# Phenylphosphonic Acid Functionalized Poly[aryloxyphosphazenes]

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ABSTRACT: A method for the synthesis of phenylphosphonic acid functionalized poly[aryloxyphosphazenes] is described. Diphenyl chlorophosphate was used as the phosphonating agent and was allowed to react with lithio-functionalized aryloxyphosphazenes, followed by treatment with aqueous sodium hydroxide. Subsequent acidification with aqueous hydrochloric acid yielded phenylphosphonic acid functionalized poly[aryloxyphosphazenes]. These polymers are candidates for use as proton-conducting membranes in fuel cells.

## Introduction

One of the main issues impeding the development of direct methanol fuel cells (DMFCs) for portable power and automotive applications is the lack of polymeric materials with suitable membrane properties. The use of polymeric membranes as electrolytes for fuel cell applications was first demonstrated in the Gemini space flight in 1965.<sup>1</sup> These early polymer electrolyte fuel cells (PEFCs), based on hydrogen and oxygen, used membranes fabricated from sulfonated polystyrene. However, these membranes had relatively short lifetimes due to the fuel cell's aggressive thermo-oxidative environment, resulting in free-radical cleavage of the hydrocarbonbased polymer backbone. Thus, PEFC research over the past decade has concentrated on the use of polymeric membranes with greater thermo-oxidative and chemical stability such as the perfluorosulfonic acid polymers typified by Nafion (DuPont). Nafion-based fuel cells using current technology require either an onboard source of pure hydrogen or the reforming of hydrocarbon fuels to produce hydrogen, a process that is not environmentally benign.

Direct methanol fuel cells allow the use of direct (nonreformed) methanol in place of hydrogen. The major advantages of DMFCs are that the methanol can be stored much easier than hydrogen and can be distributed using the infrastructure already in place for gasoline. However, DMFCs based on perfluorosulfonic acid membranes suffer from decreased performance resulting from methanol crossover and poor thermal stability at temperatures greater than 100 °C.<sup>2-6</sup> Methanol diffusion through the membrane from the anode to the cathode side of the cell is directly oxidized at the cathode. This leads to decreases in fuel efficiency and cathode performance and results in lower overall fuel cell performance. Thus, the advancement of direct methanol fuel cells demands the design of novel polymeric membranes, specifically designed for use in DM-FCs.

Polyphosphazenes are macromolecules with the basic structure shown in Figure  $1.^{7-14}$  The methods of synthesis and postsynthesis modification available for polyphosphazenes allow high loadings of acidic units throughout the polymeric material. The synthesis of polyphosphazenes bearing sulfonic acid or carboxylic acid has been examined previously. Methods for the



Figure 1. General structure of a polyphosphazene.

synthesis of poly[aryloxyphosphazenes] bearing carboxylic acid units were developed by Allcock and coworkers in 1989 and 1992.<sup>15,16</sup> The sulfonation of poly[aryloxyphosphazenes] via SO<sub>3</sub> was developed by Montoneri, Gleria and co-workers in 1989<sup>17</sup> and sulfonation via concentrated or fuming sulfuric acid by Allcock and co-workers in 1991.<sup>18</sup> Pintauro et al. have investigated the use of sulfonated polyphosphazenes as fuel cell membranes since 1996.<sup>7,19</sup> In this paper, we describe the synthesis of the first poly[aryloxyphosphazenes] bearing phosphonic acid units.

The phosphorylation of hydroxy-functionalized aryloxyphosphazenes, leading to phosphorus-oxygencarbon linkages, has been examined by us in the past.<sup>20</sup> However, cleavage of phosphate ester bonds can occur due to their limited thermal and chemical stability, which may result in loss of the pendent phosphate group.<sup>21</sup> For this reason we had previously examined the incorporation of dialkyl phosphonate groups into aryloxyphosphazenes attached through phosphonate (phosphorus-carbon) linkages.<sup>14</sup> In this route, high polymeric aryloxyphosphazenes bearing bromophenoxy side groups were treated with *n*-butyllithium followed by diethyl chlorophosphate. The use of a direct phosphorus-carbon bond ensures greater thermal and chemical stability,<sup>21,22</sup> which should provide more versatile materials. This approach has now been extended to produce poly[aryloxyphosphazenes] functionalized with diphenyl phosphonate groups, which are subsequently hydrolyzed to phenylphosphonic acid groups. The reaction sequence employed in this work is shown in Scheme 1. We are currently evaluating membranes of these polymers for fuel cell applications.<sup>23,24</sup> They have markedly lower methanol diffusion characteristics than Nafion 117 and appear to be superior to the sulfonated polyphosphazene analogues also.<sup>23,24</sup>

