

# Synthesis and characterization of diethyl-*p*-vinylbenzyl phosphonate monomer: precursor of ion exchange polymers for fuel cells

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Synthesis of diethyl-*p*-vinylbenzyl phosphonate (DE*p*VBP) monomer and its homopolymer, precursors of ion exchange materials, are reported. DE*p*VBP monomer was synthesized by means of Michaelis-Arbusov reaction of *p*-vinylbenzyl chloride with triethyl phosphite in the presence of cupric chloride using chlorobenzene as solvent with a yield of 75%. Homopolymer was synthesized by free radical polymerization reaction using AIBN as a free radical initiator at 70 °C in DMF. The structures of the compounds were determined from NMR, FT-IR and Raman spectroscopy. Good thermal stability of homopolymer (up to 200 °C) indicates that these compounds are excellent candidates to be used in the development of new proton exchange membranes for fuel cells.

**Keywords:** Ion exchange polymers; Phosphonated polymers; Metallorganic compounds

## 1. Introduction

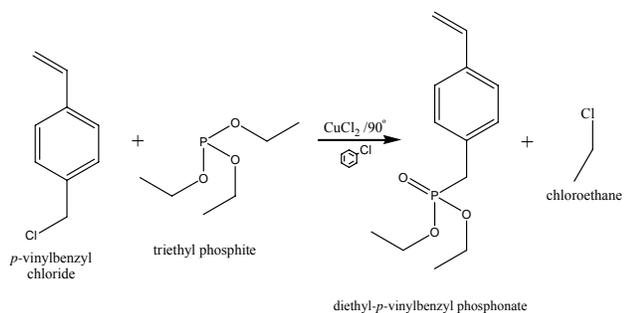
An ion exchange material is a solid that exchanges one ion for another ion. The process of ion exchange involves the change of atoms but with conservation of charge. The ion-containing polymers, such as ion-exchange resins, polyelectrolytes, and ionomers, are an important class of materials which have found use in many areas, such as fuel cells [1], water splitting [2], electro-organic synthesis [3], catalysis [4], and nanoparticles synthesis [5].

To date proton-exchange membrane fuel cells (PEMFC) are the most versatile method for power generation [6]. The proton conducting membranes employed in PEMFCs are today typically based on polymers with hydrated sulfonic acid units. Perfluorinated sulfonic acid membranes have been successfully employed as proton conductors in fuel cells based mainly on the catalytic oxidation of hydrogen [7]. The acid units of the polymer works as proton source and are dissociated by water which acts as the proton solvent and thus facilitates the proton transport [7].

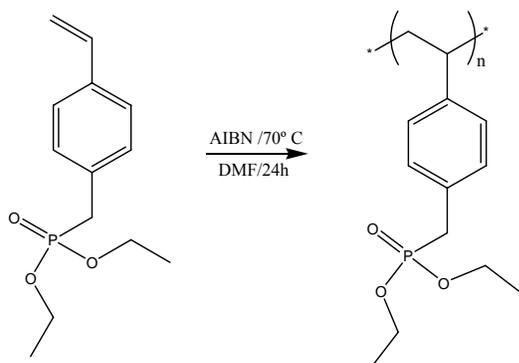
Acid group-containing polymers have attracted much attention as solid electrolyte membranes in batteries and fuel cells. In particular, the polymers functionalized with phosphonic acid have recently attracted attention as an alternative material for proton-exchange membrane fuel cells to sulfonic acid copolymers. There have been several reports of phosphonic acid-containing polymers as membranes for fuel-cell applications [8]. They have lower acidity than sulfonic acids; however, their better chemical and thermal stability with respect to corresponding sulfonic acid-functionalized polymers offers potential advantages. However, phosphonic acid groups grafted onto the polymer

main chains used as alternative ion exchange group have not been widely investigated due to the difficulty to produce C-P bonds [9, 10]. Also, most of these syntheses involve a large number of reactions steps [6]. A simple way to prepare phosphonated materials is the modification of available molecules with phosphorylating agents using the Arbusov or Michaelis-Becker reactions, in which alkyl halides react with trialkyl phosphites to form dialkyl alkylphosphonates [11, 12]. Diethyl-vinylbenzyl phosphonate is a very interesting monomer that has been synthesized by Cabbaso and co-workers [12, 13] from the reaction of vinylbenzyl chloride (a mixture of *meta* and *para* isomers 7:3) with triethyl phosphite in presence of 6-*ter*-butyl-2,4-dimethylphenol, with a 68 % yield.

