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Synthesis and Mechanism of PBI Phosphonate, Poly[2,2′-(-*m*-phenylene)-5,5′-Bibenzimidazole Phosphonate Ester], and its Polyphosphonic Acid Derivatives

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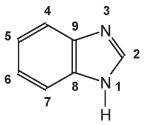
ABSTRACT: Polybenzimidazole diethyl phosphonates ($PBIP_{Et}$) of high phosphorus content (as high as ~13%) have been synthesized by reacting poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] (PBI) with diethyl phosphite and a peroxide, in *N,N*-dimethylacetamide solution, via a free radical mechanism. The phosphonate ester groups are linked directly to the aromatic backbone thus establishing a strong −(O═)P−Ph− bond. The highly phosphonylated products dissolve in lower alcohols and the corresponding polyphosphonic acids ($PBIP_{OH}$) dissolve in aqueous sodium hydroxide (pH ~ 7−8); membranes composed of either polymer are readily prepared. $PBIP_{OH}$ displayed high thermal stability as well as charge densities as high as ~9 mequiv of H^+/g. Model compounds benzimidazole and 2,2′-diphenyl-5,5′-bibenzimidazole have been phosphonylated under similar conditions in order to resolve phosphonylation mechanism, and some aspects of a rather complicated oxidative substitution. Benzoic acid is a byproduct of reactions involving benzoyl peroxide supporting a mechanism that involves breakdown of the peroxide into radicals followed by reaction with the phosphite ester and subsequent attack of phosphorus centered radicals on an aromatic ring. In the case of PBI, phosphonylation appears to occur preferentially at the C_4 and C_7 positions of the benzimidazole rings (on the benzene ring adjacent to the fusion points) as well as on the *m*-phenylene rings ortho- to the linkage with benzimidazole. The observed substitution pattern is likely controlled by the resonance stability of the radical adduct.

Introduction

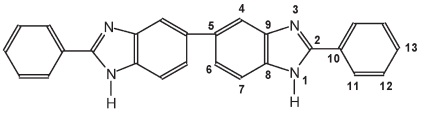
Functionalization of macromolecules with phosphonate ester groups has been shown to impart many desirable properties such as solubility in a wide variety of organic solvents,[1−4] miscibility with other polymers,[4,5] metal coordinating ability[1−3,6−8] and adhesive properties.[9−13] Most of the unique properties are due to the −C−P═O group which is a proton acceptor and thus enables the macromolecule to form a hydrogen bond and interact with Lewis acids. Additionally, the polyphosphonate esters may be hydrolyzed to the corresponding polyphosphonic acids. The latter have gained intense interest as membrane materials for use in electrochemical cells,[14−20] selective ion exchange resins,[21,22] and absorbents.[23] Polyphosphonates endure the harsh conditions that are imposed in these processes provided that the macromolecular mainframe is stable. To such category belongs polybenzimidazoles, a class of aromatic polymers well-known to possess chemical and thermal stability.[24,25] Among the polybenzimidazoles, poly[2,2′-(-*m*-phenylene)-5,5′-bibenzimidazole] (PBI) possesses an attractive combination of mechanical strength, thermal and chemical stability and tractability. Because of the many attractive properties of PBI, and its commercial availability, its sulfonic acid[15,16,26−29] and phosphonic acid derivatives[15,17] have received a great deal of contemporary interest as membrane materials for high temperature polymer electrolyte membrane (PEM) fuel cells.

Strategies for attachment of phosphonate containing groups to polymers include Arbuzov reactions,[4,30] Friedel−Crafts chemistry,[31] aromatic substitution through palladium catalysis[19] and reaction of polymeric anions with phosphorus halides[32] or haloalkyl phosphonates.[15] A route by which direct attachment of a phosphonyl group (via the phosphorus atom rather than alkyl moiety) to the aromatic backbone of a high polymer like PBI has been sought for various reasons, primarily because high substitution per unit polymer could be attained, and since the Ph−P bond is stronger than Ph−C−P.

While investigating a route suggested by Fields et al.[33,34] for low molecular weight aromatic compounds, we have demonstrated as is reported herein that benzimidazole and 2,2′-diphenyl-5,5′-bibenzimidazole[25](DPB) can be heavily phosphonylated with a dialkyl phosphite ($HP(O)(OR)_2$) in the presence of a peroxide yielding aryl phosphonate esters.



Benzimidazole



DPB

Pursuing this chemistry we were able to attain Polybenzimidazole diethyl phosphonates ($PBIP_{Et}$) with degrees of substitution (DS) ~ 3 (three diethyl phosphonyl groups per PBI repeat) through free radical aromatic substitution (Scheme 1).

Model compounds formed by phosphonylations of benzimidazole and DPB served to facilitate structural characterization of $PBIP_{Et}$ products. Di- and triphosphonylated products were obtained upon phosphonylation of DPB, while a monophosphonate was obtained in the case of benzimidazole. The PBI

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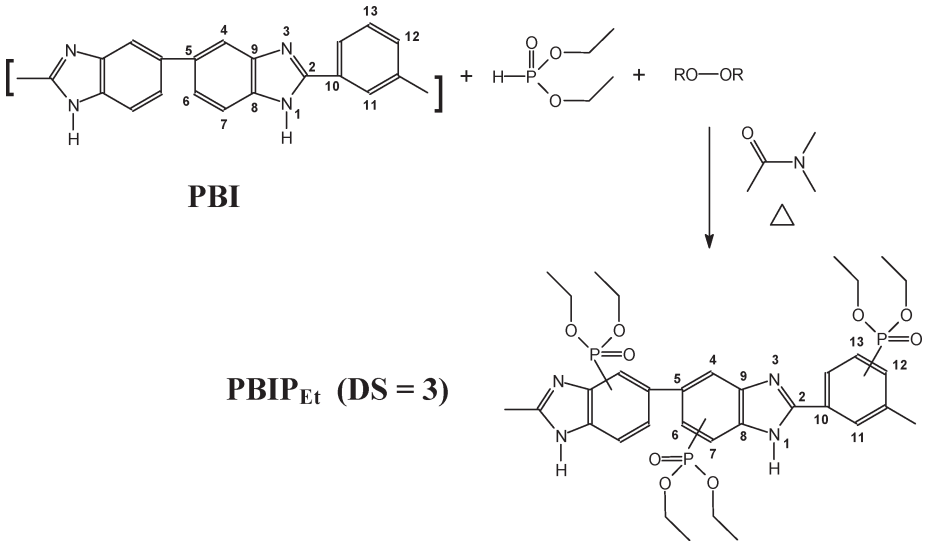
Scheme 1. Free Radical Phosphonylation of PBI



phosphonic acids ($PBIP_{OH}$) formed by hydrolysis of the corresponding esters yielded ion exchange membrane materials with high ionic charge density. With all this said, a substitution reaction via peroxide chemistry is an intricate pathway, especially when reactions are conducted on macromolecules with multiple activation sites and side-reactions are possible. In this manuscript we wish to report the synthesis, the characterization, and the reaction mechanism with all of its pitfalls.

Experimental Section

Materials. PBI (Celanese 1.0 IV) was fractionated by extraction with refluxing *N,N*-dimethylformamide (DMF), followed by extraction of the remaining insoluble fraction with dimethyl sulfoxide (DMSO) at 180 °C. The high molecular weight DMSO soluble portion ($M_n \sim 37\,000$, $M_w \sim 70\,000$) was precipitated with methanol and dried under vacuum at 100 °C for 24 h. PBI ($M_n \sim 29\,000$, $M_w \sim 73\,000$), as well as the model compound 2,2′-diphenyl-5,5′-bibenzimidazole (DPB), were also synthesized in house by condensation of 3,3′-diaminobenzidine with isophthalic acid (8 wt % solids in polyphosphoric acid, 200 °C, 5 h) and benzoic acid, respectively, according to a procedure described by Iwakura et al.[35] Benzimidazole (Aldrich 98%), isophthalic acid (Aldrich 99%) and benzoic acid (Aldrich 99%) were recrystallized from water and dried under vacuum for 24 h at 25 °C. 3,3′-Diaminobenzidine tetrahydrochloride dihydrate (Aldrich Tech.) was converted to free base and recrystallized from water after decolorization with carbon. Benzoyl peroxide, BPO (Aldrich, 75% in water) was dried under vacuum for 24 h at 25 °C and then recrystallized from chloroform/methanol solution. *N,N*-Dimethylacetamide, DMAc (Aldrich 99%), DMF (J. T. Baker) and diethyl phosphite, DEP (Aldrich 94%) were vacuum distilled from calcium hydride immediately before use. Trimethylsilyl chloride (Aldrich 98%), di-*tert*-butyl peroxide, DTP (Aldrich 98%), potassium iodide (Fisher reagent grade), ethyl acetate (Burdick & Jackson, HPLC), methanol (Burdick & Jackson, HPLC), and acetonitrile (Aldrich, HPLC grade) were used as received.

Instrumental Information. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a 600 MHz Bruker AVANCE NMR spectrometer employing DMSO-d_6 or D_2O solutions. The ^{13}C and ^{31}P spectra were proton decoupled and $^1H^{31}P$ spectra optimized for 10 ppm coupling constants (J_3, *ortho* to phosphorus). FTIR spectra were run on Nicolet Impact 400 and 750 spectrometers. HPLC/MS analyses were conducted at 70 eV with a Nucleosil C18 (5 μm, 4.6 × 250 mm) analytical column in conjunction with a HP 1100 mass spectrometer. A 50/50(v/v) acetonitrile/water to 100% acetonitrile gradient containing 0.1% trifluoroacetic acid was employed as the mobile phase. Solid probe mass spectra were performed using Polaris Q and Thermo Finnigan MAT 95 XP spectrometers. Temperature was ramped from 30 to 400 at 20 °C/min. Molecular weight characterization of the PBIs and $PBIP_{Et}$s has already been described.[36]

Synthesis. *Phosphonylation of PBI* (*$PBIP_{Et}1$*). In a typical reaction, 5 g (0.02 mol) of PBI and 200 mL of DMAc were added to a 500 mL three-necked round-bottom flask equipped with a magnetic stir bar, nitrogen inlet nozzle, dropping funnel and condenser. Under a light nitrogen purge, the mixture was stirred vigorously and heated to completely dissolve the polymer. At 125 °C, a mixture of 19.5 g (0.08 mol, 5 equiv) of BPO and 125 mL (0.97 mol, 60 equiv) of DEP was added dropwise over the course of 30 min to the PBI solution. At this point NMR analysis of the polymer revealed DS ∼ 2. Subsequently, an additional 15 equiv of BPO were added to the solution in small amounts (∼0.5 g portions) over the next 90 min. (Alternatively, the peroxide may be dissolved in a minimum amount of DMAc (∼1 g of BPO/5 mL of DMAc) and added dropwise to the reaction mixture). The temperature was kept below 140 °C. The reaction solution was then cooled and poured into acetone/hexane (50/50 v/v) to precipitate the polymer. The result was 21.3 g of a reddish-brown powder soluble in methanol, ethanol, DMF, DMAc, and DMSO; DS = 3.1. Molecular weight was measured to be as follows: $M_n = 74\,700$; $M_w = 142\,000$.

Products with lower degrees of substitution were obtained by employing procedures similar to that for $PBIP_{Et}1$ but with fewer equivalents of peroxide and phosphite. A $PBIP_{Et}$ with DS = 0.33 was formed using 5 equiv of BPO and 7 equiv of DEP added dropwise as a solution (30 wt %) in methylene chloride, with continuous removal of the methylene chloride by distillation. The molecular weight was measured to be as follows: $M_n = 39\,950$; $M_w = 79\,900$. The use of 7.5 equiv of BPO and 50 equiv of DEP yielded a product with DS = 2.4. Portions of the reaction mixture may also be removed at various intervals during the addition of the peroxide/phosphite mixture providing a range of products with varying degrees of substitution. When 5 equiv of BPO and 60 equiv of DEP were added dropwise at 125 °C over 30 min and the mixture analyzed by ^1H NMR the DS was found to be 2.1. When a second 5 eq. BPO was then added to the same reaction mixture the DS increased to 2.8. Ten additional equivalents achieved a DS = 3.1. Use of DTP (5 equiv) in place of BPO together with 60 eq. DEP at 130 °C achieved a DS = 2.2 ($PBIP_{Et}2$), though the solution would often become cloudy and clear upon addition of small amounts (0.1 g/14 mL solution) of a base such as triethylamine. Heating PBI with diethyl phosphite

in the absence of a peroxide (PBIDEP) at 120 °C for 2 h similarly resulted in precipitation and products with low phosphorus content.

When a PBI of higher molecular weight, or greater polydispersity, was phosphonylated such as that synthesized in house ($M_n \sim 29\,000$; $M_w \sim 73\,000$) more dilute polymer solutions were required to prevent gelation. In such cases addition of 10 equiv of BPO and 120 equiv of DEP to a PBI solution (1.6 wt %) in DMAc resulted in a DS = 2.3 while use of 60 equiv of DEP according to the same procedure yielded a DS = 2.0. In another procedure, 5 equiv of BPO and 125 equiv of DEP were added to a 0.8 wt % PBI solution over 40 min at 120 °C followed by continued heating for 20 min. Subsequently, 50% by volume of the solvent was removed by vacuum distillation followed by addition of 5 equiv of BPO dissolved in DMAc (~1 g/5 mL). Heating was maintained an additional 2 h at 130 °C. A $PBIP_{Et}$ with DS = 2.8 was the result.