### **Results and Discussion**

**Phosphonation of Phosphazenes via Lithiophenoxy Intermediates.** The treatment of lithiophenoxy





phosphazene intermediates with electrophiles, such as diphenylchlorophosphine, triphenyltin chloride, and (triphenylphosphine)gold(I) chloride, has been studied previously.<sup>25</sup> However, the interaction of lithiophenoxy phosphazene intermediates with phosphoryl electrophiles such as diethyl chlorophosphate and diphenyl chlorophosphate was found previously to be a complex reaction that resulted in insoluble products with only slight evidence of phosphonation.<sup>20</sup> More recent work in our laboratories has shown that phosphonation via lithiophenoxy imtermediates is possible with diethyl chlorophosphate and results in 80-85% conversions of the bromine atoms in high polymeric aryloxyphosphazenes to diethyl phosphonate groups.<sup>14</sup>

In this previous work we reported that phosphonation was afforded by the addition of a polymer containing 20% bromophenoxy side groups in THF solution at -75 °C to a solution of *n*-butyllithium in THF at -75 °C, followed by quenching of the reaction with diethyl chlorophosphate. Our initial investigations had found that phosphonation of a polymer by the addition of *n*-butyllithium to a solution of the polymer in THF at -75 °C followed by treatment with diethyl chlorophosphate resulted in an insoluble material. The reason for the formation of insoluble materials in the early investigations is still not fully understood, and we have now found that soluble polymers may be obtained via either method. Thus, here we report the phosphonation of poly-

[aryloxyphosphazenes] via lithiophenoxy intermediates formed via addition of *tert*-butyllithium to a solution of the polymer in THF at -75 °C. The lithiated polymers were then treated with diphenyl chlorophosphate, and subsequent basic hydrolysis and acidification yielded phenylphosphonic acid groups as shown in Scheme 1. Solutions of bromophenoxy functionalized polymers 2a-**2c** in THF at -75 °C were treated with *tert*-butyllithium over 30-60 min, followed by the rapid addition of diphenyl chlorophosphate. This resulted in about 50% conversion of the initial bromophenoxy groups to diphenyl phosphonate ester groups (polymers **3a-3c**). After precipitation into 2-propanol, the polymers in THF were treated with 1.0 M NaOH over 24 h. Subsequent acidification and purification yielded polymers 4a-4cin which half of the phenyl ester groups had been displaced by hydroxide as determined by multinuclear NMR and elemental analysis.

**Interaction of Bromophenoxy Poly[aryloxyphosphazenes] with** *n***-Butyllithium and** *tert***-Butyllithium.** Previous investigations into the use of lithiophenoxy intermediates as a means of side group construction in polyphophazenes had made use of *n*butyllithium as the lithiating agent, typically employing ~8 mol equiv with respect to amount of bromine in the starting polymer.<sup>14,20,25</sup> We have found that maximum lithium-halogen exchange can be achieved with as little as 4 mol equiv of *n*-butyllithium. However, attempts to



Figure 2.  $^{31}P$  NMR spectra of polymers 2c (bottom), 3c (middle), and 4c (top).

decrease the amount of *n*-butyllithium further results in significantly lower conversions. In this work we have used *tert*-butyllithium and have found that 2 mol equiv is sufficient to achieve maximum lithium—halogen exchange. This decrease in the amount of the lithiating agent allows cleaner reactions as well as a decrease in the amount of phosphonating reagent required.

