# RAPID COMMUNICATION

## Phosphonic Acid-Based Amphiphilic Diblock Copolymers Derived from ROMP

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### INTRODUCTION

Forming nanostructures with controlled size and shape is one of the most challenging tasks in material science. Amphiphilic block copolymers are of special interest because of their ability to self-assemble on the nanoscale. The formation of micelles has potential applications such as in drug delivery,[1] biosensors,[2] and gene therapy.[3] Ring-opening metathesis polymerization (ROMP) is a versatile technique for the preparation of well-defined block copolymers with narrow distribution of molecular weights. Several amphiphilic block copolymers obtained by the ROMP pathway have been investigated in the literature and were shown to form micelles and nanoparticles,[4–14] and used as drug delivery materials.[15–17] Phosphorus-containing polymers have broad application areas; besides their flame-retardant properties,[18] they are also used in biomaterials for their adhesive properties to metals, bone, and dentin.[19–22] The incorporation of phosphonic acid into acrylic monomers used in the dental industry can promote both biocompatibility and adhesion to the teeth, because of the formation of calcium phosphonates and phosphonate complexes.[21,23–25] Phosphonates, corresponding anions of phosphonic acid, have strong interactions with and adsorb very powerfully onto mineral surfaces.[26] Phosphonic acid-based polymers have also found several applications such as chelating agents for heavy metal salts,[27,28] ion-exchange resins,[29] and fuel cell membranes.[30–32]

In this study, we present an approach for the synthesis of phosphonic acid type block copolymers derived from ROMP using "Grubbs' third generation catalyst" [$(H_2$-Imes$)(3$-Br-py$)_2$-$(Cl)_2$Ru = CHPh]. Block copolymer components, monomers **2** and **3**, were synthesized by a nucleophilic exchange reaction and Mitsunobu coupling, respectively, using easily accessible starting material exo-oxabicyclo-[2.2.1]hept-5-ene-2,3-dicarboximide, **1** (Scheme 1). Then, **2** and **3** were polymerized sequentially to form block copolymers, **4a–c**, with a high control of polymerization (Scheme 2).

By cleavage of the phosphonate groups via transesterification with trimethylsilylbromide (TMSiBr) followed by the hydrolysis of the silylester group, the polymers were transformed into amphiphilic block copolymers, **5a–c** (Scheme 2). The hydrodynamic radii of the formed micelles were investigated by dynamic light scattering (DLS). The diameter of the micelles can be varied through changes in the composition of the block copolymers while the overall polymer length is kept constant.[6] Three series of block copolymers were synthesized by keeping the molecular weight constant ($M_{n,th} = \sim$20,000 g/mol) with varying compositions (4:1; 1:1; 1:4, by weight ratio for monomers **2** and **3**). For all of the series, the overall monomer/catalyst ratio was kept constant (60:1).

### EXPERIMENTAL

#### Materials and Measurements

Exo-oxabicyclo-[2.2.1] hept-5-ene-2,3-dicarboximide, **1**, was synthesized according to the literature procedure.[33]

