Phosphonic Acid Functionalized Polyethylene Glycol and Derivatives

Mohamed Essahli,[1,2] François Ganachaud,[2] Martin In,[3] Bernard Boutevin[2]

[1]*Laboratoire de Chimie Organique, Faculté des Sciences et Techniques, BP 2202 Fès, Morocco*
[2]*Institut Charles Gerhardt, UMR5253 CNRS/UM2/ENSCM/UM1, Ingénierie et Architectures Macromoléculaires, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale 34296 Montpellier Cedex 5, France*
[3]*Laboratoire des Colloïdes, Verres et Nanomatériaux, Université Montpellier 2, CC 026 Place Eugène Bataillon 34095 Montpellier Cedex 05, France*

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ABSTRACT: This article describes the functionalization of polyethylene glycol, mono or bifunctional, and a nonionic surfactant by phosphonic acids without the need for protection of the functional group. The functionalization is performed in two steps, first an esterification by thioglycolic acid, secondly a radical addition of vinyl phosphonic acid on the thiol group. All products were obtained quantitatively and characterized by ^{1}H-, ^{13}C-, ^{31}P-NMR spectroscopy techniques, MALDI, and step-by-step chemical titrations. Enhanced thermal properties were found while phosphonylating polyethylene glycol, particularly when the sulfur atom was oxidized into a sulfone group. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 483–490, 2008

Key words: polyethylene glycol; phosphonic acid; telomerization

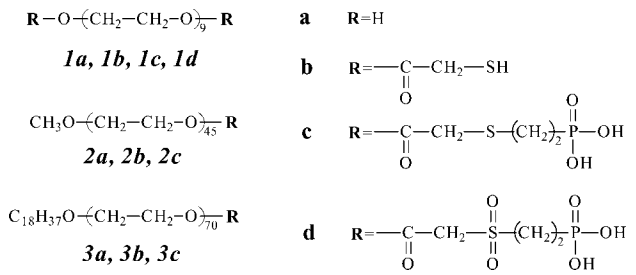
INTRODUCTION

Incorporation of phosphonic groups into polymer chains confers upgraded properties, including adhesion, emulsifying easiness, or greater resistance to corrosion or fire. Applications generally set the nature of the organophosphorus constituent, as well as the position and content of this constituent in the polymer chains. The generation of a C—P bond is rather difficult to achieve, and one generally prefers the introduction of a spacer link bearing a reactive function on the ω-end, whether it is an alcohol, an epoxy, or an amino group.

Reports on polyethylene glycol modification by phosphorus-containing groups are very scarce. In a series of articles, Weiss et al.[1–3] described the functionalization of polyethylene long-chain polymers with phosphonyl dichloride, and then derived into methyl or polyethylene glycol (PEG) ester phosphonates. A variety of characterization techniques were used on these polymers, including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), or Fourier transform infrared (FTIR). Phosphonylation decreased the crystallinity of polyethylene as well as increased water sorption. Pretula et al. and later on Bezdushna et al. have introduced dimethyl hydrogen phosphonate into a polyethylene glycol chain by trans-esterification.[4–7] For the latter team, the random copolymers exhibiting P—OCH_3 functions on both ends were hydrolyzed into phosphonic acid groups, whereas hydrogen phosphonate P—H inner groups could be derived into oxirane groups by radical or phase transfer catalysis. These polymers are thought of value for drug targeting because of their low cytotoxicity. Alternatively, Dworak et al. and Penczek et al.[8,9] have studied the functionalization of phosphoric and phosphonic molecules onto a MPEG-*b*-poly(glycidol) copolymer to generate, after hydrolysis, a polymer exhibiting double hydrophilicity. Likely, Sedlák and Cölfen[10] have functionalized amino groups of PEG-*b*-polyethyleneimine copolymers by vinyl phosphonic acid quantitatively by a Michael addition process. To our knowledge, only one team reported the synthesis of a singly phosphonylated monofunctional derivative of a PEG polymer chain, prepared by controlled anionic polymerization; amino end groups were converted to mono and diphosphonates by the Mannich-Moedritzer reaction followed by hydrolysis.[11] All these polymers were readily used in the growth and/or stabilization of $CaCO_3$ crystal suspensions in water.

Vinyl or allyl phosphonates and phosphonic acids are commercially available but do not easily polymerize. On the other hand, they react quantitatively in a radical catalyzed thiol-ene process. For instance, Pelaprat et al.[12] studied the telomerization of vinyl and allyl dimethylphosphonates onto alkylthiols.

Correspondence to: F. Ganachaud (francois.ganachaud@enscm.fr).



Scheme 1 Structure of the products prepared in this study.