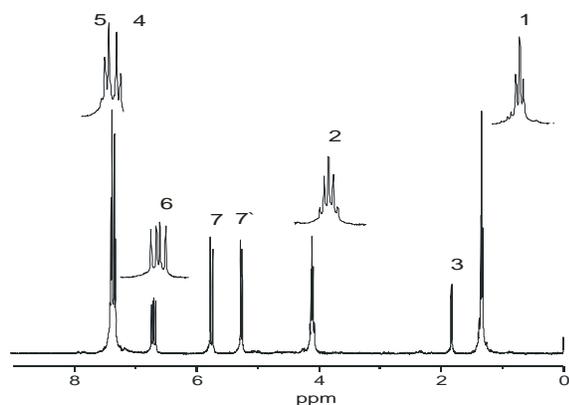
In the present work, we report the synthesis, characterization, and polymerization of diethyl-*p*-vinylbenzyl phosphonate (DE*p*VBP) monomer. It was prepared by means of Michaelis-Arbusov reaction using a modified Cabbaso method, where the main differences were the use of CuCl<sub>2</sub> and chlorobenzene as inhibitor agent of the monomer polymerization and solvent, respectively, in air atmosphere. Also, we use only the *para* isomer of vinylbenzyl chloride compound (with a purity of 98%) as precursor of the DE*p*VBP monomer. It was purified by flash chromatography (silica gel, chloroform) obtaining a yellow liquid with a yield of 75%. The polymerization of DE*p*VBP was carried out via free radicals, using 2,2'-azobisisobutyronitrile (AIBN) as a free radical initiator and



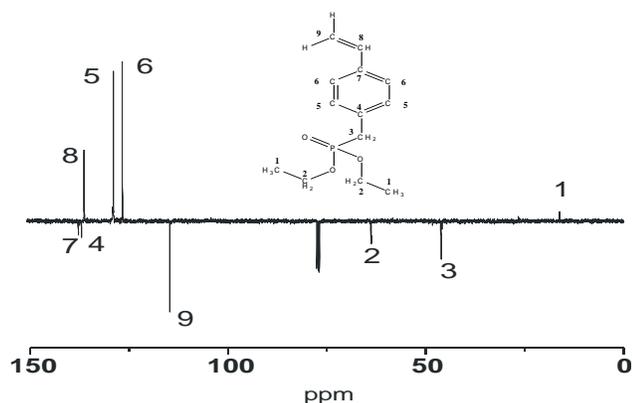
**Scheme 1.** Michaelis-Arbusov reaction of diethyl-*p*-vinylbenzyl phosphonate.



**Scheme 2.** Free Radicals polymerization of the diethyl-*p*-vinylbenzyl phosphonate.



**Figure 1.** <sup>1</sup>H-NMR spectrum of the DEpVBP monomer



**Figure 2.** <sup>13</sup>C APT NMR spectrum and molecular structure of the DEpVBP monomer.

dimethylformamide as solvent at 70°C with 24 hours reaction time in argon atmosphere. Formation and molecular structures of the synthesized compounds were confirmed from their infrared (IR), and Raman spectra as well as from their elemental analysis. Thermal stability of homopolymer was studied by thermogravimetric analysis (TGA).

## 2. Experimental Section

### 2.1. Materials

Triethyl phosphate (98% purity), *p*-vinylbenzyl chloride, CuCl<sub>2</sub> and AIBN, each with 99% purity, were purchased from Aldrich. Initiator AIBN was recrystallized using methanol. All solvents were used as delivered.