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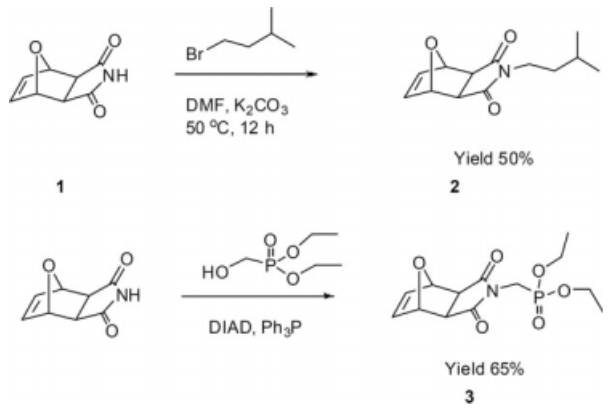
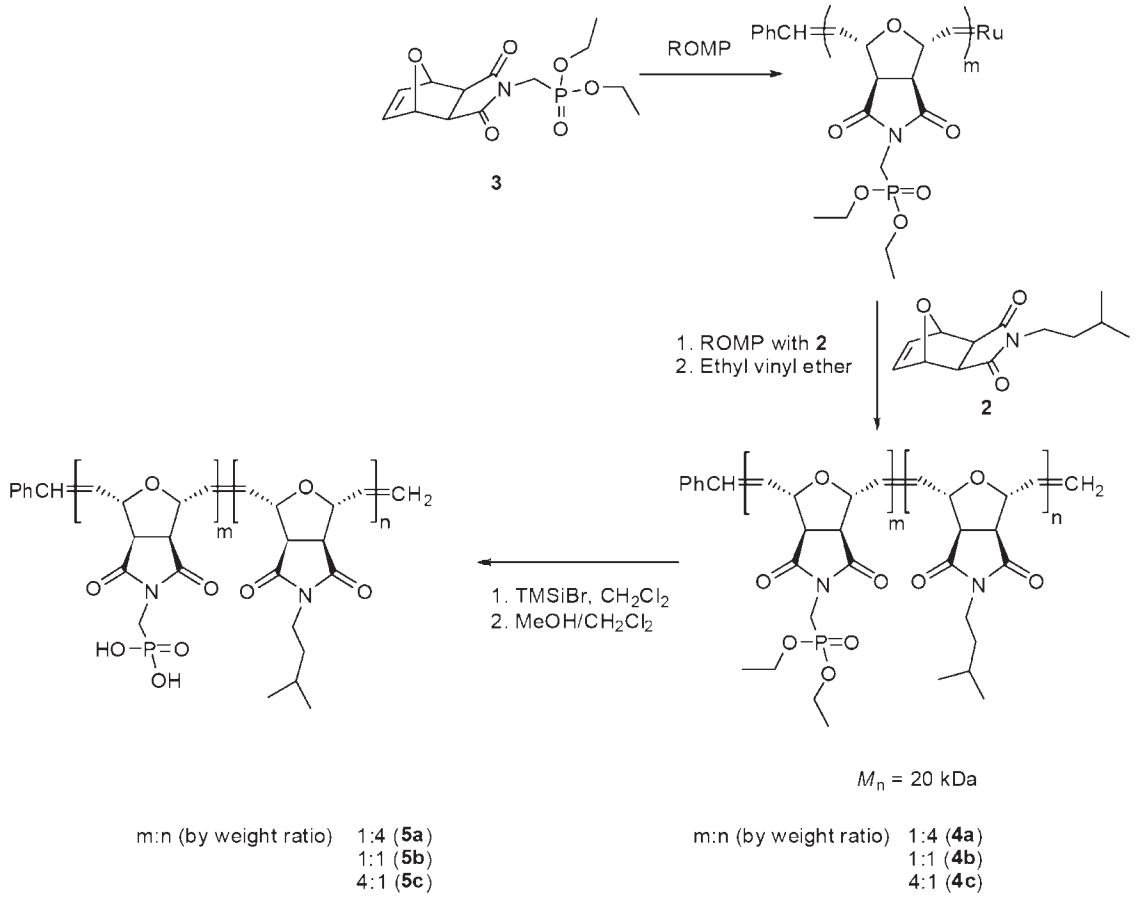



**Scheme 1.** Synthetic pathway for the monomers used in this study.

(Tricyclohexylphosphine) (1,3-dimesitylmidazolidine-2-ylidine)benzylideneruthenium dichloride, the second generation Grubbs' catalyst, was purchased from Strem Chemicals. Grubbs' third generation catalyst [$(H_2$-Imes)(3-Br-py)$_2$-$(Cl)_2$Ru = CHPh] was freshly prepared according to a literature procedure.[34] Furan, maleic anhydride, isopentyl bromide, dimethylformamide (DMF), $K_2CO_3$, and trimethylsilyl bromide (TMSiBr) were obtained from Aldrich and used as received. Deutoriated solvents were purchased from Cambridge Isotopes Aldrich. $CH_2Cl_2$ was distilled over $CaH_2$ and degassed with nitrogen. All experiments were carried out under inert atmosphere.

The $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded using a Bruker Avance400 spectrometer operating at the appropriate frequencies using either residual $CDCl_3$ or DMF-$d_7$ as internal reference (for $^1$H and $^{13}$C) or 85% $H_3PO_4$ as external reference (for $^{31}$P). Molecular weights and polydispersity indices (PDIs) were determined by gel permeation chromatography (GPC) in dimethylformamide (DMF) (1.0 mL/min) with LiBr (0.05 M) at 50 °C using a PL GPC 50 system equipped with two PL Resipore® columns (3 $\mu$m, 300 mm × 7.5 mm) and referenced against linear poly(methyl methacrylate) standards. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was performed on a Perkin–Elmer Spectrum One spectrometer equipped with a Universal Diamond ATR sampling accessory. HRMS-FAB data were acquired on a JEOL JMS 700 mass spectrometer.




