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# Synthesis of poly(aryl ether)s bearing phosphonated side-chains from phosphonate ester-containing bisphenols

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## Abstract

As part of our project research to design aromatic polymers with pendant acid groups, we have paid efforts to synthesize phosphonic acid-containing poly(aryl ether)s (PAEs) from functionalized monomers. To this end, two bisphenol monomers bearing phosphonic ester groups were synthesized. A study of the polymerization reaction via model compound preparation point out specific experimental conditions to prevent side reactions between phosphonic ester functions and phenolate monomers. Based on these experimental optimised conditions, different PAEs with high molecular weights were prepared. Free acid phosphonic groups-containing PAE were obtained by subsequent controlled hydrolysis of phosphonate ester groups.

## Keywords

Phosphonate ester-containing bisphenol, Phosphonated poly(aryl ether)s, Aromatic nucleophilic substitution.

## 1. Introduction

Because of their specific chemical structure, phosphonic acid groups provide interesting properties<sup>[1]</sup>. Therefore, phosphonic acid-containing polymers have aroused interest in many different domains, such as materials for dental cements<sup>[2, 3]</sup>, adhesion promoters<sup>[4]</sup>, anti-corrosive coatings<sup>[5]</sup>, chemical sensors<sup>[6]</sup>, scale inhibitor in water treatment<sup>[7]</sup> or even for fuel cells membranes<sup>[8-10]</sup>. In the frame of the development of new high performance thermostable materials, the synthesis of innovative macromolecular structures is of outmost importance. In this context, the design of phosphonic acid-containing aromatic and heterocyclic polymers could provide interesting properties and open new perspectives for the development of high performance materials.

A convenient approach used to introduce phosphonic acid groups along a polymer chain consists in the chemical-modification of high molecular weight pre-existing polymers. In this respect, different aromatic and heterocyclic polymer structures have been investigated, such as (poly(phosphazene)s<sup>[11-14]</sup>, poly(oxadiazoles)s<sup>[15]</sup>, poly(paraphenylene)s<sup>[16]</sup>, poly(benzimidazole)<sup>[17]</sup>, poly(diimidazopyridine)s<sup>[18]</sup> and the most extensively studied poly(aryl ether)s. Phosphonic acid groups can be incorporated by different chemical reactions (Arbusov or Michaelis–Arbusov reaction<sup>[19]</sup>, lithiation and direct phosphonation<sup>[20]</sup>, reaction with a phosphonate containing reactant<sup>[21]</sup> or a iodobenzoyl reactant<sup>[22]</sup>, by nickel-catalyzed<sup>[23, 24]</sup> or palladium catalysed phosphonation<sup>[25-27]</sup>, N-alkylation<sup>[28]</sup> or even by polymerization of vinylphosphonic side-chains<sup>[29]</sup>....). However, due to harsh reaction conditions (long reaction times, high temperature and low yields), such post-modifications usually induce some undesirable chain breaking or cross-linking. As a consequence, this strategy leads to a limited control of the degree of modification and also of the structural integrity of polymers. On the other hand, the polymerization of a functionnalized precursor is considered as a much more promising approach. In this connection, some phosphonated aromatic monomers have been described so far (Figure 1). They either present phosphonate ester or phosphonic acid groups which are directly grafted on the aromatic structure (4, 7, 10, 11, 12) or bounded on a side-chain (1, 9, 2, 3, 5, 6, 8). In all cases, multi-step syntheses are required to design such specific monomers.

Different types of polymers were prepared from these monomers. Alvares et al<sup>[30]</sup> report the synthesis of phosphonic acid containing polyimides based on diamine (1). Yasuda and co-

workers<sup>[31]</sup>, describe the synthesis of diamine (2) and studied its polymerization with a non functionalized diamine (CARDO) and NTDA.

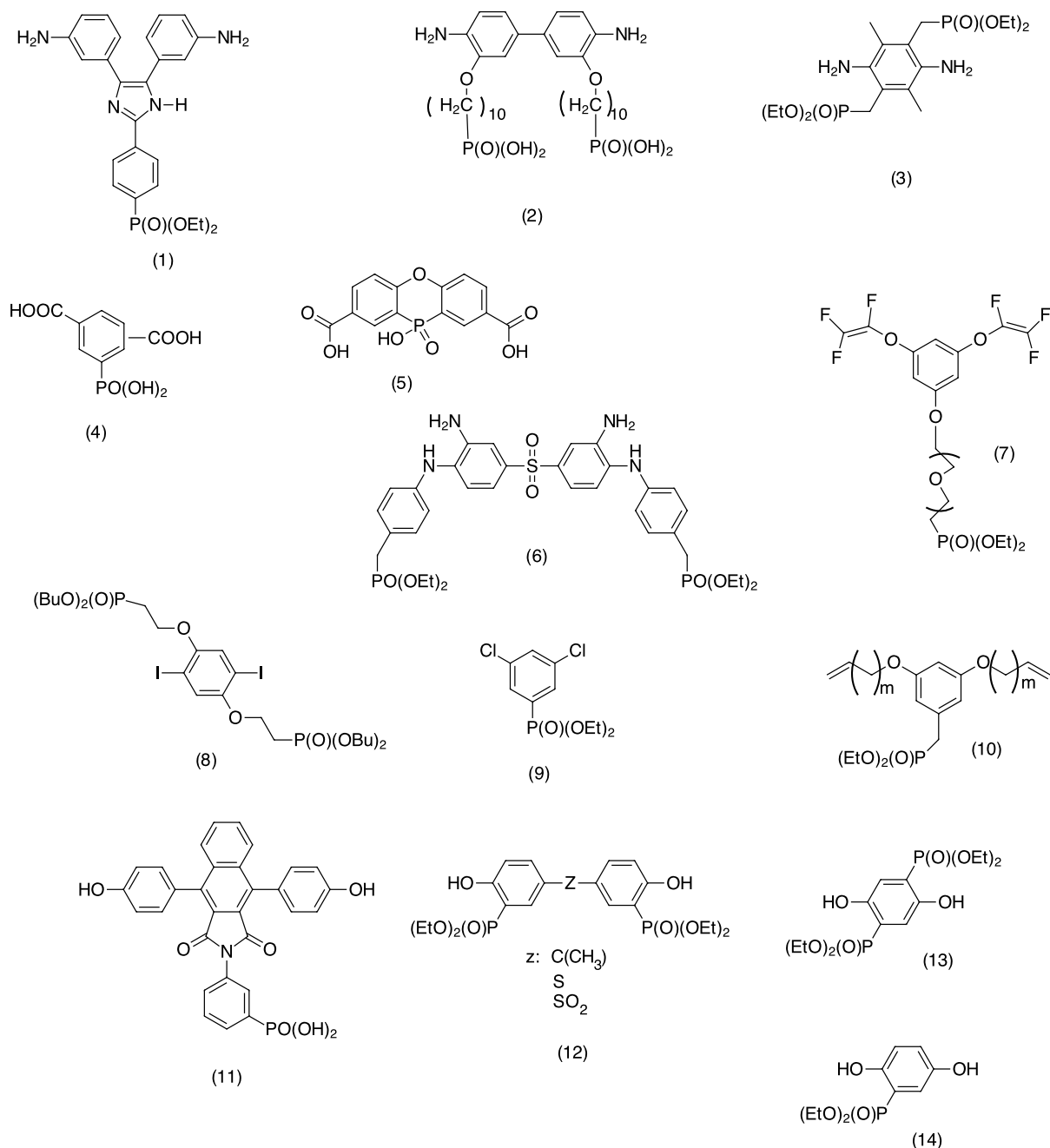


Figure 1. Phosphonate ester and phosphonic acid containing precursors

Finocchiaro et al.<sup>[32]</sup> describe the synthesis of polyamides from phosphonated diamine monomer (3). In 2001, based on 2-dicarboxyphenylphosphonic acid (4) the synthesis of phosphonic acid containing polybenzimidazoles was reported by Toyobo<sup>[33]</sup>. The synthesis of the phosphonate ester of this monomer was recently described by Bauer et al.<sup>[34]</sup> Similarly, Shaplov and co-workers described the para isomer and synthesized functionalized poly(1,3,4-

oxadiazole)s<sup>[15]</sup>. 10-hydroxy-10-oxo-10H-10 $\lambda^5$  phenoxaphosphine-2,8 dicarboxylic acid (5) and diamine (6) were used by Ponomarev et al. to synthesize remarkable thermooxidative resistant polybenzimidazoles<sup>[35, 36]</sup>. Monomer (5) was used as well to synthesize 2,3,5,6-tetraaminopyridine-based poly(heteroarylene)s<sup>[37]</sup>. Other polycondensation reactions were investigated, such as the cyclodimerization of phosphonate bistrifluorovinylether monomer (7)<sup>[38]</sup>, the Sonogashira polymerization of (8) with 1,4 diethynylbenzene<sup>[39]</sup>, or the Colom coupling reaction with (9)<sup>[16]</sup>. Very recently, phosphonic acid containing polyethylene structures were synthesized by step-growth metathesis of functionalized monomer (10)<sup>[40]</sup>. However, materials with rather low molecular weight were usually reported. The synthesis of phosphonic acid-containing Poly(aryl ether)s was also considered from different functionalized bisphenol monomers ((11)<sup>[41, 42]</sup>, (12)<sup>[43-45]</sup>, (13)<sup>[45-48]</sup> and (14)<sup>[49]</sup>). Rather few examples of the incorporation of these phosphonated precursors in the synthesis of poly(aryl ether)s by aromatic nucleophilic substitution are reported. When copolymerized with 4,4'-difluorodiphenylsulfone or 4,4'-difluorotriphenylphosphine oxide, only low molecular weight polymers are described from the diphosphonated bisphenols. The authors ascribe this result to the sterical hindrance of the bulky phosphonate groups present on the functionalized biphenol<sup>[48]</sup>. High molecular weight polymers were however synthesized by 4,4'-difluorodiphenylsulfone and the monophosphonated bisphenol (14) or using a more reactive comonomer such as decafluorobiphenyl<sup>[47]</sup>. High molecular weight poly(aryl ether)s containing from 25% to 100% of a phosphonic acid containing bisphenol-imide (11) are also reported by Meng et al.<sup>[50]</sup>

Besides the difficulties encountered for the synthesis of the phosphonated precursors, the direct polycondensation of these functionalized monomers (whatever the nature of the polymerization reaction) often results in the formation of low molecular weight oligomers. This is generally ascribed to possible strong aggregations phenomena, phosphonic acid condensation reactions or low reactivity of the functionalized monomer. As a result, the synthesis of high molecular weight polymers with a high extend of phosphonic acid groups is rather challenging. In this article, we describe the straightforward synthesis of two side-chain phosphonate ester-containing bisphenols. A thorough study of an aromatic nucleophilic substitution involving this precursor was then performed on a model molecule in order to identify possible undesirable side-reactions that could be detrimental during a polycondensation reaction. In the light of the obtained results, new insights are given for the synthesis of high molecular weight phosphonate esters and phosphonic acid-containing poly(aryl ether)s.