They used a slight excess of thiol to avoid the generation of secondary products, particularly while telomerizing vinyl phosphonates. The hydrolysis of methyl or ethyl esters was shown to proceed readily using the silylation technique, followed by methanol or NaI hydrolysis. Using similar thiol-ene reaction, Bunel and coworkers prepared different polyols functionalized by phosphonate diethyl esters; they introduced these polymers into polyurethanes to further test the fireproofing of the modified resins. In a first approach,[13] the 1-thioethyldiethylphosphonate was prepared and grafted to a polybutadiene oligomer possessing two (or more) alcohol groups. Later on, they simplified the procedure by telomerizing vinyl and allyl phosphonates onto a mercaptodiol.[14]

In this article, we present the functionalization of PEG-based molecules, namely a difunctional PEG 400 molecule (**1a**), monofunctional derivative of PEG (**2a**), and a nonionic surfactant Brij 700 (**3a**) (Scheme 1). Thioglycolic acid (TA) was first grafted onto the hydroxylated chain-end(s) of the polymers before working out a radical telomerization of vinyl phosphonic acid onto the sulfide moiety (Scheme 2). The originality of the technique lies in the use of the acid vinyl monomer, thus saving for the alkyl phosphonate hydrolysis step.[15] To our knowledge, PEG molecules derivatization with phosphonated groups was never performed this way. We purposely chose to use cheap and readily available commercial starting materials, because the final polymers were originally intended to be used in cement formulations. Quantification and characterization of the intermediate and final polymers were however thoroughly done by ^{1}H-, ^{13}C-, ^{31}P-NMR spectroscopy techniques, MALDI, and step-by-step chemical titrations. Thermal analyses and a small angle neutron scattering study complete the plot to confirm the phosphonic functionality of thus prepared hydrophilic ionomers.

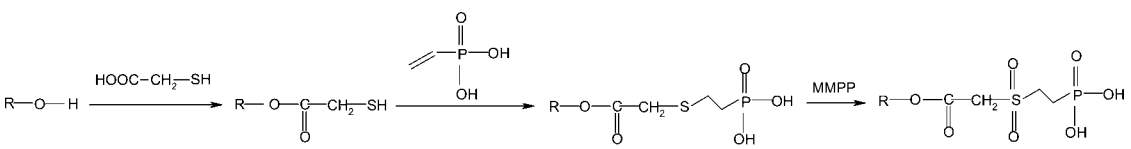
EXPERIMENTAL

Materials

All materials, including solvents, were purchased from Aldrich (St. Quentin Fallavier, France) and used without further purification, unless stated. Bis(monoperoxyphthalate) magnesium hexahydrate (MMPP), *p*-toluenesulfonic acid monohydrate (98.5%), TA (99%), vinylphosphonic acid (VPA) (97%), and azobis-isobutyronitrile (AIBN) (98%, recrystallized in methanol) were of analytical grade. PEG (M_n = 400 g mol^{-1}), monomethyl polyethylene glycol (MPEG) (M_n = 2000 g mol^{-1}) and polyethylene glycol (100) stearyl ether or Brij 700 were characterized by MALDI to check for purity (not shown). PEG400 (**1a**) exhibited only one peak distribution, separated by one EG unit of 44 g mol^{-1}, and centered around 480 g mol^{-1}, close from purchaser theoretical value of 400 g mol^{-1}. MPEG (**2a**) showed a more complex spectrum, where two populations could be detected, centered around 2200 and 3800 g mol^{-1}. Both populations exhibited the same expected monofunctionality. Brij 700 (**3a**) showed a conventional complex distribution, where only $C_{18}H_{37}$ composed the alkylated part whereas the PEG chains were evenly distributed; the chain-end was shown uniquely hydroxylated. The main peak of the distribution was centered on a PEG chain-length of typically 70 units, compared to the 100 expected (see a compilation of molar masses in Table I).

Methods

^{1}H- and ^{31}P-NMR spectra were recorded on a Bruker AC 400 apparatus at room temperature. In the latter technique, protons were irradiated to suppress the P—H coupling. References were set by tetramethylsilane and orthophosphoric acid (H_3PO_4 85 wt %), respectively. Chemical shifts (δ) were expressed in ppm, using s, d, t, q, m for singlet, doublet, triplet, quadruplet, and multiplet, respectively, and coupling constants (*J*) in Hz. FTIR spectra were accumulated on a Nicolet 510 P spectrophotometer, with the band positions expressed in cm^{-1} and a typical error of 2.5 cm^{-1}. Size exclusion chromatography (SEC) was carried out in *N,N*-dimethylformamide using a



Scheme 2 General strategy for VPA grafting onto polyethylene glycol derivatives.

TABLE I
Number Average Molar Masses (in g mol^{-1}) and Distribution (When Available) as Obtained by Different Techniques (Namely SEC, MALDI-TOF, ^{1}H-NMR, and Chemical Titrations)

Product	$M_{n,SEC}$ (M_w/M_n)	$M_{n,MALDI}$ ± SD	$M_{n,NMR}$	$M_{n,titr.}$	T_g	T_2	T_{10}	T_{90}
1a	430 (1.08)	480 ± 60	380	–	−69	7 (T_c)	243	340
1b	–	610 ± 110	530	550[a]	−60	–	274	390
1c	–	830 ± 110	750	750[b]	−28	–	239	544
1d	–	–[c]	820	–		169 (T_i)	123	–
2a	1870 (1.06)	1920 ± 300	2090	–	–	–	–	–
2b	–	2070 ± 230	2160	1470[a]	–	–	–	–
2c	–	1980 ± 270	–[d]	1590[b]	–	–	–	–
3a	3030 (1.09)	3190 ± 420	–[d]	–	–	–	–	–
3b	–	3190 ± 420	–[d]	3200[a]	–	–	–	–
3c	–	3150 ± 370	–[d]	3320[b]	–	–	–	–

Values given by the purchaser are 400, 2000, and 4670 g mol^{-1} for **1a**, **2a**, and **3a**, respectively. For PEG polymers, are added their transition temperatures (in °C) as determined by DSC (glass transition T_g, crystallization T_c, isotropic transition T_i), and decomposition temperatures T_{10} and T_{90} as obtained from ATG (where 10% and 90% weight loss were recorded, respectively).