**Scheme 2.** Synthesis of block copolymers via ROMP.

**Table 1.** Overview of the ROMP of Monomers **2** and **3**

| Diblock Copolymer | $m$[a] | $n$[b] | Mole Ratio[c] ($m/n$) | Mole Ratio[d] ($m/n$) | $M_{n,block\ th}$ (g/mol)[e] | $M_{n,block\ (NMR)}$ (g/mol)[f] | $M_{n,block\ (GPC)}$ (g/mol)[g] | PDI[g] |
|---|---|---|---|---|---|---|---|---|
| **4a** | 13 | 68 | 0.19 | 0.19 | 20,075 | 21,070 | 24,448 | 1.13 |
| **4b** | 32 | 43 | 0.74 | 0.80 | 20,185 | 22,300 | 24,040 | 1.15 |
| **4c** | 51 | 17 | 3.00 | 3.10 | 20,060 | 21,700 | 21,527 | 1.09 |

[a] Theoretical degree of polymerization (DP) of monomer **3**.
[b] Theoretical DP of monomer **2**.
[c] Theoretical ratio of monomers in the block copolymer.
[d] Ratio of block determined via integration of the $^1$H NMR spectra.
[e] Theoretical number-average molecular weight ($M_n$).
[f] $M_n$ calculated by end-group analysis with $^1$H NMR in $CD_2Cl_2$.
[g] $M_n$ and polydispersity index (PDI) were determined by GPC in DMF relative to linear poly(methyl methacrylate) standards.

### Synthesis of 2 {4-(3-Methyl-butyl)-10-oxa-4-aza-tricyclo[5.2.1.0$^{2,6}$]dec-8-ene-3,5-dione}

A mixture of isopentyl bromide (7.56 g, 50.1 mmol), potassium carbonate (3.71 g, 26.7 mmol), and **1** (2.12 g, 12.7 mmol) was stirred in deoxygenated and dry DMF (20 mL) at 50 °C for 12 h. After cooling to room temperature, the solution was diluted with ethyl acetate, washed with water and brine, dried, and evaporated under reduced pressure. The crude product was purified (recyrstallized by hexane), and monomer **2** was obtained as a white solid. Yield: 1.62 g (~53%). TLC (1:20 Methanol/$CH_2Cl_2$, $R_f = 0.6$). $^1$H NMR ($CDCl_3$, $\delta$): 6.49 (s, 2H), 5. 24 (s, 2H), 3.48 (t, $J = 5.6$ Hz, 2H), 2.81 (s, 2H), 1.53 (m, 1H), 1.40 (m, 2H), 0.90 (d, $J = 6.3$, 6H). $^{13}$C NMR ($CDCl_3$, $\delta$): 176.24, 136.53, 80.88, 47.36, 37.48, 36.26, 25.89, 22.31. IR (cm$^{-1}$): 2948.3 (m), 1766.5 (m), 1693.9 (s), 1439.1 (s), 1402.7 (s), 1357.9 (m), 1329.1 (s), 1299.6 (m), 1279.6 (m), 1187.8 (s), 1139.9 (m), 1099.3 (m), 1046.8 (w), 1015.0 (s), 957.9 (m), 946.1 (m), 884.5 (s), 866.1 (s), 856.8 (s), 825.1 (m), 804.2 (m), 782.8 (w), 761.8 (m), 724.5 (s), 7048 (s). HRMS (EI) *calcd*. for $C_{13}H_{17}NO_3$: 235.28 Found: 235.25.

### Synthesis of 3 {3,5-Dioxo-10-oxa-4-aza-tricyclo[5.2.1.0$^{2,6}$]dec-8-en-4-ylmethyl)-phosphonic acid diethyl ester}

To a dry round-bottomed flask were added **1** (3.01 g, 13.2 mmol), triphenylphosphine (4.75 g, 18.1 mmol), diethyl (hydroxymethyl)phosphonate (2.8 mL, 19.0 mmol), and dry THF (30 mL). The mixture was stirred under $N_2$ at room temperature, and diisopropyl azodicarboxylate (3.8 mL, 19.4 mmol) was added via syringe over a 10-min period. The mixture was stirred for 48 h at ambient temperature. The mixture was then concentrated and precipitated by addition of diethyl ether. The solid product was purified by column chromatography on silica gel using ethyl acetate/methanol/hexane (4:1:1, v/v; $R_f = 0.5$) mixtures to yield 2.41 g (61% yield) of a white crystalline solid. $^1$H NMR ($CDCl_3$, $\delta$): 6.52 (s, 2H), 5. 26 (s, 2H), 4.10–4.20 (m, 4H), 3.90 (d, 2 H, $J = 11$ Hz), 2.91 (s, 2H),1.32 (t, 6 H, $J = 7$ Hz, $CH_3$). $^{13}$C NMR ($CDCl_3$, $\delta$): 174.7 (C=O), 136.5 (C=C), 80.9 (C—O), 62.9 an 62.8 (O—*C*H$_2$—CH$_3$—phosphonate), 47.5 [*C*H—C(=O)], 35.09 and 35.03 (d, $CH_2P$) 16.32 and 16.24 ($CH_3$—phosphonate). $^{31}$P NMR ($CDCl_3$, $\delta$): 18.51. IR (cm$^{-1}$): 703 (s), 725 (s), 807 (m), 835 (s), 881 (s), 955 (s), 1007 (s), 1053 (m), 1094 (m), 1241 (s), 1319 (s), 1378 (m), 1399 (s), 1699 (s), 1769 (w), 2985 (w). HRMS (EI) *calcd*. for $C_{13}H_{18}NO_6P$: 315.26 Found: 315.24.