The efficiency of the lithium-halogen exchange reactions was estimated by elemental analysis. Previous work showed that the rate of lithium-halogen exchange is rapid up to the point where  $\sim$ 50% of the total side groups bear a lithium atom.<sup>25</sup> For polymers with less than 50% bromophenoxy substituents, maximum lithiumhalogen exchange was usually achieved within 30 min. The lithiation times for the polymers used in this work were adjusted accordingly (30 min for 2a, 45 min for **2b**, and 60 min for **2c**), resulting in >90% lithiumhalogen exchange in all cases. The molecular weight  $(M_n)$ = 950 000, PDI = 1.5) of the phosphonated polymer 3c, estimated by GPC, was about three-quarters that of the parent polymer (**2c**,  $M_n = 1\ 270\ 000$ , PDI = 1.8). This has been attributed to backbone cleavage by tertbutyllithium and is consistent with the results found in our previous work.14

**Interaction of Lithiophenoxy Polyphosphazene** Intermediates with Diphenyl Chlorophosphate. In our previous paper we reported the phosphonation of lithio-functionalized poly[aryloxyphosphazenes] by the dropwise addition of diethyl chlorophosphate into a solution of the lithiated polymer at -78 °C.14 Initial attempts to phosphonate the lithiated polymers 2a-2cvia the dropwise addition of diphenyl chlorophosphate resulted in precipitation of the polymer and formation of an insoluble product. However, soluble products were obtained by the rapid addition of diphenyl chlorophosphate. <sup>31</sup>P NMR spectroscopy of the purified product, 3c, revealed two phosphorus peaks in addition to those associated with the polymer backbone as shown in Figure 2 and is representative of all the phosphonated polymers. The major peak at  $\delta$  12.2 ppm was assigned to the desired diphenyl phosphonate ester in  $\sim$ 50% yield with respect to the number of bromophenoxy units initially present. The minor peak at  $\delta$  27.8 ppm has been attributed to an intramolecular coupling reaction in

Scheme 2. Intramolecular Coupling with Diphenyl Chlorophosphate



which diphenyl phosphonate ester sites on the polymer react with a second lithiophenoxy side group on the same polymer backbone, resulting in a phosphorus bridge between two aryloxy side groups as shown in Scheme 2. This was attributed to an intramolecular reaction rather than the analogous intermolecular crosslinking reaction due to the high solubility of the polymers. Presumably, intermolecular cross-linking does occur during dropwise addition of diphenyl chlorophosphate, yielding insoluble products.

The treatment of diester chlorophosphates with organometallic compounds has previously been described as a complex reaction due to the possibility of the ester groups reacting to form phosphine oxides.<sup>26</sup> To confirm the <sup>31</sup>P NMR assignment of a phosphorus bridge as shown in Scheme 2, diphenylphosphinic chloride was treated with phenol in THF using triethylamine as an HCl acceptor. <sup>31</sup>P NMR and an APCI mass spectrum of the reaction mixture confirmed the formation of the phenyl ester of diphenylphosphinic chloride [*m*/*z* 295 MH<sup>+</sup>] with a <sup>31</sup>P NMR resonance at  $\delta$  28.4 ppm.

A second model reaction was carried out to determine the possibility of a diphenyl phosphonate ester group reacting with a second lithiophenoxide group. Thus, 4-bromoanisole was treated with 1 equiv of *t*-BuLi in THF at -75 °C followed by rapid addition of 0.5 equiv of diphenyl chlorophosphate. In addition to the peak at  $\delta$  13.0 ppm characteristic of the diphenyl phosphonate ester, <sup>31</sup>P NMR spectroscopy also revealed a small peak at  $\delta$  29.9 ppm. APCI mass spectral data of the reaction mixture indicated the presence of ions with masses m/z341 MH<sup>+</sup> [CH<sub>3</sub>OPhP(O)(OPh)<sub>2</sub>] and 355 MH<sup>+</sup> [(CH<sub>3</sub>- $OPh)_2P(O)(OPh)$ , thus confirming the possibility of multiple substitution on diphenyl chlorophosphate by aryllithium reagents. Moreover, the chance of multiple substitution is significantly greater when two lithiophenoxy units are forced into close proximity by linkage to the same polymer chain as shown in Scheme 2. In an attempt to avoid this side reaction multiple attempts were made in which the lithiated polymer 2b at -75°C in THF was cannulated into a solution of diphenyl chlorophosphate, also at -75 °C in THF. <sup>31</sup>P NMR spectroscopy of the purified product revealed only the peaks associated with the polymer backbone and that of the diphenyl ester ( $\delta$  12.2 ppm), but with significantly lower yields, typically 20-25% conversion, with respect to the number of bromophenoxy units initially present.