## 2. Experimental Section

### 2.1. Materials

2,2-Bis(4-hydroxyphenyl)propane (Bisphenol A) (Sigma-Aldrich) was recrystallized from toluene, 4,4'-difluorobenzophenone (ACROS) was purified by crystallization from a petroleum ether / ethyl acetate mixture, 4,4'-difluorodiphenyl sulfone (Aldrich) was purified by sublimation and 5-chloropentanone (Alfa Aesar) was distilled prior to use. Dimethyl sulfoxide (DMSO) (VWR Chemical Co.), toluene (SDS Chemical Co.), potassium carbonate and other chemicals (phenol, triethyl phosphite, 4-fluorobenzophenone, etc.) were commercially available and used as received.

### 2.2. Characterization Methods

Nuclear magnetic resonance ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR) spectra were recorded on a Bruker Avance 400 spectrometer operating at the following frequencies of 400.16 MHz for  $^1\text{H}$ , 100.63 MHz for  $^{13}\text{C}$ , 376.48 MHz for  $^{19}\text{F}$  and 161.99 MHz for  $^{31}\text{P}$ . Tetramethylsilane was used as the internal standard for  $^1\text{H}$  and  $^{13}\text{C}$  spectra whereas 85%  $\text{H}_3\text{PO}_4$  was used as the reference for  $^{31}\text{P}$  analyses.

Thermogravimetric analyses (TGA) were performed on a TA Instruments Q50. Samples were heated under air at  $10^\circ\text{C}/\text{min}$ . The polymer glass transition temperatures ( $T_g$ ) were determined by Differential Scanning Calorimetry (DSC) with a Mettler-Toledo DSC822e equipment (measurements were performed at a heating rate of  $10^\circ\text{C}/\text{min}$ , under nitrogen) and by Thermo mechanical analyses (TMA) on a TA Instruments model Q400 (measurements were performed under nitrogen, at a heating rate of  $10^\circ\text{C}/\text{min}$ , in the penetration mode, on thin polymer films).

The polymer molecular weights were evaluated by Size Exclusion Chromatography (SEC) in DMF containing 0.05M LiBr. The system used was equipped with an AGILENT G1310A pump, two PLgel Mixed D columns thermostated at  $70^\circ\text{C}$  and a Wyatt optilab differential refractive index detector. Molecular weights (denoted  $M_{n(PS)}$  and  $M_{w(PS)}$ ) were determined from a polystyrene calibration curve.

### 2.3. Synthesis of Reagents and Monomers

*Synthesis of 1-Chloro-4,4-di(p-hydroxyphenyl)-pentane (I).* 41.68 g (0.3456 mol) of freshly distilled 5-chloropentanone, 130.126 g (1.3826 mol) of phenol, few drops of mercaptoacetic acid and few drops of sulfuric acid were introduced in a 250 mL three-necked round bottom flask. HCl was then bubbled through the reaction medium, at room temperature. The reaction

proceeded overnight. The solid obtained was dispersed into water. The product was isolated by filtration and purified by column chromatography (successively with CH<sub>2</sub>Cl<sub>2</sub> and acetone), leading to 1-chloro-4,4-di(p-hydroxyphenyl)-pentane as a pure white powder (83.4% yield). <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): δ (ppm) 1.49 (m, 5H), 2.07 (m, 2H), 3.54 (t, 8Hz, 2H), 6.65 (d, 8Hz, 4H), 6.95 (d, 8Hz, 4H). <sup>13</sup>C NMR (d<sub>6</sub>-DMSO): δ (ppm) 27.5, 28.1, 38.7, 43.8, 45.9, 114.6, 127.7, 139.6, 154.9.

*Synthesis of 1-Iodo-4,4-di(p-hydroxyphenyl)-pentane (II).* 23.3 g (8.01 · 10<sup>-2</sup> mol) of 1-chloro-4,4-di(p-hydroxyphenyl)-pentane were dissolved in 122 mL of reagent grade acetone. 48.04 g (0.32 mol) of NaI were added to the solution and the reaction mixture was heated at reflux. The evolution of the reaction was monitored by <sup>1</sup>H NMR. After the reaction was completed, the solvent was evaporated and the target product was isolated from the remaining NaI salts by extraction with dichloromethane. The organic layer was then concentrated and dried under vacuum. 22.6 g (74% yield) of 1-iodo-4,4-di(p-hydroxyphenyl)-pentane were obtained. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): δ (ppm) 1.47-1.56 (m, 5H), 2.02-2.07 (m, 2H), 3.2 (t, 4Hz, 2H), 6.65 (d, 8Hz, 4H), 6.94 (d, 8Hz, 4H), 9.17 (OH). <sup>13</sup>C NMR (d<sub>6</sub>-DMSO): δ (ppm) 9.90, 28.2, 29.53, 42.9, 44.3, 115.1, 128.2, 140.1, 155.4.

*Synthesis of Ethyl 4,4-di(p-hydroxyphenyl)pentanephosphonate (A).* 1 g (2.6 mmol) of 1-iodo-4,4-di(p-hydroxyphenyl)-pentane were introduced in a 25 mL round bottom flask equipped with a nitrogen inlet and a condenser. 0.869 g (5.2 mmol) of triethylphosphite were added dropwise. The reaction mixture was then heated at 110 °C and the evolution of the reaction was monitored both by <sup>1</sup>H and <sup>31</sup>P NMR. After the reaction was completed, the excess of triethylphosphite was distilled at 160 °C under vacuum. Ethyl 4,4-di(p-hydroxyphenyl)pentanephosphonate was obtained as a vitrous product with 95% yield. The polymer-grade phosphonated monomer was obtained as a white powder by flash chromatography. <sup>31</sup>P NMR (d<sub>6</sub>-DMSO): δ (ppm) 31.78. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): δ (ppm) 1.17 (t, 1.8 Hz, 3H), 1.28-1.30 (m, 2H), 1.48 (s, 3H), 1.60-1.68 (m, 2H), 3.86-3.96 (m, 4H), 6.63 (d, 8Hz, 4H), 6.93 (d, 8Hz, 4H), 9.2 (OH). <sup>13</sup>C NMR (d<sub>6</sub>-DMSO): δ (ppm) 16.1, 17.6, 24.7 (d 27.4, 42.3, 44.1, 60.6 114.5, 127.6, 139.6, 154.8.

*Synthesis of 1-Bromo-3-(trifluoroacetylphenyl)-propane (III).* In a three-necked round bottom flask equipped with a condenser, a magnetic stirrer and a nitrogen inlet, 23.47 g (0.176 mol) of AlCl<sub>3</sub>, were suspended in 240 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was cooled in an ice bath. 21.94 g (0.104 mol) of trifluoroacetic anhydride were added and temperature was kept below 5°C. A solution made out of 16 g (0.08 mol) of 1-Bromo-3-phenylpropane in 80 mL

CH<sub>2</sub>Cl<sub>2</sub> was added dropwise. After the end of the addition, the reaction mixture was stirred 30 minutes at room temperature. The evolution of the reaction was monitored by thin layer chromatography. After completion of the reaction, the mixture was poured into water. The product was isolated by extraction (EtOAc). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated. The yellowish liquid was distilled (85 °C - 5 · 10<sup>-2</sup> mbar) giving 20.38 g (86% yield) of a colorless liquid. <sup>19</sup>F NMR (d<sub>6</sub>-DMSO): δ (ppm) -70.75. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): δ (ppm) 2.17 (m, 2H), 2.88 (t, 2H, J = 8 Hz), 3.55 (t, 2H, J = 6.5 Hz), 7.55 (d, 2H, J = 8 Hz), 8.0 (d, 2H, J = 8 Hz). <sup>13</sup>C NMR (d<sub>6</sub>-DMSO): δ (ppm) 33.3, 33.8, 34, 118.89 (CF<sub>3</sub>), 127.7, 129.5, 130.1, 150.2, 179.69 (q).

*Synthesis of 1,1-Bis-(3,5-dimethyl-4-hydroxyphenyl)-1-(4-(3-bromopropyl)-phenyl)-2,2,2-trifluoroethane (IV).* In a three-necked round bottom flask were introduced 15 g (0.0508 mol) of freshly distilled 1-bromo-3-(trifluoroacetylphenyl)-propane (III), 20 g (0.163 mol) of 2,6-dimethylphenol and 0.346 g (0.002 mol) of zinc chloride. HCl was bubbled through the reaction mixture and temperature was raised up to 100 °C and maintained overnight. The reaction mixture was poured into water, washed with deionized water and dried under vacuum. 22.84 g (86.2% yield) of crude product were obtained. <sup>19</sup>F NMR (d<sub>6</sub>-DMSO): δ (ppm) -57.68. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): δ (ppm) 2.07 -2.14 (m, 5H), 2.72 (t, 2H), 3.51 (t, 2H), 6.57 (s, 4H), 6.96 (d, 2H), 7.19 (d, 2H), 8.38 (OH). <sup>13</sup>C NMR (d<sub>6</sub>-DMSO): δ (ppm) 16.9, 32.8, 33.5, 34.3, 62.8 (q), 123.5, 127.9, 129.3, 129.4, 130.3, 138.1, 139.8, 152.5.

*Synthesis of 1,1-Bis-(3,5-dimethyl-4-hydroxyphenyl)-1-(4-(3-iodopropyl)-phenyl)-2,2,2-trifluoroethane (V).* 22 g (0.0422 mol) of (5) and 25.29 g (0.168 mol) of NaI were suspended in 115 mL of reagent grade acetone, in a 250 mL single-neck round bottom flask equipped with a magnetic stirrer and a condenser. The reaction mixture was heated at reflux. The evolution of the reaction was monitored by <sup>1</sup>H NMR. After completion of the reaction, the sodium bromide formed during the reaction was filtered and the filtrate was evaporated, giving an orange solid. Remaining traces of NaI were removed by extraction (CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O). The organic phase was evaporated and dried in vacuo, giving (V) with 87.5% yield. <sup>19</sup>F NMR (d<sub>6</sub>-DMSO): δ (ppm) -57.67. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): δ (ppm) 2.05 -2.08 (m, 5H), 2.66 (t, 2H), 3.23 (t, 2H), 6.55 (s, 4H), 6.94 (d, 2H), 7.17 (d, 2H), 9.6 (OH). <sup>13</sup>C NMR (d<sub>6</sub>-DMSO): δ (ppm) 8.12, 17.4, 34.7, 35.6, 63.3 (q), 123.9, 128.4, 129.8, 129.9, 130.8, 138.7, 140.1, 152.9.

