5) to the organosilane-substituted PBI polymers, **6**, as an example (Figure 6). These differences are also observed in the ^{13}C{^{1}H} NMR spectra between 2-phenylbenzimidazole and 1-methyl-2-phenybenzimidazole.[27] The resonance of the methylene group between the silicon and the PBI backbone is observed in both ^{1}H NMR (~3.80−4.20 ppm) and ^{13}C{^{1}H} NMR (~35−40 ppm) spectra for all of the compounds shown in Figures 7 and 8. The methyl groups on silicon for **1**−**6** are near ~0.00 ppm for both ^{1}H NMR and ^{13}C{^{1}H} NMR spectra. Because of the low concentrations, we did not do any experiments to assign all of the resonances

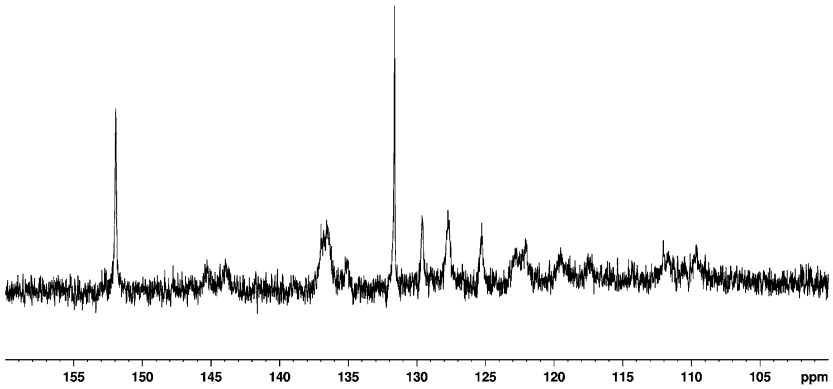


Figure 5. $^{13}C\{^1H\}$ NMR spectrum of precipitated PBI in DMAc-d_9 (aromatic region).

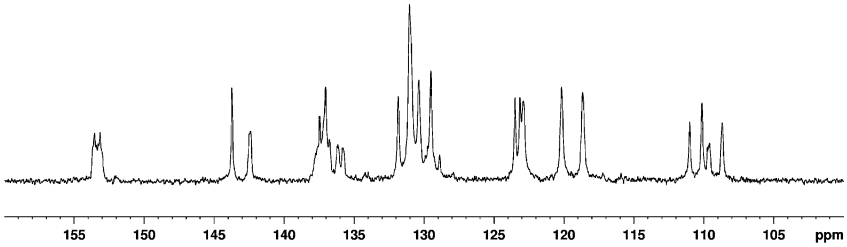


Figure 6. $^{13}C\{^1H\}$ NMR spectrum of (decyl)Me_2SiCH_2-(PBI) **(6)** in $CDCl_3$ (aromatic region).

Table 1. Solvent Solubility of Selected Polymer Derivatives

	solubility, g of polymer/mL of solvent				
polymer	THF	$CHCl_3$	CH_2Cl_2	DMAc	NMP
parent PBI (Celazole)[a]	not soluble	not soluble	not soluble	partially soluble	partially soluble
precipitated PBI	not soluble	not soluble	not soluble	soluble	soluble
(methyl)Me_2SiCH_2-PBI (**1**)	0.2−0.25	0.2−0.25[b]	0.01−0.05	soluble	soluble
(vinyl)Me_2SiCH_2-PBI (**3**)	0.2−0.25	0.2−0.25[b]	swells, slightly soluble	soluble	soluble
(allyl)Me_2SiCH_2-PBI (**4**)	0.2−0.25	0.2−0.25[b]	swells, slightly soluble	soluble	soluble

[a] Soluble in DMSO; partially soluble in DMF; 0.05−0.06 g/mL in formic acid.[1] [b] Elevated temperature (∼50 °C) and constant stirring.

Table 2. Macromolecular Weight Determination and Yield

polymer	"batch mode" M_w (g/mol)[a]	theoretical M_w (g/mol)[b]	yield (%)
parent PBI (precipitated)	8000−10000[c]	N/A	N/A
(methyl)Me_2SiCH_2-PBI **(1)**	10000−15000	12 224−15280	∼50
(phenyl)Me_2SiCH_2-PBI **(2)**	*d*	*d*	15
(vinyl)Me_2SiCH_2-PBI **(3)**	10000−15000	12800−16000	∼50
(allyl)Me_2SiCH_2-PBI **(4)**	35000−45000	13472−16840	∼50
(hexyl)Me_2SiCH_2-PBI **(5)**	35000−45000	15584−19480	∼50
(decyl)Me_2SiCH_2-PBI **(6)**	65000−80000	18272−20272	∼50

[a] Solvent = THF (tetrahydrofuran). [b] Assuming two substitutions per repeat unit and using the precipitated M_w range. [c] Solvent = DMAc (*N*,*N*-dimethylacetamide). [d] Not determined.

