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Phosphonic acid-containing homo-, AB and BAB block copolymers via ATRP designed for fuel cell applications

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ABSTRACT

The synthesis of various block copolymers containing phosphonic acid moieties is described. Poly(styrene)/PDEVBP AB block copolymers were obtained by atom transfer radical polymerization (ATRP) of diethyl *p*-vinylbenzyl phosphonate (PDEVBP). Subsequently, BAB block copolymers with tailored architecture composed of the phosphonated monomer and poly(ether ether ketone) were obtained by a combination of polycondensation chemistry and ATRP. The quantitative deprotection of the ethyl phosphonates led to the corresponding free phosphonic acids, which can be applied as polymer electrolyte membranes for fuel cells. In addition, all materials showed high thermal stability. The proton conductivity properties of the ionomers were investigated. The phosphonic acid-containing (co)polymers exhibited a linear increase of the conductivity with the temperature with a maximum value of 4.5×10^{-4} S/cm in anhydrous conditions.

1. Introduction

Proton-exchanging membrane fuel cells (PEMFC) have gained considerable attention in both academia and industry as a substitute for conventional fuel driven engines in automotives [1–3]. The most important component of the PEMFC is the proton-exchanging polymer electrolyte membrane bearing protogenic groups as a source for protons, which ensures efficient proton transport through the formation of a dynamic hydrogen bond network [4–6]. Phosphoric and phosphonic acid derivatives in particular are considered suitable candidates as ionomers because of their efficient proton transport according to the Grotthuss mechanism [6–14]. They are both amphoteric and possess a relatively high dielectric constant [6,12]. Moreover, they are able to perform even in anhydrous conditions. The combination of these properties is an important requirement for membranes operating in a high temperature regime [12–14].

In order to apply these ionomers in proton-exchanging membranes, they have to be incorporated into a polymer matrix, which is typically a high performance polymer such as poly(benzimidazole) [15–17]. The major disadvantage of these membranes is that water, which is formed during the operation of the fuel cell, dilutes and washes out the acid. To overcome these problems, covalent bonding of the acid to a suitable polymer matrix is suggested [18–21]. An extensively studied example which proves this concept is poly(vinylphosphonic acid) (PVPA), a polymer exhibiting the highest local concentration of phosphonic acid groups [12,13,22,23]. The “nominally dry” PVPA shows a conductivity of about 10^{-3} S/cm at 160 °C in low humidity atmosphere [13]. However, this polymer suffers from the so-called “condensation” problem, which describes the anhydride formation of the phosphonic acids. This side reaction blocks the proton transport and leads to a significant irreversible loss of proton conductivity [13].

Therefore, the synthesis of a new type of polymeric phosphonic acids with optimized architectures and minimum or no anhydride formation is still needed. We propose the formation of membranes with a gyroid-type 3D structure. In such materials, the proton-conducting layer would be separated from the second phase, acting as a scaffold to stabilize the membrane. Similar structures have already been obtained by block copolymers. The development of synthetic protocols, therefore, for the synthesis of amphiphilic block copolymers containing phosphonic acid moieties is essential. Amphiphilic statistical copolymers bearing phosphonic acid esters can be obtained via free radical copolymerization of the corresponding monomers [24–29]. However, the synthesis of block copolymers requires living polymerization techniques. As ionic polymerization has failed, here controlled radical polymerization [30–34] is considered a suitable alternative method.

Some attempts have already been made at the nitroxide-mediated radical polymerization of diethyl vinylbenzylphosphonate (DEVBP). However, low polymerization rates, nonlinear dependence of conversion upon molecular weight and polymers with rather broad molecular weight distributions were obtained [35,36]. We chose atom transfer radical polymerization (ATRP) as an alternative

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because it provides well-defined homo- and block copolymers of numerous monomers [31–34].

In this paper, we report the homopolymerization of DEVBP by copper-mediated ATRP. The efficiency of the method was proven by synthesizing AB block copolymers of DEVBP with styrene. In addition, BAB block copolymers of PDEVBP with poly(ether ether ketone) (PEEK) were successfully obtained. In this approach, a bisfunctional telechelic macroinitiator based on PEEK was used in the ATRP. The hydrolysis of the synthesized polyphosphonates led to the corresponding phosphonic acid-containing homo- and block copolymers. In order to prove the applicability of the polymers as proton exchanging membranes for fuel cells, the thermal stability as well as the proton conductivity was investigated.

2. Experimental section

2.1. Materials

All chemicals were obtained from commercial sources and used without further purification unless otherwise noted. Tris[2-di(benzyl acrylate) aminoethyl] amine (BzA_6TREN) was synthesized via Michael addition of benzylacrylate and tris(2-aminoethylamine) according to the literature [37]. The monomer diethyl vinylbenzylphosphonate (DEVBP) was obtained using the Arbuzov reaction starting from *p*-vinylbenzyl chloride [26]. The product was purified by column chromatography on silica, eluting first the unreacted vinylbenzyl chloride with CH_2Cl_2 and then changing to ethyl acetate for the elution of DEVBP. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.33 (d, 2H), 7.21 (dd, 2H), 6.66 (dd, 1H), 5.7 (d, 1H), 5.2 (d, 1H), 4.22–3.98 (m, 4H), 3.11(d, 2H), 1.26 ppm (t, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) 136.3, 136.1, 130.9, 129.7, 126.17, 113.5, 61.8, 34.4, 32.3, 16.2; ^{31}P NMR (202 MHz, $CDCl_3$): δ (ppm) 25.6; FD-MS: *m*/*z* 254.5 [calcd. 254.27].

2.2. Homopolymerization of DEVBP (polymers ***1a–i***)

ATRP of DEVBP was performed in bulk using the CuBr/Ligand catalytic system. The ligands used to form a catalytic complex with CuBr were 2,2′-bipyridine (bpy), 4,4′-di-tertbutyl-2,2′-bipyridine (dTbpy), *N*,*N*,*N*′,*N*′,*N*″-pentamethyl diethylene triamine (PMDETA) and BzA_6TREN.

2.2.1. Representative polymerization

An oven-dried Schlenk flask was charged with the desired amount of monomer, CuBr and ligand (L). The flask was purged with argon for 0.5 h before adding the initiator α-methylbenzyl bromide (1 mol% related to the monomer). The mixture was deoxygenated by several freeze–pump–thaw cycles and placed in an oil bath adjusted to the desired polymerization temperature. Polymerization was allowed to proceed until the mixture became very viscous and further stirring was impossible. The polymer was dissolved in CH_2Cl_2 and precipitated in hexane. The sample was purified by redissolving in a minimum amount of CH_2Cl_2 and passing through a short column filled with neutral Al_2O_3. After evaporation of the solvent the polymer was dried in vacuum at room temperature for at least 12 h. The yields of polymerization were measured gravimetrically. ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 1.1 (b, 8H), 1.8 (b, 1H), 2.97 (b, 2H), 3,88 (b, 4H), 6.3–6.9 (b, 4H); ^{31}P NMR (202 MHz, DMSO-d_6, triphenylphosphine (TPP) as standard) δ (ppm): 27.7 (s).

2.3. Synthesis of the poly(styrene) macroinitiators (***2***)

The poly(styrene) macroinitiators **2** were synthesized via ATRP in bulk using 0.5, 1, and 2 mol% of initiator α-methylbenzyl bromide with CuBr/PMDETA catalytic system for 24 h at 110 °C. The polymers were precipitated in methanol, redissolved in CH_2Cl_2 and passed through a column of neutral Al_2O_3 to remove the catalyst. The yields varied between 75 and 85%.

2.4. ATRP of DEVBP using poly(styrene) macroinitiators. Synthesis of AB block copolymers (***3a–d***)

AB block copolymers of poly(styrene) and PDEVBP were obtained by performing ATRP using the desired amount of the macroinitiator in 50% anisole solution at 110 °C for 48 h with different CuBr/L catalytic systems. All mixtures were degassed by three freeze–pump–thaw cycles prior to polymerization. The molar ratio of 1:6 for Cu(I) to the ligand was taken in all cases. The polymerizations were quenched by the addition of CH_2Cl_2. The copolymers were precipitated in hexane, washed and dried overnight. For purification the samples were dissolved in CH_2Cl_2, passed through a column of neutral Al_2O_3 and dried to constant weight after evaporation of the solvent. The molecular weights of the products were calculated from the corresponding ^1H NMR spectra.

