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Synthesis and characterization of ionomers based on telechelic phosphonic polyether or aromatic polyesters

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ABSTRACT

A new method to prepare ionomers bearing terminal ionic groups has been developed by modification of different hydroxyl terminated oligomers and using vinyl phosphonic acid as reagent. The different oligomers have been characterized by NMR, MALDI-TOF, SAXS, SEM-EDX, thermal analysis and their ionic crosslinking was achieved using different cations. Characterization of the network was performed and proved that an efficacious crosslinking was reached depending on the nature of the cations.

1. Introduction

Ionomers are polymers which contain ionic groups able to lead to crosslinked networks [1–7]. These functional groups are usually distributed all along the polymer chains (Nafion®, Surlyn®) but can also more rarely be located at the chain ends (halato ionomers). These ionic polymers can be used as viscosity modifiers [8–17].

Phosphorus compounds are used for their good thermal resistance. The ionization potential value of phosphonic acids $R–PO(OH)_2$ is intermediate between sulfonic and carboxylic acid ones due to its intermediate pK_a and these acids are known for their complexing properties [18].

Ionomers bearing phosphonic groups have already been studied but their synthesis was very difficult to carry out [19]. Wu and Weiss [20] tried to synthesize ionomers containing phosphonic acid groups and showed that the direct copolymerization of styrene with vinyl phosphonic acid was hard to perform. These previous studies showed that the best way was the use of phosphonate compounds which were hydrolyzed in the second step. Unfortunately, hydrolysis was difficult to reach and needed drastic experimental conditions.

Our research group is also involved in the synthesis of phosphonic compounds, by the telomerization reaction. For instance, we studied the addition of thioethylene glycol $HS(CH_2)_2OH$ or thioglycolic acid $HSCH_2CO_2H$ on diethyl allyl phosphonate leading to monoadducts with yield close to 90% and without any by-products [21–23]. Recently, we achieved the one step synthesis of phosphonic acid compounds bearing a perfluorinated or alkyl chain by telomerization of vinyl phosphonic acid with mercaptans as chain transfer agents [24].

In the present paper, we report the synthesis of telechelic phosphonic ionomers based on polyether or aromatic polyethylene terephthalate (PET) oligomers using this simple telomerization reaction. Our readily processable synthesis needed two steps without any drastic conditions and permitted to easily convert alcohol or amine groups into phosphonic groups leading to phosphonic based ionomer compounds. Our study was focused on Terathane® 650 (polytetramethylene glycol ether) which brought flexibility to polymers and on an aromatic polyester diol obtained through the glycolysis of PET with diethylene glycol (DEG) [25,26]. The use of these two different oligomers permitted to evaluate the influence of the chain structure on the properties of the halato-telechelic ionomers.

2. Experimental

2.1. Materials

Polyethylene terephthalate (PET) (T74F9) was purchased from Tergal Fibre Company (Gauchy, France) in the form of pellets with a melting point of about 252 °C and a density close to 1.40 g cm^{-3}.

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Acetonitrile, diethylene glycol (DEG), methanol, sodium sulfate (Na_2SO_4), Terathane® 650 (Tera), thioglycolic acid, toluene, *p*-toluene sulfonic acid (PTSA), vinyl phosphonic acid (VPA), zinc acetate dihydrate (ZnAc), sodium hydroxide (NaOH), calcium nitrate tetrahydrate ($Ca(NO_3)_2$), from Sigma–Aldrich (St Quentin Fallavier, France), were of analytical grade and were used without further purification. Azobisisobutyronitrile (AIBN) was recrystallized from methanol.

2.2. Instrumentation

NMR spectra were recorded on Bruker spectrometers (Wissembourg, France) AC200 (200 MHz), Avance 250 (250 MHz) or Avance 400 (400 MHz) with tetramethylsilane as reference for ^{1}H NMR. The chemical shifts are reported in parts per million, where s is a singlet, d a doublet, t a triplet, and m a multiplet. Unless otherwise specified, all the spectra were recorded from $CDCl_3$ solutions.

IR spectra were recorded on a Nicolet (Madison, WI) 510P Fourier Transform InfraRed (FTIR) spectrometer apparatus with 2 cm^{-1} accuracy.

DSC measurements were performed on a Mettler DSC-30 instrument. Thermograms were recorded at 10 °C min^{-1} heating/cooling rate.