$PBIP_{Et}1$. ^{1}H NMR (600 MHz in DMSO-d_6), δ (ppm): 1.25 (br, 6H, CH_3CH$_2$O), 2.04 (br, 0.3H, CH_3C=O), 2.83 (br, 0.3H, N(CH_3)CH$_2$), 4.23 (br, 4H, CH$_3$CH_2O), 5.80 (br, 0.1H N-(CH$_3$)CH_2), 7.38−8.60 (br m, 2.2H, Ph−*H*). ^{13}C NMR (150 MHz in DMSO-d_6), δ (ppm): 16.27 (*C*H$_3$CH$_2$O), 22.44 (*C*H$_3$C=O), 34.75 (N(*C*H$_3$)CH$_2$), 55.38 (N(CH$_3$)*C*H$_2$), 62.52 (CH$_3$*C*H$_2$O), 114.58−151.80 (br, Ph−*C*), 151.80 (NH−*C*=N), 169.90 (CH$_3$*C*=O). ^{31}P NMR (243 MHz in DMSO-d_6 at 80 °C), δ (ppm): 14.26−16.94, ((CH$_3$CH$_2$O)$_2$*P*O). FTIR (film form, cm^{-1}): 2992.5, 2938.8, 2905.2 (m, aliphatic CH); 1663.8 (m, amide C=O); 1450.9, 1394.8 (m, imidazole ring C=C, C=N); 1254.7 (s, P=O); 1052.9, 1027.7 (s, POEt); 974.5 (m, POC). Anal. Calcd for $PBIP_{Et}1$ DS(diethyl phosphonyl) = 3.1: P, 13.25. Found: P, 13.79.

$PBIP_{Et}2$. ^{1}H NMR (600 MHz in DMSO-d_6), δ (ppm): 1.04 (br, 6H, CH_3CH$_2$O), 2.93 (br, 1.6H, PhCH_2P), 3.60−4.07 (br, 5H, CH$_3$CH_2O + H$_2$O), 7.61−9.88 (br m, 3.6H, Ph−*H*). ^{13}C NMR (150 MHz in DMSO-d_6), δ (ppm): 16.63 (*C*H$_3$CH$_2$O), 35.82, 34.93 (minor, Ph*C*H$_2$P), 59.75, 62.48 (CH$_3$*C*H$_2$O), 112.67−170.91 (br, Ph−*C*). ^{31}P NMR (243 MHz in DMSO-d_6), δ (ppm): 1.63 (0.5P, (OH)$_2$*P*O), 11.81 (0.9P, (CH$_3$CH$_2$O)(OH)*P*O), 19.08 (1.3P, (CH$_3$CH$_2$O)$_2$*P*=O), 32.57 (1P, (CH$_3$CH$_2$O)$_2$*P*OCH$_2$). FTIR (film form, cm^{-1}): 2984.3, 2948.7 (s, aliphatic CH); 2627.9, 2496.1, 2360.6 (s, POH); 1636.4, 1475.6, 1446.1, 1400.5 (m, imidazole ring C=C, C=N); 1202.2 (s, P=O); 1046.7 (s, POEt); 947.5 (m, POC). Anal. Calcd for $PBIP_{Et}2$ DS(diethyl phosphonyl) = 2.2: P, 11.23. Found: P, 9.16.

PBIDEP. ^{1}H NMR (300 MHz in DMSO-d_6), δ (ppm): 1.20, 1.43 (br, 6.6H, CH_3), 3.93, 4.48 (br, 4.6H, CH_2), 5.74 (br, 0.5H, P−*H*), 7.63, 7.77, 7.93, 8.33, 9.15 (113H, Ph−*H*). ^{13}C NMR (75 MHz in DMSO-d_6), δ (ppm): 115.92 (broad), 122.72, 125.23, 128.02, 130.19, 131.31, 136.49, 139.78 (broad), 151.71(Ph−*C*), minor peaks at 25.56, 66.78, 67.46. FTIR (film form, cm^{-1}): 3620−3180 (s, NH); 3066.4 (s, aromatic CH); 1629.1, 1534.3, 1445.2, 1289.1 (m, aromatic and imidazole ring C=C, C=N); 851.5, 806.9 (m, out of plane bending CH). Anal. Found: P, < 0.6%.

Hydrolysis of $PBIP_{Et}1$ ($PBIP_{OH}1$). $PBIP_{Et}1$ (19 g) and 200 mL dry DMF were added to a 500 mL three-neck flask fitted with a magnetic stir bar, nitrogen inlet nozzle, condenser and a dropping funnel. Under a light nitrogen purge, 41 mL (0.324 mol) of trimethylsilyl chloride was added dropwise with stirring followed by the addition of 54 g (0.324 mol) potassium iodide. The mixture was then heated to 85−90 °C for 90 min. Afterward deionized water was added to the solution causing precipitation of the polymer. The polymer precipitate was then vacuum filtered and washed with deionized water and then with acetone. After drying, 13.7 g of a brown polymer soluble in water (pH ~ 8) but insoluble in water (pH ≤ 5) was obtained. Strong, pliable, water insoluble films were prepared by solution casting from aqueous base and ion exchanging with dilute acid. $PBIP_{Et}1$ was also hydrolyzed under basic conditions with hot aqueous sodium hydroxide. ^{31}P NMR indicates partial hydrolysis with formation of monoethyl phosphonyl groups, (CH$_3$CH$_2$O)(HO)PO.

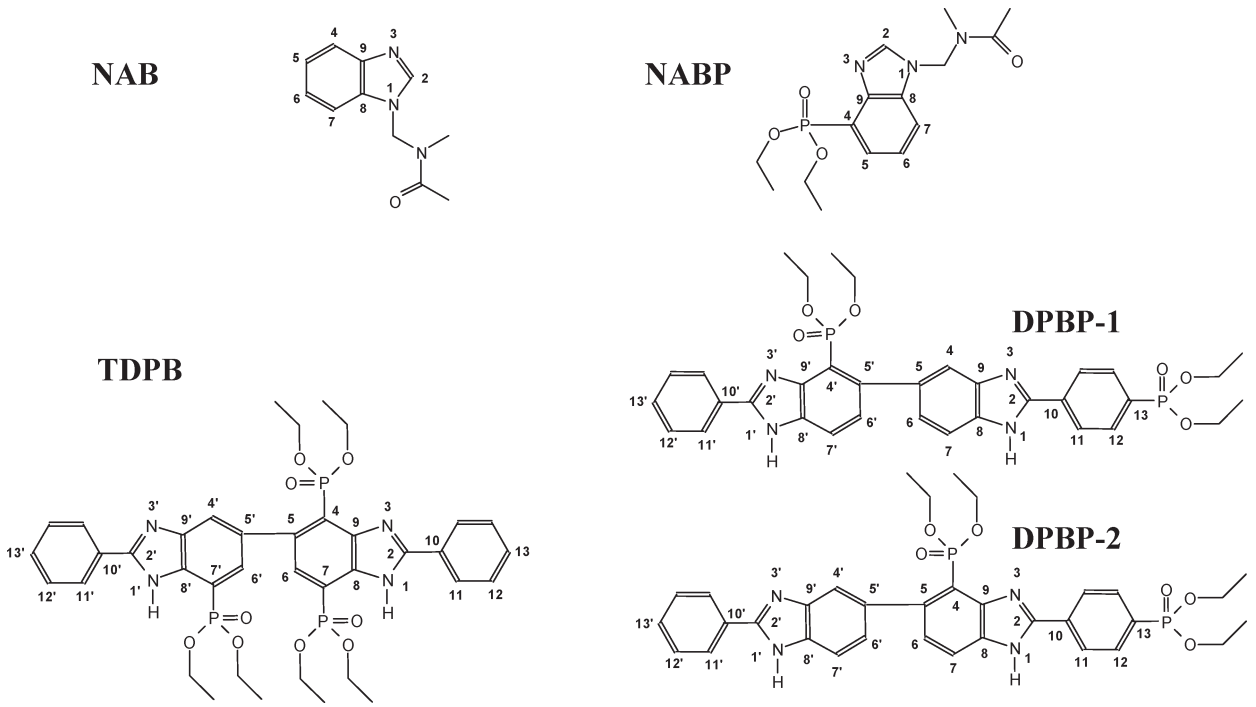
$PBIP_{OH}1$. ^{1}H NMR (600 MHz in D$_2$O as Na$^+$ salt), δ (ppm): 7.28−9.03 (br m, Ph−*H*). ^{13}C NMR (150 MHz in D$_2$O as Na$^+$ salt), δ (ppm): 114.22−141.49 (br, Ph−*C*), 154.01 (NH-*C*=N). ^{31}P NMR (243 MHz in D$_2$O as Na$^+$ salt), δ (ppm): 9.20 - 10.49 (br, (HO)$_2$*P*O). FTIR (H$^+$ film form, cm^{-1}): 2800 − 2200 (br, POH); 1621.8, 1557.4, 1456.5 (s, imidazole ring C=C, C=N); 1157.3 (s, P=O); 1065.2, 994.0, 940.5 (s, POH). Anal. Calcd for $PBIP_{OH}$ DS (phosphonic acid) = 3.1: C, 42.92; H, 2.73; N, 10.01; P, 17.39. Found: C, 40.29; H, 3.16; N, 8.53; P, 14.90. Ion exchange capacity (IEC, mequiv of H$^+$/g dry polymer), for DS = 3.1, 9.4; for DS = 2.4, 8.1; for DS = 0.33, 1.9 by titration. Alkaline hydrolysis: ^{1}H NMR (600 MHz in D$_2$Oas Na$^+$ salt), δ (ppm): 0.77−1.46 (br, 6H, CH_3CH$_2$O), 3.49−3.91 (br, 3.7H, CH$_3$CH_2O), 7.60−8.61 (br m, 3H, Ph−*H*). ^{31}P NMR (243 MHz in DMSO-d_6), δ (ppm): 11.20, 13.28, 14.18, 14.83, 15.50, ((CH$_3$CH$_2$O)(HO)*P*O).

Phosphonylation of Benzimidazole in DMAc Solution. Benzimidazole, 3 g (0.03 mol), was dissolved in 120 mL DMAc in a 250 mL three neck round-bottom flask fitted with a magnetic stir bar, nitrogen inlet nozzle, dropping funnel and condenser. Under a gentle nitrogen purge, the solution was heated to 100 °C and 12.2 g (0.05 mol) BPO dissolved in 65 mL (0.58 mol) DEP was added dropwise to the solution over 30 min. The mixture was then maintained at 100 °C for 3.5 h. Subsequently, DMAc and excess DEP were removed by vacuum distillation at 42−80 °C (8 Torr). The pot residue, a light yellow viscous oil, was separated into acidic and basic portions by dissolution in methylene chloride, extraction with 1 M NaOH and 1 M HCl followed by neutralization and back extraction. From the NaOH extract was recovered 6.28 g benzoic acid. A flash chromatography column (3 × 35 cm) using silica gel (0.04 - 0.06 mm particle size, 230−400 mesh) as the stationary phase and ethyl acetate/methanol (5/1 v/v) as the mobile phase was employed for separation of the HCl extract. The two major products isolated were *N*-(*N*-methyl acetamidomethyl) benzimidazole (NAB), a white crystalline solid, 2.73 g (53%) and *N*-(*N*-methyl acetamidomethyl) benzimidazole diethyl phosphonate (NABP), a light yellow oil, 1.43 g (17%). NAB and NABP are soluble in common organic solvents such as methanol, acetone, methylene chloride, chloroform, ethyl acetate and toluene.

N-(N-Methyl acetamidomethyl) Benzimidazole (NAB, Scheme 2). ^{1}H NMR (600 MHz in DMSO-d_6), δ (ppm): 2.02 (s, 3H, CH_3C=O), 2.96 (s, 3H, N(CH_3)CH$_2$), 5.76 (s, 2H, N(CH$_3$)CH_2), 7.20 (m, 2H, H_5,H_6), 7.67 (m, 2H, H_4,H_7), 8.34 (s, 1H, −N−C*H*=N−). ^{13}C NMR (150 MHz in DMSO-d_6), δ (ppm): 22.07 (*C*H$_3$C=O), 35.09 (N(*C*H$_3$)CH$_2$), 55.10 (N(CH$_3$)*C*H$_2$), 111.45 C_7, 119.89 C_4, 122.37 C_6, 123.15 C_5, 133.69 C_9, 143.86 C_8, 144.98 C_2, 171.61 (CH$_3$*C*=O). FTIR (NaCl, cm^{-1}): 3093.3, 3066.4, (m, aromatic CH); 2938.8 (m, aliphatic CH), 1662.7 (s, amide C=O); 1501.5, 1387.3, 1353.7 (m, imidazole ring, C=C, C=N). Anal. Calcd for $C_{11}H_{13}N_3O$: C, 65.01; H, 6.44; N, 20.67. Found: C, 64.05; H, 6.22; N, 20.09.

N-(N-Methyl acetamidomethyl) Benzimidazole Diethyl Phosphonate (NABP, Scheme 2). ^{1}H NMR (600 MHz in DMSO-d_6), δ (ppm): 1.20 (t, 6H, CH_3CH$_2$O), 2.03 (s, 3H, CH_3C=O), 3.00 (s, 3H, N(CH_3)CH$_2$), 4.09 (m, 3.8H, CH$_3$CH_2O), 5.80 (s, 2H, N-(CH$_3$)CH_2), 7.35 (td, 1H, H_6), 7.64 (dd, 1H, H_5), 7.95 (d, 1H, H_7), 8.48 (*s*, 1H, −N−C*H*=N−). ^{13}C NMR (150 MHz in DMSO-d_6), δ (ppm): 16.66 (*C*H$_3$CH$_2$O), 22.05 (*C*H$_3$C=O), 35.21 (N-(*C*H$_3$)CH$_2$), 55.32 (N(CH$_3$)*C*H$_2$), 62.10 (CH$_3$*C*H$_2$O), 116.13 C_7, 119.58 C_4, 122.60 C_6, 127.53 C_5, 133.90 C_8, 144.08 C_9, 146.08 C_2, 171.78 (CH$_3$*C*=O). ^{31}P NMR (243 MHz in DMSO-d_6), δ (ppm): 18.85 ((CH$_3$CH$_2$O)$_2$*P*O). FTIR (NaCl, cm^{-1}): 3070, (w, aromatic CH); 3000, 2950, 2900, (m, aliphatic CH), 1653.7 (s, amide C=O); 1489.6, 1420.9, 1385.1, 1349.3 (m, imidazole ring, C=C, C=N); 1247.8 (s, P=O); 1056.7.1, 1026.9 (s, POEt); 967.2 (m, POC). Anal. Calcd for $C_{15}H_{22}N_3O_4P$: C, 53.09; H, 6.54; N, 12.38; P, 9.13. Found: C, 53.99; H, 6.26; N, 11.93; P, 8.47.