*Synthesis of 1,1-Bis-(3,5-dimethyl-4-hydroxyphenyl)-1-(4-(3-diethylphosphonatopropyl)-phenyl)-2,2,2-trifluoroethane (B).* In a three-necked round bottom flask equipped with a magnetic stirrer, a nitrogen inlet and a condenser were introduced 10 g (0.0191 mol) of 1,1-



Bis-(3,5-dimethyl-4-hydroxyphenyl)-1-(4-(3-bromopropyl)-phenyl)-2,2,2-trifluoroethane (respectively 21 g (0.036 mol) of (V)) and 6.58 ml of triethylphosphite (resp 12.7 ml ). The reaction mixture was heated at 110 °C for 12 hours. The temperature was raised to 160 °C in order to distill off all remaining volatile compounds. The vitreous resulting product was dissolved in dichloromethane and purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>, EtOH), giving 8.5 g (76.6% yield) resp 17.2 g (80.4% yield) of polymer grade (B). <sup>19</sup>F NMR (d<sub>6</sub>-DMSO): δ (ppm) -57.52. <sup>31</sup>P NMR: (d<sub>6</sub>-DMSO): δ (ppm) 31.49. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): δ(ppm) 1.18 (t, 6H), 1.6-1.8 (m, 4H), 2.06 (s, 12H), 2.63 (t, 2H), 3.94 (m, 4H), 6.54 (s, 4H), 6.93 (d, 2H), 7.15 (d, 2H), 8.4 (OH). <sup>13</sup>C NMR (d<sub>6</sub>-DMSO): d (ppm) 16.1, 16.19, 22.9, 23.7, 25.1, 34.8(d), 60.78, 63.2 (q), 123.5, 127.9, 129.3, 130.4, 138.1, 140.3, 152.5.

*Study of the reaction of potassium carbonate on hemi-phosphonate ester groups*

2 g (0.0082 mol) of diethyl[(4-methylphenyl)methyl]phosphonate, 3.48 g (0.033 mol) of potassium carbonate, 25 ml of toluene (cyclohexane) and 11.5 ml of DMSO were introduced in a three-necked round bottom flask equipped with a nitrogen inlet, a mechanical stirrer and a dean stark trap. The reaction medium was heated at 140 °C (110°C) for 4 hours. After azeotropic distillation of the water formed, the reaction medium was heated at 160 °C (110 °C) for 20 hours. Samples were directly withdrawn from the reaction medium and few drops of deuterated DMSO were added. Quantitative <sup>31</sup>P NMR spectra were recorded at 30 °C.

*Model molecule synthesis*

1 g (0.0025 mol) of (A), 1.021 g (0.005 mol) of 4-fluorobenzophenone, 0.718 g (0.0052 mol) of potassium carbonate were suspended in 10 ml of DMSO. The reaction mixture was heated at 160 °C for 9 hours. The evolution of the reaction was monitored both by <sup>19</sup>F and <sup>31</sup>P NMR. After the reaction was completed (as evidenced by <sup>19</sup>F NMR), the reaction medium was poured into acidic water. The resulting beige compound was filtrated, washed with petroleum ether and dried under vacuum (yield 89.5%).

**2.4. General procedures for the synthesis of phosphonate ester-containing poly(aryl ether)s**

*Synthesis of phosphonate ester-containing poly(aryl ether ketone)s (PAEK).*

2 g (5 mmol) of Ethyl 4,4-di(p-hydroxyphenyl)pentanephosphonate (A), 2.19 g (10 mmol) of 4,4'-difluorobenzophenone, 1.13 g (5 mmol) of Bisphenol A and 4.2 g (30 mmol) of potassium carbonate, 20 mL of DMSO (or NMP, or DMAC) and 15 mL of toluene were introduced in a two-necked reactor equipped with a nitrogen inlet and a mechanical stirrer. The reaction mixture was heated at 140 °C for 4 hours. After azeotropic distillation of the

water formed, the temperature was raised to 160 °C-180 °C and heated for 24 to 39 hours. After cooling, the mixture was poured into water. The resulting polymer was collected by filtration, washed with water and dried under vacuum at 80 °C, for 4 hours.

*Typical procedure for the synthesis of phosphonate ester-containing poly(aryl ether nitrile)s*  
*Synthesis of PAEN-40 A*

In a two-necked reactor, equipped with a nitrogen inlet and a mechanical stirrer, 0.436 g (1.91 mmol) of bisphenol A, 0.5 g (1.27 mmol) of phosphonate ester-containing bisphenol (A), 0.443 g (3.19 mmol) of 2,6-difluorobenzonitrile, 0.968 g (7.01 mmol) of potassium carbonate and 4.14 mL of DMSO were added and heated at 100 °C for two days. At the end of the polymerization, the reaction mixture was poured into water. The white fibrous polymers were collected by filtration, thoroughly rinsed with water and finally dried under vacuum.

*Typical procedure for the synthesis of phosphonate ester- containing poly(aryl ether sulfone)*  
*Synthesis of PAES-40A*

In a two-necked reactor, equipped with a nitrogen inlet and a mechanical stirrer, 0.523 g (2.29 mmol) of bisphenol A, 0.6 g (1.52 mmol) of phosphonate ester-containing bisphenol (A), 0.972 g (3.8 mmol) of 4,4'-difluorodiphenylsulfone, 1.16 g (8.4 mmol) of potassium carbonate and 6.5 mL of DMSO were added and heated at 80 °C for two days. At the end of the polymerization, the reaction mixture was poured into water. The white fibrous polymers were collected by filtration, thoroughly rinsed with water and finally dried under vacuum.

*Typical procedure for the synthesis of phosphonate ester and decafluorobiphenyl-containing poly(aryl ether)s*

*Synthesis of PAE10F-40A*

Into a three-neck round bottom flask equipped with a mechanical stirrer and a nitrogen inlet, were charged 1.064 g (3.18 mmol) of decafluorobiphenyl, 0.436 g (1.91 mmol) of bisphenol A, 0.5 g (1.27 mmol) of (A) and 0.968 g (7.01 mmol) of potassium carbonate. Then, 6 mL of DMAC were added and the mixture was stirred at 70 °C for 24h. The viscous reaction mixture was diluted with 8mL of DMAC, cooled to room temperature and precipitated in water, filtered off, washed with water and methanol. The white fibrous polymer was filtered and dried at 80 °C under vacuum.

*Synthesis of PAE10F-40B*

Into a three-neck round bottom flask equipped with a mechanical stirrer and a nitrogen inlet,

were charged 1.458 g (4.37 mmol) of decafluorobiphenyl, 0.5918 g (2,6 mmol) of bisphenol A, 1 g (1.73 mmol) of (B) and 1.31 g (9.5 mmol) of potassium carbonate. Then, 9 mL of DMAC were added and the mixture was stirred at 70 °C for 48h. The viscous reaction mixture was diluted with 6mL of DMAC, cooled to room temperature and precipitated in water, filtered off, washed with water and methanol. The white fibrous polymer was filtered and dried at 80 °C under vacuum.

### ***2.5 Film elaboration***

Polymer thin films were prepared by casting 20 wt% polymer solutions in NMP onto a glass substrate. The films were dried under nitrogen at 50 °C overnight and successively treated one hour at 80 °C, 120 °C, 150 °C and 180 °C. Films were peeled off by immersion in water.

### 3. Results and Discussion

#### 3. 1. Synthesis of Ethyl 4,4-di(*p*-hydroxyphenyl)pentanephosphonate (A)

Monomer (A) was synthesized in three steps, according to the synthetic route depicted in Figure 2.

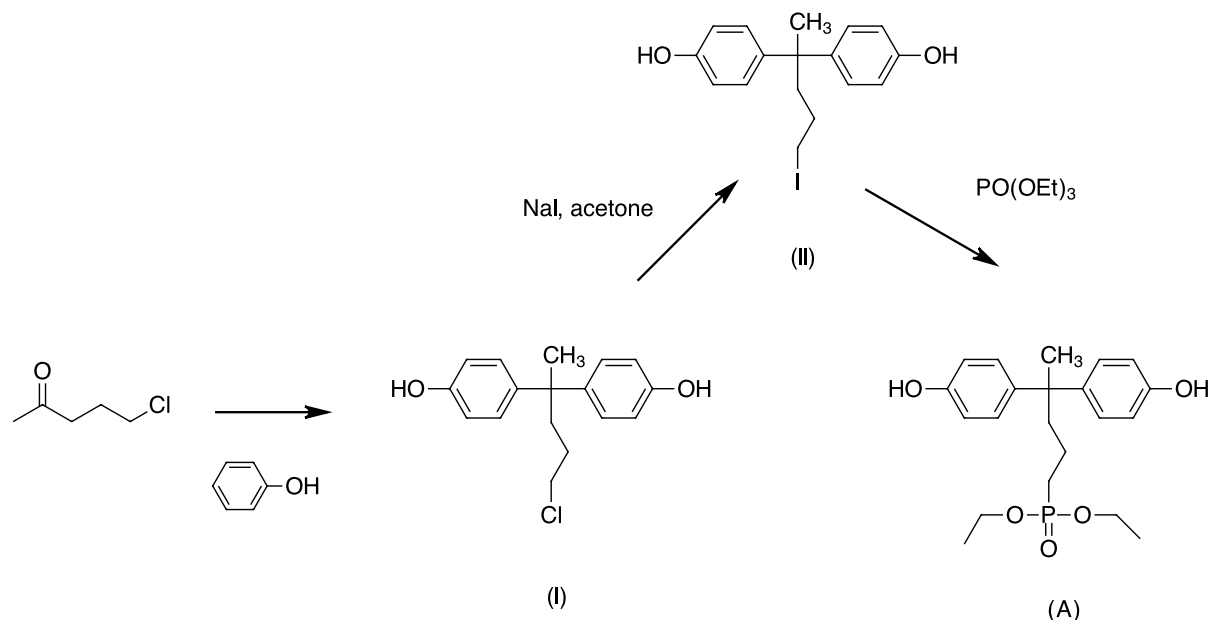


Figure 2. Synthesis of Ethyl 4,4-di(*p*-hydroxyphenyl)pentanephosphonate (A)

The first step is the condensation reaction of phenol with 5-chloropentanone in acidic medium leading to the formation of 1-Chloro-4,4-di(*p*-hydroxyphenyl)-pentane (I) (the pure product was isolated with 83.4% yield). The iodine analogue of (I) was then obtained by halogen exchange, in the presence of sodium iodide (74% yield). Finally, this intermediate compound (II) was reacted at 110°C with triethylphosphite in Arbusov reaction. The crude product was obtained with a quasi-quantitative yield. Compound (A) was obtained as a white powder. The purity of the intermediates as well as of the phosphonate-containing monomer were confirmed by HPLC (see supporting information Figure S1) and multi-nuclei NMR. <sup>1</sup>H NMR spectrum of the phosphonate ester bisphenol is reported in Figure 3.