Efficiency of Phosphonation Reactions. The overall efficiency of the phosphonation method with respect to percent conversion of the initial bromine atoms present was determined by <sup>31</sup>P NMR spectroscopy. Phosphonation of polymers 2a-2c via lithiophenoxy intermediates proceeded with ~50% conversion of the bromophenoxy side groups to diphenyl phosphonate

Table 1. DSC Data for Polymers 2a-2c, 3c, and 4a-4c (n/o = Not Observed)

polymer	<i>T</i> <sub>g</sub> (°C)	$T_{\rm m}(^{\circ}{\rm C})$	polymer	<i>T</i> <sub>g</sub> (°C)	$T_{\rm m}(^{\circ}{\rm C})$
2a	11	154	<b>4a</b>	42	n/o
2b	11	156	<b>4b</b>	42	n/o
2c	13	133	<b>4</b> c	44	n/o
3c	34	n/o			

ester side groups (polymers 3a-3c). Figure 2 shows the <sup>31</sup>P NMR spectra of the parent polymer **2c** and the corresponding phosphonated polymer **3c**. Polymer **2c** shows only a broad resonance attributed to the overlapping signals of the phosphorus atoms in the polymer backbone. The spectrum of the phosphonated product **3c** contains an even broader resonance between  $\delta$  –16.5 and  $\delta$  -24.0 ppm also attributed to the phosphorus atoms in the phosphazene backbone. In addition, two distinct resonances were detected at  $\delta$  12.2 ppm (diphenyl phosphonate phosphorus) and  $\delta$  27.8 ppm (bridged phosphonate phosphorus). The total percentage of lithiophenoxy groups that had reacted with the diphenyl chlorophosphate was 70%. However, only  $\sim$ 50% of the lithiophenoxy groups resulted in formation of the diphenyl phosphonate ester. As discussed earlier, elemental analysis revealed that >90% of the initial bromine atoms had been lithiated. Thus, rather than incomplete lithiation, the limiting factor in the overall reaction appears to be side reactions of the highly reactive lithiophenoxy intermediate, which may occur during the addition of diphenyl chlorophosphate. This is also consistent with observations made using diethyl chlorophosphate.<sup>14</sup>

Basic Hydrolysis of Diphenyl Ester Side Groups. Hydrolysis of the diphenyl phosphonate ester groups was accomplished by treatment of a THF solution of the phosphonated polymers with 1.0 M NaOH over 24 h. During this reaction the polymer precipitates from solution, at which point little further hydrolysis takes place. Figure 2 shows the <sup>31</sup>P NMR spectra of the phosphonated polymer 3c and the corresponding hydrolyzed product 4c after conversion to the acid form and subsequent purification. The <sup>31</sup>P NMR spectra indicated that for each of the polymers 4a-4c, approximately half of the phenyl ester groups had been hydrolyzed. Typical hydrolysis product ratios were 5% diester ( $\delta$  13.9 ppm), 40% monoester/monoacid ( $\delta$  10.5 ppm), and 5% diacid ( $\delta$  14.1 ppm). The peak at  $\delta$  22.7 ppm was attributed to partial hydrolysis of the lone phenoxy substituent on the bridged phosphonate product. Analysis of polymers 4a-4c by GPC to determine the effect of the hydrolysis conditions on the molecular weights was not possible due to the limited solubility of these polymers. However, a model reaction was carried out in which poly[bis(4-methylphenoxy)phosphazene] was treated with 1.0 M NaOH in THF over 24 h. GPC analysis revealed no change in the molecular weight of this polymer, confirming the stability of the phosphazene backbone to the basic hydrolysis conditions.