Scheme 2. Products Obtained from the Phosphonylation of Benzimidazole and DPB[a]



[a] Two different structures are proposed for DPBP, though DPBP-1 is more likely based on mass spectral data.

Phosphonylation of 2,2′-Diphenyl-5,5′-bibenzimidazole (*DPB*) *in the Presence of BPO*. To a 250 mL three neck flask fitted with a magnetic stir bar, nitrogen inlet nozzle, dropping funnel, and condenser were added 1 g (0.003 mol) of DPB and 40 mL (0.31 mol) of DEP. Under a gentle nitrogen purge the solids were allowed to dissolve after which 3.2 g (0.01 mol) of BPO dissolved in 30 mL of DEP was added dropwise. About one-quarter of the BPO solution was added at 25 °C, the remainder added at 70 °C. Upon complete addition, the solution temperature was raised to 100 °C for 1 h followed by removal of excess DEP by vacuum distillation. Benzoic acid (1.2 g) was isolated from the dark brown residue by dissolution in methylene chloride and extraction with 1 M NaOH followed by acidification and back extraction. The remainder was separated using a 3 × 38 cm silica gel column (0.04−0.06 mm particle size, 230−400 mesh) with ethyl acetate followed by ethyl acetate/ethanol 85/15 (vol) followed by ethanol as the mobile phase. The tar-like products consisted of two products that were identified by NMR as 2-(*p*-diethyl phosphonyl phenyl)-2′-phenyl-5,5′-bibenzimidazole-4-diethyl phosphonate (DPBP) and 4,7,7′-tri(diethyl phosphonyl)-2,2′-diphenyl-5,5′-bibenzimidazole (TDPB). DPBP, R_f = 0.2 (ethyl acetate, silica gel), was isolated as a white powdery material, 0.15 g (9%), while TDPB, R_f = 0.6 (ethyl acetate/ethanol 85/15 (v/v), silica gel), was a light yellow powder, 0.22 g (11%). A large portion of the product displayed long elliptical spots upon TLC analysis while the ^{1}H NMR spectra showed rather broad poorly resolved bands characteristic of phenylated or higher molecular weight materials. The products were soluble in common organic solvents such as methanol, acetone, methylene chloride, chloroform, ethyl acetate, and toluene.

2-(p-Diethyl phosphonyl phenyl),2′-phenyl-5,5′-bibenzimidazole-4-diethyl Phosphonate (*DPBP Scheme 2*). ^{1}H NMR (600 MHz in DMSO-d_6), δ (ppm): 0.98, 1.28 (m, CH_3CH$_2$O), 3.87, 4.25 (m, CH$_3$CH_2O), 7.28 (d, 1H, H_6), 7.48 (t, 1H, $H_{13'}$), 7.54−7.58 (m, 6H, $H_{12,12',6',7'}$), 7.66, 7.67 (d, 2H, $H_{4',7}$), 8.22 (d, 4H, $H_{11,11'}$), 12.07 (s, N-*H*). ^{13}C NMR (150 MHz in DMSO-d_6) δ (ppm): 18.18, 19.11 (*C*H$_3$CH$_2$O), 63.19, 63.22 (CH$_3$*C*H$_2$O), 115.17−123.92 $C_{4',6',7,7'}$, 125.15 C_6, 127.50, 128.20 $C_{11,11'}$, 129.90, 130.59, 131.68 $C_{12,12'}$, 130.98 $C_{13'}$, 135.82−143.88 $C_{4,5,5',8,8',9,9',10,10',13}$, 152.74, 154.38 $C_{2,2'}$. ^{31}P NMR (243 MHz in DMSO-d_6) δ (ppm): 16.76, 18.30 ((CH$_3$CH$_2$O)$_2$*P*O). FTIR (NaCl, cm^{-1}): 1474.6, 1450.7, 1388.1, 1301.5 (m, aromatic and imidazole ring C=C, C=N); 1250.7 (s, P=O); 1050.7, 1026.9 (s, POEt); 976.1 (m, POC). Anal. Calcd for $C_{34}H_{36}N_4O_6P_2$: C, 62.00; H, 5.51; N, 8.50; P, 9.41. Found: C, 61.33; H, 5.93; N, 7.81; P, 8.55.

4,7,7′-Tri(diethyl phosphonyl)-2,2′-diphenyl-5,5′-bibenzimidazole (*TDPB, Scheme 2*). ^{1}H NMR (600 MHz in d_6-DMSO), δ (ppm): 1.03, 1.27 (m, CH_3CH$_2$O), 3.90, 4.22, 4.26 (m, CH$_3$-CH_2O), 7.50 (t, 1H, $H_{13,13'}$), 7.56−7.60 (m, 6H, $H_{6,12,12',13,13'}$), 7.67 (d, 1H, $H_{6'}$), 7.85 (s, 1H, $H_{4'}$), 8.25 (m, 4H, $H_{11,11'}$), 12.1 (s, N-*H*). ^{13}C NMR (150 MHz in d_6-DMSO), δ (ppm): 16.69, 17.12 (*C*H$_3$CH$_2$O), 62.23, 62.93, 63.23 (CH$_3$*C*H$_2$O), 118.45 (broad) $C_{4'}$, 127.87, 128.27 $C_{11,11'}$, 129.41 $C_{6'}$, 118−130.5 $C_{6,12,12'}$, 131.22, 131.73 $C_{13,13'}$, 135−146 $C_{4,5,5',7,7',8,8',9,9',10,10'}$, 154.12, 154.64 $C_{2,2'}$. ^{31}P NMR (243 MHz in DMSO-d_6), δ (ppm): 16.69, 18.32, 18.85 ((CH$_3$CH$_2$O)$_2$*P*O). FTIR (NaCl, cm^{-1}): 3065.9 (m, aromatic CH); 2986.0, 2940.9, 2906.2 (m, aliphatic CH); 1476.8, 1451.1, 1383.7, (m, aromatic and imidazole ring C=C, C=N); 1253.1 (s, P=O); 1049.1, 1025.4 (s, POEt); 971.9 (m, POC). Anal. Calcd for $C_{38}H_{45}N_4O_9P_3$: C, 57.43; H, 5.71; N, 7.05; P, 11.69. Found: C, 57.19; H, 5.48; N, 6.93; P, 12.0.

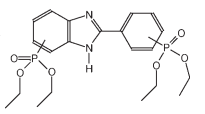
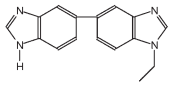
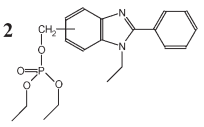
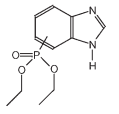
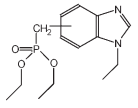
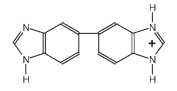
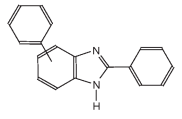
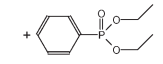
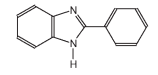
Phosphonylation of 2,2′-Diphenyl-5,5′-bibenzimidazole (*DPB*) *in the Presence of DTP*. To a 50 mL three neck round-bottom flask equipped with a magnetic stir bar, nitrogen inlet nozzle, dropping funnel, and condenser were added 0.7 g (0.002 mol) of DPB, and 28 mL of DEP. Dissolution was complete upon gentle heating. A mixture of 1.32 g (0.009 mol) of DTP and 14 mL of DEP was added dropwise to the DPB solution over 1 h at 130 °C under a light nitrogen purge. Heating was continued at 130 °C for 6 h after which a second 1.32 g portion of DTP was added dropwise. The dark brown mixture was maintained at 130 °C for a total of 20 h.

Excess DEP was removed under reduced pressure and the brown residue separated on a silica gel column (3 cm ×35 cm) with ethyl acetate followed by ethyl acetate/methanol 50/50 (vol) and finally methanol as the mobile phase. Two major phosphonylated DPB fractions were isolated, DPBP-a, 0.26 g,

Table 1. HPLC and Pyrolysis MS Data of Polymers and Model Compounds

product	major mass spectral fragments (*m*/*z*)
PBI	solid probe (400 °C): 270 (0.3%), 235 (0.2%), 91 (0.4%, benzimidazole − HCN), 77 (3%, C_6H_5), 64 (3%, benzimidazole − 2HCN), 44 (CO_2, 100%).
$PBIP_{Et}1$	solid probe (234 °C): 466 (3%), 438 (3%), 410 (3%), 381 (5%), 355 (5%), 264 (18%, $(NC)_2C_6H_3PO(OCH_2CH_3)_2$), 257 (5%, $OOCC_6H_4PO(OCH_2CH_3)_2$), 255 (6%), 239 (24%, $NCC_6H_4PO(OCH_2CH_3)_2$), 213 (6%), 194 (4%), 137 (12%, $PO(OCH_2CH_3)_2$), 109 (22%, $PO(OH)OCH_2CH_3$), 81 (43%, $PO(OH)_2$).
$PBIP_{Et}2$	solid probe (287 °C): 388 (55%), 296 (90%), 261 (65%), 253 (8%).
DPBP-a	Solid probe (125 °C): 167 (3%, $CH_2OPO(OCH_2CH_3)_2$), 137 (46%, $PO(OCH_2CH_3)_2$), 123 (100%, $CH_2PO(OH)OCH_2CH_3$), 109 (28%, $PO(OH)OCH_2CH_3$), 81 (40%, $PO(OH)_2$).
DPBP-b	solid probe (179 °C): 137 (3%, $PO(OCH_2CH_3)_2$), 123 (8%, $CH_2PO(OH)OCH_2CH_3$), 109 (23%, $PO(OH)OCH_2CH_3$), 81 (15%, $PO(OH)_2$).
NAB	HPLC: 204 ($M + H^+$).
NABP	HPLC: 340 ($M + H^+$).
DPBP	HPLC: 659 ($M + H^+$), 330.
TDPB	solid probe (399 °C): 794 (14%, M^+), 686 (100%), 658 (25%, $M - PO(OCH_2CH_3)_2$), 77 (16%, C_6H_5).

Table 2. Structures Corresponding to Mass Spectral Fragments

Fragment	*m*/*z*	Fragment	*m*/*z*
1 	466 +H=467 -H=465 - CH_2CH_2 = 438 - 2 CH_2CH_2 = 410	5 	261 (-H)
2 	388	6 	254 +H=255 -H=253
3 	296	7 	235
4 	270	8 	213
		9 	194

R_f = 0.8 (ethyl acetate/methanol 60/40 (vol), silica gel), and DPBP-b, 0.49 g, R_f = 0.2 (ethyl acetate/methanol 50/50 (vol), silica gel).

DPBP-a. ^{1}H NMR (600 MHz in DMSO-d_6), δ (ppm): 1.24 (br, 6H, CH_3CH_2O), 3.53−4.05 (br, 3.9H, CH_3CH_2O), 7.55−8.60 (m, 2.5H, Ph−*H*). ^{13}C NMR (150 MHz in DMSO-d_6), δ (ppm): 16.64 (CH_3CH_2O), 29.46 (minor, $PhCH_2P$), 41.92 (CH_3CH_2N), 62.36 (CH_3CH_2O), 111.91−153.98 (Ph−*C*). ^{31}P NMR (243 MHz in DMSO-d_6), δ (ppm): 5.04−20.00, 28.79−34.09. FTIR (NaCl, cm^{-1}): 2986.9, 2929.7, 2909.5 (s, aliphatic CH), 1444.3, 1389.3 (m, aromatic and imidazole ring C=C, C=N); 1250.6 (s, P=O); 1052.1, 1028.2 (s, POEt); 966.0 (m, POC). Anal. Found: P, 12.2.

DPBP-b. ^{1}H NMR (600 MHz in DMSO-d_6), δ (ppm): 1.25 (br, 6H, CH_3CH_2O), 3.51−4.05 (br, 4H, CH_3CH_2O), 7.59−8.60 (br, 2.6H, Ph−*H*). ^{13}C NMR (150 MHz in DMSO-d_6), δ (ppm): 16.80 (CH_3CH_2O), 29.47 (minor, $PhCH_2P$), 41.84 (CH_3CH_2N), 62.33 (CH_3CH_2O), 111.77−143.22 (Ph−*C*). ^{31}P NMR (243 MHz in DMSO-d_6), δ (ppm): 1.58−20.09, 28.79−34.76. FTIR (NaCl, cm^{-1}): 2984.5, 2939.5, 2907.4 (s, aliphatic CH), 1446.1, 1395.3 (m, aromatic and imidazole ring C=C, C=N); 1246.6 (s, P=O); 1053.9, 1026.8 (s, POEt); 972.7 (m, POC). Anal. Found: P, 12.9%.

Molecular Weight. The phosphonylation of PBI did not affect significantly the molecular weight of these polymers, beside what should be accepted from adding the phosphonate groups, indicating that no substantial degradation took place. Therefore, we will not elaborate on this subject here, but in the report by Yuan et al.[36]

Mass spectral data as well as possible fragment structures are given in Tables 1 and 2.