### Synthesis of Diblock Copolymers (4a–c)

Typically, 0.25 g (0.79 mmol) of monomer **3** was dissolved in dichloromethane ($CH_2Cl_2$). The required amount of catalyst (11 mg, 0.013 mmol, for copolymer **4c**, Table 1) was dissolved in $CH_2Cl_2$ in a separate flask, and then the catalyst solution was added to the monomer solution with vigorous stirring. The final monomer concentration was 0.2 M. After the polymerization of the first block had gone to completion (~10–15 min, confirmed by $^1$H NMR spectroscopy or TLC), the required amount of monomer **2** (0.053 g, 0.22 mmol for copolymer **4c**; Table 1), previously dissolved in $CH_2Cl_2$ was added to the polymerization mixture. The polymerization was allowed to continue for 20–25 min to completion. The reaction was terminated by the addition of an excess of ethyl vinyl ether while stirring for 1 h. The polymer was then precipitated in an excess of pentane and dried overnight under reduced pressure at room temperature to give a creamy white solid. Yield: 0.26 g (~85%). The molecular weights of the polymer blocks were calculated via $^1$H NMR; the ratio of the phosphonate ester peaks to the side-chain methyl peaks was used to arrive at a value for the degree of polymerization of the hydrophilic and hydrophobic blocks. As an example, spectral characterization of **4c** is given. $^1$H NMR ($CDCl_3$, $\delta$): 6.09 (br s, 2H, trans), 5.76 (br s, 2H, cis), 5.00 (br s, 2H, cis), 4.43 (br s, 2H, trans), 4.16 (br t,