Thermal Analysis of Polymers 2a–2c and 4a– 4c. DSC data for the polymers 2a–2c, 3c, and 4a–4c may be found in Table 1. Little variation was found in the glass transition temperatures ( $T_g$ ) of parent polymers 2a–2c (between 11 and 13 °C). All the parent polymers (2a–2c) displayed melting transitions ( $T_m$ ) above 130 °C. Interestingly, the  $T_m$  for 2c was ~20 °C lower than for polymers 2a and 2b. This may result from different substitution patterns of the aryloxy side groups. For polymers **2a** and **2b**, sodium 4-bromophenoxide was added to poly(dichlorophosphazene) followed by the addition of sodium 4-methylphenoxide which was used in excess. For polymer **2c** this order of addition was reversed with sodium 4-bromophenoxide used in excess. The lower  $T_m$  of polymer **2c** may indicate a more random substitution pattern of the aryloxy side groups.

Like the base polymers, little variation was found in the glass transition temperatures of the acidic polymers **4a**-**4c**. Perhaps most interesting is that the  $T_g$ 's of **4a**-**4c** are significantly higher ( $\sim 30$  °C) than those of the parent polymers. The addition of bulky substituents onto the polymer side groups should result in increased steric hindrance, especially when the bridged phosphonate species (Scheme 2) is considered. This effect was confirmed by thermal analysis of polymer 3c, which revealed a  $T_{\rm g}$  of 34 °C. Moreover, the acidic units introduce the possibility of hydrogen bonding, either to each other or potentially to the lone pair electrons on the nitrogen atoms of the polymer backbone. Although the addition of these bulky phenylphosphonic acid units should increase the free volume of the system, it is apparent that the effect of this on the  $T_g$ 's of polymers **4a**–**4c** is of only minor significance. However, evidence for this increase in free volume is found in the complete loss of polymer crystallinity indicated by the absence of melting transitions for polymers 4a-4c.

### Conclusions

In this study, we have expanded the synthetic utility of lithiophenoxy polyphosphazene intermediates. Phosphonation via lithiophenoxy intermediates resulted in  $\sim$ 50% conversion of bromophenoxy side groups to aryloxy diphenyl phosphonate ester units after the addition of diphenyl chlorophosphate. Moreover, basic hydrolysis of the phosphonated polymers with sodium hydroxide, and subsequent acidification, resulted in the conversion of about half of the phosphonate phenyl ester groups to hydroxyl groups. An advantage of this synthesis protocol is the freedom to tune the polymer composition and properties by variations in the initial aryloxy side group ratios, the degree of lithiation, the extent of phosphonation, and the amount of ester hydrolysis. These polymers are currently being evaluated by our coworkers as membrane materials for fuel cell applications.<sup>23,24</sup> They have markedly lower methanol diffusion characteristics than Nafion 117 and appear to be superior to sulfonated polyphosphazene analogues also.<sup>23,24</sup> Ongoing studies with this synthetic route will examine the variety of cosubstituents (in place of 4-methylphenoxy side groups) suitable for phosphonation and subsequent hydrolysis.

### **Experimental Section**

**Materials.** Diphenyl chlorophosphate (98%), *tert*-butyllithium (1.7 M in pentane), 4-methylphenol (99%), 4-bromophenol (99%), methyl red (0.1 wt % in H<sub>2</sub>O), and tetra(*n*butyl)ammonium bromide (99%) were obtained from Aldrich and used as received. Sodium hydride (60% suspension in mineral oil) was obtained from Fluka and used as received. Tetrahydrofuran (THF) and 2-propanol (IPA) were obtained from EM Science. THF was distilled from sodium benzophenone ketyl prior to use. Hexachlorocyclotriphosphazene (Ethyl Corp./Nippon Fine Chemical Co.) was recrystallized from heptane and sublimed at 40 °C (0.05 mmHg). Poly(dichlorophosphazene) (1) was obtained by ring-opening polymerization of hexachlorocyclotriphosphazene.<sup>27,28</sup> All reactions were carried out under an atmosphere of dry argon.