Results and Discussion

Phosphonylation of PBI. Phosphonylation of PBI was carried out by reaction with DEP in the presence of two different peroxides, BPO and DTP. This reaction apparently occurs by a free radical mechanism, since exclusion of the peroxide from the reaction resulted in little or no phosphonylation (< 0.6% P). Reactions involving low molecular weight aromatic compounds have typically been carried out in bulk, however, the insolubility of PBI in DEP necessitates a mutual solvent such as DMAc. It has been found that in the application of this chemistry to a polymer such as PBI in a solvent medium, an excess of peroxide and phosphite is required to achieve a high degree of substitution (DS ∼ 3, ∼13% P). The $PBIP_{Et}$ products were typically collected as light orange-brown powders or film, soluble in polar aprotic solvents such as DMF, DMAc and DMSO. At DS ∼ 3, the products were also soluble in lower alcohols

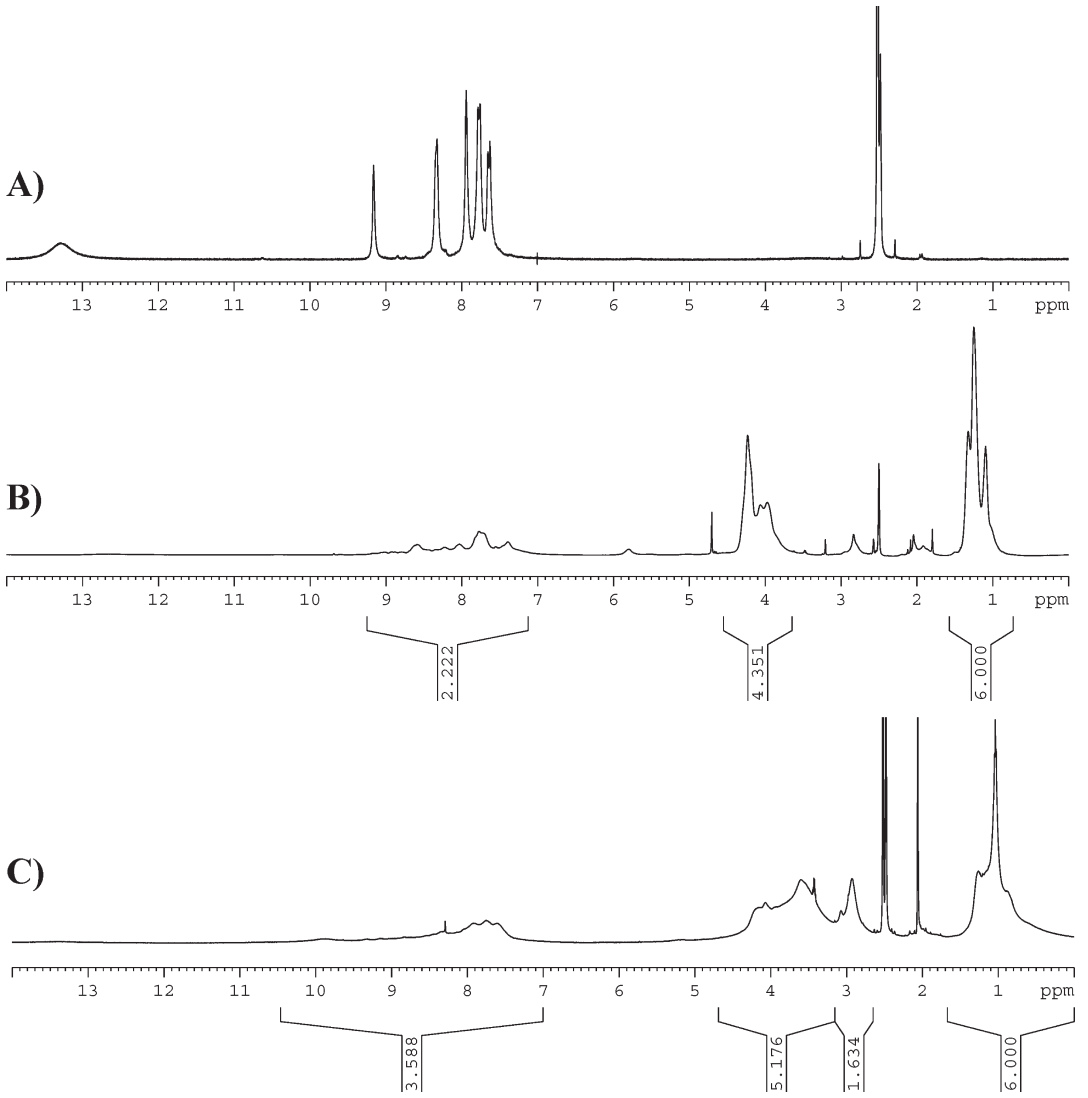


Figure 1. ^{1}H NMR (600 MHz) spectra of (A) PBI, (B) $PBIP_{Et}1$, and (C) $PBIP_{Et}2$ in DMSO-d_6.

such as methanol and ethanol. Complete hydrolysis of the phosphonate ester yielded brown film forming polyionomers soluble or swellable in dilute aqueous NaOH.

Upon phosphonylation of PBI with DEP proton resonances appear at ~1 ppm and ~4 ppm in the ^{1}H NMR spectrum corresponding to $(CH_3CH_2O)_2PO$ and $(CH_3CH_2O)_2PO$ respectively (Figure 1). The degree of substitution was estimated by comparison of the intensities of peaks arising from $(CH_3CH_2O)_2PO$ and Ph−*H* (~7−9 ppm). The observed I_{Ph-H}:I_{CH_3} of 2.2: 6 in the case of $PBIP_{Et}1$, corresponds to a DS of ~3.1. A $PBIP_{Et}$ with a DS of exactly 3 would yield a I_{Ph-H}:I_{CH_3} ratio of 7: 18 or 2.3: 6. Table 3 presents the degrees of substitution of $PBIP_{Et}$ products synthesized using varying amounts of BPO and DEP. In order to achieve a high degree of substitution (DS ≥ 2), it was necessary to employ excess BPO and DEP. Under similar conditions, a similar result was obtained with DTP. With as many as 20 eq. of peroxide a DS of at least three could be achieved. Pyrolysis mass spectrometry (Table 2) gave further evidence for a heavily phosphonylated aromatic polymer chain in the case of $PBIP_{Et}1$. A large fragment (**1**), $m/z = 466$, was observed along with m/z = 438, 410, 381, and 355, corresponding to a diphosphonylated phenyl benzimidazole chain segment with sequential loss of an ethylene fragment, C_2H_4.

Table 3. Degree of Substitution (DS) of $PBIP_{Et}$ Products Synthesized Under Different Conditions as Determined by ^{1}H NMR

equiv of DEP	equiv of BPO	concn (wt %)	DS
60	10	1.6	2.0
120	10	1.6	2.3
125	10	0.8	2.8
7	5	2.6	0.3
60	5	2.6	2.1
60	10	2.6	2.8
60	20	2.6	3.1
60	5 (DTP)	2.6	2.2

The free radical reactions under study were found to be sensitive to molecular weight, polydispersity, and initial polymer concentration. When PBI (M_w ~ 70 000, M_w/M_n ~ 1.9) was phosphonylated it was necessary to conduct the reactions in dilute (2.6 wt %) DMAc solution. At higher concentrations, the reaction mixture would visibly thicken as the phosphite/peroxide was added until the mixture could no longer be magnetically stirred. The higher polydispersity PBI (M_w ~ 73 000, M_w/M_n ~ 2.5) required even greater dilution (1 wt %). Addition of a radical to the polymer backbone followed by radical coupling among polymer chains can explain the formation of gel. Coupling of low molecular weight compounds, such as naphthalene, has been reported

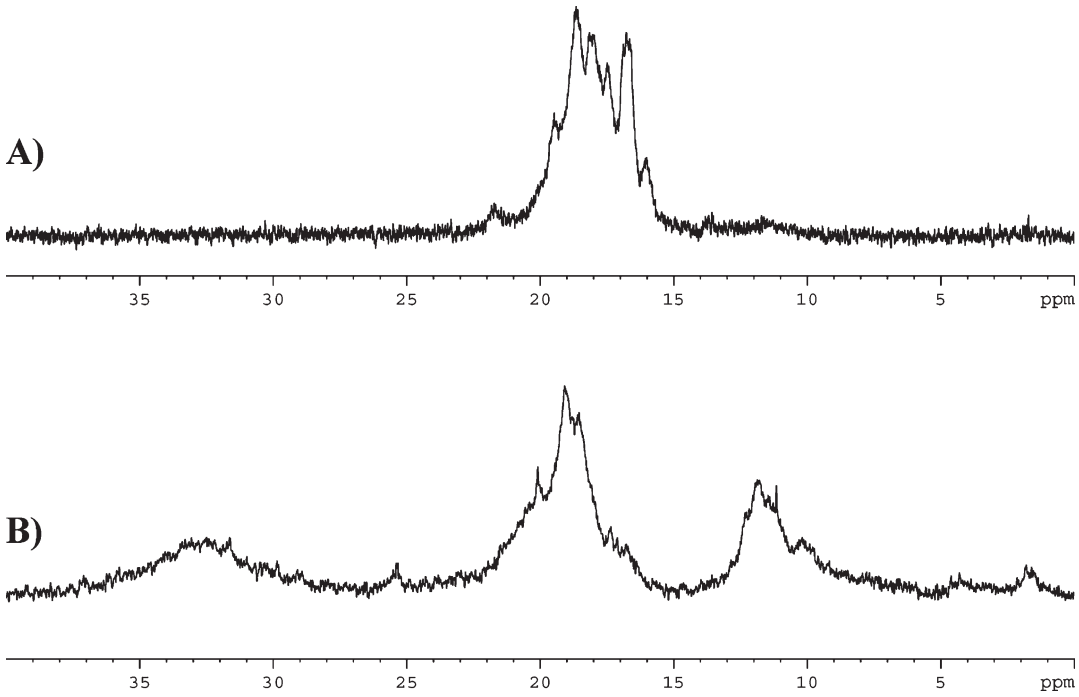


Figure 2. ^{31}P NMR (243 MHz) of $PBIP_{Et}$ synthesized with two different peroxides. (A) $PBIP_{Et}1$ synthesized with BPO. (B) $PBIP_{Et}2$ synthesized with DTP, DMSO-d_6.

during phosphonylation with DEP in the presence of a peroxide.[34]

In addition to phosphonylation, there was evidence for side reactions involving the solvent DMAc resulting in *N*-methyl acetamidomethylation ($-CH_2N(CH_3)COCH_3$) of the polymer. Minor peaks around 2, 3, and 6 ppm (Figure 1) are often present in the ^{1}H NMR spectra of $PBIP_{Et}$ phosphonylated in DMAc solution arising from the two methyl groups and methylene group, respectively. Amidomethyl radicals have been shown to form when *N*,*N*-dimethyl amides are exposed to electrophilic radical species.[37,38] Phenylation and/or benzoylation of the polymer is also possible in reactions involving BPO since thermal decomposition of BPO is known to form phenyl radical[39−41] as well as benzoyloxy radical.[42,43] The minor mass spectral fragment (**8**) $m/z = 213$, provides evidence for arylation (and subsequent phosphonylation) of the backbone.

In the case of PBI phosphonylated with DTP as the free radical source, (see Table 1, $PBIP_{Et}2$) a proton resonance around 3 ppm (Figure 1) and ^{31}P resonances around 32 ppm (Figure 2) suggest the presence of phosphonomethyl groups ($(CH_3CH_2O)_2POCH_2$) arising from methylation of the backbone with subsequent radical abstraction and coupling with a phosphite radical. Methylation of aromatic compounds by methyl radical arising from breakdown of tert-butoxy radical has been described previously.[34,44] Such ^{31}P signals are clearly absent from the spectrum of $PBIP_{Et}$ synthesized with BPO.

There is also a significant ^{31}P signal at ~12 ppm in the spectrum of $PBIP_{Et}2$ indicating the presence of (CH_3CH_2O)(HO)PO. Partial hydrolysis occurs as a result of the addition of triethylamine added to increase the solubility of the reacting components (note that alkaline hydrolysis of phosphonate esters produces only monohydrolysis where complete hydrolysis is achieved by acid[18,45,46]).

There is a possibility of alkylation of the benzimidazole residues at nitrogen stemming from the fact that phosphate esters are reported to alkylate benzimidazole.[47] The mass spectral fragments (**2**, **3**, **5**, Table 2) would be consistent with the existence of phosphonomethylation as well as ethylation of nitrogen. NMR spectra of the polymer and model compounds do not indicate that a carbon−nitrogen bond exists. Therefore, we cannot prove at the moment that diethyl phosphite alkylates the benzimidazole nitrogens as does phosphate esters. This interesting observation calls for further study. DTP has been shown to have a longer half-life than BPO in benzene solution,[48] therefore it would result in a slower phosphonylation reaction allowing the possibility of nitrogen alkylation to occur as a competing side reaction.

Model Compounds. In order to further characterize the structure and mechanism of synthesis of PBI diethyl phosphonate products two model compounds: benzimidazole and 2,2′-diphenyl-5,5′-bibenzimidazole (DPB), were subjected to similar phosphonylation conditions as those described for PBI. Major products formed from phosphonylation of benzimidazole were benzoic acid, *N*-(*N*-methyl acetamidomethyl) benzimidazole (NAB) and *N*-(*N*-methyl acetamidomethyl) benzimidazole diethyl phosphonate (NABP), see Scheme 2, indicating amidoalkylation is an important side reaction in the case of benzimidazole. Monophosphonylation of NABP at $\mathbf{C_4}$ is evidenced by the correlations of $\mathbf{H_6}$ (meta to the phosphonate group) with $\mathbf{C_4}$ and $\mathbf{C_8}$, as well as $\mathbf{C_8}$ with $\mathbf{H_6}$, NCH_2N and $\mathbf{H_2}$ in the ^{1}H^{13}C HMBC spectrum (Figure 3). *N*-Methyl acetamidomethylation was found to give rise to signals at 2, 3, and 6 ppm in the ^{1}H spectra of both NAB and NABP as was observed in the case of the $PBIP_{Et}1$. The ^{1}H^{13}C HMBC spectra of these compounds (Figures 3 and 4) correspondingly show correlation of $NC\mathbf{H_2}N$ with $\mathbf{C_2}$, $\mathbf{C_8}$, and the carbonyl carbon, attesting to the attachment of *N*-methyl acetamidomethyl groups at $\mathbf{N_1}$.

The second model compound, DPB, more accurately represents the structure of the polymer repeat unit. Acetamidomethylation side products were avoided by performing reactions in the presence of BPO under neat conditions. Phosphonylation yielded two DPB diethyl phosphonate products with well resolved NMR spectra: 2-(*p*-diethyl phosphonyl phenyl), 2′-phenyl-5,5′-bibenzimidazole-4-diethyl phosphonate (DPBP), and 4,7,7′-tri(diethyl phosphonyl)-2,2′-diphenyl-5,5′-bibenzimidazole (TDPB).