[a] Thiol titration by iodine.
[b] Acid titration by sodium hydroxide.
[c] Did not come out in MALDI.
[d] Chain ends could not be integrated because of the limiting sensitivity of NMR.

Spectra Physics SP 8810 pump at a flow rate of 0.8 mL min^{-1}, two PL Gel 5-μm Mixed-C columns, and a refractive index detector Spectra Physics SP 8430. MALDI analyses were performed on an Ultraflex from Bruker Daltonik (Bremen, Deutschland) equipped with a 50 Hz N_2 laser (wavelength 337 nm), a delayed extraction, and a reflector, at an acceleration potential of 20 kV in reflection mode. One microliter of polymer solution in THF (10 g L^{-1}) was first mixed with 10 μL of a matrix solution (DHB, 20 g L^{-1} in THF) containing 10 mg L^{-1} of sodium iodide as the cationizing agent. The final solution (1 μL) was deposited on the target and dried under air at ambient temperature before irradiation. An average of 250 consecutive projections was accumulated. External calibrations were done using polypeptide calibration kit from Bruker Daltonik prior analyses. Differential calorimetry measurements were provided by a PERKIN ELMER DSC Pyris 1, at a heating rate of 10°C/min under helium flux. TGAs were performed using an ATG DUPONT 2000 type apparatus, under air or nitrogen, between 25 and 550°C with a temperature gradient of 10°C/min. SANS experiments were performed at LLB (Saclay, France) on spectrometer PAXY. One configuration (λ = 6 Å, sample-detector distance d = 3.2 m) was used to record the data over a scattering vector range from 10^{-2} up to 10^{-1} Å^{-1}. The raw data were treated by the same standard normalization procedure in terms of time recording, sample thickness, and background correction.

Synthesis

Polyethylene glycol ester of TA (**1b**)

PEG **1a** (0.1 mol) (according to the theoretical molar mass of 400 g mol^{-1}) was mixed with TA (0.6 mol) in a 250-mL two-neck reactor headed by a Dean Stark and the volume was adjusted to 100 mL with toluene. The mixture was let at 130°C under magnetic stirring during 48 h. Solvent was evaporated, and excess TA discarded by distillation under vacuum. Yield: 100%. ^{1}H-NMR ($CDCl_3$) δ ppm: 2.05 (t, 2H, CH_2—*SH*, J = 8.2 Hz); 3.30 (d, 4H, OOC—*CH_2*—SH, J = 6.10 Hz); 3.65 (m, 4nH, —(O—*CH_2*—*CH_2*)$_n$—O); 3.90 (m, O—*CH_2*—CH_2—OOC); 4.31 (t, 4H, —*CH_2*—COO—CH_2—SH, J = 3.3 Hz). ^{13}C-NMR ($CDCl_3$) δ ppm: 26.34 (s, 2C, —*CH_2*—SH); 61.4–70.5 (m, 2nC, O—[—*CH_2*—*CH_2*—O]$_n$); 170.8 (s, 2C, CH_2—*COO*—CH_2—SH).

Phosphonic acid derived PEG (**1c**)

In a two-neck reactor equipped with a condenser and fluxed with argon, 0.11 mol of VPA, 0.05 mol of **1b** were added to a solution of AIBN (1.1×10^{-3} mol) in 50 mL of acetonitrile. The mixture was agitated at room temperature, under argon and at reflux of acetonitrile (T = 85°C) during 4 h. Under cooling, a very viscous yellowish product separated from the solvent; after extraction under vacuum at 40°C during one night, a clear viscous liquid was obtained, with a final yield of 92%. ^{1}H-NMR ($CDCl_3$) δ ppm: 2.14 (m, 4H, CH_2—*CH_2*—$PO(OH)_2$); 2.92 (m, 4H, S—*CH_2*—CH_2—$PO(OH)_2$); 3.31 (s, 4H, —*CH_2*—*S*—CH_2—CH_2—$PO(OH)_2$); 3.70 (m, 4nH, —(O—CH_2—CH_2)$_n$—O); 3.75 (m, O—*CH_2*—CH_2—OOC); 4.31 (m, 4H, —*CH_2*—COO—CH_2—S—), 8.50 (s, 4H, —PO(*OH*)$_2$). ^{13}C-NMR ($CDCl_3$) δ ppm: 25.5 (m, 2C, —*CH_2*—*S*—CH_2—CH_2—$PO(OH)_2$); 27.8 (m, 2C, —*CH_2*—$PO(OH)_2$); 33.3 (m, 2C, —S—*CH_2*—CH_2—$PO(OH)_2$); 64–70 (m, 2C, —(O—*CH_2*—*CH_2*)$_n$—O);

170.5 (t, 2C, —*COO*—CH_2—S—, J = 3.3 Hz). ^{31}P-NMR ($CDCl_3$) δ ppm: 30.1 (s, 1P).