2.5. Synthesis of α,-ω-bishydroxy-telechelic poly(ether ether ketone) (***4***)

To synthesize α,-ω-bishydroxy-telechelic poly(ether ether ketone) (**4**), 3.5 g (15,33 mmol) of Bisphenol A, 3.0218 g (13,85 mmol) of 4,4′-difluorobenzophenone and 6.35 g (46 mmol, three-fold excess) of K_2CO_3 in 50 ml DMAc and 12.5 ml toluene were mechanically stirred under a Dean–Stark trap in a nitrogen atmosphere. The reaction mixture was heated to 150 °C for 3 h, at which point the formed water was removed via azeotropic distillation with toluene. The polycondensation was further allowed to proceed at 165 °C for 20 h. After cooling to room temperature, an excess of Bisphenol A (0.167 g, 0.00073 mol) dissolved in 3 ml DMAc and 1 ml toluene were added. The system was heated for another 3 h at 165 °C. The reaction mixture was then allowed to cool to 70 °C, diluted with 40 ml of DMAc and held for another 2 h. After cooling, the mixture was poured into 600 ml of cold water acidified with several drops of glacial acetic acid. The polymer was washed with methanol and dried at 100 °C overnight. After reprecipitation from THF into water/methanol and subsequent drying, a white polymer was obtained in 85% yield, with a number-average molecular weight (M_n) of 3500 g/mol and PDI = 2.6 (measured by GPC in THF using poly(styrene) standards). ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.7 (d, four aromatic protons from the repeating unit, *ortho* to the ketone junction), 7.2–6.9 (eight aromatic protons from the repeating unit), 7.1 (d, 2H) and 6.77 (d, 2H) four aromatic protons of the end group, 5.78 (OH), 1.63 (s, CH_3 of the repeating unit), 1.57 (s, CH_3 of the end-groups); ^{13}C NMR (62.5 MHz, $CDCl_3$, 25 °C) δ (ppm): 30.97 ($\mathbf{C}H_3$), 42.36 ($\mathbf{C}$–CH_3), 117.09, 128.25, 119.52, 132.17, 146.7, 153.5, 161.4 (aromatic carbons from the repeating unit), 114.8, 127.76, 142.37, 147.4 (aromatic carbons from the end-group), 194.25 (C=O).

2.6. Synthesis of PEEK macroinitiators

2.6.1. Functionalization of polymer **4** with 2-bromoisobutyryl groups (macroinitiator **5**)

A solution of 2-bromoisobutyryl bromide (0.097 g, 4.2×10^{-4} mol, 0.052 ml) in 1 ml THF was added dropwise to a solution of polymer **4** (0.5 g, 1.4×10^{-4} mol, M_n (GPC) = 3500 g/mol, PDI = 2.6) in 10 ml dry THF at room temperature, followed by the addition of triethylamine (0.04 g, 0.06 ml in 1 ml THF). The reaction mixture was allowed to react at this temperature for 40 h. It was then precipitated in methanol, washed several times to remove residual 2-bromoisobutyryl bromide and low molecular weight by-products. After re-precipitation from THF into methanol, the macroinitiator was dried at 90 °C overnight. Yield: 87%. The polymer **5** had M_n (GPC) = 4400 g/mol and PDI = 2.2. ^{1}H NMR (250 MHz, $CDCl_3$): Along with all characteristic signals for PEEK, a new signal at 2.01 ppm was observed, corresponding to the CH_3 protons of the end-capper; ^{13}C NMR (62.5 MHz, $CDCl_3$, 25 °C) δ (ppm): In addition to the spectra of **4**, three new signals from the end-capper were observed: at 27.19 ppm a new signal corresponding to **C**H_3 groups, at 55.38 a signal from **C**–CH_3 and at 132.15 ppm a new signal corresponding to the carbonyl group of the ester formed.

2.6.2. *Functionalization of polymer **4** with α-chlorophenylacetyl groups (macroinitiator **6**)*

The macroinitiator **6** was synthesized by derivatization of **4** (0.5 g, 1.4×10^{-4} mol, M_n (GPC) = 3500 g/mol, PDI = 2.6) with α-chlorophenylacetyl chloride (5.63×10^{-4} mol) in the presence of triethylamine (0.08 ml) at 70 °C for 40 h. The product was precipitated in methanol, washed several times with water and re-precipitated from THF in methanol. Yield: 90%; M_n (GPC) = 4700, PDI = 2.0. ^{1}H NMR (250 MHz, $CDCl_3$): Three new signals were observed along with all characteristic signals for PEEK: 7.3–7.5 ppm – aromatic protons form the end-capping unit and 5.48 ppm a singlet for the CH group. ^{13}C NMR (62.5 MHz, $CDCl_3$, 25 °C) δ (ppm): In addition to the spectra of **4**, new signals for the end-capper were observed at 59.01 ppm corresponding to **C**HClPh, in the region of 129.5–132 ppm for the aromatic carbons and at 135.3 ppm a signal due to the carbonyl group of the ester.

2.7. *ATRP of DEVBP using PEEK macroinitiators. Synthesis of BAB block copolymers (**7**)*

ATRP was conducted using CuX/L as transition metal complex (X = Br or Cl), in 50% anisole solution at 110 °C for CuBr – mediated polymerization and at 130 °C for CuCl – mediated ATRP process. The reactions were stopped after the prescribed time by cooling in a water jet and quenching with CH_2Cl_2. The mixtures were then precipitated in a large excess of *n*-hexane. The products were washed several times and dried in air to constant weight. The molecular weights of the products were calculated from the corresponding ^{1}H NMR spectra. A detailed procedure for ATRP polymerization using **6**/CuCl/bpy system is given below:

4.7 mg CuCl (4.7×10^{-5} mol), 14.7 mg (9.4×10^{-5} mol) bpy and 10.88 mg (2×10^{-6} mol) of the macroinitiator **6** were dissolved in 0.5 ml anisole at room temperature under argon. The formation of the catalytic transition metal complex was evidenced by a change in color to dark brown. 0.5 g (2×10^{-3} mol) monomer DEVBP was subsequently added. The reaction mixture was then degassed by three freeze–pump–thaw cycles and immersed in a thermostated oil bath adjusted to 130 °C. After 48 h the polymerization was stopped by cooling and diluted with CH_2Cl_2. The product was precipitated in hexane, washed and dried in vacuum at room temperature. The molecular weight of the product was calculated by ^{1}H NMR and it was found to be 124 000 g/mol (Sample **7b**, Table 3).

2.8. *Hydrolysis of the DEVBP-containing materials. Preparation of poly(vinylbenzylphosphonic acid) containing homopolymers (**8**), AB (**9**) and BAB (**10**) block copolymers*

The hydrolysis of PDEVBP was performed using bromotrimethylsilane (TMSBr)/methanolysis approach. Typically, the phosphonate was reacted with a 5-fold molar excess of TMSBr relative to the phosphonate groups in CH_2Cl_2 (5% solution) at room temperature for 24 h. After evaporation of the volatiles, the silylated ester was reacted with a large excess of methanol at room temperature for 24 h. PVBPA (**8**) was obtained in quantitative yield after evaporation of the solvent under reduced pressure and drying in vacuum at room temperature for at least 12 h. ^{1}H NMR (250 MHz, methanol-d_4) δ (ppm): 1.1–2.0 (b, 3H), 2.9 (b, 2H), 6.1–7.5 (b, 4H); ^{31}P NMR (202 MHz, DMSO-d_6, triphenylphosphine (TPP) as standard) δ (ppm): 24.8 (s).

The hydrolysis of the block copolymers **3** and **7** to the corresponding phosphonic acid-containing derivatives (**9** and **10**) was performed using the same methodology.

2.9. *Characterization*

The molecular weight and PDI indexes were calculated using gel permeation chromatography (GPC). GPC measurements were performed against narrow-dispersed poly(styrene) standards on a Waters 150CALC/GPC device with UV and RI detectors equipped with a Styragel columns using THF at 30 °C or DMF at 60 °C as the mobile phase.