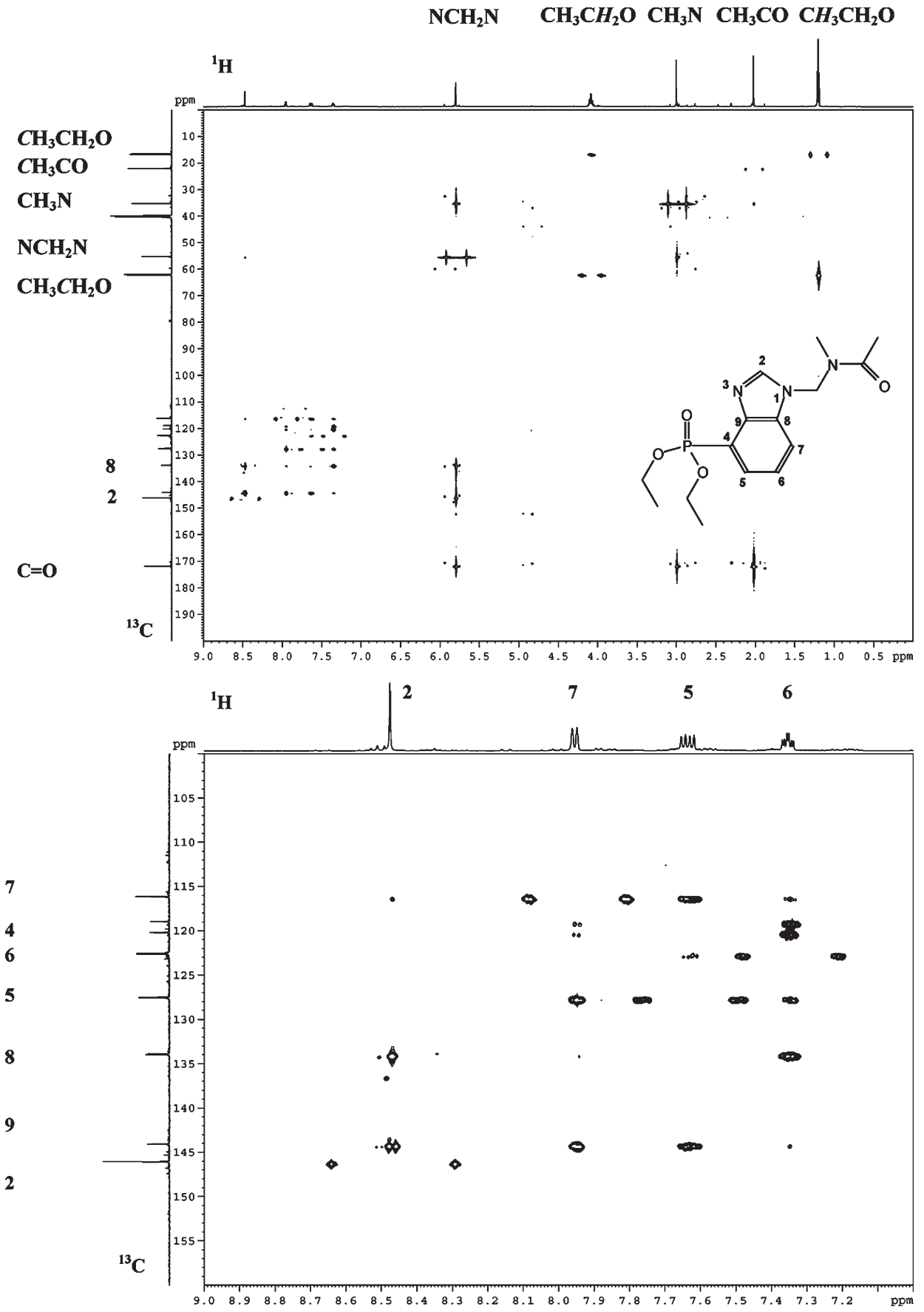


Figure 3. $^{1}H^{13}C$ HMBC (600 MHz) spectrum of N-(*N*-methyl acetomidomethyl) benzimidazole diethyl phosphonate, DMSO-d_6.

Position of phosphonylation in both compounds can be inferred from Figures 5 and 6.

Phenyl ring protons at 7.5−7.6 ppm (H_{12}, H_{13}) and 8.3 ppm (H_{11}) occur in both molecules, however, major differences

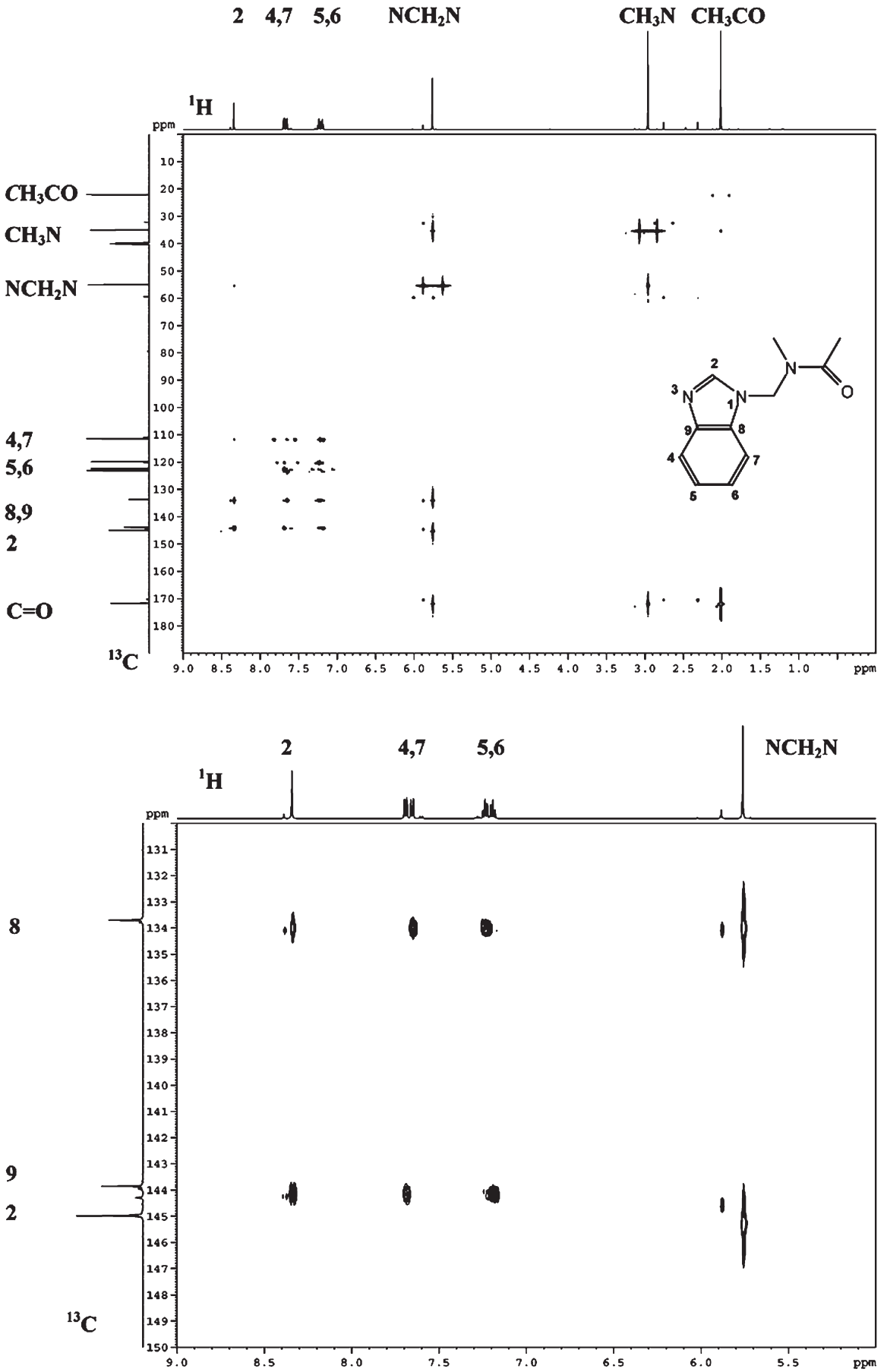


Figure 4. $^{1}H^{13}C$ HMBC (600 MHz) spectrum of *N*-(*N*-methyl acetomidomethyl) benzimidazole, DMSO-d_6.

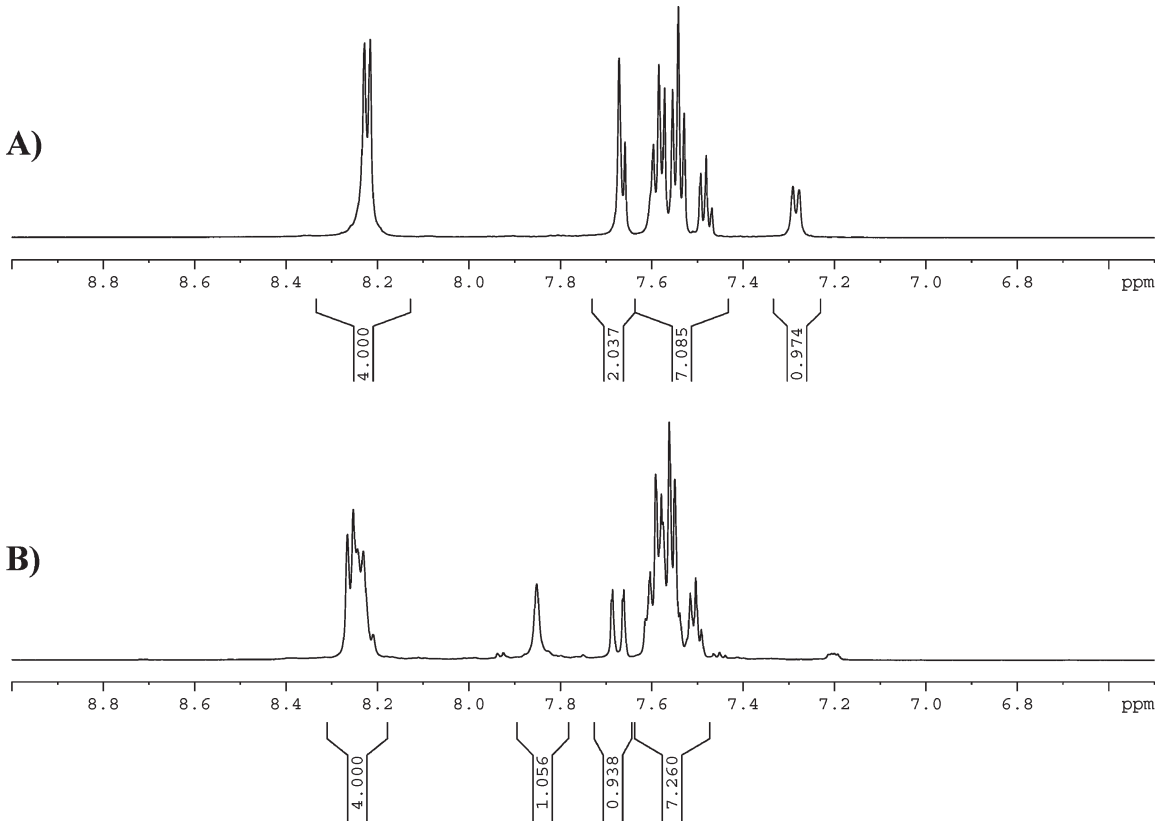


Figure 5. ^{1}H NMR (600 MHz) spectra of (A) DPBP and (B) TDPB, DMSO-d_6.

in the ^{1}H spectra include a proton shifted upfield to 7.3 ppm in the case of DPBP and two protons at 7.7 and 7.9 ppm in the case of TDPB indicating differences in benzimidazole ring substitution. DPBP is apparently phosphonylated at $\mathbf{C_4}$, since $\mathbf{H_6}$ (meta position) is shifted upfield to 7.3 ppm and shows only a weak correlation with phosphorus. DPBP is also apparently phosphonylated on the phenyl ring at $\mathbf{C_{13}}$ as the protons at 7.6 ppm ($\mathbf{H_{12}}$) correlate with phosphorus at 16.8 ppm. Two unsubstituted phenyl rings in TDPB are suggested by the intensity ratio, $I_{7.5\text{-}7.6}$:$I_{8.3}$, of 7H:4H in the ^{1}H NMR spectrum (Figure 5). This ratio completely accounts for all the phenyl protons, as the 7.5−7.6 ppm region hosts four $\mathbf{H_{12}}$, two $\mathbf{H_{13}}$ and one benzimidazole ring proton, $\mathbf{H_6}$, while the peak at 8.3 ppm represents the remaining four $\mathbf{H_{11}}$ protons. Triphosphonylation occurring on the bibenzimidazole ring system is evinced by the three distinct phosphorus signals at 16.7, 18.3, and 18.9 ppm in the ^{31}P NMR spectrum. The ^{1}H^{31}P HMQC spectrum shows phosphorus (18.9 ppm) at $\mathbf{C_{7'}}$ of the monophosphonylated benzimidazole ring correlating with $\mathbf{H_{6'}}$ (doublet) at 7.7 ppm. Diphosphonylation of the other benzimidazole ring, with phosphorus positioned at $\mathbf{C_4}$ and $\mathbf{C_7}$, can be similarly justified. The ^{31}P signal at 16.7 ppm (substitution at $\mathbf{C_4}$) shows no cross peak, while phosphorus at 18.3 ppm ($\mathbf{C_7}$) correlates with $\mathbf{H_6}$ at 7.6 ppm (shifted upfield by being positioned meta to the phosphorus group at $\mathbf{C_4}$). Mass spectrometry revealed $m/z = 659$ and $m/z = 794$ for DPBP and TDPB respectively, corresponding to molecular ions. The appearance of $m/z = 330$ in the HPLC/MS spectrum of DPBP indicates formation of phosphonylated benzimidazole fragments (barring protonation of the second imidazole ring of the DPB structure yielding a dication). Breakdown of the diphosphonylated DPB structure into equal monophosphonylated phenyl benzimidazole fragments supports DPBP-1 (the appearance of m/z = 194 would support DPBP-2).