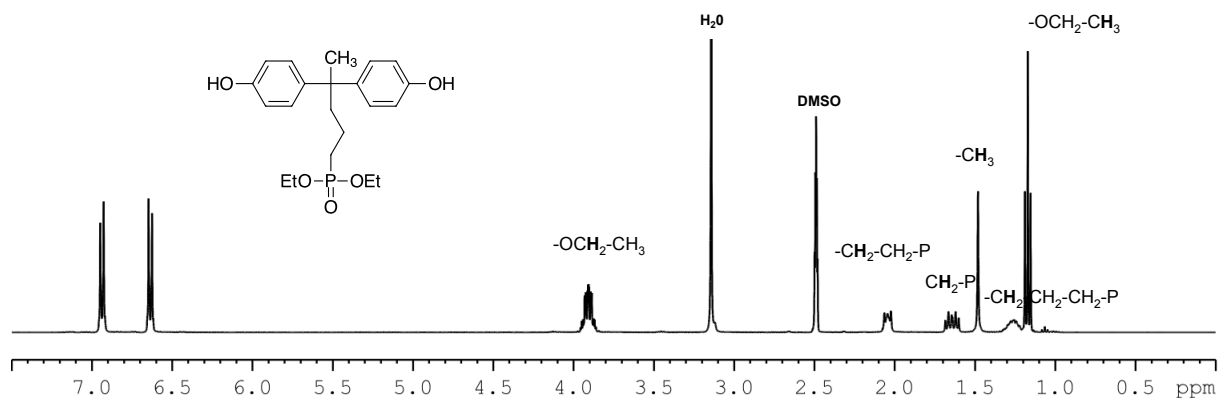


Figure 3.  $^1\text{H}$  spectrum ( $\text{d}_6\text{-DMSO}$ ,  $50^\circ\text{C}$ ) of compound (A)

### 3. 2. Synthesis of 1,1-Bis-(3,5-dimethyl-4-hydroxyphenyl)-1-(4-(3-diethylphosphonatopropyl)-phenyl)-2,2,2-trifluoroethane (B).

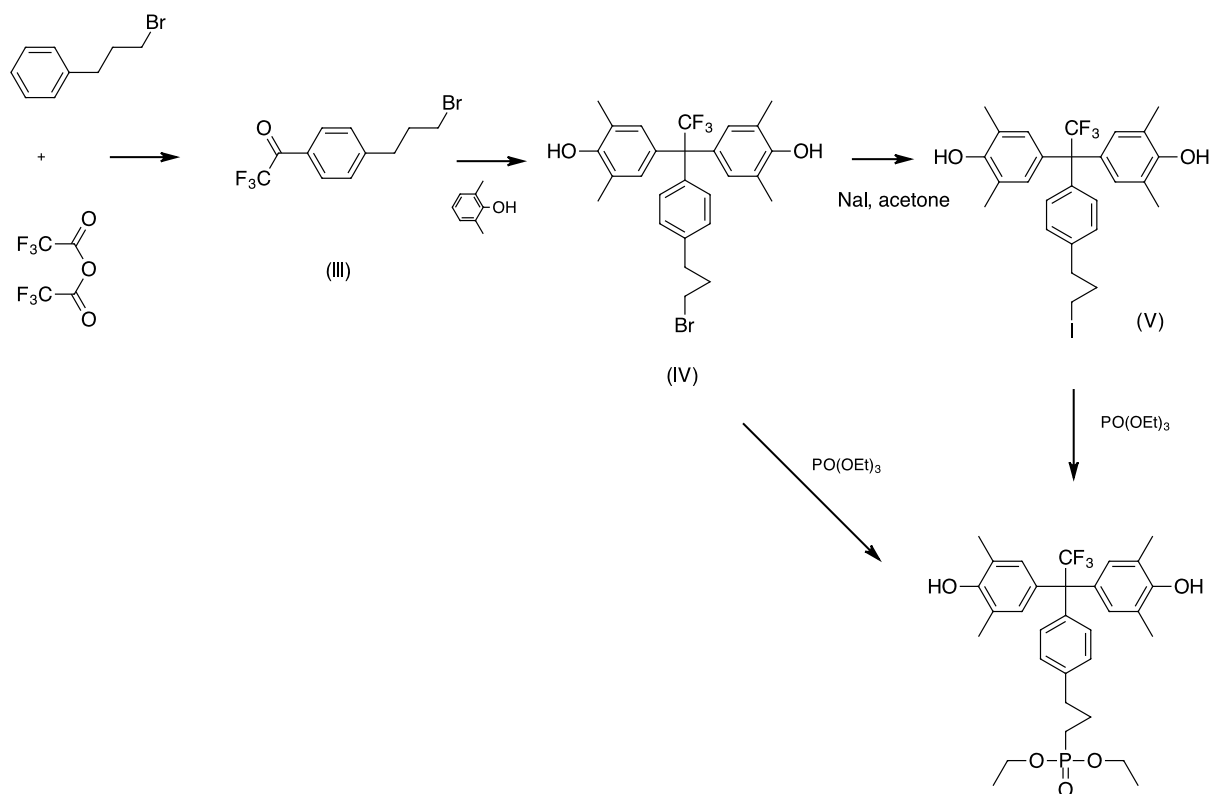


Figure 4. Multi-steps synthesis of phosphonate ester-containing bisphenol (B)

According to the synthetic pathway described in Figure 4, 1,1-Bis-(3,5-dimethyl-4-hydroxyphenyl)-1-(4-(3-diethylphosphonatopropyl)-phenyl)-2,2,2-trifluoroethane (B) could be synthesized in three or four steps. First a Friedel/Crafts reaction of trifluoroacetic anhydride with 1-bromo-3 phenylpropane gives 1-bromo-3-(trifluoroacetylphenyl)-propane (III) with 86% yield. 2,6-Dimethylphenol was then condensed on this freshly distilled

precursor in acidic medium leading to the formation of 86% of 1,1-Bis-(3,5-dimethyl-4-hydroxyphenyl)-1-(4-(3-bromopropyl)-phenyl)-2,2,2-trifluoroethane (IV). This bromoalkyl compound was used without further purification in a halogen exchange reaction involving NaI in acetone. The Arbusov reaction could be either performed with the bromo or iodo precursors (IV and V), in the presence of triethylphosphite, at 110 °C. However, a better yield was obtained with compound V. Monomer grade diethylphosphonate diphenol (B) was produced from a purification of the crude product by flash chromatography and its structure was confirmed by HPLC (see supporting informations Figure S1) and NMR characterizations.  $^1\text{H}$  NMR is reported in Figure 5.

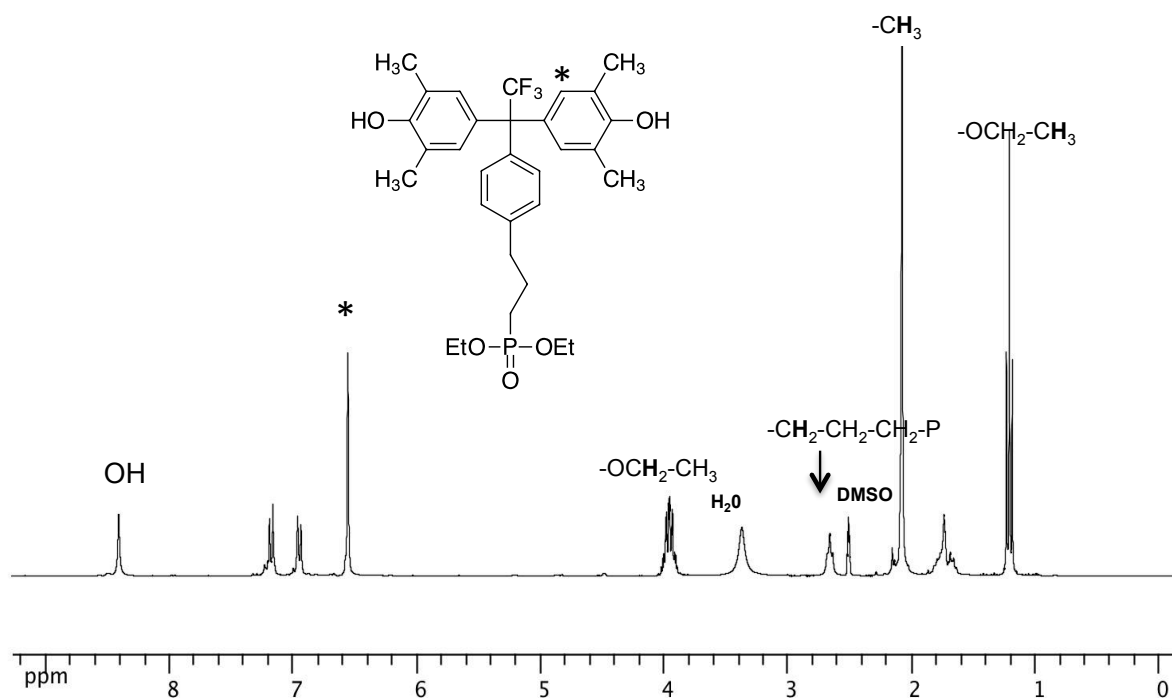


Figure 5.  $^1\text{H}$  spectrum ( $\text{d}_6\text{-DMSO}$ ) of compound (B)

### 3.3 Regeneration of phosphonic acid groups by dealkylation

When performed in basic conditions (KOH / EtOH), the dealkylation reaction of phosphonate esters is known to exclusively produce hemi-ester derivatives<sup>[51]</sup>. In such experimental conditions, the hemi-ester phosphonate potassium salt was characterized by a  $^{31}\text{P}$  peak at 19.2 ppm and after re-acidification in mild conditions, the acid analogue was characterized by a  $^{31}\text{P}$  peak at 28.5 ppm. In the frame of this work,  $^{31}\text{P}$  NMR was used to precisely identify the structure of the phosphorus containing compounds formed. Indeed, the phosphorus atoms

present either in a phosphonate ester, phosphonic acid or hemi-ester, both in their acid or salt forms are characterized by different resonance peaks.