^{1}H NMR, ^{13}C NMR and ^{31}P spectra were recorded in $CDCl_3$ and DMSO-d_6 on a Bruker DPX 250, Bruker AMX 300 or Bruker DRX 500 spectrometer. The solvent proton or carbon signals were used as internal standard for the ^{1}H NMR and ^{13}C NMR measurements respectively, while triphenylphosphine (TPP) was applied for the calibration of the ^{31}P NMR measurements.

Thermal gravimetric analyses (TGA) were performed on a Perkin Elmer TGA 7 thermogravimetric analyzer (10 K/min heating rate in nitrogen atmosphere).

Temperature-dependent conductivity in dry conditions was measured using a Schlumberger SI1260 impedance/gain phase analyzer with a dielectric interface in the frequency range from 10^{-1} to 10^6 Hz and in the temperature regime from 20 to 160 °C. The measurement was performed in a Novocontrol cryostat (Novocontrol, Hundsangen, Germany). The sample was placed between two Pt electrodes and controlled with nitrogen gas. Conductivity measurements in pure water vapor ($p(H_2O) = 1$ atm) were carried out on a Hewlett–Packard 4192A LF AC-impedance analyzer in a double-walled temperature-controlled glass chamber with heated gas inlet and outlet. The sample was placed in a porous glass cylinder and contacted with Pt/C electrodes from E-Tek.

3. Results and discussion

3.1. *Polymerization of DEVBP*

For the first time, copper-mediated ATRP has been applied as a polymerization technique for DEVBP [38]. One of the very important factors influencing the efficiency of this type of polymerization is the appropriate choice of the initiating system. As the most effective initiators in ATRP have similar structures as the monomers [31], an aromatic bromide, i.e. α-methylbenzyl bromide, was chosen. The selection of the ligand is also an efficient way to control the ATRP process by modifying the solubility and reactivity of the catalyst. It has been observed that the lower redox potential of the catalyst leads to a higher polymerization efficiency [30,31,39]. In principle, the activity of the catalytic complex increases with the increasing of the number of nitrogen coordination sites of the ligand, which subsequently decreases the redox potential of the complex formed [39].

Four different ligands were evaluated to coordinate to Cu(I)Br, namely 2,2′-bipyridine (bpy), 4,4′-di-tertbutyl-2,2′-bipyridine (dTbpy), *N,N,N′,N′,N″*-pentamethyl diethylene triamine (PMDETA) and tris[2-di(benzyl acrylate)aminoethyl]amine (BzA$_6$TREN) (Fig. 1). Bpy and dTbpy are bidentate ligands possessing two nitrogen atoms in the molecule and therefore two complexing centres. PMDETA is a tridentate ligand incorporating three coordinating centres, while

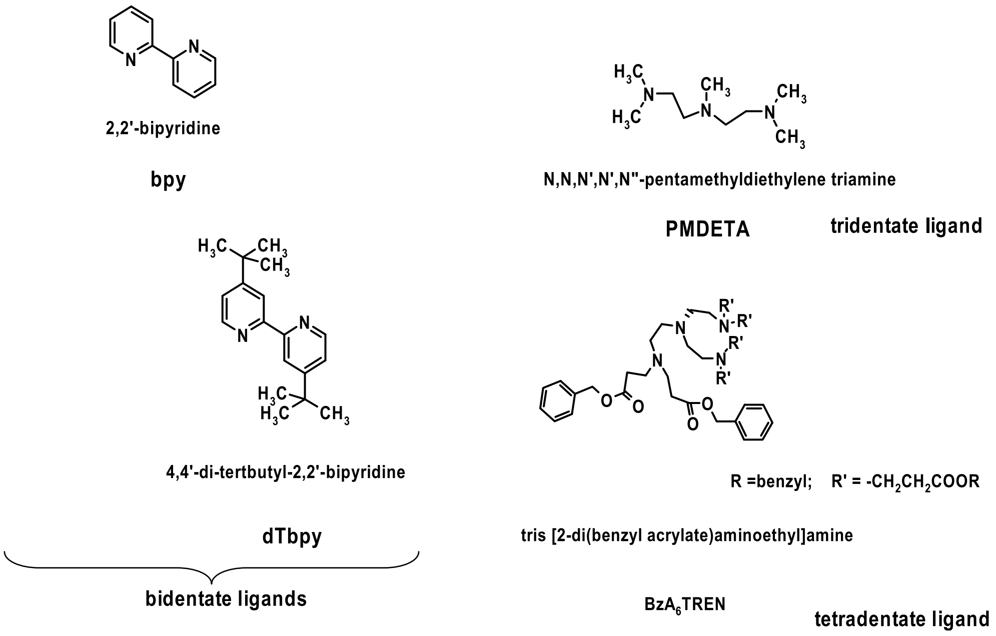


Fig. 1. Ligands used in the ATRP polymerization of DEVBP.

BzA_6TREN belongs to a group of tripodal ligands with four nitrogen atoms.

The presence of the phosphonate group was expected to cause problems during the ATRP process by stabilizing the propagating radicals and thus leading to extremely slow polymerization rates and difficulties in controlling the molecular weight and molecular weight distributions (PDI). For that reason, a combination of α-methylbenzyl bromide exhibiting high initiating efficiency and a less reactive catalytic complex comprised of CuBr/bpy was initially selected (Table 1, Sample **1a**). The polymerization was performed in bulk, using a molar ratio of monomer to initiator to Cu(I) to bpy of 100:1:1:6 with target molecular weight of 2.56×10^4 g/mol as calculated from the applied monomer to initiator molar ratio. After 24 h at 90 °C, no polymerization was observed. The heating was continued for another 24 h at 110 °C, which led to a polymer with a very low PDI of 1.2 and a molecular weight much higher than expected (Sample **1a**, Table 1). The polymer yield was only 50% after 48 h, indicating a very slow propagation rate. The low polymerization yield, along with the much higher than expected M_n, could be caused by low initiator efficiency, combined with a chain transfer to the polymer during the propagation step. The alkyl substitution of bpy at the 4 and 4′ positions was reported to improve the catalytic activity of the complex by increasing its solubility [39]. A set of polymerizations using this ligand was carried out at 110 °C applying different concentrations of dTbpy relative to the CuBr (Samples **1b**–**c**, Table 1). However, in both cases the molecular weights of the polymers were much lower than expected and the PDIs in the range of 1.6–1.7, which suggests that significant termination reactions occurred at the early stages of the polymerization.

PMDETA is known to have pronounced catalytic activity compared to the bipyridine ligands [39]. Therefore, several experiments with CuBr/PMDETA as catalytic complex were performed using different Cu(I) to ligand molar ratios and reaction temperatures. A polymer with M_n close to the expected one and PDI of 1.5 was obtained when the catalytic complex was composed of Cu(I) and PMDETA in 1:1 molar ratio at 90 °C, indicating a controlled process (Sample **1d**, Table 1). The polymer was obtained after 16 h in 53% yield. An extremely fast polymerization rate was observed when the concentration of the ligand was increased to 1:6 relative to Cu(I) leading to a polymer with very high molecular weight and broad PDI in 30% yield (Sample **1e**, Table 1). Besides the concentration of the ligand during the formation of the catalytic complex, it was found that the polymerization temperature influences the degree of polymerization and the macromolecular characteristics of the obtained polymers (Samples **1f**–**g**, Table 1). Applying an initial concentration of the components of 100:1:0.5:0.5 at 110 °C gave an oligomer ($M_n = 1.2 \times 10^3$ g/mol) with low PDI in 59% yield (Sample **1f**). However, a polymer with high molecular weight and PDI of 1.2 was obtained when the molar ratio of 1:6 of CuBr-to-PMDETA was used at the same temperature (Sample **1g**).

Table 1
ATRP of DEVBP.

Sample	[M]:[In]:[Cu(I)]:L	L	Time (h)	T (°C)	Yield (%)	M_n (g/mol)	PDI
1a	100:1:1:6	Bpy	48	[a]	50	1.5×10^5	1.2
1b	100:1:1:3	dTbpy	20	110	82	1×10^3	1.7
1c	100:1:1:6	dTbpy	12	110	30	3×10^3	1.6
1d	100:1:1:1	PMDETA	16	90	53	2.2×10^4	1.5
1e	100:1:1:6	PMDETA	0.5	90	30	1.4×10^5	2.5
1f	100:1:0.5:0.5	PMDETA	24	110	59	1.2×10^3	1.3
1g	100:1:1:6	PMDETA	16	110	55	1.6×10^4	1.2
1h	100:1:1:6	BzA_6TREN	24	110	77	1×10^3	2.0
1i	100:1:1:10	BzA_6TREN	0.7	110	65	1×10^4	1.9

[a] $\Delta = 90$ °C for 24 h and 110 °C for another 24 h.