In contrast, the DPB diethyl phosphonate products generated in the presence of DTP showed poorly resolved spectra even after separation by column chromatography and are apparently complex mixtures of isomers. Peaks ranging from around 1 to 35 ppm in the ^{31}P NMR spectra also indicate that some fraction of the phosphonate ester may have been converted to phosphate during reaction with the peroxide. The mass spectral fragments 167 and 123 consistent with $CH_2OPO(OCH_2CH_3)_2$, and $CH_2PO(OH)(OCH_2CH_3)$ were detected in the analysis of these products, however, the ^{31}P spectrum of $PBIP_{Et}1$ indicates that conversion of phosphonate to phosphate is insignificant if at all.

Detailed Structural Analysis of $PBIP_{Et}$. Though the PBI backbone differs from benzimidazole and DPB in that *m*-phenylene linkages are present, the spectra of $PBIP_{Et}$ incorporate certain features of the phosphonylated model compounds. Figure 7 displays the ^{31}P NMR spectra of DPBP, TDPB and $PBIP_{Et}$. Overlapping peaks occur in the ^{31}P spectrum of $PBIP_{Et}$ (DS ∼ 2.5) at 18−19 ppm providing evidence for substitution at the $\mathbf{C_4}$ and $\mathbf{C_7}$ positions of benzimidazole as in the case of DPBP and TDPB. Significant peaks also appear at 16−18 ppm supporting phosphorus substitution at the $\mathbf{C_4}$ position of a benzimidazole ring system already substituted at $\mathbf{C_7}$, *m*-phenylene ring substitution or phenylation of the polymer backbone with subsequent phosphonylation. Figure 8 depicts the ^{1}H^{31}P HMQC spectra of two different $PBIP_{Et}$ samples, DS ∼ 0.5 and DS ∼ 3, run at 80 °C to improve peak resolution.

Phenylene ring substitution at $\mathbf{C_{12}}$ is supported by phosphorus correlating with protons at 8.1 and 8.5 ppm ($\mathbf{H_{12}}$ and $\mathbf{H_{13}}$) in the spectrum of $PBIP_{Et}$ (DS ∼ 0.5). In this $PBIP_{Et}$, the phosphorus peaks further downfield correlating with the protons at 7.3 ppm (as in the case of DPBP) and 7.9 ppm support the presence of phosphorus located at $\mathbf{C_4}$ and $\mathbf{C_7}$ respectively (Figure 8A). Correlation of phosphorus with a

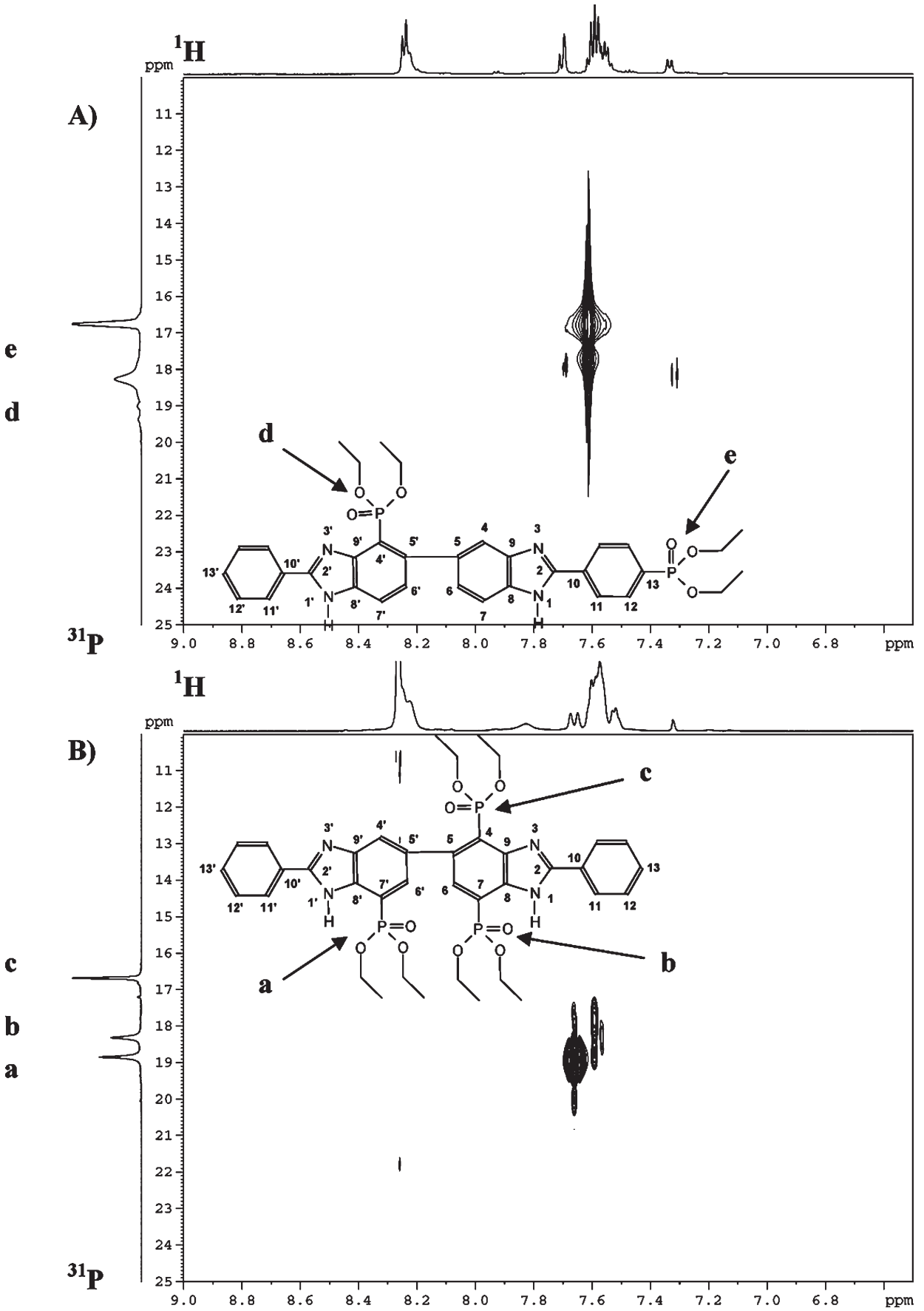


Figure 6. $^{1}H^{31}P$ HMQC (600 MHz) spectra of (A) DPBP and (B) TDPB in DMSO-d_6.

proton at 8.9 ppm can be seen corresponding to phosphonylation of an end group (likely isophthaloyl). This peak is more pronounced in lower molecular weight polymers ($M_n \sim 5000$), correlations of this type become less pronounced

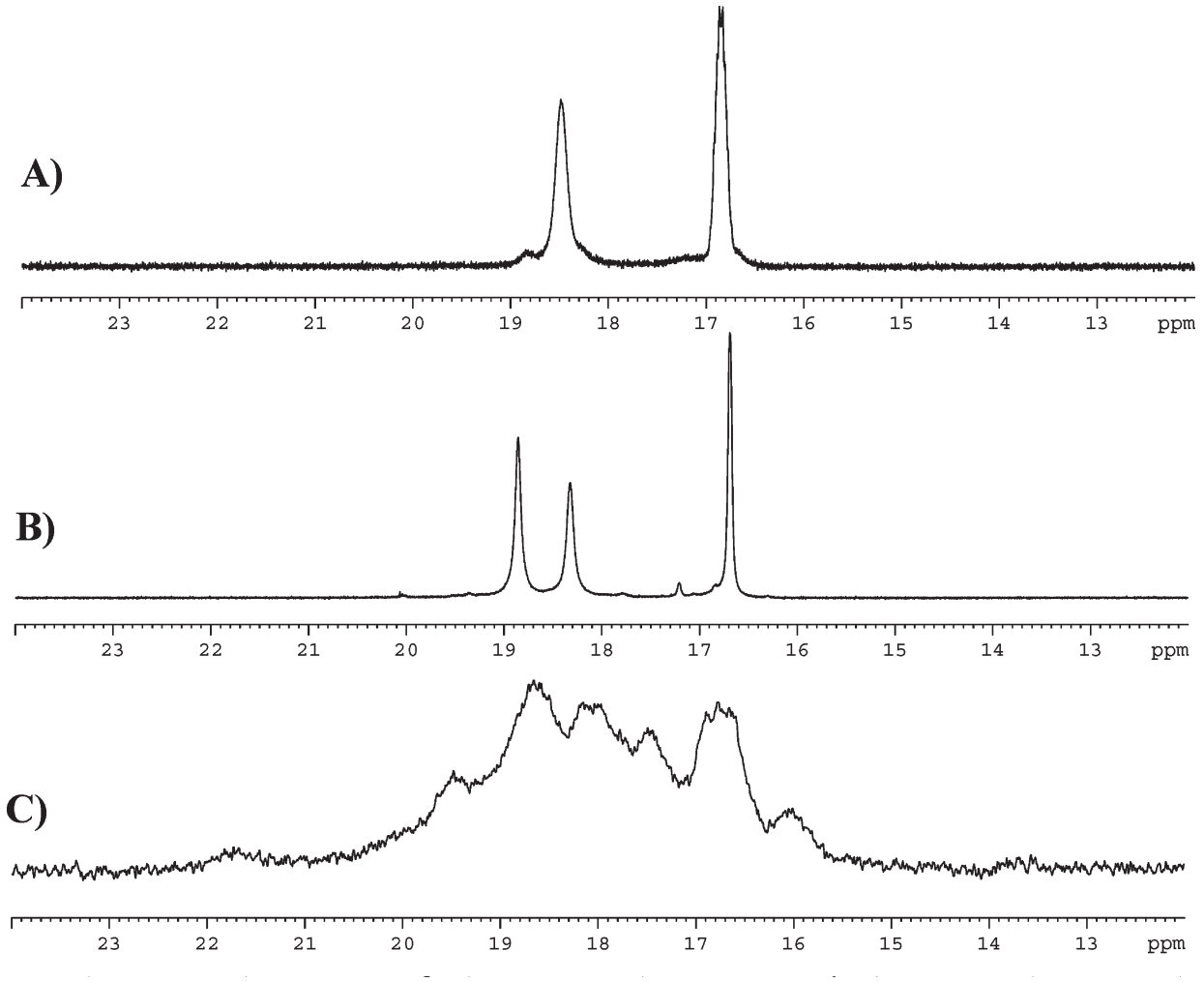


Figure 7. ^{31}P NMR (243 MHz) spectra of (A) DPBP, (B) TDPB, and (C) $PBIP_{Et}$ (DS ~ 2.5) in DMSO-d_6.

or barely discernible at higher levels of phosphonylation. In the more heavily phosphonylated polymers (DS ~ 3, Figure 8B) phosphorus can be seen to correlate with protons at 7.7−8.0 ppm ($\mathbf{H_6}$) indicative of phosphorus substitution at $\mathbf{C_7}$ (as in the case of TDPB). Additional phosphorus peaks further upfield also become much more pronounced indicating additional substitution. Figure 9 depicts the $^1H^{31}P$ spectrum of $PBIP_{Et}$ (DS ~ 2.5). The large phosphorus peak at ~17 ppm shows no strong correlations with ^{1}H (as seen in the case of TDPB) providing evidence for the addition of phosphorus to the $\mathbf{C_4}$ position of a benzimidazole ring already substituted at $\mathbf{C_7}$. The phosphorus peak at ~17.5 ppm correlating with ^{1}H at ~7.6 ppm that is absent from the spectra of DPBP and TDPB may arise from phosphonyl phenylation or phosphonyl benzoylation. At slightly higher substitution (DS ~ 3, Figure 8B), the phosphorus peak furthest upfield correlates with a proton at 8.5 ppm possibly resulting from substitution at $\mathbf{C_{13}}$.

The pyrolysis mass spectrum of heavily substituted $PBIP_{Et}$ synthesized with BPO shows several mass fragments supporting the phosphonylation of benzimidazole as well as phenylene moieties. The fragments m/z = 466 and 255 are consistent with diphosphonylated phenyl benzimidazole and phosphonylated benzimidazole, while the minor peaks m/z = 213 and 257 are consistent with the scission of diethyl phosphonylphenyl and diethyl phosphonylbenzoyl resulting from reaction of the polymer backbone with BPO. Since phenyl benzimidazoles are reported to yield benzonitrile upon fragmentation,[49] the fragments, m/z = 239 and m/z = 264 indicate the release of diethyl phosphonyl derivatives of benzonitrile and phenylene dinitrile, respectively, arising from phosphonylation of *m*-phenylene rings along the PBI backbone. The minor peak m/z = 194 also indicates a small quantity of unsubstituted phenyl benzimidazole segments.

The ^{1}H and ^{31}P NMR spectra of $PBIP_{Et}2$ (Figures 1 and 2) are rather poorly resolved indicating a highly irregular structure. The presence of phosphonomethyl groups in addition to phosphonyl groups would greatly contribute to such irregularity.