The dealkylation of the phosphonate ester-containing bisphenol (A) was performed at room temperature in acetonitrile, in the presence of chlorotrimethylsilane and sodium iodide. Such conditions are well-known to give phosphonic acid functions<sup>[52]</sup>. The evolution of the reaction was monitored by  $^{31}\text{P}$  NMR spectroscopy. As shown in Figure 6, the peak initially present at 31.3 ppm, (characteristic of the phosphonate ester groups) progressively disappears. An intermediate compound (corresponding to the hemi-phosphonic acid analogue) is characterized by the apparition of a peak at 28.5 ppm. The final formation of the corresponding phosphonic acid bisphenol (A-OH) is confirmed by the appearance of the peak at 26.4 ppm.

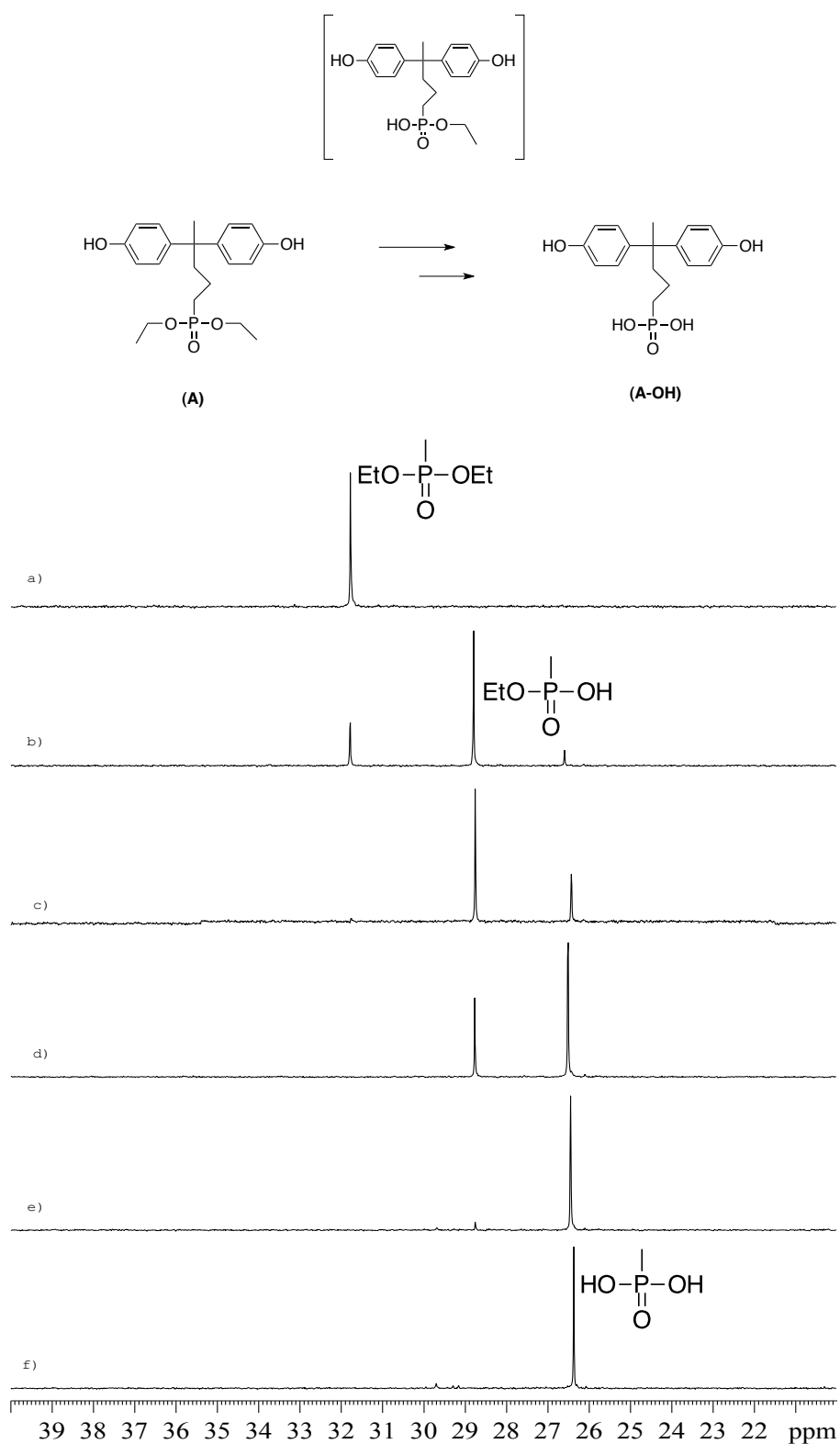


Figure 6.  $^{31}\text{P}$  NMR. (DMSO- $d_6$ , 80°C). Dealkylation of bisphenol phosphonate ester (A) in its phosphonic acid analogue (A-OH). a)  $t=0$  min, b)  $t=10$  min, c)  $t=40$  min, d)  $t=3$ h, e)  $t=2$  days, f) 2 days+ excess NaI



On the  $^1\text{H}$  NMR spectrum (Figure 7), the complete disappearance of the triplet at 1.17 ppm and the multiplet at 3.86-3.96 ppm, respectively associated to the protons of methyl and methylene groups of the ethyl phosphonate function confirms the formation of the phosphonic acid product.

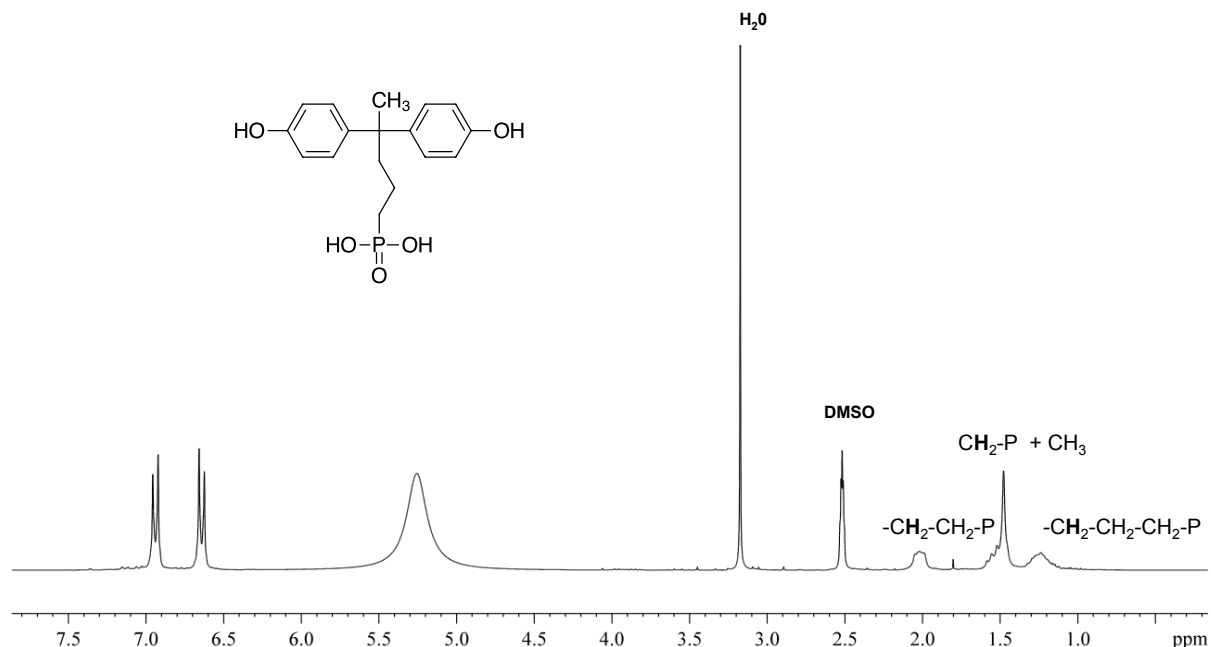


Figure 7.  $^1\text{H}$  NMR spectrum of phosphonic acid containing bisphenol (A-OH).

Although the phosphonic acid bisphenol (A-OH) was isolated as a monomer-grade monomer, this precursor was rather unstable in acidic form and could not be successfully used to synthesize polymers. As a result, both phosphonate ester precursors (A and B) were directly used for polymer synthesis and phosphonic acid groups were regenerated thereafter.

### 3. 4. *Synthesis of phosphonic acid containing poly(arylether)s (PAE)*

The phosphonate ester-containing poly(aryl ether)s were first synthesized in a polar aprotic solvent (DMSO). Bisphenol monomers (A) and (B) were polycondensed with different comonomers (4,4'-difluorobenzophenone, 2,6-difluorobenzonitrile, 4,4'-difluorodiphenylsulfone or decafluorobiphenyl) as illustrated in Figure 8.