The tripodal ligand BzA_6TREN, however, did not show further improvement in the control of the ATRP of DEVBP (Samples **1h**–**i**). Applying 100:1:1:6 molar ratio of the reagents gave an oligomer with a broad PDI of 2.0 in 77% yield (Sample **1h**), while a polymer with M_n of 1×10^4 g/mol and the same broad PDI was obtained when the concentration of the ligand was further increased as Cu(I) to $L = 1{:}10$ (Sample **1i**).

The phosphonates belong to a special class of monomers possessing diverse reactivity in radical processes. Several groups studied the radical polymerization of phosphonated monomers gave contradictory information about the real mechanism of initiation and propagation and have found to be extremely complicated [40–42]. In addition, the presence of the phosphonate group causes difficulties to control the macromolecular characteristics of the produced polymers by stabilizing the growing macroradicals.

Similar problems with the control over the ATRP process were observed by Huang and Matyjaszewski in the polymerization of dimethyl(1-ethoxycarbonyl)vinyl phosphate [43]. A possible explanation for the difficulties in the ATRP polymerization of the phosphonate-containing monomer could be the complexation of the Cu ion with the phosphonate group of the monomer through the phosphoryl oxygen [43,44].

Several attempts to calculate M_n of the PDEVBP via ^{1}H NMR spectroscopy were done in order to prove the controlled character of the ATRP. The evaluation was performed by comparison of the relative intensities of the signal at 5.32 ppm, which is characteristic for the $C\underline{H}$–Br end group, and any of the signals for the PDEVBP at 2.93 ppm (CH_2 at the benzyl position), 3.86 ppm (CH_2 of the ethyl ester group) or the aromatic region at 6.15–7.10 ppm. Such calculation was possible only for polymers with M_n below 1×10^4 g/mol and relatively narrow PDIs. Thus, the calculated number average molecular weight from the ^{1}H NMR spectrum of a PDEVBP sample was 9.0×10^3 g/mol, which is in good agreement with the value obtained by GPC, M_n of 8.4×10^3 g/mol (the sample is not listed in Table 1). This polymer exhibited a PDI of 1.6. However, it was not possible to perform such calculation for the narrow-dispersed polymers having higher molecular weight, due to the very low intensity of the signal for the methyne proton of the ending repeating unit.

The homopolymerization of DEVBP via copper-mediated ATRP was studied as a model. An evaluation of several ligands in combination with CuBr was performed in order to identify a suitable catalytic system leading to polymers with an M_n close to the theoretical one in reasonable good conversions and apply them to a further block copolymer synthesis. Thus, CuBr/PMDETA was found to be the best catalytic system for the copper-mediated ATRP of DEVBP. Polymers with controlled molecular weight and relatively narrow PDI in the range of 1.2–1.5 were obtained depending on the molar ratio of the transition metal and the ligand during the formation of the catalyst and the polymerization temperature.

3.2. Synthesis of poly(styrene)/PDEVBP AB block copolymers

The ability to polymerize DEVBP via copper-mediated ATRP was further investigated in order to synthesize well-defined amphiphilic block copolymers. In this case, narrow-dispersed polystyrene macroinitiators **2** were applied leading to AB type block copolymers (**3a**–**d**) comprised of hydrophobic polymer and phosphonate containing-polymer. For that purpose, polystyrene macroinitiators (**2**) of different molecular weights were first synthesized via ATRP in bulk using α-methylbenzyl bromide as initiator and CuBr/PMDETA as a catalytic system.

The molecular weight of the macroinitiators varied from 6.0 to 21.5×10^3 g/mol with PDIs in the range of 1.23–1.4. The influence of the CuBr/L catalytic system on the copolymerization and copolymer composition was studied using different ligands to coordinate with Cu(I)Br during the formation of the catalyst (Table 2).

Attempts to measure the molecular weight and PDI indexes of the copolymers via GPC failed, probably due to the strong interaction of the materials with the chromatography columns independent of the degree of polymerization of DEVBP. Thus, the molecular weights of the block copolymers were calculated by ^{1}H NMR (Table 2, Fig. 2).

The molecular composition of the block copolymers and the number-average molecular weight (M_n) of the PDEVBP block were calculated from the relative intensities of the ^{1}H NMR signals at 2.9 ppm corresponding to the $\mathbf{CH_2}$–Ph group from the phosphonate-containing polymer and the aromatic protons of both polystyrene and PDEVBP (5 H and 4 H respectively) at 6.4–7.3 ppm.

The conversion of DEVBP strongly depended on the type of the ligand used for the formation of the catalytic complex. The non-substituted bidentate ligand bpy was inactive in the ATRP polymerization. The reaction mixture was heterogeneous during the polymerization and no copolymers were obtained within 72 h. However, a very low conversion of about 4% was observed when the *tert*-butyl substituted bpy (dTbpy) was used in the formation of the catalytic complex (**3a**).

The other two ligands, PMDETA and BzA_6TREN exhibited a pronounced effect on the solubilization of the Cu(I) and the polymerizations of DEVBP in all cases were homogeneous. Surprisingly, both ligands showed similar catalytic activity in spite of the different number of coordinating centers. Polymers with maximum conversion of about 32% were obtained independently of the molecular weight of the applied polystyrene macroinitiator (**3b**–**d**).

3.3. Synthesis of PEEK/PDEVBP BAB block copolymers

It is known that the PDI indexes of block copolymers are of minor importance for their bulk morphology and self-assembly. Moreover, a broad range of micro- and mesoscopic ordering can be easily achieved by simple tailoring the composition of polydisperse block copolymers [45–47]. ATRP is a powerful technique offering an easy access to block copolymers especially when a combination of a chain-growth and step-growth processes is desired. There are several examples in the literature dealing with such combination, where polysulfones and poly(carbonates) were the common examples for step-growth polymers, while polystyrene, poly(methylmethacrylate) or poly(n-butyl acrylate) were usually applied as chain-growth polymers [32–34]. In this paper, we report

Table 2
ATRP of DEVBP using polystyrene macroinitiators.

Sample	M_n of 2 g/mol (GPC)	Ligand	M_n Block B (^{1}H NMR) g/mol	Conversion%	M_n Total (M_n Block A + M_n Block B) g/mol
3a	6×10^3	dTbpy	1.0×10^3	3.92	7.0×10^3
3b	6×10^3	PMDETA	8.2×10^3	32.2	1.4×10^4
3c	21.5×10^3	BzA_6TREN	8.1×10^3	31.9	3.0×10^4
3d[a]	21.5×10^3	PMDETA	81.4×10^3	32.0	10.3×10^4

Reaction conditions: 50% anisole solution; $\Delta = 110\,^{\circ}C$; time: 48 h. [M]-to-[**2**] = 100:1.
M_n of the macroinitiators **2** (Block A) was measured by GPC calibrated with narrow-dispersed poly(styrene) standards in THF at 30 °C.
[a] [M]-to-[**2**] = 1000:1.