The favored positions of substitution are difficult to determine though PBI appears to be substituted at $\mathbf{C_7}$, $\mathbf{C_4}$, and $\mathbf{C_{12}}$ (*m*-phenylene) in common with DPB and benzimidazole. Figure 10 displays the ^{31}P NMR spectra of $PBIP_{Et}$ at 80 °C with varying degrees of phosphonylation (DS ~ 0.5, 1.0, 1.7, 3). Substitution at $\mathbf{C_7}$, $\mathbf{C_4}$ and $\mathbf{C_{12}}$ can be seen from the outset with $\mathbf{C_7}$ substitution being favored as shown by an intensity ratio, I_{C7}:I_{C12}:I_{C4} = 1.9: 1.2: 1.0. End group substitution, however, also occurs (overlap with $\mathbf{C_7}$ substitution at ~ 17−18 ppm). As degree of substitution increases ^{31}P resonances further upfield ($\mathbf{C_{13}}$, $\mathbf{C_4}$ disubstituted benzimidazole, phosphonyl phenyl) clearly increase in intensity. The broadened peak corresponding to $\mathbf{C_4}$ substitution also shows a gradual shift upfield with increasing substitution overlapping with phosphorus at $\mathbf{C_7}$. Integration of the phosphorus multiplet given by $PBIP_{Et}$ (DS ~ 3, Figure 10D) gives an approximate intensity ratio, I_{C4}:I_{C7}:I_{C12} = 1.2: 1.1: 0.9

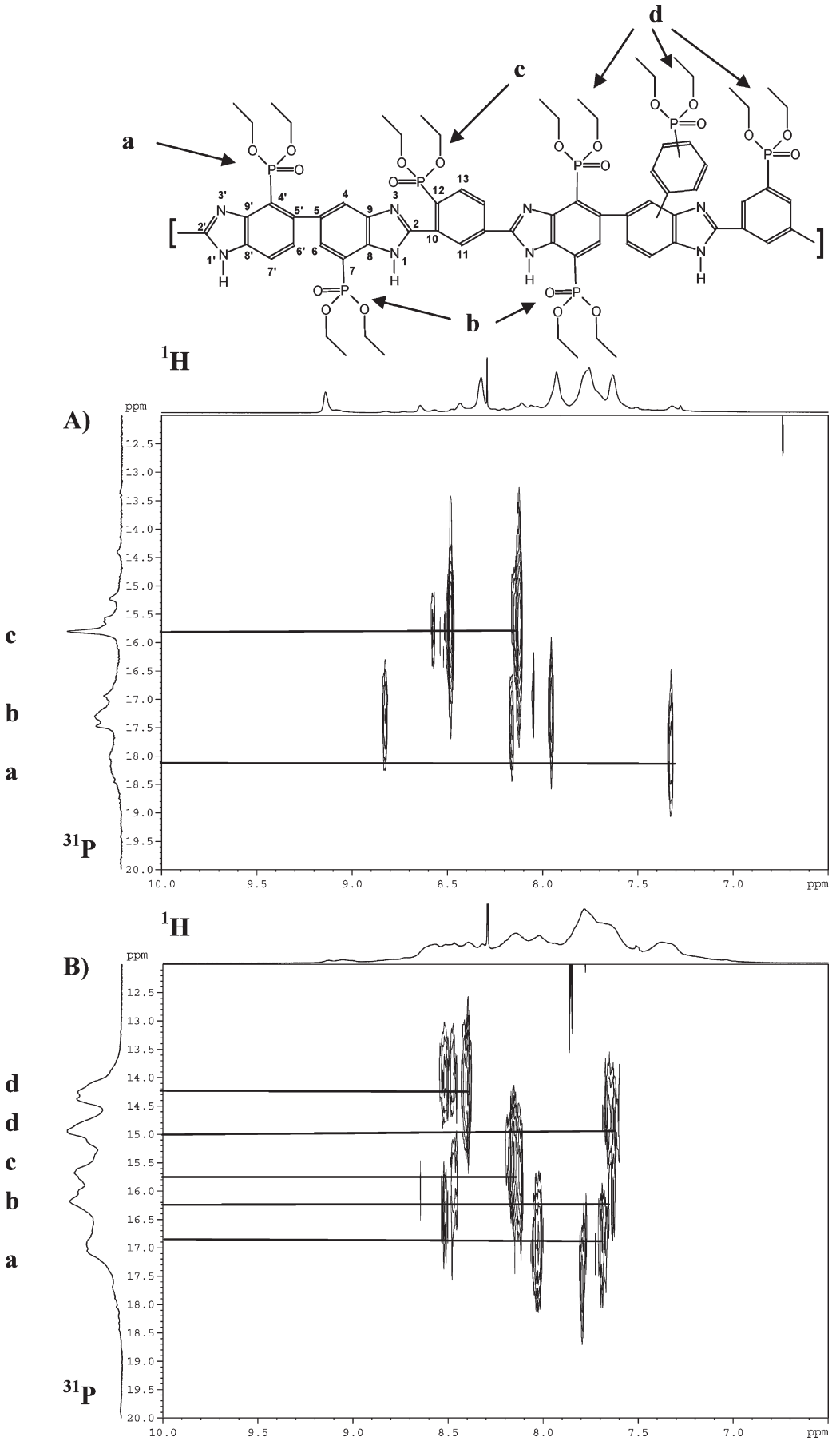


Figure 8. $^{1}H^{31}P$ HMQC (600 MHz) spectra of (A) $PBIP_{Et}$ (DS ~ 0.5) and (B) $PBIP_{Et}$ (DS ~ 3), 80 °C, DMSO-d_6.

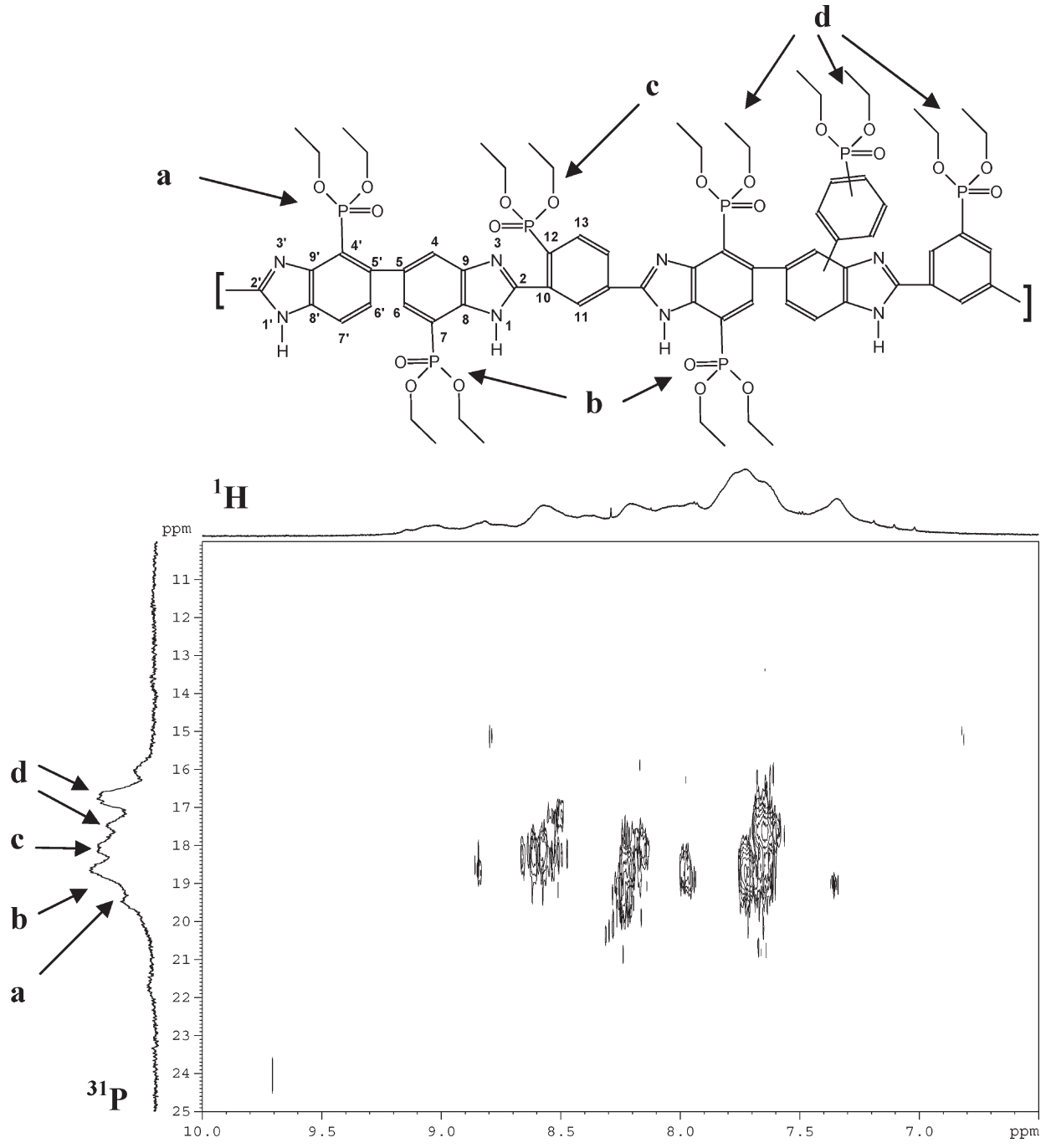


Figure 9. $^{1}H^{31}P$ HMQC (600 MHz) spectrum of $PBIP_{Et}$ (DS ~ 2.5), DMSO-d_6.

if the peak at ~17 ppm is attributed to largely C_4 substitution. It appears that when the DS is high, benzimidazole and phenylene rings are substituted at the C_7, C_4, and C_{12} to about an equal extent.

Reaction Mechanism. Phosphonylation at C_4 and C_7 in this system involving PBI is strongly supported by work with benzimidazole and DPB as model compounds. A mechanism involving abstraction of the P−H proton from diethyl phosphite with subsequent addition of a diethyl phosphonyl radical to the PBI backbone followed by reaction with another radical to restore aromaticity, as shown in Scheme 3, is supported by this work. That benzoyloxy radicals are initially formed with subsequent formation of phosphorus based radicals is supported by the fact that benzoic acid is generated as a byproduct of reactions involving BPO. Additionally, peroxide was necessary in order to achieve significant phosphonylation levels. Stability of the radical adduct is likely the reason for the preference for positions C_4 and C_7 of the benzimidazole rings. Scheme 4 shows that addition of a phosphite radical to C_4 or C_7 maintains the aromaticity of the imidazole ring in two of the three resonance contributors.

The radicals formed from breakdown of the peroxide may also abstract protons from the solvent forming *N*-methyl acetamidomethyl radicals which in turn give rise to *N*-methyl acetamidomethylated products. Decomposition of BPO in DMF solution is known to form benzoic acid in addition to *N*-benzoylmethyl *N*-methyl formamide.[37] That *N*-methyl acetamidomethylation and phosphonylation occur at different sites is likely the result of differing chemical affinities of the electrophilic diethyl phosphonyl radicals[50,51] and nucleophilic

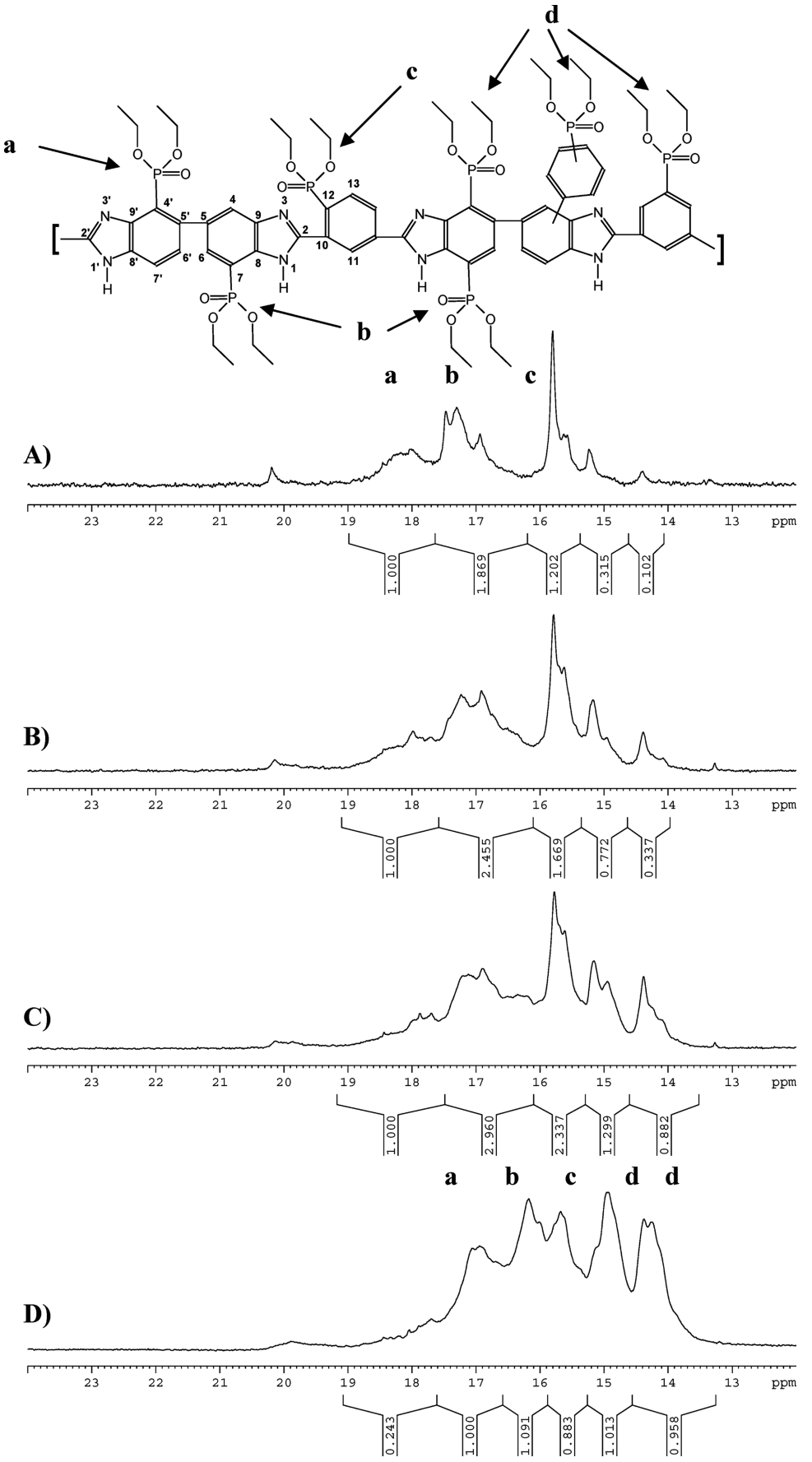
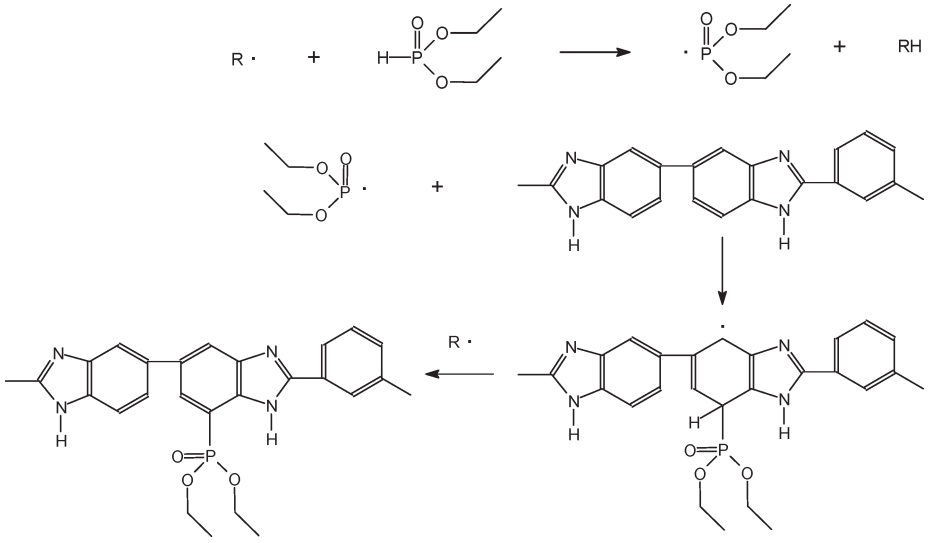
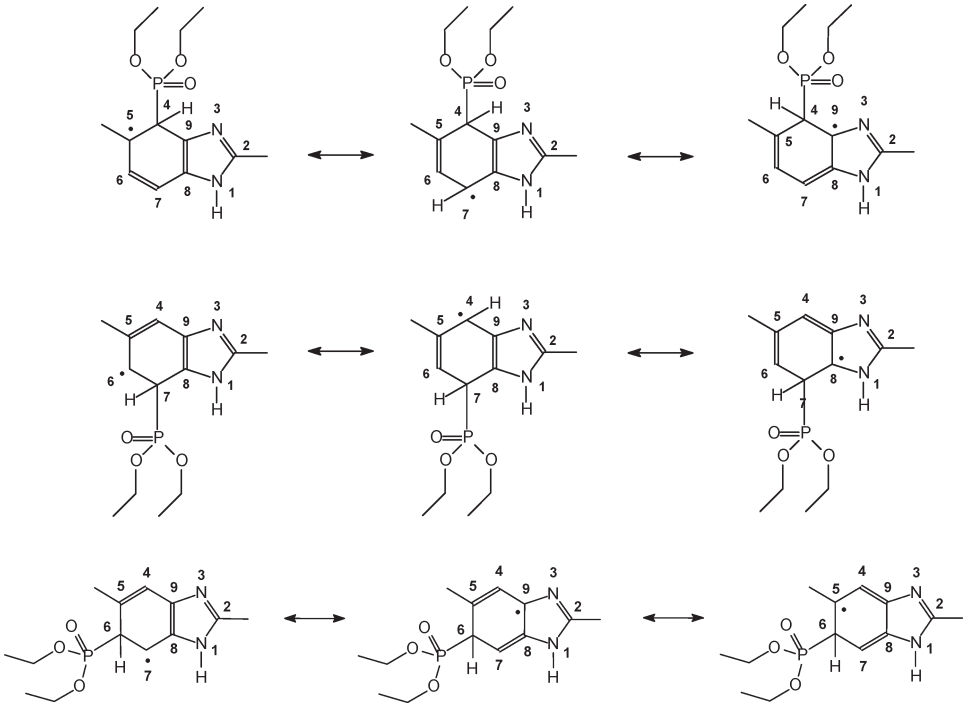