MALDI-TOF mass spectrometry analyses were performed on an Ultraflex time-of-flight mass spectrometer (Bruker Daltonik, Bremen, Germany) equipped with a 337 nm, 50 Hz N_2 laser, a delayed extraction and a reflector. Analyses were performed at an accelerating potential of 20 kV in reflectron mode. The polymer solution (1 μL of a 10 g L^{-1} solution in THF) was mixed with 10 μL of matrix solution (DHB, 20 g L^{-1} in THF) and with 1 μL of cationizing agent (10 mg L^{-1} of sodium iodide in THF). The final solution (1 μL) was deposited onto the target and dried in air at room temperature before irradiation. The mass spectra represent averages over 250 consecutive laser shots. External calibrations were performed with peptide standards (Burker Daltonic, Bremen, Germany).

Small angle X-ray scattering (SAXS) experiments were carried out in transmission configuration on solid powders in 1 mm diameter glass capillaries. A copper rotating anode X-ray source (4 kW) with a multilayer focusing "Osmic" monochromator giving high flux (10^8 photons/s) and punctual collimation was employed. An "Image plate" 2D detector was used. Diffraction curves were obtained giving diffracted intensities as a function of the wave vector q. Diffracted intensities were corrected by exposition time, transmission and intensity background coming from diffusion by an empty capillary.

For crystalline solids, the characteristic distance d_{hkl} between reticular plans *hkl* can be evaluated from the position of the corresponding Bragg peaks observed on the diffractograms. Bragg distance d_{hkl} can be calculated from Bragg's law:

$$2d_{hkl}\sin\theta = \lambda \tag{1}$$

with 2θ is the diffraction angle and $\lambda_{CuK\alpha} = 1.5418$ Å.

q is related to θ by the equation:

$$q = \frac{4\pi\sin\theta}{\lambda} \tag{2}$$

d_{hkl} can be deduced from Eqs. (1) and (2):

$$d_{hkl} = \frac{2\pi}{q_{hkl}} \tag{3}$$

where q_{hkl} is the q value corresponding to the associated Bragg peak position.

Scanning electron microscopy coupled with X-ray (SEM-EDX) analyses was performed on a LEICA apparatus (resolution: 50 nm) to analyze the different elements present in the sample. Characterization of each element (except hydrogen) was obtained by X-ray spectroscopy under electron flux. For this purpose, an electron beam was focused on the surface to be analyzed and emitted X photons were detected. Thanks to the energy emitted by the elements, an X-ray spectrum was obtained. Two types of analyses were performed. An overall analysis of the surface was achieved giving an average composition of the sample. Furthermore a probe was used to inspect different surfaces within a 1 μm^3 scale in order to reach the distribution of the different chemical elements in the cross-section of the material. EDX analyses were performed at the surface of the film. To compare the heights of the peaks, all analyses were performed at the same magnification with an electron beam tension of 7 kV and count numbers.

2.3. Titrations

2.3.1. Volumetric titration of free thiol functions

The volumetric titration of free thiol is based on a redox process

$$2RSH + I_2 \rightarrow RSSR + 2HI$$

$$I_2 + HI \rightarrow H^+ + I_3^-$$

The sample (m, grams) was titrated by an iodine aqueous solution ($N = 0.1$ mol L^{-1}) under vigorous stirring until the color changes from colorless to pale yellow (showing the presence of I_3^- ions). Then, the molecular weight M (in g mol^{-1}) of the telechelic thiol compound could be calculated according to:

$$M = 2 \times \frac{m}{n_{\text{thiol}}} = 2 \times \frac{m}{N_{I_2} \times V_{I_2}} \times 1000$$

where N_{I_2} and V_{I_2} represent the normality and the volume of iodine solution, respectively, and n_{thiol} the mole number in free thiol functions in the sample.

2.3.2. Volumetric titration of acid function

Volumetric titration of acid function was achieved according the general procedure. m Grams of the sample was dissolved in a mixture of 20 mL of THF with 4 mL of water. Then this solution was titrated with an aqueous solution of sodium hydroxide (0.1025 mol L^{-1}). The indicator for the titration of the two acidities of phosphonic acid groups was phenolphthalein. The molecular weight M (in g mol^{-1}) of the diphosphonic acid compound was calculated according to the following equation that takes into account the two acid protons of phosphonic acids:

$$M = 4 \times \frac{m}{n_{\text{acid}}} = 4 \times \frac{m}{V \times T} \times 1000$$

with V = volume of the potassium hydroxide solution (mL), m = weight of the sample (g), T = molarity of the sodium hydroxide solution (mol L^{-1}).