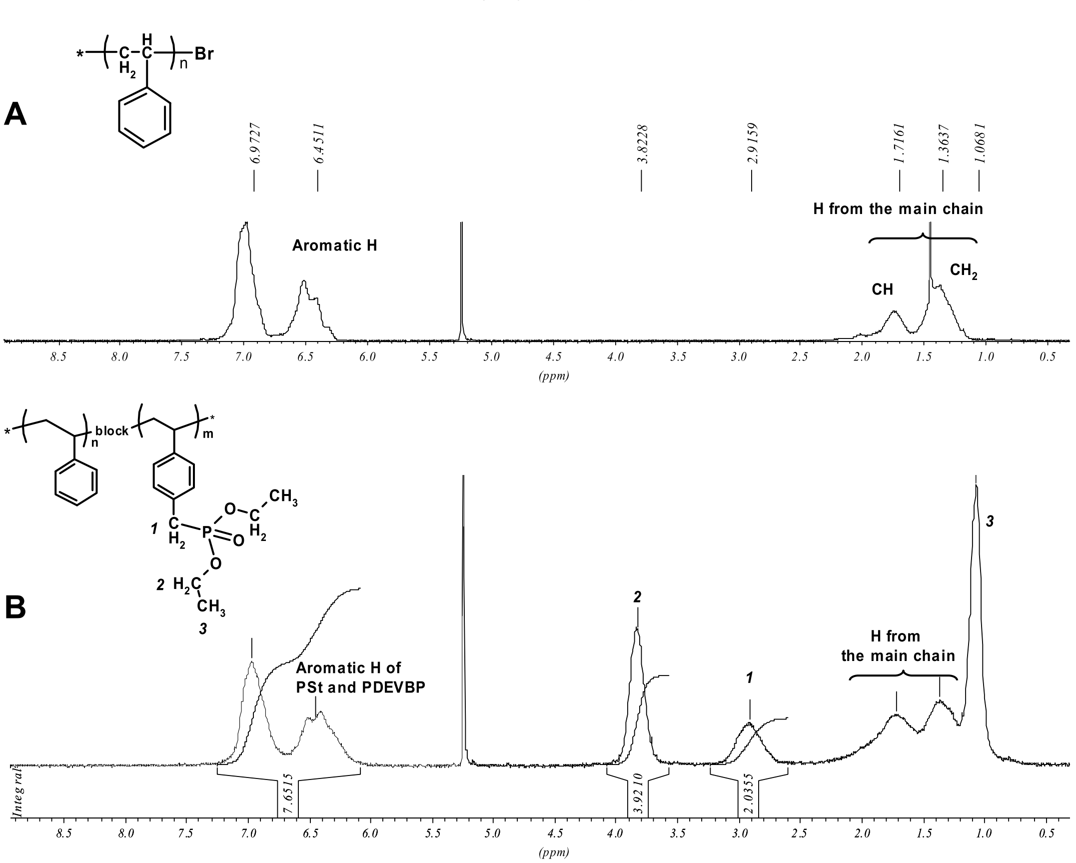


Fig. 2. ^{1}H NMR of the polystyrene macroinitiator (A) and of the corresponding AB block copolymer Sample **3b**, Table 2 (B).

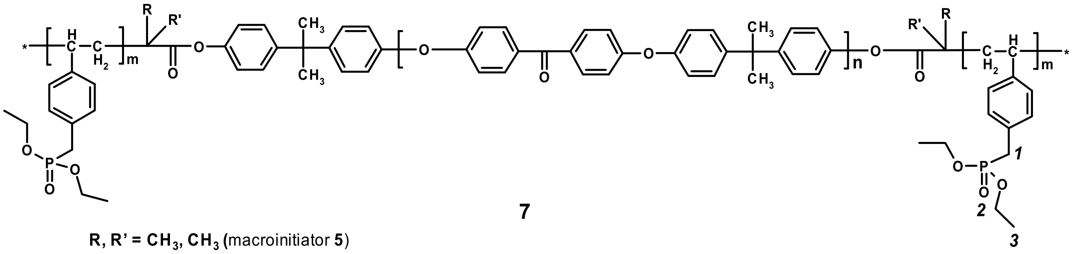
the synthesis of poly(ether ether ketone) (PEEK)/PDEVBP BAB block copolymers (Fig. 3) using a combination of polycondensation and copper-mediated ATRP. For that reason a bifunctional PEEK macroinitiator was applied.

We chose a telechelic PEEK as suitable step-growth polymer for the formation of BAB block copolymers with DEVBP. A bishydroxy-telechelic PEEK (**4**) with a targeted molecular weight of 4000 g/mol (degree of polymerization = 10) was synthesized via nucleophilic aromatic substitution (S_NAR) between 4,4′-difluorobenzophenone and Bisphenol-A in *N*,*N*′-dimethylacetamide at 165 °C in the presence of anhydrous K_2CO_3. An excess of Bisphenol A over difluorobenzophenone was used in order to control the functionality and molecular weight. After re-precipitation from THF into water/methanol, polymer **4** was obtained in 85% yield. The molecular weight of the polymer was calculated using GPC and ^{1}H NMR spectroscopy. The result from GPC (THF as eluent at 25 °C) gave $M_n = 3500$ g/mol and PDI of 2.6.

In the ^{1}H NMR spectrum of polymer **4** (Fig. 4A), the signal at 1.63 ppm corresponds to 6 protons from the methyl groups of the repeating unit (**5**), the signal at 1.57 ppm corresponds to the methyl protons of the end group. At 5.78 ppm there is a signal corresponding to the terminal OH-groups. In the region of 6.9–7.2 ppm there are signals assigned to the eight aromatic protons of the repeating unit (*ortho* to the ether junction, **2**,**3**). The two doublets at 6.7 and 7.1 ppm correspond to the four aromatic protons of the end groups. The signal at 7.7 ppm results from absorption of the repeating unit (*ortho* to ketone junction, **1**). Thus, integration of these regions allowed the determination of the chain length of the polymer. The molecular weight of the PEEK was calculated by comparison of the signals at 7.7 ppm and 6.7 ppm, resulting in $M_n = 4000$ g/mol. PEEK with a target degree of polymerization of 5 and 20 was synthesized in a similar manner.

Subsequently, two different macroinitiators were synthesized by esterification of the polymer **4** with either 2-bromoisobutyryl bromide (macroinitiator **5**) or α-chlorophenylacetyl chloride (for macroinitiator **6**) (Scheme 1).

The derivatization of **4** with α-chlorophenylacetyl chloride led to macroinitiator **6** containing a chloride group at the benzyl



7

R, R' = CH_3, CH_3 (macroinitiator **5**)

R, R' = Ph, H (macroinitiator **6**)

Fig. 3. PDEVBP-*block*-PEEK-*block*-PDEVBP synthesized via ATRP.

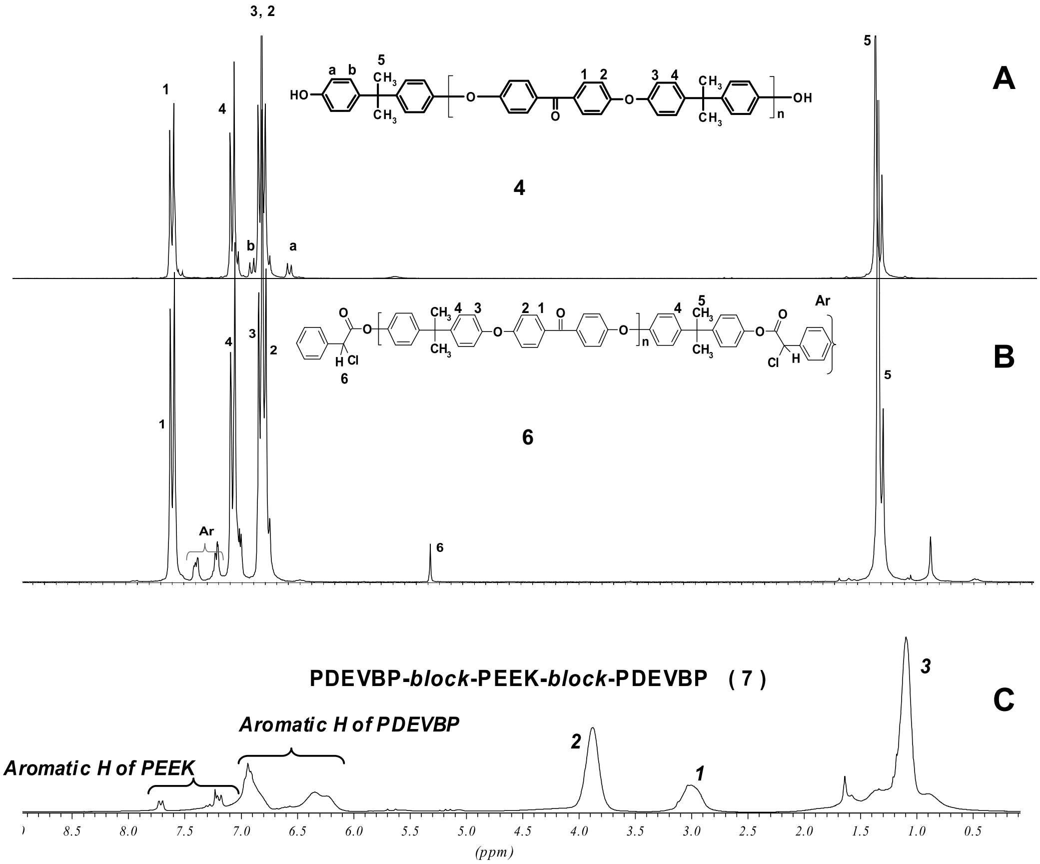


Fig. 4. ^{1}H NMR spectra of the starting PEEK **4** (**A**), the macroinitiator **6** (**B**) and the resulting PDEVBP/PEEK BAB block copolymer (**C**). The signals for the BAB block copolymer are assigned from Fig. 3.

position and was expected to be efficient for the ATRP polymerization of styrene and diethyl *p*-vinylbenzyl phosphonate, which can be considered as functionalized styrene. In an analogous way, the macroinitiator **5** was synthesized using 2-bromoisobutyryl bromide. The macroinitiators were prepared using an excess of the acyl halide via a triethylamine catalysed esterification reaction and both were isolated in approximately 90% yield after purification and were characterized by ^{1}H and ^{13}C NMR spectroscopy.