### 2.2. Synthesis of diethyl-*p*-vinylbenzyl phosphonate (DEpVBP) monomer

DEpVBP monomer was prepared by means of Michaelis-Arbusov reaction (scheme 1) according to modified method from the reference 13. A 50 mL three-necked flask equipped with a mechanical stirring device, reflux condenser and thermometer was charged with 1.23 mL (7.04 mmol) of triethyl phosphite, 2 mL (14.19 mmol) of *p*-vinylbenzyl chloride, 2 g (7.03 mmol) of CuCl<sub>2</sub> as inhibitor of the polymerization of *p*-vinylbenzyl chloride and 1 mL of chlorobenzene as solvent. The mixture was heated to 90 °C for 2 h. After this period, the reaction mixture was cooled at room temperature and the unreacted triethyl phosphite was removed at room temperature in vacuum. The crude product was purified by flash chromatography on silica gel using chloroform, and dried at room temperature in vacuum for 12 h, obtaining 1.35 g (yield 75%) of DEpVBP monomer as a yellow liquid. Elemental analysis found: C 61 % and H 7.2%; calculated for C<sub>13</sub>H<sub>19</sub>PO<sub>3</sub>: C 61.41 % and H 7.48%. <sup>1</sup>H NMR (400 MHz, d<sub>3</sub>-chloroform): δ 7.39 (d, 8.04 Hz, 2H, Ar-H), 7.33 (d, 8.2 Hz, 2H, Ar-H), 6.70 (m, 1H, CH=C), 5.76 (d, 17.57 Hz, 1H, C=CH<sub>2</sub>), 5.27 (d, 10.98 Hz, 1H, C=CH<sub>2</sub>), 4.11 (m, 4H, O-CH<sub>2</sub>), 1.82 (s, 2H, CH<sub>2</sub>-P), 1.33 (t, 6.96 Hz, 6H, C-CH<sub>3</sub>). <sup>13</sup>C APT NMR (100 MHz, d<sub>3</sub>-chloroform): δ 16.02 (CH<sub>3</sub>), 46.02 (CH<sub>2</sub>), 63.69 (CH<sub>2</sub>), 114.75 (CH<sub>2</sub>=), 126.51 (Ph), 129.03 (Ph), 136.35 (CH=), 136.95 (Ph), and 137.75 ppm (Ph). FT-IR (KBr pellets): 3088, 2979, 2929, 2868, 2342, 1913, 1828, 1681, 1630 (vinyl C=C), 1608 (Ar C=C stretch), 1569, 1512, 1479, 1443, 1421, 1405, 1375, 1266 (P=O stretch), 1214 1166, 1113, 1099 (P-O-C stretch), 1032 (P-O-C stretch), 989, 912, 843, 730, 682, 629, 542, 483 and 430 cm<sup>-1</sup>.

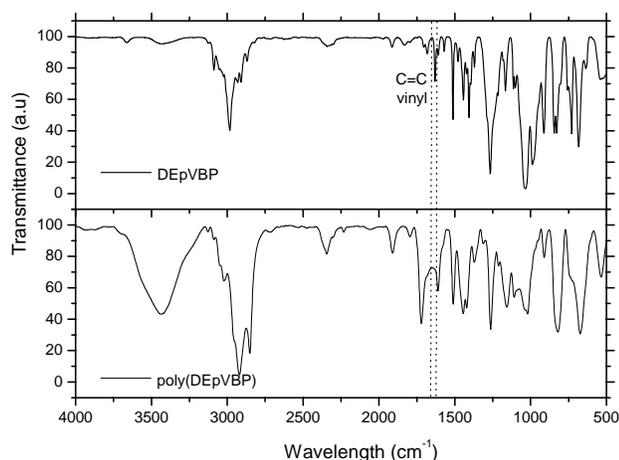


Figure 3. IR spectra of the DEpVBP and poly(DEpVBP).

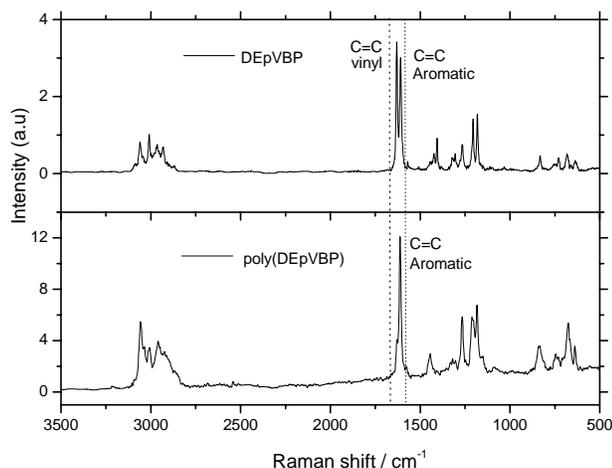


Figure 4. Raman spectra of the DEpVBP and poly(DEpVBP).