Sulfonated phosphonic acid PEG (**1d**)

In a one-neck reactor, 2.5 mmol of **1c** were dissolved in 20 mL of methanol cooled at 0°C to which was added 5.25 mmol of MMPP. Reaction proceeded under magnetic stirring during 12 h, after which the solvent was discarded on a rotavapor. Excess salt reactant was extracted by a water/acetone mixture (20/80, v/v). Yield: 92%. ^{1}H-NMR (D_2O) δ ppm: 1.80 (m, 4H, —*CH_2*—$PO(OH)_2$); 3.37 (m, 4H, —*CH_2*—*S*—CH_2—$PO(OH)_2$); 3.58 (m, 4nH, —(O—*CH_2*—*CH_2*)$_n$—O); 3.72 (m, O—*CH_2*—CH_2—OOC); 4.30 (m, 4H, —*CH_2*—COO—CH_2—S—). ^{31}P-NMR (D_2O) δ ppm: 28.2 (s, 1P).

MPEG ester of TA (**2b**)

Similar procedure as for **1b** synthesis was carried out, except that a catalytic amount of *p*-toluene sulfonic acid was added as a catalyst. The remaining TA was extracted from a basic concentrated $NaHCO_3$ water solution, and the organic phase dried by Na_2SO_4 and filtered. Final yield: 94%. ^{1}H-NMR ($CDCl_3$) δ ppm: 2.05 (s, 1H, CH_2—*SH*); 3.30 (d, 2H, *CH_2*—SH, J = 8.3 Hz); 3.40 (s, 3H, *CH_3*—O); 3.66 (m, 4nH, —(O—*CH_2*—*CH_2*)$_n$—O); 3.94 (m, O—*CH_2*—CH_2—OOC); 4.30 (m, 2H, —*CH_2*—COO—CH_2—SH). ^{13}C-NMR ($CDCl_3$) δ ppm: 26.34 (s, 1C, R—*CH_2*—SH); 61.4–70.5 (m, 4nC, O—[—*CH_2*—*CH_2*—O]$_n$); 170.8 (s, 2C, *R*—CH_2—*COO*—CH_2—SH).

MPEG phosphonic acid (**2c**)

Similar procedure as for **1c**, except that excess VPA needed to be extracted by NaCl saturated water after acetonitrile evaporation. The organic phase was dried on Na_2SO_4. Yield: 94%. ^{1}H-NMR ($CDCl_3$) δ ppm: 1.96 (m, 2H, *S*—CH_2—*CH_2*—$PO(OH)_2$); 2.85 (m, 2H, —S—*CH_2*—CH_2—$PO(OH)_2$); 3.22 (d, 2H, —*CH_2*—*S*—CH_2—CH_2—$PO(OH)_2$, J = 6.10 Hz); 3.31 (s, 3H, *CH_3*—O); 3.59 (m, 4nH, —(O—*CH_2*—*CH_2*)$_n$—O); 3.67 (m, O—*CH_2*—CH_2—OOC); 4.23 (t, 2H, —*CH_2*—COO—CH_2—*S*—CH_2, J = 3.3 Hz). ^{31}P-NMR ($CDCl_3$) δ ppm: 28.8 (s, 1P).

Brij 700 ester of TA (**3b**)

Same as before, expect that the final product was precipitated in diethyl ether. Yield: 93%. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.8 (t, 3H, *CH_3*, J = 6.8 Hz) 1.18 (m, 32H, CH_3—(*CH_2*)$_{16}$—CH_2); 1.52 (t, 2H, CH_3—(CH_2)$_{16}$—*CH_2*, J = 6.5 Hz); 1.92 (t, 1H, CH_2—*SH*, J = 8.3 Hz); 3.22 (t, 2H, *CH_2*—SH, J = 7.9 Hz); 3.58 (m, 4nH, (*CH_2*—*CH_2*—O)$_n$); 3.80 (m, O—*CH_2*—CH_2—OOC); 4.22 (m, $C_{18}H_{37}$—O—*CH_2*—); 4.61 (t, 2H, *CH_2* —COO—CH_2—SH, J = 2.7 Hz).

Phosphonic acid derivative of Brij700 (3c)

Same procedure as before, with the final product precipitated in diethylether. Yield: 92%. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.8 (t, 3H, CH_3, J = 6.8 Hz) 1.18 (m, 32H, CH_3—(*CH_2*)$_{16}$—CH_2); 1.52 (t, 2H, CH_3—(CH_2)$_{16}$—*CH_2*, J = 6.5 Hz); 1.78 (m, 2H, *CH_2*—P); 2.7 (m, 4H, S—*CH_2*); 3.22 (t, 2H, *CH_2*—S, J = 7.9 Hz); 3.58 (m, 4nH, (*CH_2*—*CH_2*—O)$_n$); 4.61 (t, 2H, *CH_2*—COO—CH_2—SH, J = 2.7 Hz); 8.4 (2H, s, $PO(OH)_2$).^{31}P-NMR ($CDCl_3$) δ ppm: 28.9 (s, 1P).

Chain end titration

Sulfide titration by iodine

A known mass of the pure product was dissolved in 10 mL of water and titrated by a 0.1*N* iodine solution until a clear yellow color appears, showing the presence of I_3^-. The average molar mass of the thiolated polymer was given by

$$\overline{M}_n = \frac{pm_{\text{thiol}} \times 1000}{N_{\text{iodine}} V_{\text{iodine}}} \quad (1)$$

where p is the number of SH functions (1 or 2) in the titrated product, m_{thiol} the exact mass of the product (g), N_{iodine} the normality of the iodine solution, and V_{iodine} the exact volume poured in the beaker (cm^3).