In the ^{1}H NMR spectrum of **6** (Fig. 4B) three new signals of the end-capper were observed: at 5.48 ppm there is a signal corresponding to methyne protons (C**H**) and at 7.3 and 7.5 ppm two signals related to the five aromatic protons from the end-group. The number average molecular weight of the macroinitiator **6** (Table 3) was calculated by evaluation of the relative intensities of the signals at 7.7 ppm (4H from the repeating unit) and 5.48 ppm (methyne protons of the end-groups). In the ^{1}H NMR spectrum of **5** the signal for the OH-groups disappeared and a new signal at 2.01 ppm was observed, corresponding to 6 protons from the two methyl groups of the end-capper. The number average molecular weight of **5** ($M_n = 4700$ g/mol) was calculated in a similar way to **6** by comparison of the signals at 7.7 ppm and 2.01 ppm (CH_3 protons of the end-groups). The number average molecular weights calculated by ^{1}H NMR spectroscopy for both macroinitiators were in good agreement to the values obtained by GPC using poly(styrene) standards.

The macroinitiators were not soluble in the DEVBP monomer, thus anisole was used as a suitable solvent for the experiments.

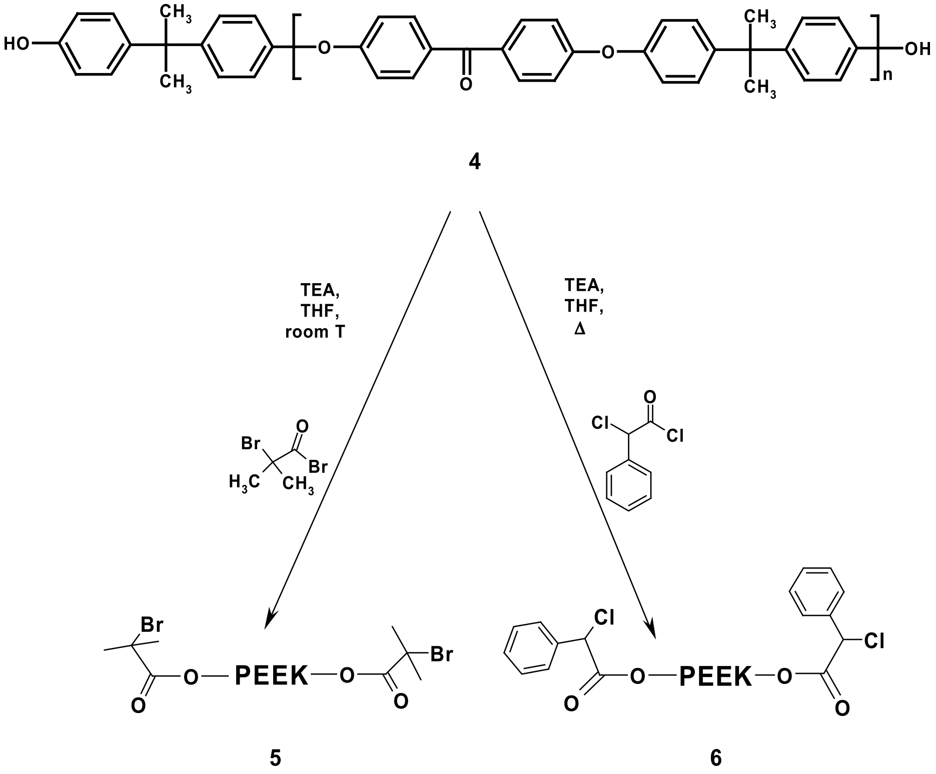
ATRP of DEVBP initiated by macroinitiator **5** was carried out at 110 °C for 48 h. As the solubility of the copper complexes in the polymerization media is a decisive criterion for the efficiency of the ATRP process, the four different ligands, already tested for the homopolymerization of this monomer and in the syntheses of the polystyrene/PDEVBP AB block copolymers, were examined in order to obtain BAB block copolymers of different compositions, i.e. bpy, dTbpy, PMDETA and the tripodal BzA$_6$TREN. However, PEEK/PDEVBP BAB block copolymers were obtained only when the tripodal BzA$_6$TREN ligand was applied to coordinate with CuBr. The concentration of the macroinitiator was varied from 0.1 to 1 mol% relative to the monomer. In both cases, poor initiator efficiency was observed. The conversion of DEVBP to the desired block copolymer was found to be relatively low, i.e. 35% and 40% respectively. A possible reason for the lower efficiency of the bromo-functionalized macroinitiator could be the structural difference of the initiating group. The nature of the initiating unit plays a crucial role in the initiating and propagating steps of the ATRP process.

Copper-mediated ATRP polymerization of DEVBP initiated by macroinitiator **6** was carried out in 50% anisole solution at 110 °C (with CuBr) and at 120–130 °C (with CuCl) using various ligands to form active transition metal complexes.

The mixed initiating system based on R–X/Cu–Y (X, Y = Cl or Br) has been extensively investigated [33,42,48]. This technique has been successfully applied for various monomers and shows better control over the polymerization when compared to the R–X/Cu–X.

Several experiments to polymerize DEVBP via ATRP initiated by macroinitiator **6** with different CuBr/L catalytic systems were performed. However, in all cases the transition metal complex was not active and no polymerization was observed.

PEEK/PDEVBP BAB block copolymers of various compositions (**7a**–**k**) were successfully obtained applying ATRP of DEVBP initiated by macroinitiator **6** and using CuCl/L catalytic system. All block copolymers were characterized by ^{1}H NMR spectroscopy (Fig. 4C).



Scheme 1. Synthesis of well-defined telechelic PEEK macroinitiators suitable for ATRP.

The methyl and methylene protons of the ethyl ester group were observed at 1.1 and 3.9 ppm respectively. At 3.0 ppm the signal of the methylene protons at the benzyl position was observed, while in the region 1.1–2 ppm there was a broad signal for the protons of the PDEVBP main chain. The signal at 6.3–6.9 ppm was assigned to the aromatic protons of the PDEVBP block. All these signals exist in the ^{1}H NMR spectra of the BAB block copolymer in conjunction with the characteristic signals of the PEEK. The degree of polymerization (DP) of DEVBP and the molecular weight of the products were calculated by evaluating the relative signal intensities of the aromatic protons of PEEK (7.7 ppm 4H from the repeating unit) and the aromatic protons from PDEVBP (6.3 ppm).