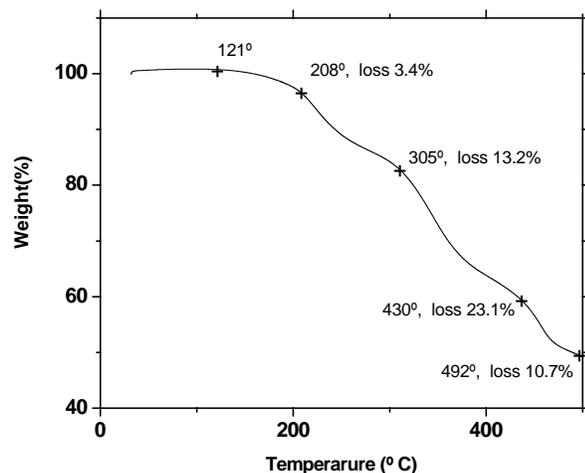


Figure 5. TGA curve of poly (DEpVBP).

### 2.3. Synthesis of homopolymer poly(diethyl-*p*-vinylbenzyl phosphonate)

DEpVBP monomer was polymerized by free radicals reaction in DMF using AIBN as a free radical initiator (scheme 2). 0.635 g of monomer and 8.62 mg (2 wt % of the monomer) of initiator were charged in a glass test tube containing 1 mL of DMF, which was bubbled with argon gas for 20 min. The test tube was then sealed under argon and placed in a constant temperature (70 °C) water bath for 24 h. After this period, the reaction mixture was cooled to room temperature, and the polymer was isolated by precipitation of the product in cold water (10 times the volume of the reaction mixture) and with subsequent drying at 90 °C in vacuum for 2 h. The homopolymer in form of a light brown solid was obtained with a 68 % yield (0.432 g).

### 2.4. Characterization

<sup>1</sup>H NMR and <sup>13</sup>C APT NMR spectra of the samples were recorded on JEOL 400 (400 MHz/100 MHz) NMR spectrometer, using deuterated chloroform and tetramethyl silane (TMS) as the internal reference. IR spectra were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrophotometer, with a spectral resolution of 4 cm<sup>-1</sup>. For FTIR studies, 1 mg of solid sample was mixed with 99 mg of dry KBr homogeneously to make pellets of 7 mm diameter and 0.5 mm thick. Raman spectra were recorded on a Raman Perkin-Elmer system 2000 spectrophotometer.

Elemental analysis of the samples was carried out on a Perkin-Elmer C, H, N analyzer (model 2400). Thermogravimetric measurements of the compounds were carried out with a Mettler-Toledo thermal analyzer TGA/SDTA 851. The measurements were performed from room temperature to 500 °C, at a heating rate of 10°C/min under nitrogen atmosphere.

## 3. Results and discussion

### 3.1. Monomer characterization

Formation and molecular structure of the DEpVBP was confirmed from their <sup>1</sup>H NMR, <sup>13</sup>C APT NMR, infrared, and Raman spectra. Figure 1 shows the <sup>1</sup>H NMR spectrum of the DEpVBP monomer and the results are summarized in the Table 1. The most important signals for the compound, which indicate its formation were the multiplet at 6.70 ppm assigned to the proton on the CH=C group, the doublets at 5.76 and 5.27 ppm assigned to the protons on the CH<sub>2</sub>=C, the multiplet at 4.11 ppm assigned to the protons on O-CH<sub>2</sub>, the singlet localized at 1.82 ppm corresponding to the protons of P-CH<sub>2</sub>, and the triplet at 1.33 ppm for the protons of CH<sub>3</sub>-C group.

The <sup>13</sup>C APT NMR spectrum of the DEpVBP (Figure 2) revealed nine signals. The main signals that confirming the formation of compounds were localized at 114.74 and

136.35 ppm corresponding to the C atoms of the vinyl group; the signals at 16.02 and 63.69 ppm due to the C atoms on the CH<sub>3</sub> and CH<sub>2</sub> of the diethyl-phosphonate group, respectively.