Figure 10. ^{31}P NMR (243 MHz) spectra of $PBIP_{Et}$ with (A) DS = 0.5, (B) DS = 1.0, (C) DS = 1.7, and (D) DS = 3.0, 80 °C, DMSO-d_6.

Scheme 3. Free Radical Mechanism of PBI Phosphonylation



Scheme 4. Structure of Phosphonate Radical Adduct



amidomethyl radicals.[38] In the case of benzimidazole, which bears a proton in the $\mathbf{C_2}$ position, phosphonylation in DMAc solution in the presence of BPO resulted in acetamidomethylation to a large degree lending support to the involvement of the $\mathbf{H_2}$ proton. Ishida et al[52] described the formation of products coupled at the $\mathbf{N_1}$ and $\mathbf{C_2}$ positions from thermal decomposition of 2-aryloxybenzimidazoles. A radical mechanism is believed to occur involving abstraction of $\mathbf{N_1}$ protons or a proton shift resulting in nitrogen based radicals. Treatment of PBI with BPO and an excess of DEP in DMAc solution resulted in a minor amount of *N*-methyl acetamidomethylation providing an excess of phosphite was present. Since PBI lacks an $\mathbf{H_2}$ proton, a mechanism involving radical abstraction of the N−H proton followed by recombination may occur in the case of *N*-methyl acetamidomethylation of PBI.

Hydrolysis of PBI Diethyl Phosphonates. When $PBIP_{Et}$s are subjected to hydrolysis using hot concentrated HCl or bromotrimethylsilane,[53,54] the resulting products ($PBIP_{OH}$) will swell strongly or dissolve when placed in aqueous sodium hydroxide solution (e.g., pH∼8). At DS ∼ 3 the polymer will completely dissolve but precipitate when the solution is acidified (pH < 5). $PBIP_{Et}$1 with a DS ∼ 3.1, as determined by ^{1}H NMR, would theoretically possess an ion exchange capacity (IEC) of 11.2 mequiv of H^+/g upon hydrolysis, though titration of $PBIP_{OH}$1 with NaOH gave 9.4 mequiv H^+/g (Figure 11). $PBIP_{OH}$ with lower degrees of substitution, e.g., DS = 0.33 and 2.4, yielded IECs of 1.9 mequiv of H^+/g (theoretical ∼2.0) and 8.1 mequiv of H^+/g (theoretical ∼9.6) respectively. Incomplete hydrolysis, the formation of P−O−P bridges or bound water (resulting in increased weight of the polymer sample) could account for the lower experimental values.

Thermal Stability of PBI, $PBIP_{Et}$, and $PBIP_{OH}$. Thermogravimetric curves of high phosphorus content $PBIP_{Et}$ and

$PBIP_{OH}$ are compared with that of parent PBI in Figure 12. PBI and $PBIP_{OH}$ each showed a slight decrease in weight at ~100 °C, however, in both cases there was not another major weight decrease until >400 °C. There is likely loss of bound water from both polymers as well as formation of P−O−P bridges in the case of $PBIP_{OH}$. $PBIP_{Et}$, however, begins to undergo significant degradation around 300 °C. $PBIP_{OH}$ therefore appears to possess high thermal stability which make these materials excellent candidates for ion exchange and PEM fuel cell membranes.[55]

Conclusion

Free radical aromatic substitution employing a dialkyl phosphite ester in conjunction with an organic peroxide, was successfully carried out on the heteroaromatic compounds benzimidazole and 2,2′-diphenyl-5,5′-bibenzimidazole. PBI was also successfully phosphonylated by this pathway with as many as three diethyl phosphonyl groups per PBI repeat unit. The limited solubility of PBI, however, necessitated the use of DMAc as a solvent and significant dilution was necessary to prevent gelation of the solution. Gelation in this case is presumably caused by radical reactions between polymer chains. While DMAc is effective in conducting the primary reaction (i.e., phosphonylation), it was found to cause a side reaction, particularly in the case of benzimidazole resulting in the appearance of *N*-methyl acetamidomethyl groups in the products.

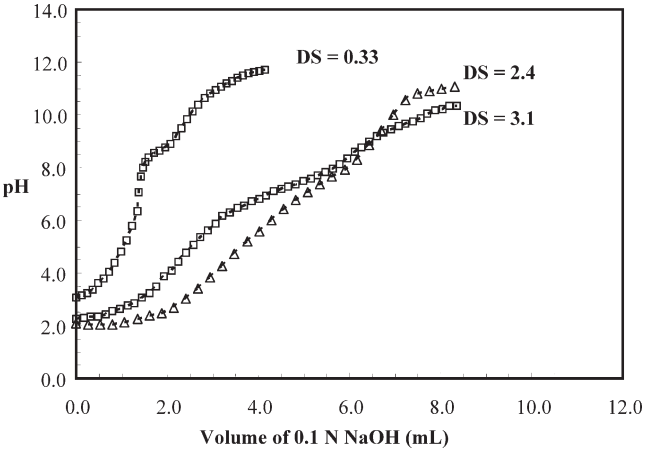


Figure 11. Titration curves of different degrees of substitution $PBIP_{OH}$ resins.

This work supports a mechanism involving breakdown of the peroxide into radicals followed by abstraction of the H−P proton of the phosphite ester with subsequent attack of phosphorus centered radical upon an aromatic ring. Benzoic acid, generated from the breakdown of benzoyl peroxide into benzoyloxy radicals, was isolated as a byproduct of reactions involving benzimidazole and DPB where BPO was the radical source. Additionally, the reaction did not occur to any appreciably extent in the absence of peroxide. Phosphonylation appears to occur preferentially at the $\mathbf{C_4}$ and $\mathbf{C_7}$ positions of the benzimidazole nuclei, and in the case of PBI, at the $\mathbf{C_{12}}$ position of the *m*-phenylene rings. Resonance stability of the radical adduct can explain the preference of this substitution pattern. Reactions in DMAc solution involving benzimidazole gave a significant portion of *N*-(*N*-methyl acetamidomethyl) benzimidazole indicating possible involvement of the imidazole ring *N*=CH−N proton with subsequent radical shift. This appears to be the main amidation pathway since this side reaction occurs to only a small degree in the case of PBI. Radical abstraction followed by recombination may also occur, though further investigation in this area is required. When DTP was employed as the radical source, NMR and mass spectroscopy indicate that the reaction involves methylation of the PBI backbone. Methyl radical formed from breakdown of *tert*-butoxy radicals is likely involved in such cases.

The polymeric phosphonate esters are readily hydrolyzed to the corresponding PBI phosphonic acids. Aqueous solutions of the sodium salt are easily formed with polymers of high phosphorus content and films are readily cast from such solutions. In protonic form, however, the phosphonic acids displayed water insolubility and high thermal stability at charge densities as high as ~9 mequiv of H^+/g. This material is being tested as a fuel cell membrane for 12 months.

The phosphonylation chemistry described in this work can be applicable to other all-aromatic polymers. In particular, other members of the polybenzimidazole class soluble in polar aprotic amide solvents can be expected to undergo such phosphonylation reactions. Applicability of such chemistry in other solvent systems or in solid state requires further investigation.

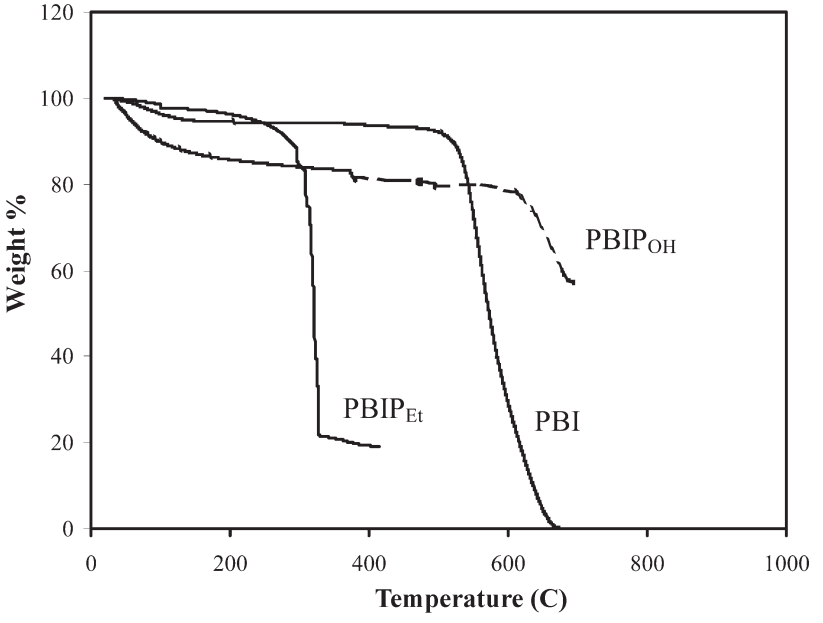


Figure 12. Thermogravimetric curves of PBI, PBI diethyl phosphonate ($PBIP_{Et}$), and PBI phosphonic acid ($PBIP_{OH}$).

While this work proves that PBI and model compounds can be heavily phosphonylated, it was discovered that a number of side reactions and substitutions are involved. It is not surprising that such a polymer with multiple activation sites on its monomeric unit would produce a highly complex structure when exposed to radical substitution.

Abbreviations

BPO	benzoyl peroxide
DEP	diethyl phosphite
DMAc	*N,N*-dimethylacetamide
DMF	*N,N*-dimethylformamide
DPB	2,2′-diphenyl-5,5′-bibenzimidazole
DPBP	2-(*p*-Diethyl phosphonyl phenyl)-2′-phenyl-5,5′-bibenzimidazole-4-diethyl phosphonate
DS	degree of substitution
DTP	di-*tert*-butyl peroxide
HMBC	heteronuclear multiple bond coherence
HMQC	heteronuclear multiple quantum correlation
NAB	*N*-(*N*-methyl acetamidomethyl) benzimidazole
NABP	*N*-(*N*-methyl acetamidomethyl) benzimidazole diethyl phosphonate
PBI	poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole]
$PBIP_{Et}$	poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] diethyl phosphonate
$PBIP_{OH}$	poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] phosphonic acid
TDPB	4,7,7′-tri(diethyl phosphonyl)-2,2′-diphenyl-5,5′-bibenzimidazole

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Supporting Information Available: Text discussing the NMR spectra including structures and figures showing ^{1}H NMR spectra of DPB, isophthalic acid and oligomeric PBI, as well as ^{13}C NMR spectra of PBI and $PBIP_{Et}$, the $^{1}H^{13}C$ HMQC spectra of PBI, DPBP, and TDPB, the $^{1}H^{13}C$ HMBC spectra of DPBP and TDPB, the $^{1}H^{1}H$ COSY spectra of $PBIP_{Et}$ and DPBP, and pyrolysis mass spectra, and a table containing structures corresponding to mass spectral fragments of $PBIP_{Et}$ and TDPB. This material is available free of charge via the Internet at http://pubs.acs.org.

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