Acid–base titration of phosphonic derivatives

An exact amount m of product is weighed, dissolved in 10 mL of water and let to fast agitation for 30 min. The acid is then titrated by a 0.1025*N* NaOH solution using phenolphthaleine as a colored indicator. The average molar mass of the polymer was thus given by

$$\overline{M}_n = \frac{pm_{\text{acid}} \times 1000}{N_{\text{base}} V_{\text{base}}} \quad (2)$$

where p is the number of exchanged protons (2 or 4), N_{base} the normality of the NaOH solution, and V_{base} the poured volume to shift the mixture color (cm^3).

RESULTS AND DISCUSSION

In the following, we describe the functionalization pathway exclusively for PEG, because the procedure is identical for the monofunctional derivative of PEG

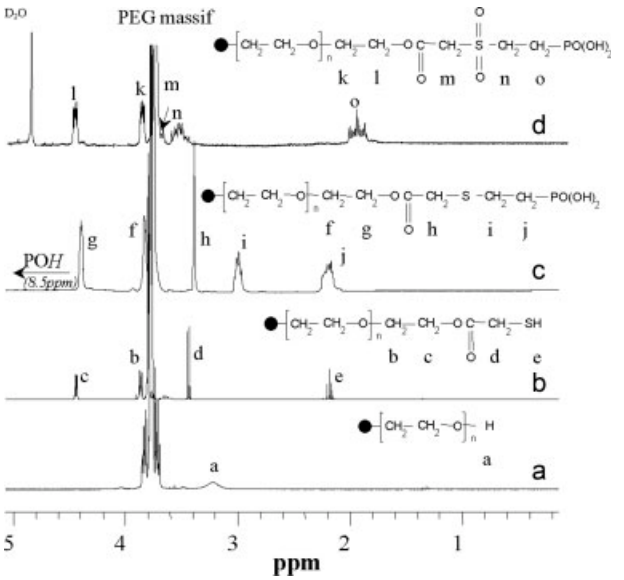


Figure 1 ^{1}H-NMR spectra of the different step-molecules synthesized starting from PEG400 **1a** (for details, see the Experimental section; only one chain-end is represented on the graph). **1a**, **1b**, and **1c** in $CDCl_3$; **1d** in D_2O.

and for Brij surfactant (only the extraction of the products after each step differed according to the nature of the polymer functionalized; see Experimental section). Basically, the esterification of TA onto polyethylene glycol was performed at reflux of toluene (130°C) during 48 h, without acid catalyst (which is required for the synthesis of **2b**). The equilibrium was shifted toward the ester synthesis by trapping water into a Dean Stark. At the end of the reaction, the excess of TA was removed by distillation under vacuum (96°C at 5 mmHg). Proton NMR, apart from the characteristic peaks of the PEG molecule, showed the vanishing of the peak at 3.08 ppm (signal a in Fig. 1, molecule **1a**) and the building of a new peak corresponding to the protons of methylenes in vicinity of thiol at 3.30 ppm (signal d in Fig. 1, molecule **1b**). The triplet showing up at 2.05 ppm corresponds to SH moieties (signal e in Fig. 1, molecule **1b**) and the peaks at 3.90 and 4.31 ppm those of the CH_2 close to ester groups (signals b and c in Fig. 1, molecule **1b**), thus confirming the transformation of alcohol into ester group. Carbon NMR spectrum of product **1b** shows two new peaks, located at 26.34 and 170.8 ppm, corresponding to the ester carbon and methylene group close to the thiol.

The second reaction, i.e., stoichiometric addition of VPA onto the thiol of **1b**, was performed using a radical catalyst. The kinetics of functionalization was followed by ^{31}P-NMR, from the integration of peak corresponding to the adduct at 30 ppm and the one assigned to excess VPA, resonating at 14 ppm. The reaction was quite fast, because quantitative conversion was reached after 4 h time (not shown). The extraction of product **1c** was rather easy, because it demixed from acetonitrile at room temperature and could thus be separated in a funnel. After drying under vacuum at 40°C overnight, the final viscous