2.4. Synthesis

2.4.1. Glycolysis of PET by DEG

The PET pellets (50.0 g: 0.26 mol (in PET monomer units)), diethylene glycol (27.6 g: 0.26 mol), and 0.50 g of zinc acetate (ZnAc) (1 w/w% in respect to PET) were added into a 500 mL reactor equipped with a mechanical stirrer, a nitrogen inlet and a vacuum outlet. The reactor was heated under nitrogen at 240 °C for 2 h. The mixture was cooled for 5 min and ethylene glycol vapors were removed under reduced pressure (18 mm Hg) for 5 min. The cooled product (PETDEG) appeared as a white paste.

2.4.2. Functionalization of oligomers by thioglycolic acid

The α,ω-hydroxy oligomers (Tera or PETDEG) were esterified with a large excess of thioglycolic acid (6 mol of acid functions in respect to 1 mol of hydroxyl group) in refluxing toluene, in the presence of paratoluenesulfonic acid (0.1 mol/mol% in respect to acid functions) as catalyst, for 24 h.

The residual thioglycolic acid was removed by water extraction in the presence of sodium bicarbonate. The organic layer was dried with sodium sulfate (Na_2SO_4) and the solvent was evaporated under vacuum. TeraSH was obtained from Tera and PETDEGSH from PETDEG. The thiol functions were titrated to determine the molecular weights of the dithiol compounds: $M_{\text{PETDEGSH}} = 586\ \text{g mol}^{-1}$; $M_{\text{TeraSH}} = 792\ \text{g mol}^{-1}$.

2.4.3. Addition of thiol compounds onto vinyl phosphonic acid

The radical addition of α,ω-dithiol compounds (TeraSH or PETDEGSH) onto vinyl phosphonic acid was performed in stoichiometric conditions, in the presence of AIBN (1 mol/mol% in respect to thiol function) as initiator, under argon atmosphere, in refluxing acetonitrile, for 4 h.

After cooling, the addition products were insoluble in acetonitrile. The desired compounds were recovered by filtration. Then, acetonitrile traces were removed under vacuum (1 mbar).

TeraSP from TeraSH and PETDEGSP from PETDEGSH were obtained with molecular weights calculated using the titration of acid functions: $M_{\text{PETDEGSP}} = 800\ \text{g mol}^{-1}$; $M_{\text{TeraSP}} = 994\ \text{g mol}^{-1}$.

2.4.4. Ionomer synthesis

Ionomer TeraSPZn1 was synthesized by mixing 1 mol of TeraSP with 1 mol of ZnAc in methanol. The formation of a white precipitate was observed. It was filtrated, washed several times with hot methanol to eliminate free acetic acid or remaining ZnAc and finally dried under vacuum (1 mbar) for 48 h at 60 °C. This compound was a transparent solid resin totally insoluble in usual solvents at room temperature. Ionomer TeraSPZn2 was synthesized according to the same procedure with 2 mol of ZnAc.

The ionomer TeraSPCa1 was synthesized by mixing 1 mol of TeraSP with 1 mol of $Ca(NO_3)_2{\cdot}4H_2O$ previously dissolved in methanol. TeraSPCa2 was prepared with 2 mol of $Ca(NO_3)_2{\cdot}4H_2O$ according to the same procedure. For both ionomers, methanol and HNO_3 were evaporated under vacuum (60 °C, 1 mbar).

The ionomers TeraSPNa was synthesized by dissolving 1 mol of TeraSP in methanol and adding 4 mol of NaOH to neutralize the phosphonic acid functions. The ionomer was recovered after evaporation of methanol (60 °C, 1 mbar), and appeared as a white powder.