Formation of the DEpVBP is also evident from their FTIR and Raman spectra (see Fig. 3 and Fig. 4). IR spectrum revealed strong absorption bands due to the P=O stretching vibration mode at 1266 cm<sup>-1</sup>, P-O-Et stretching at 1099-1020 cm<sup>-1</sup>, P-O-C stretching at 989 cm<sup>-1</sup>, all corresponding to the -PO(CH<sub>2</sub>CH<sub>3</sub>) group; C=C stretching vibration mode at 1630 cm<sup>-1</sup> of vinyl group; and C=C stretching at 1608 cm<sup>-1</sup> of phenyl group. These assignments were based on literature vibrational studies of organic and phosphonate materials [14-17]. On the other side, in the Raman spectrum the signals corresponding to the C=C stretching modes of the vinyl and phenyl groups appeared at 1630 cm<sup>-1</sup> and 1607 cm<sup>-1</sup>, respectively.

### 3.2. Polymer characterization

The poly(DEpVBP) homopolymer was found to be soluble in several polar solvents like ethanol, methanol, DMF, and DMSO; but insoluble in toluene, cyclohexane, and water. Formation of the homopolymer was followed by Raman and IR spectroscopies. Fig. 3 and Fig. 4 show the IR (4000-400 cm<sup>-1</sup>) and Raman (in the spectral range of 3500-500 cm<sup>-1</sup>) of the monomer and polymer, indicating the region correspond to the C=C stretch. It is clear from Raman spectra that the principal evidence of polymer formation came from the disappearance of the signal due to C=C stretching vibration mode of vinyl group of the monomer. In the IR spectrum of the polymer (Figure 3) also the absorption band due to C=C stretching of the vinyl group is absent.

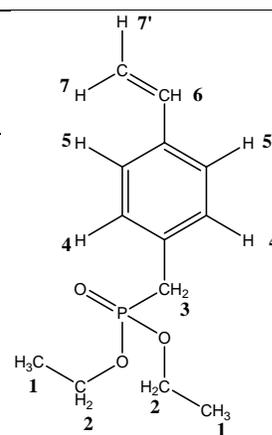
Thermal stability of the poly(DEpVBP) was studied through thermogravimetric measurements realized at a heating rate of 10°C/min under nitrogen atmosphere. Figure 5 Thermogravimetric curve of the polymer shows distinct regions of weight loss with the increase of temperature. The first, a gradual weight loss of about 3.4 % in the temperature range 120-208 °C was attributed to the evaporation of water and DMF. In the second region (208-305 °C), about 13.2 % of the weight loss was associated to the partial thermal degradation of poly(DEpVBP) due to the loss of the ethyl ester group of the vinylbenzyl phosphate. Thermal degradation of VBP due to the loss of ester groups has been reported at 240-250 °C [13]. Progressive thermal degradation of the polymer observed between 305 and 500 °C, is probably due to the degradation of the main chain of polymer and the degradation of P-C bonds of the pendant group of polymer. These results indicate that the poly(DEpVBP) synthesized is stable until 208 °C. Above this temperature, the degradation of polymer occurs in several steps, resulting in the loss of about 47 % of the weight of polymer.

### 4. Conclusions

DEpVBP monomer was synthesized by means of Michaelis-Arbusov reaction using CuCl<sub>2</sub> as inhibitor agent and chlorobenzene as solvent, with a yield of 75%. Synthesis process permits to improve the yield on reported (68%). Poly(DEpVBP) synthesized by free radicals polymerization shows a good thermal stability until 208 °C. Molecular structures of the synthesized compounds were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C APT NMR, IR, and Raman spectroscopies. Owing to the ion exchange capacity conferred by the phosphonate group and the good thermal

**Table 1.** Assignment of <sup>1</sup>H-NMR peak positions of the DEpVBP monomer.

Chemical Shift δ (ppm)	Integration	Multiplicity	J <sub>H-H</sub> (Hz)	Assignment
7.39	2	d	8.04	H <sup>5</sup>
7.33	2	d	8.2	H <sup>4</sup>
6.70	1	m	---	H <sup>6</sup>
5.76	1	d	7.57	H <sup>7</sup>
5.27	1	d	10.98	H <sup>7'</sup>
4.11	4	m	---	H <sup>2</sup>
1.82	2	s	---	H <sup>3</sup>
1.33	6	t	6.96	H <sup>1</sup>



s = singlet, d = doublet, t = triplet and m = multiplet

stability of polymer, the DEpVBP and poly(DEpVBD) is under study by our research group for the synthesis of copolymers useful as polymer exchange membranes for fuel cells.

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