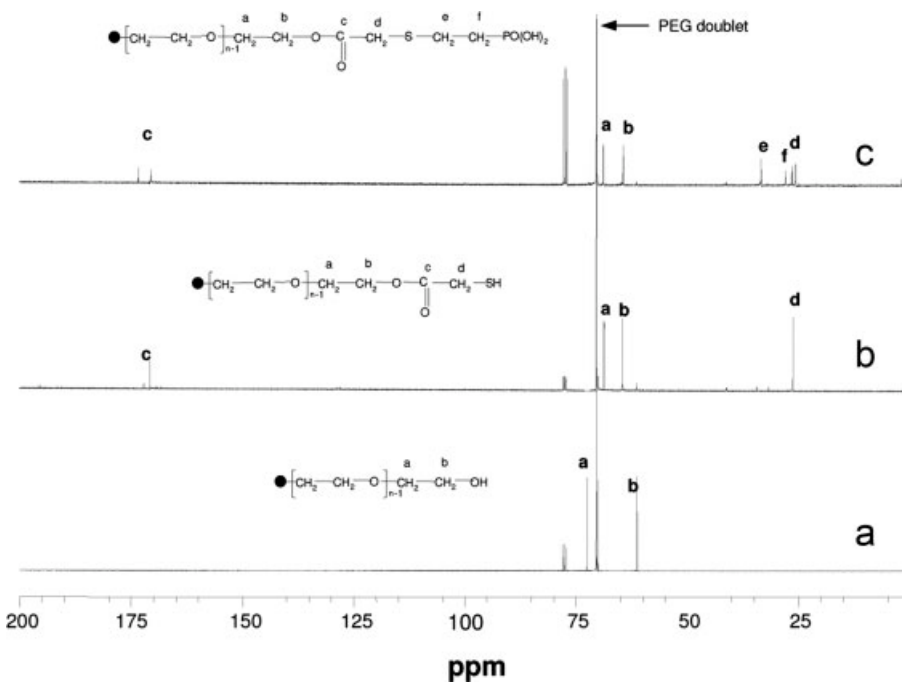


Figure 2 ^{13}C-NMR spectra in $CDCl_3$ of the different step-molecules **1b** and **1c** synthesized starting from PEG400 **1a** (for details, see the Experimental section; only one chain-end is represented on the graph).

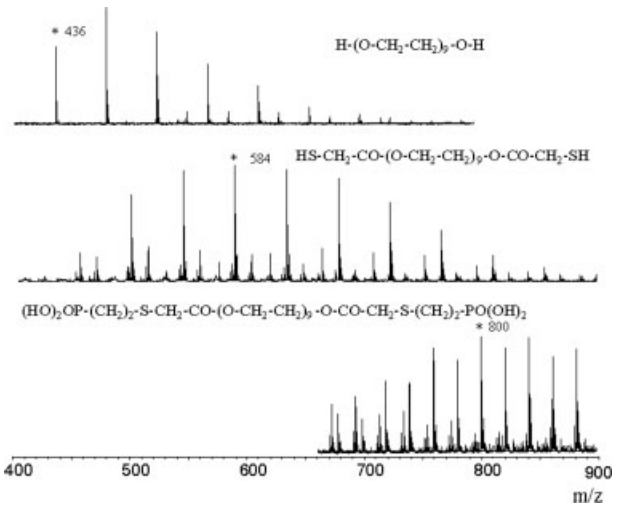


Figure 3 MALDI distributions of **1a**, **1b**, and **1c**. Tagged with an asterisk are the corresponding structure given on the graph, with their actual molar masses in g mol^{-1}.

liquid was analyzed by ^{1}H-NMR to confirm the phosphonic functionality, according to the chemical shifts, the methylene peaks adjacent to the phosphonylated group (2.14 ppm, signal j in Fig. 1, molecule **1c**) and at each side of the sulfur atom (2.92 and 3.31 ppm, signals i and h in Fig. 1, molecule **1c**). The signal of the acid group showed up at 8.50 ppm, whereas vinyl peaks at 5.70 and 6.20 ppm have totally vanished (not shown). On the carbon NMR spectrum (Fig. 2, molecule **1c**), the two new methylene groups arising from VPA addition are traced at 27.8 and 33.3 ppm.

In a view to depress the faint bad smell of the final molecule **1c**, we proceeded to an oxidation of the sulfur atom into sulfone groups, using MMPP as a mild reagent.[16] The reaction was carried out in methanol, at 0°C, for 12 h using a slight excess of MMPP, after which the polymer was isolated by precipitation in a water/acetone mixture. The remaining white powder was soluble only in polar protic solvents (water, methanol); ^{1}H-NMR was thus carried out in deuterated water. A striking shift of about 1 ppm was observed for the peak of the methylene groups in α of the sulfide [signal n at 3.37 ppm in Fig. 1(d)], whereas the peak of the methylene close to the phosphorus atom shifted downfield to 1.80 ppm [signal o in Fig. 1(d)], against 2.14 ppm for molecule **1c**. Such a decrease in chemical shift can either be explained by the changing of solvent or a ''Push-Pull'' effect of the methylene group trapped between two strong electron withdrawing groups, sulfone and phosphonic acid. The yield of **1d** was 92% after product separation.

MALDI spectra of **1a**, **1b**, and **1c** zoomed on a short scale are given in Figure 3. We did not succeed to observe **1d** by MALDI, presumably because the strong dipole–dipole interactions between sulfone groups, even in a good solvent, prevented the polymer from being properly crystallized in the several matrices tested. The peaks marked by the asterisks correspond to the initial, intermediate, and final functionalized PEG molecules where the corresponding molar masses are those expected for a number of 9 EG units (see structures in Fig. 2), when taking into account the cationization by Na^+. Note that the backgrounds of the different spectra were polluted with a second population of peaks, the distribution of which seemed not to shift from one sample to another; this noise was not further analyzed because it is out of the scope of this (industrial) study.

FTIR were also done systematically on the molecules **1a–c**, which showed overlapped spectra (Fig. 4). After the esterification step, the vanishing of OH band around 3500 cm^{-1} and the appearing of the ester band at 1735 cm^{-1} and thiol band at 2552 cm^{-1} was observed. The monoaddition of VPA discarded this latter band, as well as generated a new broad band centered around 2300 cm^{-1} and a bump at 2873 cm^{-1} ascribed to the P—OH band. Finally, oxidation of the sulfide atom produced broad peaks at 3500 cm^{-1}, presumably due to water uptake, and at 1650 cm^{-1}.