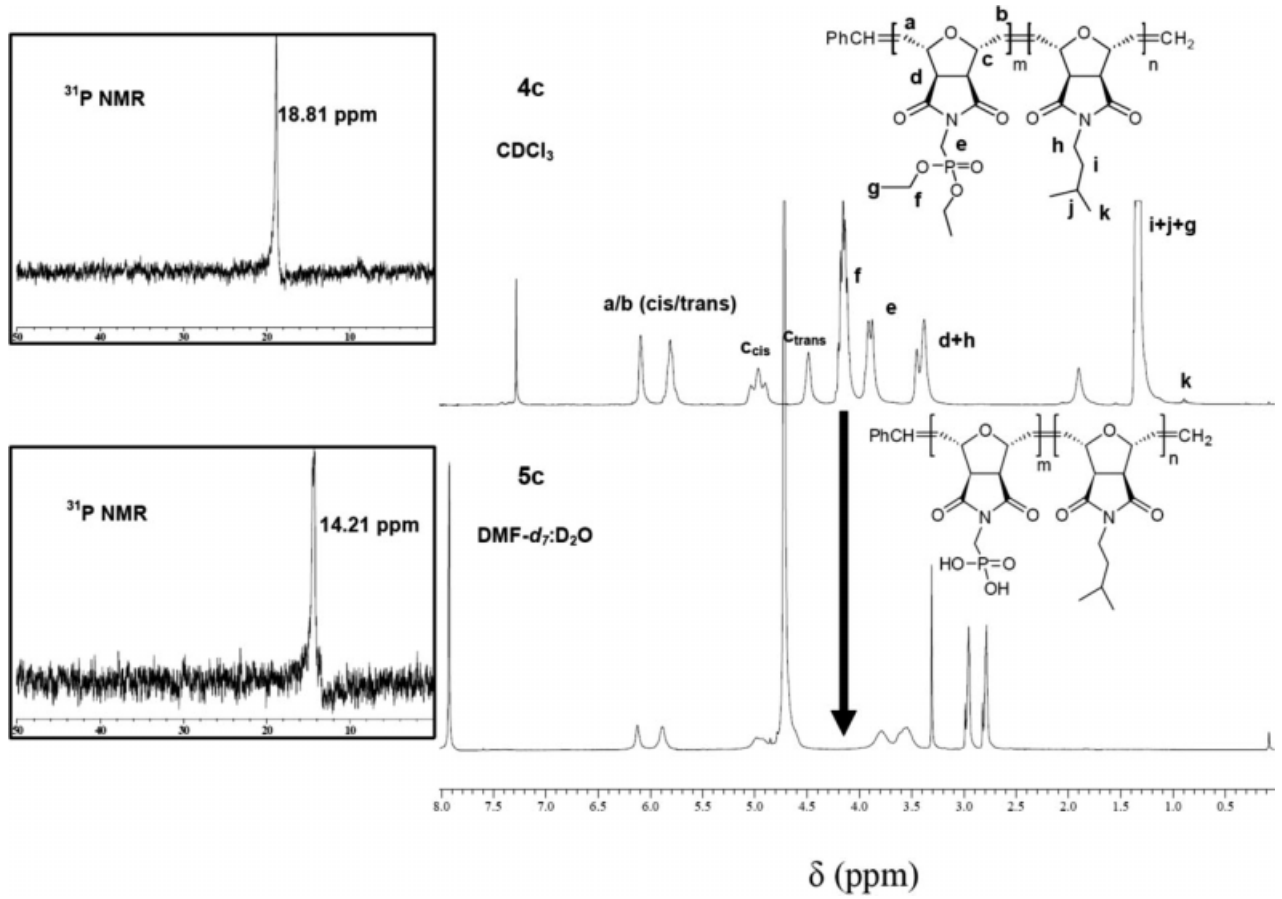



**Figure 1.** $^{1}$H NMR spectra of before and after cleavage of the phosphonate ester group of the polymer **4c** and **5c**, respectively, (spectrum **4c** is performed in $CDCl_3$, spectrum **5c** in DMF-$d_7$:$D_2O$). Methylene peaks were not observed in DMF-$d_7$:$D_2O$ because of micellization of the polymer. The insets are corresponding $^{31}$P NMR spectra of the respective polymers.

4H), 3.49 (br s, 2H), 3.38 (br t, 2H), 3.32 (br s, 2H), 1.60 (m, 2H), 1.45–1.47 (m, 3H), 1.34 ( br t, 6H), 0.84 (t, 2H). $^{31}$P NMR ($CDCl_3$, $\delta$): 18.82. IR ($cm^{-1}$): 847 (m), 968 (s), 1007 (s), 1047 (s), 1156 (m), 1244(s), 1320 (m), 1402 (m), 1710 (s), 1779 (w), 2985 (w). GPC (DMF, polymethylmethacrylate standards): $M_n$ = 21,500 g/mol (calculated $M_n$ = 20,060 g/mol), PDI = 1.09, cis/trans ratio = 1:1 (determined by $^{1}$H NMR).

### Synthesis of Polymers (5a–c) by Deprotection of (4a–c)

In the same manner as discussed in the literature,[35] trimethylsilyl bromide (1.5 mL, 11.5 mmol) was added slowly to a solution of **4c** (0.14 g, 0.0075 mmol) in 8 mL of dry dichloromethane. After being stirred under refluxing conditions for 4 h, excess trimethylsilyl bromide and the solvent were removed by under reduced pressure. Twenty milliliters of methanol/$CH_2Cl_2$ (3:1 v/v) solvent mixture was added and stirred for 48 h at room temperature. Solvent was evaporated, and the polymer was purified by addition of excess methanol. In the process, 0.13 g (99% yields) of creamy white solid polymer, **5c**, was obtained. The same procedure was applied for the synthesis of **5a–b**. As an example, the $^{1}$H NMR characterization of **5c** is given. $^{1}$H NMR [DMF-$d_7$/$D_2O$ (1:1), $\delta$]: 6.09 (br s, 2H, trans), 5.86 (br s, 2H, cis), 5.00 (br s, 2H, cis), 4.71 (br s, 2H, trans, coincide with solvent peak), 3.63 (br s, 2H), 3.50 (br t, 2H), 3.32 (br s, 2H), Methylene peaks were not observed due to micelle formation. Disappearance of phosphonate peaks was clearly observed by $^{31}$P NMR and IR spectra as well. $^{31}$P NMR [DMF-$d_7$/$D_2O$ (1:1), $\delta$]: 14.21 (s). IR: ($cm^{-1}$) 3386 (br w), 2917 (w), 1779 (w), 1696 (s), 1407 (m), 1384 (m), 1319 (m), 1153 (s), 998 (s), 931 (s), 818 (m), 752 (w).