Table	2.	Reaction	Condition	is for t	he Pre	paration	of Po	lymers	2a-	-2c
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polymer	(NPCl <sub>2</sub> ) <sub>n</sub> , g (mol)	4-bromophenol, g (mol)	NaH, g (mol)	4-methylphenol, g (mol)	NaH, g (mol)	% yield
2a	20.0 (0.173)	23.9 (0.138)	5.52 (0.138)	46.7 (0.432)	16.5 (0.413)	59
2b	20.0 (0.173)	29.9 (0.173)	6.91 (0.173)	37.4 (0.346)	13.8 (0.346)	64
2c	23.0 (0.199)	82.4 (0.476)	19.1 (0.476)	17.2 (0.159)	6.4 (0.159)	58

**Equipment.** High-field <sup>1</sup>H (360 MHz) and <sup>31</sup>P (146 MHz) NMR spectra were obtained using a Bruker AMX-360 spectrometer; <sup>13</sup>C (126 MHz) spectra were obtained using a Bruker AMX-500 spectrometer. The <sup>31</sup>P and<sup>13</sup>C spectra were proton-decoupled. <sup>31</sup>P NMR spectra were referenced to external 85% H<sub>3</sub>PO<sub>4</sub> with positive shifts recorded downfield from the reference. <sup>1</sup>H and <sup>13</sup>C were referenced to external tetramethylsilane. All NMR spectra were obtained in *d*<sub>7</sub>-DMF unless otherwise noted with chemical shifts recorded in ppm and coupling constants recorded in hertz.

Molecular weights were estimated using a Hewlett-Packard HP1090 gel permeation chromatograph equipped with a HP-1047A refractive index detector. The samples were eluted with a 0.1 wt % solution of tetra(*n*-butyl)ammonium nitrate in THF. The GPC system was calibrated with polystyrene standards (Polysciences). Elemental analyses were preformed by Quantitative Technologies of Whitehouse, NJ.

DSC measurements were carried out using a Perkin-Elmer-7 thermal analysis system equipped with a PC computer. Glass transition temperatures were obtained by heating the polymer samples from -80 to 80 °C at a rate of 10 °C/ min, under an atmosphere of dry nitrogen. Melting transitions were obtained by heating the polymer samples from 50 to 200 °C at a rate of 10 °C/min. Calibration was preformed using cyclohexane for -80 to 80 °C scans and indium for 50 to 200 °C scans.

**General Procedure for the Preparation of Polymers** 2a-2c. The specific reaction conditions used for these syntheses are listed in Table 2. The general experimental procedure was adapted from a previously published procedure as follows.14 4-Bromophenol was dissolved in 50-100 mL of THF and added dropwise to a suspension of sodium hydride in 100-300 mL of THF. 4-Methylphenol was dissolved in 50-100 mL of THF and added dropwise to a suspension of sodium hydride and tetra(n-butyl)ammonium bromide (1.0 g, 3.0 mmol) in 100-200 mL of THF. The first sodium aryloxide (sodium 4-bromophenoxide for 2a and 2b, sodium 4-methylphenoxide for 2c) was added dropwise to the stirring solution of poly-(dichlorophosphazene) (1) in 600 mL of THF in an autoclave and stirred for 30 min. The second aryloxide (sodium 4-methylphenoxide for 2a and 2b, sodium 4-bromophenoxide for 2c) was then added dropwise to the autoclave. The autoclave was pressurized to 1 atm with argon, sealed, and heated to 150 C. After 18-20 h the autoclave was cooled to room temperature, and the contents precipitated into 15 L of acidified H<sub>2</sub>O (30 mL of concentrated HCl). The polymer was reprecipitated from THF (polymers 2a and 2b) or dioxane (polymer 2c) 3 times into 95% ethanol (1×),  $H_2O$  (1×), and hexanes (1×). Prior to the last precipitation the polymer solution was vacuumfiltered. The desired product was dried at <0.1 mmHg for 24 h at room temperature to yield a white solid. <sup>1</sup>H NMR ( $d_8$ -THF):  $\delta$  2.2 (singlet, 3H × y, -Ar*CH*<sub>3</sub>) and  $\delta$  6.5–7.0 (multiple peaks, 4H, -O*Ar*Br and -O*Ar*CH<sub>3</sub>). <sup>31</sup>P NMR ( $d_8$ -THF):  $\delta$ -18.2 (br, -P=N-). <sup>13</sup>C NMR ( $d_8$ -THF):  $\delta$  21.2,  $\delta$  118.2,  $\delta$ 121.7,  $\delta$  123.9,  $\delta$  130.8,  $\delta$  133.2,  $\delta$  134.7,  $\delta$  150.3, and  $\delta$  151.6.  $M_{\rm n}$  for all polymers was >500 000 with PDI < 2. DSC data may be found in Table 1.