Table 3. Differential Scanning Calorimetry and Thermal Gravimetric Analysis Data

polymer	thermal transitions	initial weight loss and temp under N_2 (°C)
parent PBI (Celazole)	T_g = 450 °C[a]	512
precipitated PBI	*b*	512
(methyl)Me_2SiCH_2-PBI (**1**)	*b*	448
(phenyl)Me_2SiCH_2-PBI (**2**)	*b*	430
(vinyl)Me_2SiCH_2-PBI (**3**)	249 °C	464
(allyl)Me_2SiCH_2-PBI (**4**)	239 °C	451
(hexyl)Me_2SiCH_2-PBI (**5**)	*b*	390
(decyl)Me_2SiCH_2-PBI (**6**)	*b*	382

[a] From the manufacturer. [b] No detectable thermal transitions up to 500 °C.

to the N-substituted PBI polymers. However, the NMR data are consistent with the compounds being the expected modified PBI materials.

The molecular weights that were determined for **1** and **3**−**6** (Table 2) are lower than the values that Reynolds et al.[22] reported. However, Reynolds et al. synthesized organo-sulfate PBI polymers that may have other problems determining the molecular weight due to the highly ionic behavior of the polymer. They used aqueous 0.3 N NaOH for their analysis to overcome the ionic behavior, but there is the possibility of aggregation with the organo-sulfate PBI on itself in the aqueous solution (organic vs aqueous portions). In this paper, a "batch mode" molecular weight determination was used with all of the N-substituted PBI polymers in organic solvents. It was found the parent PBI (precipitate) in DMAc was in agreement with the previously determined value of 8000−10 000 g/mol from Kojima et al.[28] Also, the filtration/precipitation processes described in this paper may have reduced the quantity of higher molecular weight polymer when comparing the values to Reynolds et al. In Table 2, the molecular weights are within the calculated values for two substituted PBIs, and the results correspond with two added pendant groups per polymer repeat unit of the polymer backbone. However, as Reynolds observed elevated molecular weights after modification, we also observed the larger molecular weight values. For polymers that were substituted with larger functional groups the corresponding molecular weights tended to be higher than expected possibly due to polymer aggregation in solution.

The thermogravimetric analyses (TGA) for **1**−**6** show initial weight losses for compounds **1**−**4** that are within 60 °C of the parent PBI; however, **5** and **6** had lower decomposition temperatures (Table 3). This is possibly due to hexyl and decyl

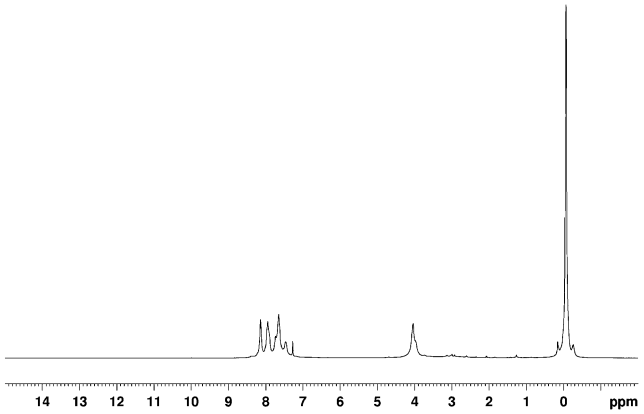


Figure 7. A representative ^{1}H NMR spectrum: (methyl)Me_2SiCH_2-(PBI) **(1)** in $CDCl_3$.

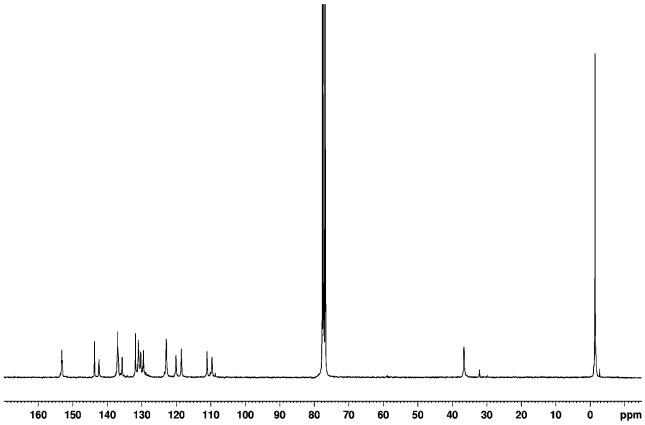


Figure 8. A representative {^{1}H}^{13}C NMR spectrum: (methyl)Me_2-$SiCH_2$-(PBI) **(1)** in $CDCl_3$.

alkyl-substituted chain degradation at lower temperatures. From our data, differential scanning calorimetry (DSC) does not provide any information with regard to glass transitions (T_g) for any of the compounds, including the parent PBI polymer. However, compounds **3** and **4** show small exotherms that possibly indicate that the vinyl and allyl groups are reacting and cross-linking.

Conclusions

The synthetic route described in this paper has expanded previous reactions to include a number of soluble hybrid organic−inorganic PBI-based polymers that exhibit similar thermal properties as the parent PBI. Six different N-substituted organosilane polymer derivatives ($-CH_2SiMe_2R$; R = methyl, vinyl, allyl, hexyl, phenyl, and decyl) were synthesized, and all of the modified polymers are much more soluble in organic solvents than the parent polybenzimidazole. Interpretation of the NMR spectra indicates that the polybenzimidazole is almost fully substituted by the organosilane moieties (two substituents per repeat unit). Some of the modified polymers exhibit high thermal transitions/degradations that are within 60 °C of the parent polymer. The molecular weights are within the expected values for the substituted parent PBI, except for the larger functional groups. Overall, this postpolymerization polymer modification route provides a straightforward synthetic method that can be carried out at room temperature and give moderate yields and provide materials that could be more amenable to processing.

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