### Dynamic Light Scattering

The hydrodynamic diameters of the micelles were determined by DLS using a Protein Solutions model

MS800/12 instrument with polarized light (824 nm) and a measuring angle of 90° relative to the incident beam. Before analysis, the solutions were filtered through disposable 0.22-$\mu$m pore size filters. The cumulant method was used to obtain an average particle diameter and polydispersity index (PDI). The values presented are the mean of at least six measurements (two micellizations per diblock copolymer, and at least three DLS measurements per micellar sample).

### Micellization

A solution of the block copolymers, **5a–c**, in THF/Milli Q water (deionized water, resistance > 18.2 MΩ) was sonicated for 10 min (5 mg in 5 mL THF/Millipore water (1:1 v/v)). The organic solvent was removed by dialysis (membrane with MWCO = 7500–15,000) of the solution against Milli Q water for 2 d. The final polymer concentration was ~1 mg/mL after dialysis.

## RESULTS AND DISCUSSION

A novel phosphonate-functionalized oxanorbornene monomer (**3**) was prepared according to the general synthetic route shown in Scheme 1. A key feature of the synthesis was the Mitsunobu coupling of hydroxymethylphosphonate and **1**. Literature assignments were used for the characterization of the phosphonate peaks of **3**.[36] Characteristic signals appeared at 1.3 and 4.1 ppm in the $^{1}$H NMR spectra and 16.3 and 62.9 ppm in the $^{13}$C NMR spectra, which can be assigned to the new aliphatic bonds. In addition, $^{13}$C NMR showed the characteristic doublet shifts from 33.0 to 35.1 ppm due to the hetero-coupling between the C-nucleus and the P-nucleus.[37] The $^{31}$P NMR spectrum showed the phosphonate ester peak at 18.8 ppm (Fig. 1, inset spectrum, polymer **4c**).

In general, in the synthetic route for the diblock synthesis by ROMP, the first monomer was homopolymerized at room temperature in dry dichloromethane until complete conversion occurred, as observed by TLC, $^{1}$H NMR, or GPC. The second monomer was then added as soon as the first monomer was completely consumed, thus, block copolymers with narrow molecular weight distribution were achieved. Table 1 summarizes the resulting block copolymers, **4a–c**.

All polymers were obtained with low polydispersities and molecular weights close to the theoretical values. Characterization of the diblock copolymers before deprotection was done using NMR techniques. The completion of polymerization was indicated by the total disappearance of the characteristic monomer olefin protons at 6.5 ppm and the appearance of the backbone double bond (cis/trans) signals at 5.8–6.1 ppm. The ratio of the number of repeat units of the phosphonate blocks ($m$, Scheme 2) to the number of repeat units of the hydrophobic block ($n$, Scheme 2) were analyzed by comparing the corresponding $^{1}$H NMR peaks. For example, the phosphonate ester peak (P—OC$H_2$CH$_3$) at 4.16 ppm indicated four proton units, while the methylene peak (six protons) at 0.92 ppm was due to the terminal alkyl chain of the isopentyl units from the same backbone block. It was found that the ratio of the methylene peaks and the phosphonate ester peaks of the polymer **4b** was 0.50 to 0.40, resulting in the block ratio $m$:$n$ = 0.8. Using the same methodology, the actual $m$ to $n$ values for all three diblock copolymers were determined (Table 1).

The integration values of the $^{1}$H NMR peaks were found to be strongly dependent on the solvent used. The data represent the actual values correctly only if micelle formation does not occur.[6,16] For example, the most hydrophobic polymer, **4a**, was dissolved in DMF-$d_7$ and the $^{1}$H NMR spectrum showed that the integration value of the isopentyl methyl protons were too low, which are caged in the core of the micelle. However, using $CDCl_3$ or $CD_2Cl_2$ the methyl protons appeared in the $^{1}$H NMR spectrum. Figure 1 shows the $^{1}$H NMR spectrum of one of the amphiphilic block copolymers, **5c**, as a micelle form in DMF-$d_7$:$D_2O$ (the same phenomenon was also observed in THF-$d_8$:$D_2O$). The peak that corresponds to the methyl protons in the hydrophobic monomer was no longer visible. This disappearance is in agreement with the formation of core-shell micelles in which the hydrophobic block is hidden in the micelle core in a nonsolvated state.[38–40]