**General Procedure for the Preparation of Polymers 3a–3c.** The specific reaction conditions used for these syntheses are listed in Table 3. The general experimental procedure was as follows. Polymers **2a–2c** were dissolved in 1.2 L of THF at 40 °C. The polymer solution was cooled to -75 °C, and *tert*-butyllithium (1.7 M in pentane) was added dropwise. After holding at -75 °C (30 min for **3a**, 45 min for **3b**, and 60 min for **3c**), diphenyl chlorophosphate was added rapidly via syringe. The reaction was then allowed to warm to room temperature. The reaction mixture volume was concentrated to 100 mL by reduced pressure rotary evaporation, and the

Table 3. Reaction Conditions for the Preparation of Polymers 3a-3c

		v	
polymer	polymers <b>2a–2c</b> , g (mol)	<i>t</i> -BuLi (1.7 M), mL (mol)	diphenyl chlorophosphate, g (mol)
3a	4.0 (0.013)	11.34 (0.019)	30.59 (0.116)
3b	4.0 (0.012)	14.52 (0.025)	39.70 (0.150)
<b>3c</b>	4.0 (0.012)	16.70 (0.029)	45.36 (0.171)

product precipitated into isopropyl alcohol. The polymers were then used directly for the hydrolysis reactions without further purification. Characterization for **3c**: <sup>31</sup>P NMR:  $\delta$  –24 to –16 (broad overlapping peaks, 1P, –*P*=*N*–),  $\delta$  12.2 (br, 1P × 0.56, –OPh*P*(O)(OPh)<sub>2</sub>),  $\delta$  27.8 (br, 1P × 0.12, (–OPh)<sub>2</sub>*P*(O)(OPh)).  $M_{\rm n}$  = 950 000 with PDI = 1.5.

**General Procedure for the Preparation of Polymers 4a**-**4c.** Polymers **3a**-**3c** were dissolved in 400 mL of THF. 10 mL of 1.0 M NaOH was added, and the solution was stirred for 24 h. This resulted in precipitation of the polymer. 120 mL of 0.1 M HCl was then added, and the solution was stirred until the polymer redissolved. THF was removed via reduced pressure rotary evaporation, and this resulted in the precipitation of the polymer. To ensure complete conversion to the acid, the polymer was redissolved in a solution of 400 mL of THF/ 100 mL of 0.1 M HCl and again precipitated by removal of THF via reduced pressure rotary evaporation. The polymer was then cut into small pieces and soaked in water for 24 h and then dried at <0.1 mmHg for 48 h at RT to yield a white solid in >95% yield for **4a**-**4c**.