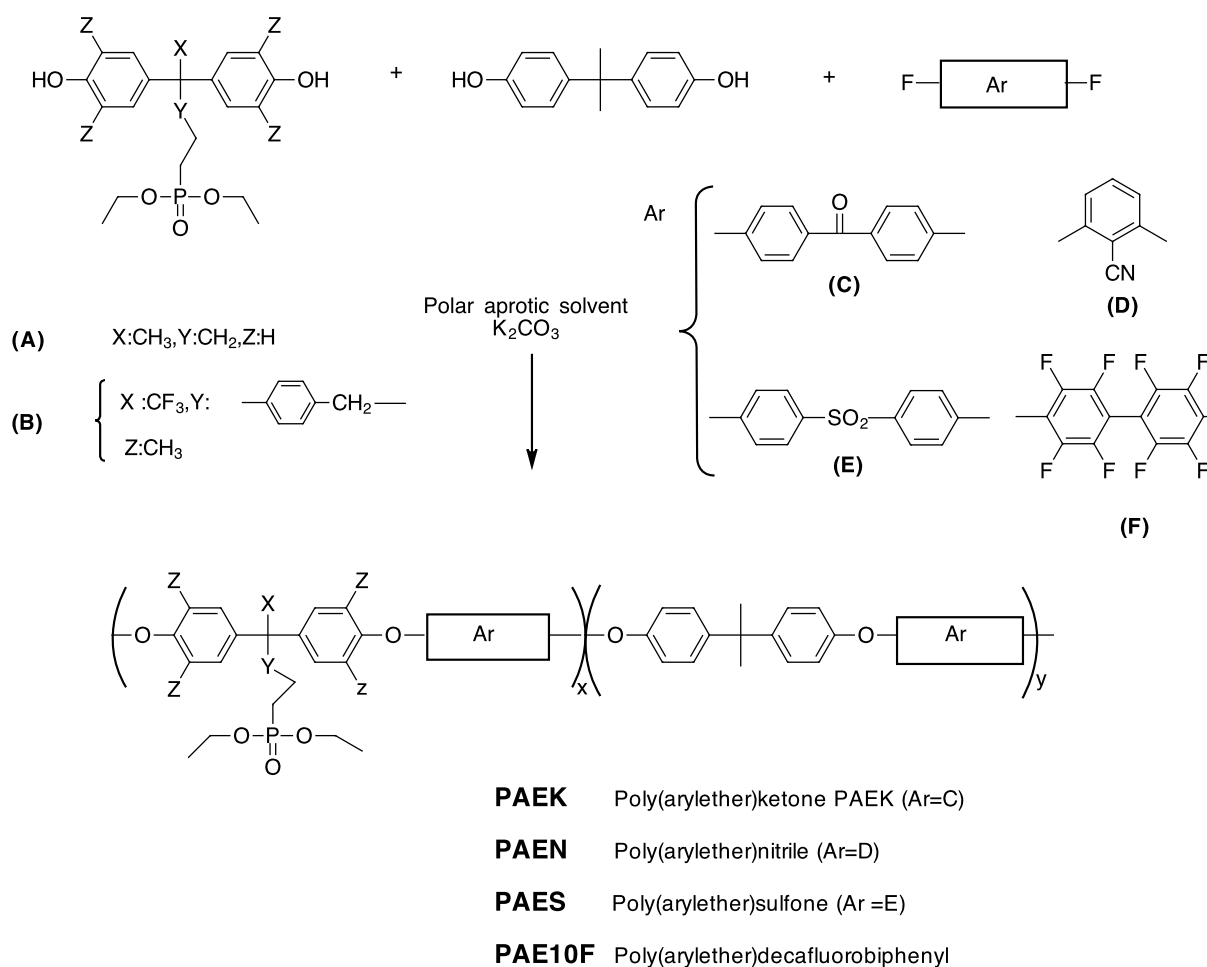


Figure 8. Synthesis of phosphonated ester containing (PAE)s

A first series of PAEKs was prepared from monomer (A) and difluorobenzophenone as comonomer. Polymerizations were classically performed at high temperature (160-180°C). The polymers were isolated in their phosphonate ester form and characterized by  $^{31}P$  and  $^1H$  NMR

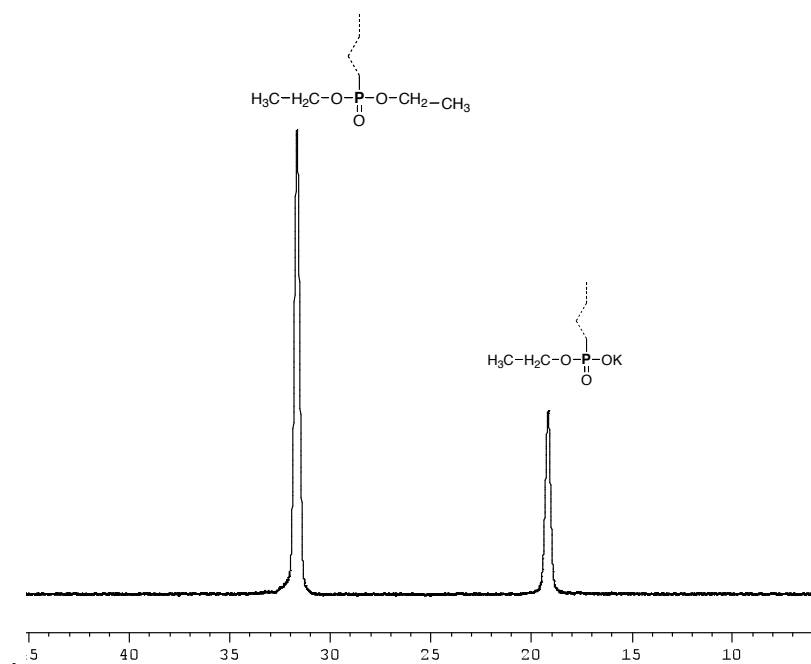


Figure 9.  $^{31}\text{P}$  spectrum of a phosphonate ester-containing (PAE)s

$^{31}\text{P}$  NMR spectrum (Figure 9) revealed the presence of two different phosphorus containing species. One major peak is present at 31.3 ppm and a second one at 19.2 ppm. In the  $^1\text{H}$  NMR spectrum, (see supported information (Figure S3), both the relative low proportion of the methylene and methyl groups respectively present at 3.93 ppm and 1.18 ppm and the presence of a second type of methylene at 3.6 ppm and methyl at 1.03 ppm suggest that the two phosphorus containing species respectively correspond to the expected phosphonate ester groups and to partially dealkylated groups (hemi-phosphonates, in their potassium salt form). This observation was confirmed by further  $^{31}\text{P}$  NMR investigation (Supporting information Figure S4). Indeed, the acidification of the polymer by addition of few drops of trifluoroacetic acid (TFA) results in the protonation of the hemi-phosphonates groups, which are therefore characterized by a peak at 28.5 ppm (figure S4 b)). In comparison, Figure S4 c) and d) correspond to the  $^{31}\text{P}$  NMR spectra of partial and quasi-complete dealkylation of the polymer, after reflux in HCl 37%. In this last case, phosphonic acid functions are characterized by a peak at 26.4 ppm.

The proportion of hemi-phosphonate groups present in the polymer at the end of the polymerization (from 22 to 61%) was proven to strongly depend on the nature of the polymerization solvent. The results are reported in Table 1.

Table 1. Effect of the polymerization solvent and reaction temperature on the formation of hemi-phosphonate species.

Ref	PO(OEt) <sub>2</sub> <sup>a</sup> (%)	PO(OEt)(OK) <sup>a</sup> (%)	T (°C)	Solvent	Reaction time (h)
PAEK1	78	22	160	DMSO	24
PAEK2	61	39	180	DMSO	24
PAEK3	39	61	160	NMP	24
PAEK4	63	37	160	DMAC	24
PAEK5	68	32	160	DMAC	39

<sup>a</sup> From <sup>31</sup>P NMR

After 24 hours reaction at 160°C, only 22% of hemi-phosphonate groups were formed in DMSO whereas 37% and 61% were respectively formed in DMAC and NMP. The reaction temperature seemed to favor as well the formation of these species as in DMSO, 39 % of hemiphosphonates were formed at 180°C (versus 22% at 160°C).

The presence of K<sub>2</sub>CO<sub>3</sub> during the polycondensation reaction was first suspected to induce the formation of hemi-phosphonate groups as the hydrolysis of phosphonate esters in a basic medium is well known to lead to such species. However, when diethyl[(4-methylphenyl)methyl]phosphonate (Supporting information Figure S5) was heated in DMSO at 160 °C for 24h in the presence of K<sub>2</sub>CO<sub>3</sub>, only 14% of dealkylation were determined by quantitative <sup>31</sup>P NMR. In addition, when the experience was performed at 110 °C, only 3.9% of dealkylation was effective.

In both cases, the proportions of hemi-phosphonate groups formed were far lower than those observed after a polymerization reaction performed in the same conditions. Furthermore, when diethyl[(4-methylphenyl)methyl]phosphonate was heated at 160 °C in the presence of K<sub>2</sub>CO<sub>3</sub> and some additional 4-fluorophenol, the proportion of hemi-phosphonate formed drastically increased. These observations suggested a possible participation of the phenate groups in this dealkylation reaction.

A dealkylation process involving exclusively the potassium carbonate should not be detrimental to the formation of high molecular weight macromolecules. Indeed, this reaction does not modify the stoichiometry ratio of monomers, which is a key parameter to obtain a polymer by polycondensation via an aromatic nucleophilic substitution reaction. However, if the phenate reagent is involved in this reaction, the polymer chain growth should be affected. To clarify this point, an investigation of a model compound obtained by reaction of the

monomer (A) with two equivalents of 4-fluorobenzophenone, using experimental conditions similar to the polymerization conditions was performed. The resulting crude product after acidification was analyzed by NMR ( $^{31}\text{P}$ ,  $^1\text{H}$ ,  $^{13}\text{C}$ ) and HPLC. As expected, the formation of a slightly hydrolyzed phosphonate product (16% of hemi-phosphonate compound) was confirmed by  $^{31}\text{P}$  NMR, by the presence of a resonance peak at 28.5 ppm, characteristic of an hemi-phosphonate group. Moreover, besides the desired model compound which was the major product, the  $^1\text{H}$  NMR clearly shows the presence of side-product(s), especially in the aromatic region (Figure 10).

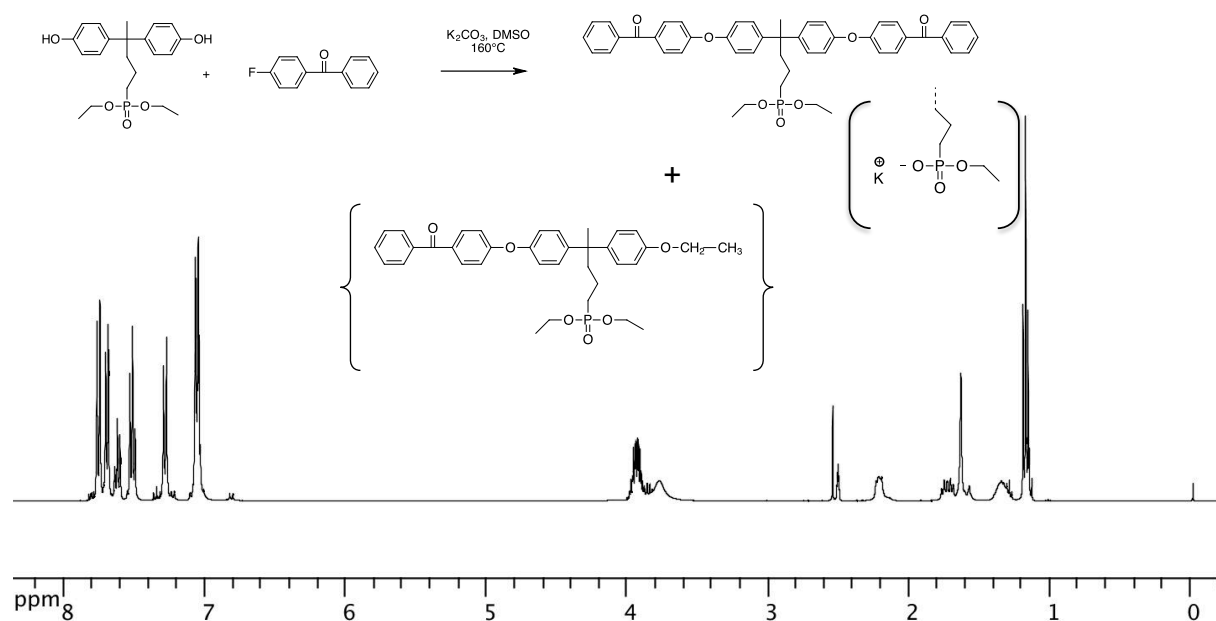


Figure 10.  $^1\text{H}$  NMR spectrum of the crude model compound

Interestingly, the HPLC analysis of the crude product confirmed the presence of at least 4 different compounds (see supporting informations Figure S2). Whereas the molar mass of the two major products were determined by mass spectroscopy, the quantity of the two last minor side-products were insufficient to allow an accurate measurement. As expected, the molar mass of the main product corresponds to the desired model compound. More surprising was the identification of a second compound with a molar mass of 600 g/mol.  $^{13}\text{C}$  NMR analyses support the formation of the the main side –product (S), by a transesterification reaction.