For the transformation to amphiphilic block copolymers, **5a–c**, the phosphonate esters were cleaved by TMSiBr and then treated with methanol/dichloromethane mixture. Before deprotection, polymers **4a–c** were soluble in DMF, chloroform, and DMSO; but after cleavage, the obtained polymers **5a–c** became insoluble in these organic solvents. Deprotection of the dialkylphosphonate **4c** to **5c** was nearly quantitative shown by NMR and FTIR spectroscopy (Figs. 1 and 2, respectively). In particular, $^{31}$P NMR and FTIR were the most informative techniques. Disappearance of the phosphonate ester peak at 4.16 ppm in $^{1}$H NMR was observed after cleavage. The $^{31}$P NMR spectrum (Fig. 1, inset spectra) showed a shift from 18.8 to 14.2 ppm, which was assigned for corresponding resonance signals of phosphonate ester and phosphonic acid. FTIR clearly revealed the disappearance of phosphonate alkyl peaks as well. A strong vibration band at 1241 cm$^{-1}$, due to the vibrations of phosphonate esters (P=O), disappeared after cleavage (Fig. 2). A broad peak was observed at ~3500 cm$^{-1}$ due to the acidic OH stretching vibrations of the free phosphonic acid. The FTIR spectra of the polymers, **4a–c**, also showed strong absorptions at ~1037 cm$^{-1}$ corresponding to P—O—C stretchings. After cleavage, disappearance of this peak could not be clearly followed due to the broadening of the spectrum at this region. The same spectral analysis can be drawn for the cleavage of the polymer series **4a–b** to **5a–b**, which are not mentioned here.

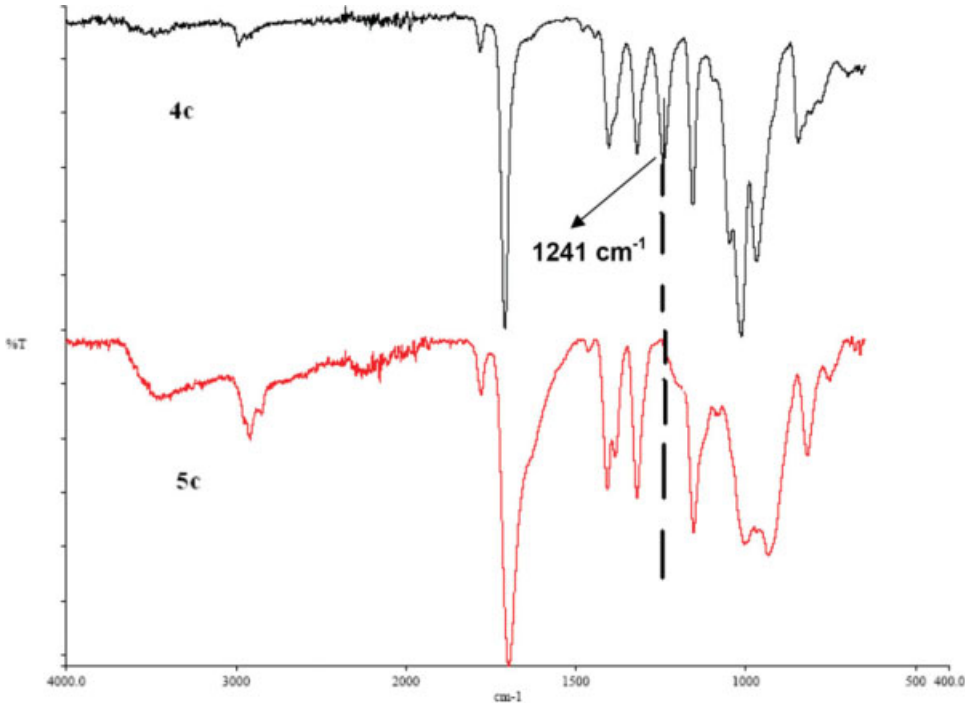



**Figure 2.** FTIR spectra of **4c** (phosphonate ester) and **5c** (deprotected **4c**, phosphonic acid) polymers. The disappearance of the characteristic IR band at 1241 $cm^{-1}$ indicates the complete cleavage of phosphonate esters. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

The molecular weight distribution and the polydispersity index of the block copolymers, **4a–c**, were determined using DMF-GPC against linear poly(methyl methacrylate) standards (Fig. 3). All of the GPC chromatograms showed a monomodal distribution confirming a defined growth of the second block. The polydispersity indices were low and in the range of 1.09 to 1.15. The molecular weight values obtained by GPC were in close agreement with the calculated theoretical molecular weights ($M_{n,th}$) (Table 1). $M_{n,th}$ was calculated in accordance with the targeted block ratios. For instance, the molecular weights of the first and second repeat units were 315 and 235, respectively; if the target block ratio was 51:17 (polymer **4c**, Table 1), then $M_{n,th} = (315 \times 51) + (235 \times 17) = 20{,}060$. It was also possible to calculate the $M_n$ of the polymers by end-group analysis of the $^1H$ NMR spectra. The relative integrations of the peaks from the polymer repeat unit versus the multiplet from the styrenic end-group at 7.3 ppm showed a good agreement with the targeted molecular weight for each type of polymer. For example, the phosphonate ester peak at 4.05 ppm was used to calculate the molecular weight of the phosphonate block in polymer **4c** and the observed molecular weight (16,185 g/mol) was close to the theoretical molecular weight of the phosphonate group (16,065 g/mol). The calculation was done as follows DP = $[(I_{phophonate}/4)/(I_{styreneendgroup}/5)] \times 315$ (MW of the phosphonate repeating unit). The same calculation procedure was applied to polymers **4a** and **4b**. GPC measurements of the phosphonic acid-based, amphiphilic block copolymers **5a–c** could not be carried out due to interaction with the column material.