The molar masses of all products used or prepared here, as obtained by the different quantitative techniques, including SEC, MALDI-TOF, ^{1}H-NMR, and chain-end chemical titrations, are given in Table I. They are in good agreement for a given sample, thus confirming the good yields reported in the Synthesis section. For instance, SEC analysis and MALDI of starting polymers give comparable average molar masses, when taking M_n as the most intense peak in this MALDI molar distribution. Note that both techniques concluded that the Brij700 contains only 70 EG units, against the 100 units claimed by the purchaser. ^{1}H-NMR is particularly suited for

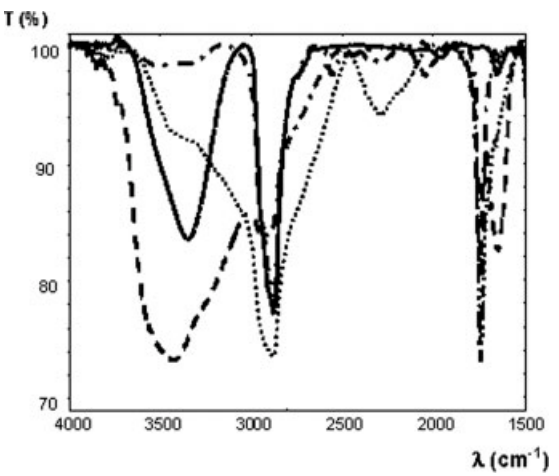


Figure 4 FTIR spectra of (—) **1a**, (- -) **1b**, (···) **1c**, (---) **1d**.

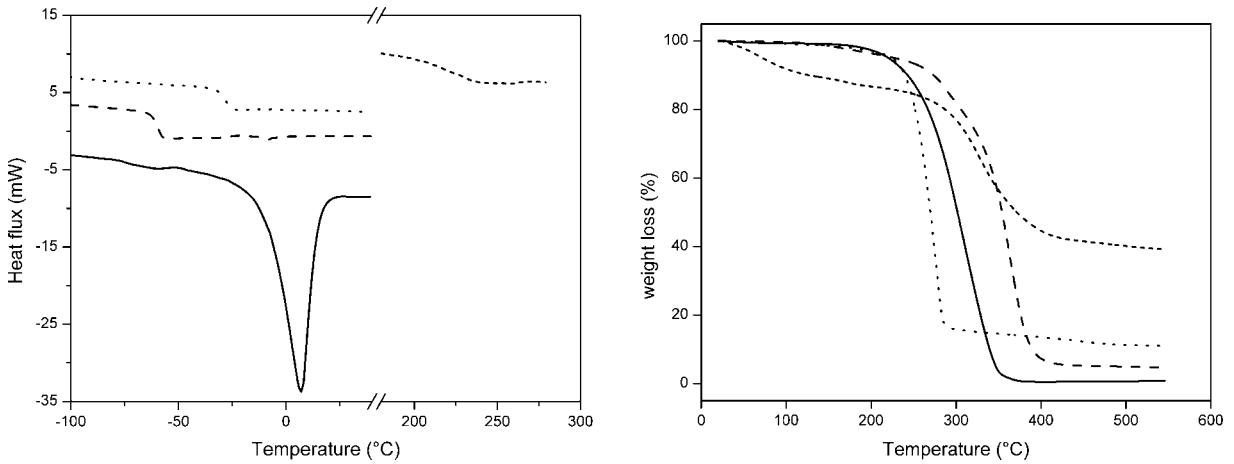


Figure 5 DSC (left) and TGA (right) thermograms of (—) **1a**, (- -) **1b**, (···) **1c**, (---) **1d**.

low molar mass materials, but integrations failed to give reproducible values for molecules prepared from Brij700. Titrations of intermediate thiol or final phosphonic acids gave molar masses in good agreement with other results, when the molecules were perfectly mono or bis hydroxylated. On the other hand, the products arising from the MPEG molecule are lower in functionality than expected, because of the nonnegligible content of large molar mass chains present in the sample (see experimental part), which may not have reacted quantitatively.

The different intermediate polymers obtained from **1a** were also analyzed by DSC and TGA. Thermograms are compiled in Figure 5 and the corresponding transition temperatures are quoted in Table I. DSC confirmed that PEG possesses both a glass transition around −70°C and a melting point at 7°C, making the polymer liquid at room temperature. Addition of TA slightly increased the first transition, and prevented crystallization, thus showing the important role of chain-ends on such short chains (DP of the PEG molecules is only 9). Addition of VPA shifted T_g toward −28°C, presumably because phosphonic acids interact through a 1 : 1 hydrogen bonding between P=O and P—OH[17] to stiff the chains. Finally, sulfonating the chains had for effect to transform the liquid material into a powder. T_g could not be observed for this material, but a mesophase/isotropic transition was measured at 169°C. Such trend confirms the tremendous influence of sulfone dipole–dipole interactions on material solidification and poor solubility in usual solvents (vide supra). ATG showed also significant differences between **1a** and **1d** molecules. The 5–10% weight loss in **1b–d** was due to water evaporation accumulated during the synthesis, particularly for the latter molecule. A second tiny transition was observed around 200°C, but this should not be ascribed to ester fragmenta-