**Polymer 4a.** <sup>1</sup>H NMR:  $\delta$  2.2 (s, 3H × 0.63, Ar*CH*<sub>3</sub>) and  $\delta$  6.3–7.8 (multiple peaks, 13H, aromatic protons). <sup>31</sup>P NMR:  $\delta$ –21.8 and –18.9 (br, 1P, –*P*=*N*–),  $\delta$  10.5 (br, 1P × 0.32, –OPh*P*(O)(OPh)(OH)),  $\delta$  13.9 (br, 1P × 0.03, –OPh*P*(O)-(OPh)<sub>2</sub>),  $\delta$  14.1 (br, 1P × 0.03, –OPh*P*(O)(OH)<sub>2</sub>),  $\delta$  23.4 (br, 1P × 0.03, (–OPh)<sub>2</sub>*P*(O)(OH)),  $\delta$  28.6 (br, 1P × 0.04, (–OPh)<sub>2</sub>*P*(O)(OPh)). <sup>13</sup>C NMR:  $\delta$  20.3,  $\delta$  117.0,  $\delta$  121.0,  $\delta$  122.3,  $\delta$  123.2,  $\delta$  124.1,  $\delta$  125.2,  $\delta$  127.5 (d, <sup>1</sup>*J*<sub>C-P</sub> = 186),  $\delta$  129.4,  $\delta$  129.5–130.0,  $\delta$  130.3,  $\delta$  133.3,  $\delta$  133.7,  $\delta$  149.5,  $\delta$  151.7,  $\delta$  152.0 and  $\delta$  154.1. Elemental analysis: found (calculated): C, 58.47 (58.41); H, 4.74 (4.55); P, 14.02 (13.88); N, 4.31 (4.44); Br, 1.48 (1.27). DSC data may be found in Table 1.

**Polymer 4b.** <sup>1</sup>H NMR: δ 2.2 (s, 3H × 0.50, Ar *CH*<sub>3</sub>) and δ 6.3–7.8 (multiple peaks, 21H, aromatic protons). <sup>31</sup>P NMR: δ –21.8 and –18.9 (br, 1P, -P=N-), δ 10.5 (br, 1P × 0.41, –OPh*P*(O)(OPh)(OH)), δ 13.9 (br, 1P × 0.04, –OPh*P*(O)-(OPh)<sub>2</sub>), δ 14.1 (br, 1P × 0.04, –OPh*P*(O)(OH)<sub>2</sub>), δ 23.4 (br, 1P × 0.05, (–OPh)<sub>2</sub>*P*(O)(OH)), δ 28.6 (br, 1P × 0.05, (–OPh)<sub>2</sub>*P*(O)(OPh)). <sup>13</sup>C NMR: δ 20.3, δ 117.0, δ 120.9, δ 121.0, δ 122.4, δ 123.1, δ 124.3, δ 125.2, δ 127.4 (d, <sup>1</sup>*J*<sub>C-P</sub> = 186), δ 129.4, δ 129.5–130.0, δ 130.3, δ 132.4, δ 133.3, δ 133.9, δ 149.5, δ 151.7, δ 151.9 and δ 154.1. Elemental analysis: found (calculated): C, 57.72 (56.77); H, 4.45 (4.31); P, 14.79 (14.40); N, 4.27 (4.21); Br, 2.25 (1.56). DSC data may be found in Table 1.

**Polymer 4c.** <sup>1</sup>H NMR: δ 2.2 (s, 3H × 0.40, Ar *CH*<sub>3</sub>) and δ 6.3–7.8 (multiple peaks, 34H, aromatic protons). <sup>31</sup>P NMR, δ –21.8 and –18.9 (br, 1P, -P=N-), δ 11.5 (br, 1P × 0.45, –OPh*P*(O)(OPh)(OH)), δ 13.8 (br, 1P × 0.06, –OPh*P*(O)-(OPh)<sub>2</sub>), δ 14.4 (br, 1P × 0.06, –OPh*P*(O)(OH)<sub>2</sub>), δ 22.6 (br, 1P × 0.03, (–OPh)<sub>2</sub>*P*(O)(OH)), δ 28.4 (br, 1P × 0.07, (–OPh)<sub>2</sub>*P*(O)(OPh)). <sup>13</sup>C NMR: δ 20.3, δ 117.0, δ 120.5, δ 121.0, δ 129.6, δ 129.5–130.0, δ 130.3, δ 132.4, δ 133.3, δ 133.9, δ 149.4, δ 151.7, δ 152.3 and δ 153.7. Elemental analysis: found (calculated): C, 55.67 (54.85); H, 4.46 (4.09); P, 14.50 (14.50); N, 4.41 (4.07); Br, 2.81 (2.51). DSC data may be found in Table 1.

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