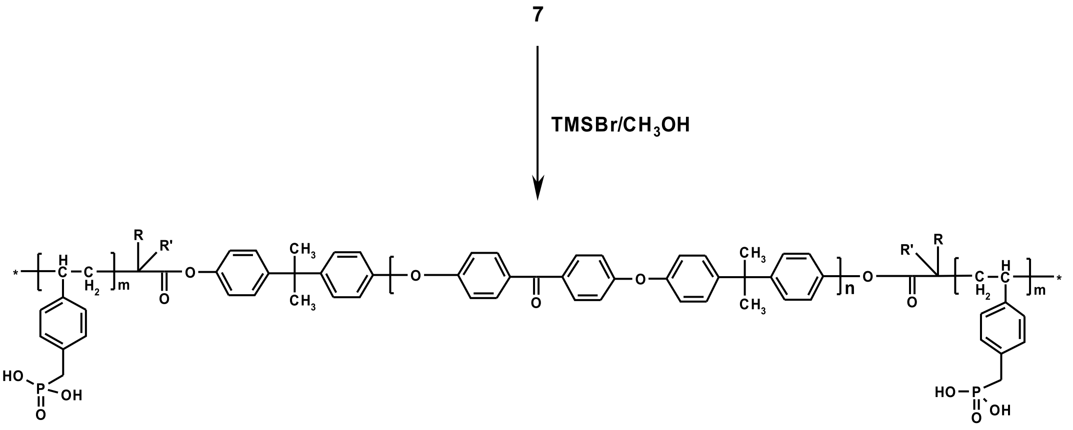
The influence of polymerization time, temperature and the type of ligand were investigated in detail (Table 3). ATRP processes initiated by RCl/CuCl/L system were generally slow. This discrepancy can be explained by the stronger C–Cl bonding. CuCl/bpy mediated ATRP polymerization of DEVBP using macroinitiator **6** did not produce block copolymers after 24 h at 130 °C. Increasing the reaction time to 48 h led to the desired products in higher conversion. Due to the observed lower polymerization rate, all of the experiments were performed for 48 h and longer.

The different solubility of the copper complexes also played a significant role. Within a polymerization time of 48 h, higher conversion of DEVBP to the BAB block copolymer was obtained using the catalytic system Cu(I)/bpy (Samples **7a**–**b**, Table 3). A concentration of 1 and 0.1 mol% of the macroinitiator was applied leading to a reasonably good conversion of 40 and 60% respectively. The influence of polymerization time and temperature was investigated using the dTbpy and BzA$_6$TREN ligands. In the conditions applied for the bpy ligand and using 1 mol% of the macroinitiator, a polymer with a lower degree of polymerization of 14 was obtained in 30% yield (Sample **7c**). Similar results were observed when the concentration of the macroinitiator was decreased (Sample **7f**). Polymers of slightly higher molecular weight were obtained when the polymerization time was increased to 72 h although the temperature of the experiment was 120 °C. The highest conversion of 70–80% (Samples **7e** and **7g**) using the same catalytic system was achieved when the polymerization was

Table 3
ATRP approach to PDEVBP-*block*-PEEK-*block*-PDEVBP (Fig. 3, Samples **7a**–**k**) using macroinitiator **6**.

Sample	[M]/[I]/[CuCl]/[L]	L	M_n of **6** (^{1}H NMR)	Reaction temperature (°C)	Time (h)	DP of DEVBP (^{1}H NMR)	M_n Product g/mol (^{1}H NMR)	Yield (%)
7a	100/1/1.5/2.5	bpy	4000	130	48	66	20 800	40
7b	1000/1/24/48	bpy	4000	130	48	472	12 4000	60
7c	100/1/2.5/20.5	dTbpy	4000	130	48	14	7400	30
7d	100/1/2/12	dTbpy	2000	120	72	22	7460	38
7e	100/1/2/20	dTbpy	4000	130	72	42	14 600	80
7f	1000/1/24/48	dTbpy	4000	130	48	198	54 000	50
7g	1000/1/24/48	dTbpy	4000	130	72	416	110 000	70
7h	100/1/3/30	BzA$_6$TREN	4000	130	48	12	6900	30
7i	1000/1/24/48	BzA$_6$TREN	4000	130	48	136	38 400	30
7j	250/1/2/12	BzA$_6$TREN	2000	120	72	59	17 000	70
7k	150/1/2/12	BzA$_6$TREN	2000	120	72	35	11 000	60

Polymerizations were performed in 50% anisole solution.
Yields were measured gravimetrically.



PVBPA/PEEK BAB block copolymer (10)

Fig. 5. Hydrolysis of the BAB block copolymers **7** to the corresponding phosphonic acid-containing compounds **10**.

performed for 72 h at 130 °C. The CuCl/BzA$_6$TREN complex showed even lower catalytic activity in comparison to the bpy and its substituted derivative (Table 3, Samples **7h**–**k**). The conversion of DEVBP was only 30% when the polymerization was allowed to proceed at 130 °C for 48 h (Samples **7h** and **7i**). Increasing the reaction time to 72 h but processing at a lower temperature of 120 °C gave polymers with a higher degree of polymerization. The maximum conversion achieved in these conditions was about 70%. Surprisingly, in all cases the tridentate ligand PMDETA was found to be inactive.

In all cases, the conversion was kept below 100% in order to avoid side reactions such as the recombination of the growing macroradicals. The molecular weight of the PDEVBP blocks and the BAB block copolymers respectively depended on the concentration of the macroinitiator. The degree of polymerization increased linearly with the concentration of the initiator. The maximum achieved degree of polymerization calculated from the ^{1}H NMR spectra was found to be 472 (Sample **7b**). The obtained polymer exhibited M_n close to the theoretical one, indicating a controlled process.

*3.4. Deprotection of the phosphonates to the corresponding phosphonic acid-containing materials (**8**, **9**, **10**)*

The conversion of PDEVBP (**1**) to the poly(vinylbenzylphosphonic acid) (PVBPA) (**8**) was carried out in a two-step procedure by first reacting the phosphonate with an excess of TMSBr to give the corresponding silylated esters, followed by methanolysis. The hydrolysis using these mild conditions was found to be quantitative. Both the starting ethyl phosphonate polymers as well as the corresponding acids were characterized by ^{1}H and ^{31}P NMR spectroscopy.

The ^{31}P NMR spectrum of PDEVBP (**1**) showed a singlet at 27.7 ppm corresponding to the phosphorous atom of the ethyl phosphonate group. PVBPA (**8**) also exhibited one singlet, with a clear chemical shift to 24.8 ppm corresponding to the phosphorous of the phosphonic acid. Besides the shift of the signal, a broadening was also observed, most probably due to the presence of hydrogen bonds. The presence of only one signal in the ^{31}P NMR spectrum of the deprotected homopolymer **8** proved the quantitative conversion of PDEVBP to the desired phosphonic acid.

The same hydrolysis conditions were applied to the AB and BAB block copolymers (Fig. 5). Based on the ^{31}P NMR results, the conversions were in all cases quantitative.

The block copolymers **10** possess ester linkages connecting both the PEEK and PVBPA blocks. Theoretically, this type of esters could be easily cleaved, however such processes usually require strong basic or acidic conditions. PVBPA is a weak acid with pK_a values of the organic phosphonic acids in the range of 2–3 [49]. Therefore it is very unlikely that such cleavage of the ester linkages could occur in the absence of any strong acid or base. In order to prove the stability of the PEEK/PVBPA BAB block copolymers, several samples bearing different acid content were immersed in water for several days,

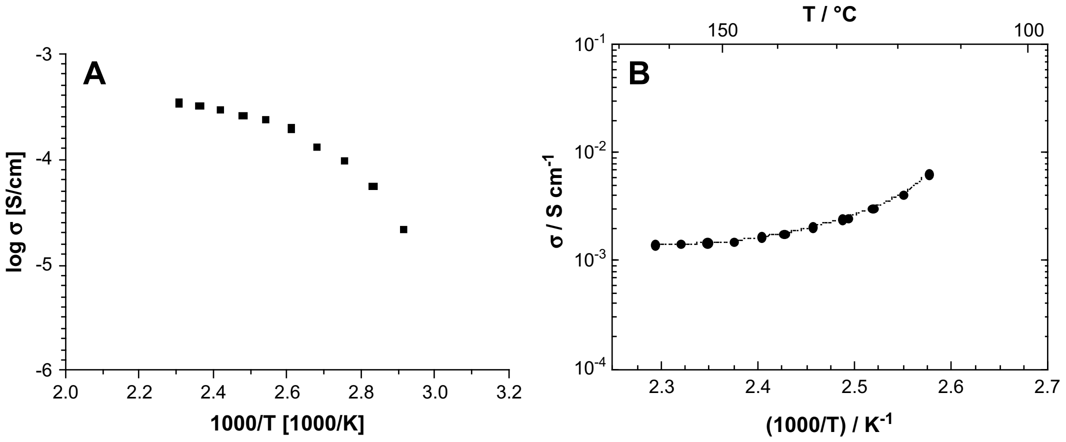


Fig. 6. Proton conductivity properties of PVBPA (**8**) in dry conditions (**A**) and in an atmosphere with 50% relative humidity (**B**).