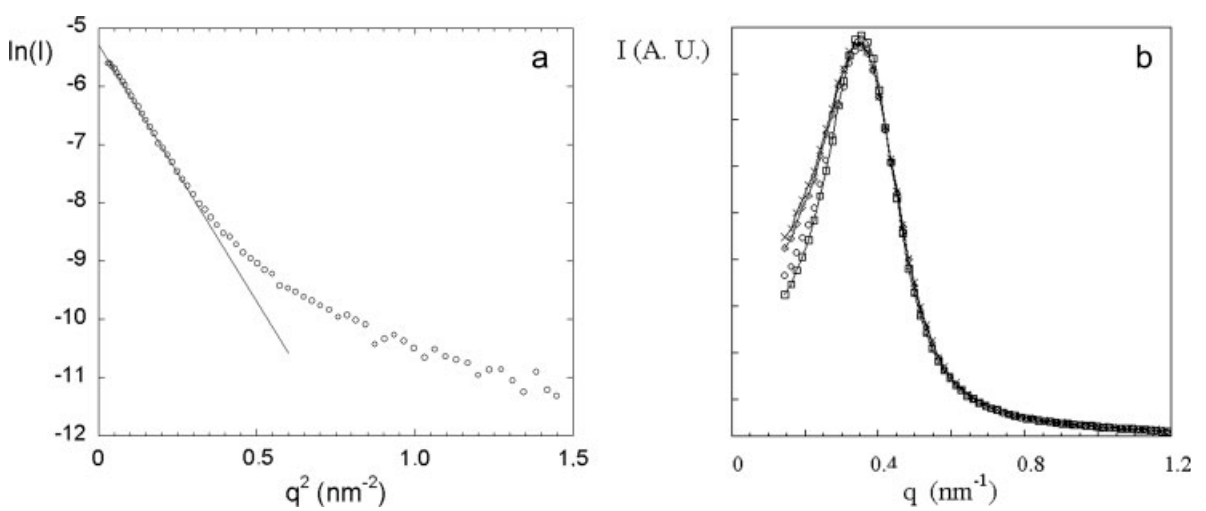


Figure 6 Neutron scattering results of **3c** micellized in deuterated water. (a) Guinier representation for **3c** at 0.5 wt %; (b) I versus q for 5 wt % solution of **3c** at various neutralization ratio.

tion, because it also occurred for **1a**. Sharp degradations were observed between 300 and 400°C, with a remaining 10 and 40% brown crust material for **1c** and **1d**, respectively (see Fig. 4). Both phosphonic acids and sulfones are known for their fireproofing properties, a result that was confirmed here.

The functionalization of Brij 700 by a phosphonic acid could not be seen by ^{1}H-NMR spectroscopy (Table I). A way to address this difficulty was to look at the physicochemical behavior of such electrosteric surfactant and, particularly, the variations on interactions between micelles of **3c** as a function of the pH. Two sets of samples were prepared in D_2O: (i) a low concentration sample (0.5 wt %) fully neutralized (x = [NaOH]/[**3c**] = 2); (ii) a series at 5 wt % with x = 0.5, 1, 1.5, and 2. The low concentration sample was reprocessed under a Guinier representation, i.e., ln(I) versus q^2, where I is the scattering intensity and q the scattering vector. In the small q limit, the approximation $I \propto \exp(-R_g^2 q^2/3)$ gives the gyration radius of the micelle [Fig. 6(a)], which best fit yields R_g = 5.1 ± 0.1 nm. When increasing **3c** concentration, micelles interact with each other and the scattering profile results from both form and structure factors. Depletion of the forward scattering and the correlation peak observed at a finite scattering vector q = 0.35 nm^{-1} revealed repulsive interactions between **3c** micelles [Fig. 6(b)]. Comparison with simulated spectra showed that the **3c** micelles at 5 wt % scatter neutrons like hard spheres of radius R_{HS} = 7.5 nm for a volume fraction of 0.2, consistent with the value of the radius of gyration obtained above and the core-shell structure of the micelles (small hydrophobic core and a water-swelled corona of phosphonated PEG). In addition, the distance of closest approach (here d = 15 nm) allows one to estimate the aggregation number of the micelles by multiplying the excluded volume ($4/3\pi R_{HS}^3$) by the molecular concentration of the copolymer (99 molecules per Å^3). An average of 175 molecules per micelles was found, which is close to values expected for a C_{18} surfactant. Besides, the position of the peak does not depend on x [Fig. 5(b)], which indicates that the aggregation number of the micelles determined essentially by intramicellar interaction is not very sensitive to the degree of phosphonic acid neutralization. However, intermicellar interactions are clearly pH-dependent, because the intensity scattered at low q decreased as sodium hydroxide concentration increased. This last result, i.e., the pH-dependence of the osmotic compressibility is a strong evidence that the corona of **3c** micelles carries weak acidic functionalities.

In conclusion, this article showed that the radical telomerization thiol-ene is an interesting and simple route to synthesize phosphonic acid functionalized polyethylene glycol and derivatives. All products were obtained in high yields and fully characterized by physical and chemical techniques. They also showed enhanced thermal properties, particularly when the sulfur atom was oxidized into a sulfone group. Such phosphonic polyethylene glycol materials are currently tested as additives in cement formulations.

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