$^{13}\text{C}$  NMR analysis shows the presence of 3 different  $^{13}\text{C}$  of methylene groups in the 55-64 ppm region (Figure 11a). The major peak, at 61.24 ppm, appears as a doublet (6.33 Hz)

because of the coupling with the neighbouring phosphorus atom and corresponds to the phosphonate group of the model compound. A second peak at 60.02 ppm also appears as a doublet (5.83 Hz) and was attributed to the hemi-phosphonate group formed by the partial dealkylation previously evidenced. Finally, a third peak appearing as a singlet at 63.37 ppm which was assigned to  $^{13}\text{C}$  of methylene groups of a phenyl ethyl ether structure. This was confirmed in the 0-18 ppm region (Figure 11b), by the presence of three different  $-\text{CH}_3$ . At 16.65 ppm, the main doublet corresponding to the phosphonate ester compound, at 16.89 ppm a small doublet is attributed to the hemi-ester form, and the last peak at 15.12 ppm is a singlet and characterizes the phenyl ether end group.

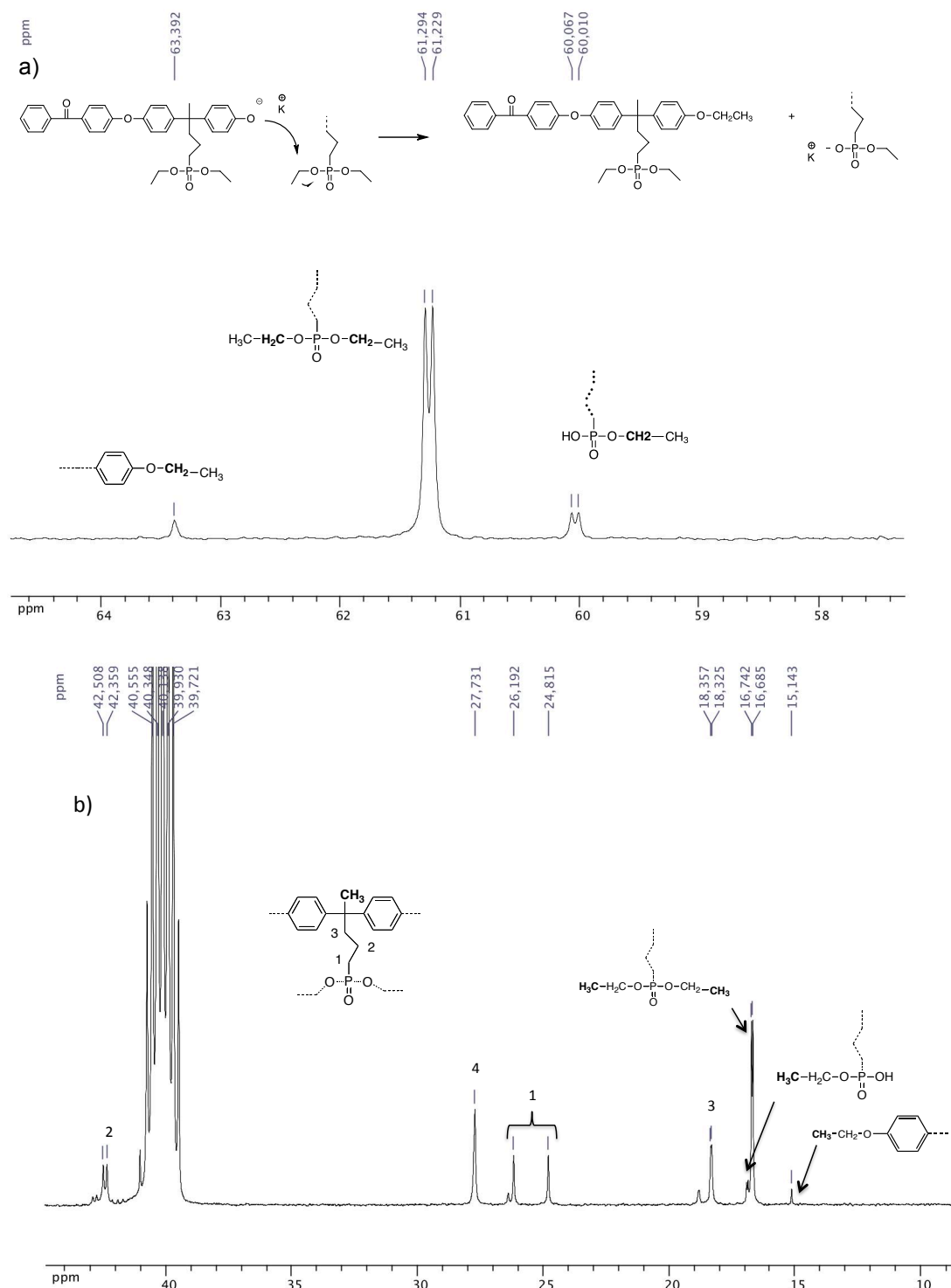


Figure 11.  $^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ ,  $50^\circ\text{C}$ ) spectra (a): 58-64 ppm region, (b): 10-45 ppm region of model compound

This interpretation of results was corroborated by those obtained by a two-dimensional HSQC analysis (see supporting informations Figure S6), namely the formation of an unwanted phenyl ethyl ether side-product. One possible explanation for the formation of this

species relies in a trans-etherification reaction between the phenate reagent and a phosphonate ester group.

Of course, such a reaction during the polymerization process should have a detrimental effect on the polymer chain growth. To avoid this problem, the reaction was performed at lower temperature and it was found that a polycondensation at temperature lower than 100°C was possible. The polymers based on 4,4'-difluorobenzophenone were unfortunately insoluble at this temperature and readily precipitated in the reaction medium. However, 2,6'-difluorobenzonitrile was successfully polymerized and lead to the formation of high molecular weight phosphonated poly(arylether)s. A series of copolymers based on monomer (A) and bisphenol A was obtained. Polymer structures were characterized by  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR (Figure 12 and Figure 13).

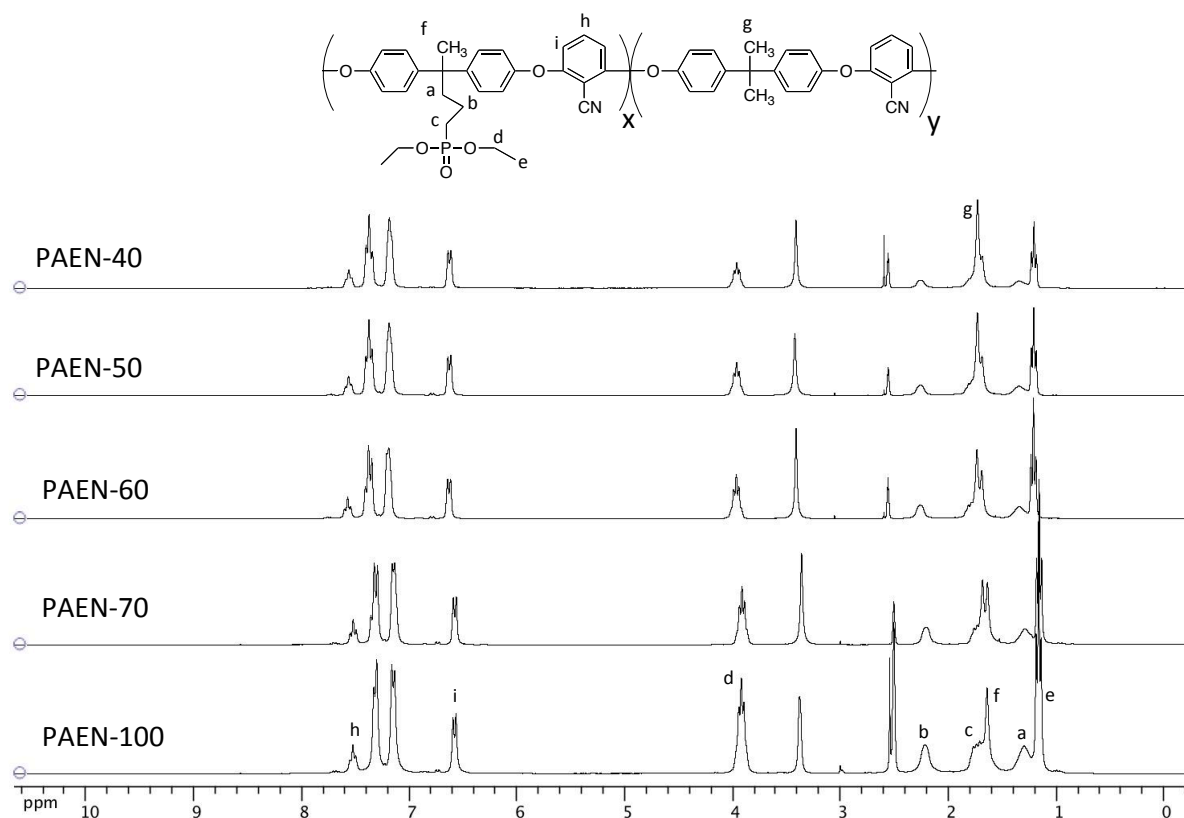


Figure 12.  $^1\text{H}$  NMR (DMSO- $\text{d}_6$ ) spectra of phosphonate ester-containing Poly(Aryl Ether)s



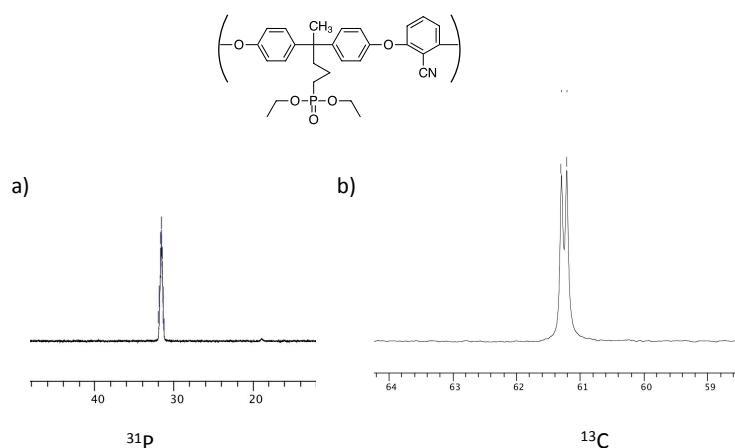


Figure 13. a)  $^{31}\text{P}$  and b)  $^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ ) of PAEN-100

As evidenced in Figure 13 a) less than 1.4% of hemiphosphonate groups were determined by  $^{31}\text{P}$  NMR, suggesting that the undesired trans-etherification side reactions were minimized. This was confirmed by the presence of a unique doublet in the 58-65 ppm region of  $^{13}\text{C}$  NMR, as reported in Figure 13 b) (there is no singlet at 63.4 ppm corresponding to  $\text{PHI-O-CH}_2\text{CH}_3$  and no doublet at 60.2 ppm attributable to the methylene group of the hemiphosphonate is visible). In this case, the very small amount of hemi-phosphonate group formed may be ascribed to a partial dealkylation due to  $\text{K}_2\text{CO}_3$ .