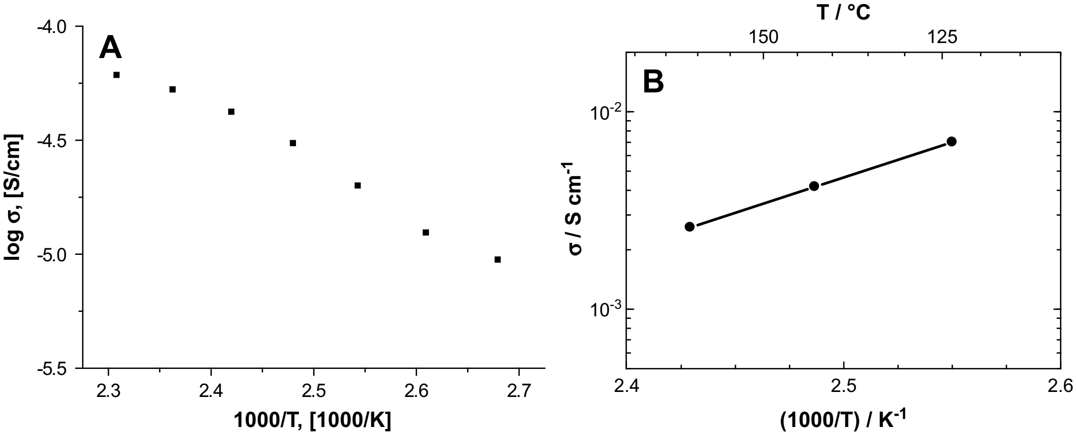


Fig. 7. Proton conductivity properties of PVBPA/PEEK BAB block copolymers **10** in dry conditions (**A**) and in an atmosphere with 50% relative humidity (**B**).

extracted with methanol, and further analyzed by ^{1}H NMR. However, PVBPA homopolymer was not obtained after the methanol extraction. Moreover, the subsequent NMR analyses did not show any change in the structure of the block copolymers. Therefore, this type of block copolymer architecture was considered as suitable for further proton conductivity experiments in dry and humidified conditions.

3.5. Properties of the phosphonic acid-containing (co)polymers

3.5.1. Proton conductivity

Essential requirements for using proton-conducting electrolytes as polymer electrolyte membranes for automotive applications are high thermal stability and an ability to transport protons between the electrodes in the fuel cell. All synthesized materials showed very good thermal stability with less than 10% weight loss up to 200 °C as confirmed by thermal gravimetric analyses. The proton conductivity properties of the PVBPA derivatives were measured by impedance spectroscopy in dry conditions and in an atmosphere with a defined relative humidity.

The measurements in anhydrous atmosphere were performed under nitrogen applying two cycles of heating and one cooling in a temperature regime 20–160 °C. PVBPA exhibited linear dependence of the conductivity with increasing temperature. A maximum value of 4.5×10^{-4} S/cm was observed at the higher applied temperature of 160 °C in anhydrous conditions under nitrogen (Fig. 6A). Alternatively, the measurements were performed in an atmosphere with defined relative humidity, using 10^5 Pa water vapor pressure, which corresponds to a 50% relative humidity. In these conditions, considered comparable to the real operating atmosphere of the fuel cell, the measured conductivity increased by about two orders of magnitude reaching a maximum value of 0.6×10^{-2} S/cm (Fig. 6B).

A similar linear increase of the value for conductivity with increasing the temperature was observed with the PVBPA-based block copolymers (**9** and **10**). Generally, the PEEK/PVBPA BAB block copolymers (**10**) exhibited about one order of magnitude lower conductivity, compared to the PVBPA homopolymer (**8**). The influence of the composition of the BAB block copolymers on the proton conductivity properties of the materials was investigated. For that reason, samples with different degrees of polymerization of DEVBP and therefore with various concentrations of the corresponding PVBPA polyelectrolyte were analysed by impedance spectroscopy in anhydrous conditions.

The deprotected polymer **7e**, Table 3 shows a maximum conductivity of about 6×10^{-5} S/cm at 160 °C (Fig. 7A). Surprisingly, no significant influence of the polyelectrolyte concentration was observed. A PEEK/PVBPA BAB block copolymer with about 7.5 times higher concentration of the phosphonic acid-containing polyelectrolyte exhibited proton conductivity in a similar range of 10^{-5} S/cm. However, a pronounced increase in the proton conductivity properties was measured in an atmosphere with 50% relative humidity, and a value of 0.75×10^{-2} S/cm was observed for the PVBPA/PEEK BAB block copolymers (Fig. 7B).

The polystyrene/PVBPA block copolymers (**9**) exhibited lower conductivity compared to the PA-containing homopolymer (**8**) and the BAB block copolymer (**10**). This could be explained by a macrophase separation between the hydrophobic styrene component and the amphiphilic PVBPA part within the AB block copolymer. This would lead to a dilution of the acid, most probably due to restricted percolation pathways and thus non-efficient proton transport, as evidenced in a significant decrease in the conductivity properties.

Such a dramatic effect was not observed for the BAB block copolymers **10** composed of PEEK and PVBPA. This might be attributed to a protonation of the carbonyl group of the PEEK by the phosphonic acid, which can contribute to the efficiency of the proton transport.

The ability of the PVBPA derivatives to conduct protons even in anhydrous state provides a possible alternative to the sulfonic acid-containing proton conducting polyelectrolytes, which are known to be dependent on the presence of water. The phosphonic acid-containing materials showed linear increase of the conductivity with the temperature in the absence of water with maximum values in the range of 10^{-5}–10^{-4} S/cm depending on the macromolecular composition. In the same experimental conditions the sulfonic acid-based systems with Nafion as a typical example do not exhibit any proton conductivity properties [4,5]. A drastic improvement of the conductivity of the PVBPA derivatives was observed when performing in an atmosphere with defined relative humidity, making them prospective candidates for high temperature operating polymer electrolyte membranes in automotive applications.

4. Conclusions

Copper-mediated ATRP was successfully applied as a suitable method for the synthesis of PDEVBP homopolymers, AB block copolymers with styrene and BAB block copolymers with PEEK middle blocks. First, the ability to polymerize the DEVBP monomer in a controlled way was studied in detail as a model reaction. A strong influence of the electron-donating phosphonate group on the specificity of the ATRP process was observed. The molecular weight and the PDI of the obtained polymers strongly depended on the type of the ligand used to form a catalytic complex with CuBr.

CuBr/PMDETA was found to give the best results in the controlled homopolymerization of DEVBP. Subsequently, the conditions in the controlled synthesis of PDEVBP via ATRP were extended to create AB and BAB block copolymers with tailored architecture, where the type of macroinitiator as well as the type of catalytic system influenced the composition of the obtained products. The transformation of the phosphonates to the corresponding phosphonic acids was performed under mild conditions in quantitative yields. The PA-containing polyelectrolytes are very attractive materials as proton-exchanging membranes for fuel cells due to their ability to perform in anhydrous conditions. The deprotected (co)polymers showed reasonable high thermal stability with less than 10% weight loss of up to 200 °C, which is a decisive criterion in the automotive industry. The proton conductivity of the PVBPA-based materials was studied by impedance spectroscopy in dry conditions and in an atmosphere with defined relative humidity. The ionomers exhibited linear increase of the proton conductivity properties with the temperature. The value of the conductivity depended on the macromolecular architecture with a maximum of 10^{-4} S/cm at 160 °C measured in dry conditions. Although these systems are not optimized with regard to block ratio or molecular weights, the values for conductivity they exhibit are already in the range of other dry membranes [12]. Altering the composition will probably also optimize the morphology and as a result the conductivity. A drastic increase in the conductivity for all materials was observed in a humidified atmosphere. At 50% relative humidity the PEEK/PVBPA BAB block copolymer exhibited conductivity of 0.75×10^{-2} S/cm, which is comparable to the properties of the Nafion membrane in fully humidified conditions. These block copolymers can be considered, therefore, as promising materials for polymer electrolyte membranes for high-temperature operating fuel cells as the PVBPA-based materials show a pronounced ability to conduct protons in both nominally dry and humidified conditions. In addition, it should not be ignored that the amphiphilic nature of the block copolymers, containing phosphonic acid functionalities, opens up a large variety of industrial applications in coatings, paints, as metal support or as stabilizers for emulsions [50–52].

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.06.011.

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