DLS was used to characterize the micelles in solution and to obtain a measure of the hydrodynamic diameter of the particles and their polydispersities. Figure 4 shows the results of the DLS analysis for the synthesized amphiphilic block copolymer series, **5a–c**. In this series, the overall monomer/catalyst ratio was kept constant (similar molecular weight; $M_n \approx 20{,}000$ g/mol), but the hydrophobic to hydrophilic ratio was

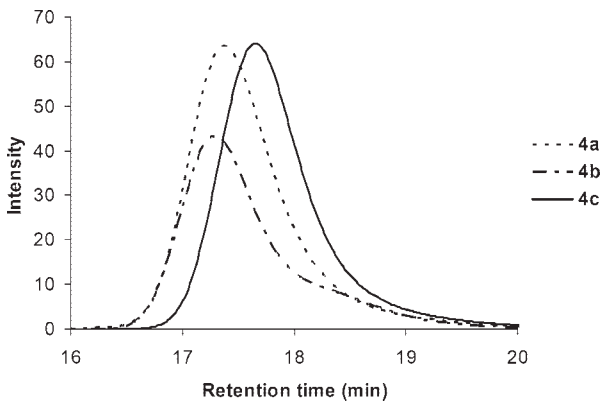



**Figure 3.** Gel permeation chromatograms for block copolymer series **4a–c**.

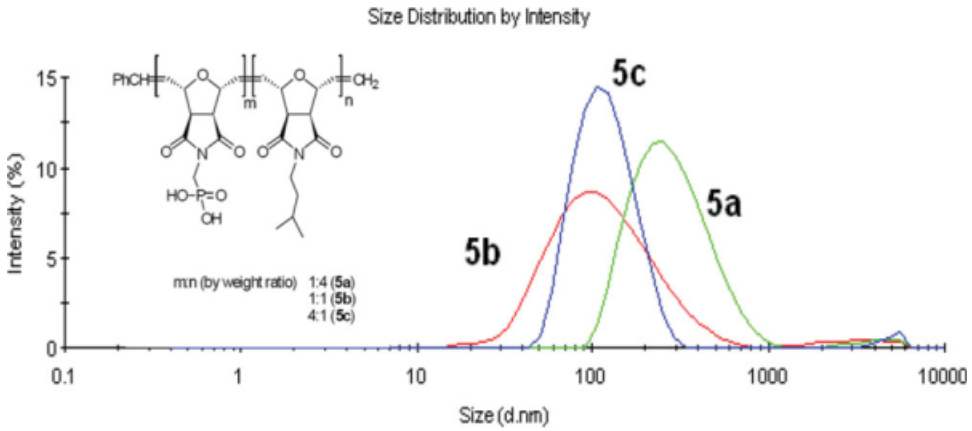



**Figure 4.** Average size distribution of ~1 wt % (in $H_2O$) solutions of polymers, **5a–c**, determined with DLS.

varied from 4:1 to 1:4, by weight. The solution of the most hydrophobic polymer **5c** stayed slightly turbid (water/THF, 1:1), whereas polymer solutions **5a** and **5b** were transparent in the same solvent mixtures. With decreasing hydrophobic group concentration in the polymer backbone, the micellar radius decreased from 301 nm for polymer **5a**, to 136 nm for **5b**, and 123 nm for **5c**. The polydispersity indices obtained via DLS were 0.2, 0.28 and 0.17 for **5a**, **5b**, and **5c**, respectively, which indicated a broad size distribution of the micelles.

## CONCLUSIONS

Novel phosphonate block copolymers were synthesized by the ROMP pathway for the first time. Quantitative deprotection of the phosphonate block to phosphonic acid produced amphiphilic block copolymers that formed micelles in a water/THF (1:1) solvent mixture. The micelle dimensions could be altered over a broad range (123–301 nm) by varying the compositions of the block copolymers while keeping the MW constant. It was observed that the core size decreased with a decrease in the hydrophobic fraction. Applications for this type of polymeric material, such as biomedical applications,[41] are currently under investigation.

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