Thin tough films were elaborated by the solvent casting method, from 20%wt polymer solutions in NMP. This result suggests that the polymers had high molecular weights. This was confirmed by size exclusion chromatography measurements (Table 2).

Table 2 Physico-chemical characterizations of phosphonate ester-containing poly(arylether)nitriles

Ref	A (%)	BisA (%)	Mn <sup>a</sup> (kg.mol <sup>-1</sup> )	Mw <sup>a</sup> (kg.mol <sup>-1</sup> )	Td <sub>5%</sub> (°C)	$\Delta_{\text{mTh}}$ (%)	$\Delta_{\text{m}}^{\text{b}}$ (%)	Tg <sup>c</sup> (°C)	Tg <sup>d</sup> (°C)
PAEN-0	0	100	33.5	59.5	455	0	0	164	157
PAEN-40	40	60	50.9	125.9	330	6	7.8	128	135
PAEN-50	50	50	34.9	75.6	318	7.2	8.9	119	124
PAEN-60	60	40	35.6	82.6	322	8.5	9.7	108	116
PAEN-70	70	30	35.7	78.5	312	9.7	11.8	103	110
PAEN-100	100	0	-	-	312	12.2	13.2	77	99

<sup>a</sup> Measured in DMF/LiBr, values determined from PS calibration, <sup>b</sup> weight loss at 350°C. <sup>c</sup> determined by DSC. <sup>d</sup> determined by TMA. -: non soluble in DMF/LiBr

The thermo-oxidative stability of the polymers was evaluated by thermogravimetry analyses (Figure 14). All polymers present good thermal stability as their 5% weight loss temperatures are above 320°C. The first weight loss (determined at 350 °C) corresponds to the decomposition of phosphonate ester groups in phosphonic acid analogues and ethylene, as already reported<sup>[53]</sup>. Condensation of two phosphonic acid groups into anhydride bridge might also occur in this temperature range. Such structures have been described and characterized by X ray analysis by Ponomarev et al.<sup>[35]</sup>. This could explain why the experimental values of the first weight losses are slightly higher than the theoretical ones.

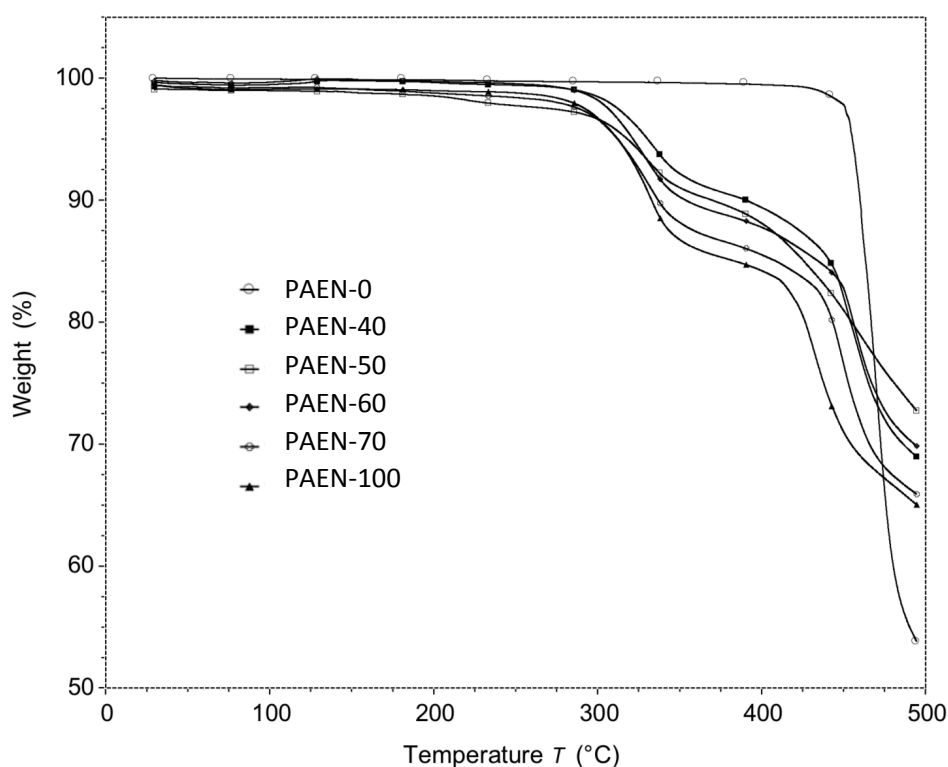


Figure 14. TGA analyses of phosphonate ester containing poly(arylether)nitriles

The glass transition temperatures were determined by DSC and TMA. Both methods evidence a drastic decrease of  $T_g$  as a function of phosphonate ester groups incorporated along the polymer chains. By plotting the evolution of the glass transition temperature versus the mol% of incorporated monomer A (see supporting information Figure S7), a linear relationship is clearly evidenced : the higher the phosphonated ester content, the lower the  $T_g$ . This could be attributed to a plasticizing effect of the alkyl side-chain.

Confirming that the low polymerization temperature is the key parameter to obtain high molecular weight polymers, 4,4'-difluorodiphenylsulfone (E) or decafluorobiphenyl (F) were successfully involved in polycondensation with both phosphonate esters-containing monomers (A) and (B).  $^1\text{H}$  NMR characterization of such structures containing 40% of phosphonated monomer are represented in Figure 15. As evidenced on these spectra, no polymer end groups are visible, which suggest that high molecular weight polymers were synthesized. This hypothesis was confirmed by the successful preparation of tough thin membranes by solvent casting method.

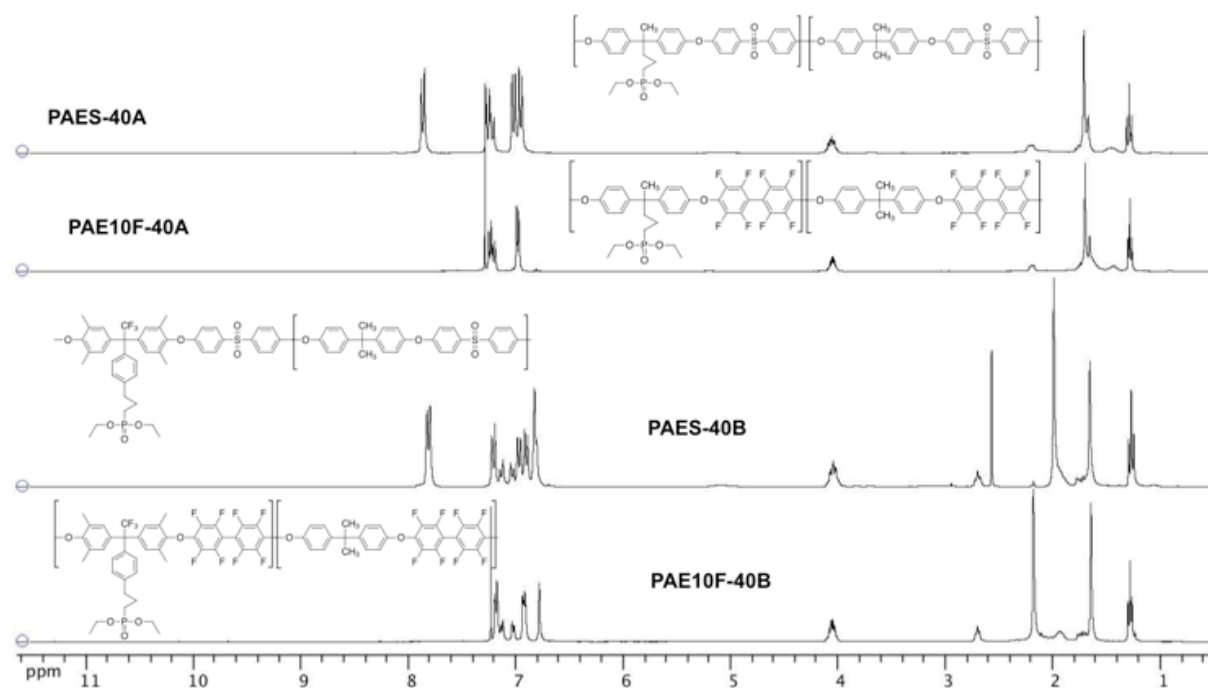


Figure 15.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) characterization of a) PAES-40A, b) PAE10F-40A, c) PAES-40B, PAE10F-40B

As mentioned elsewhere <sup>[17]</sup>, heating phosphonate esters at reflux in concentrated hydrochloric acid results in a complete hydrolysis of those groups into phosphonic acids. Subsequent dealkylation reaction in acidic media of the pre-cited polymers successfully led to phosphonic acid containing polymer analogues. Thorough physico-chemical characterization of such polymers will be reported elsewhere.

## Conclusion

In this work, two side-chain containing phosphonate ester bisphenols were successfully synthesized and characterized. Whereas the dealkylated form of the precursors were not stable enough to be polymerized by aromatic nucleophilic substitution, the phosphonate ester

analogue were incorporated in poly(aryl ether)s by direct polycondensation. When polymerizations were performed at high temperatures, the moderate molecular weights obtained were unambiguously attributed to undesirable trans-etherification reactions. As the reaction temperature was found to be a crucial parameter governing this side-reaction, new insights for the synthesis of high molecular weight phosphonate esters were proposed. While performing the polymerization at mild temperature and involving highly reactive comonomers (2,6-difluorobenzonitrile, 4,4'-difluorodiphenylsulfone, decafluorobiphenyl), high molecular weight polymers containing high proportions of phosphonate ester groups were successfully synthesized. After dealkylation reaction, high molecular weight phosphonic acid containing polysulfones were obtained.

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