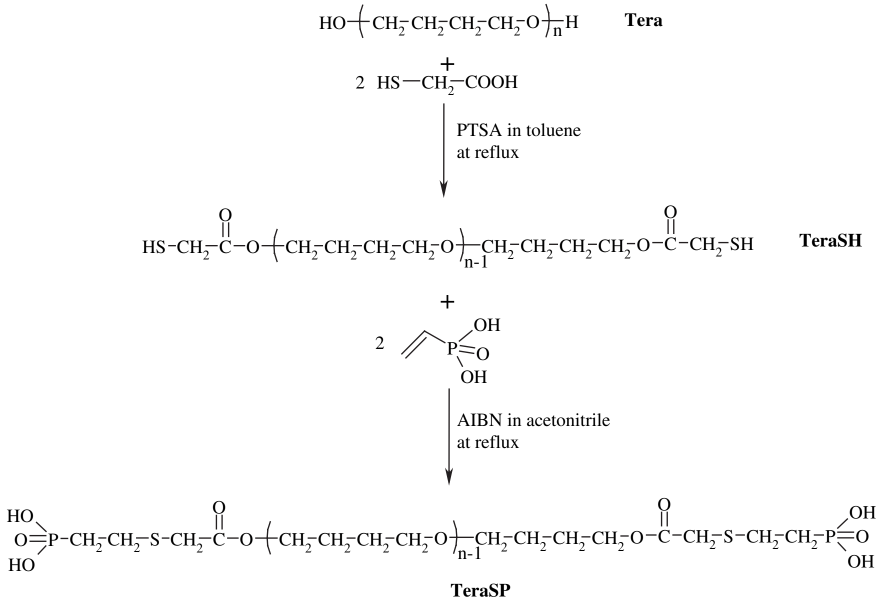
A mixture of TeraSP and PETDEGSP (50/50 mol/mol%) in methanol and ZnAc named Mixt50 was also studied under the same experimental conditions. This ionomer compound was synthesized by mixing 1 mol of PETDEGSP and 1 mol of TeraSP in methanol, and after, by adding 1 mol of ZnAc dissolved in methanol. The formation of a white precipitate was observed. It was filtrated, washed with methanol to eliminate free acetic acid and finally dried under vacuum (1 mbar). This compound was totally insoluble in usual solvents at room temperature and finally appeared at last as a transparent solid resin.

3. Results and discussion

Ionomers are usually prepared with sulfonic [27–37] or carboxylic [3,38–41] acid functions. Phosphonic acids are well known for their properties of adhesion onto metals and of flame retardance of materials but they can also be used in the synthesis of ionomers [42–44]. As the strength of ionic bonds is directly dependent on the pK_a of the acid group, phosphonic acids confer intermediate strengths contained between sulfonic and carboxylic ones which lead to the strongest and weakest ionic bonds, respectively. It also has to be noticed that the synthesis of phosphonic based ionomers is rather complicated to perform since only few monomers are available. Our new synthetic route [24] permitted to obtain telechelic phosphonic compounds from diols according to simple experimental conditions avoiding the hydrolysis of phosphonates usually described in the literature.

3.1. Terathane telechelic compounds

Thiolation reaction (Scheme 1) was achieved with thioglycolic acid in the presence of paratoluenesulfonic acid in refluxing toluene.



Scheme 1. Synthesis of the diphosphonic compound (TeraSP) issued from Terathane.

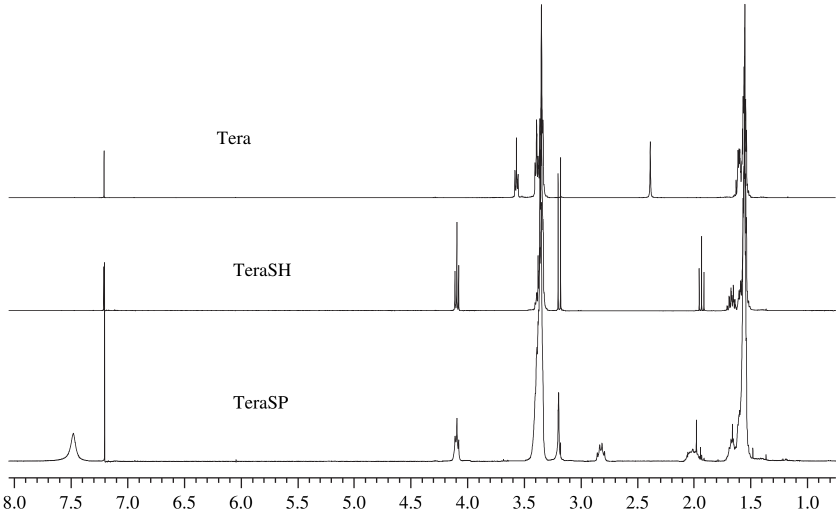


Fig. 1. ^{1}H NMR spectrum of Tera, TeraSH and TeraSP compounds ($CDCl_3$).

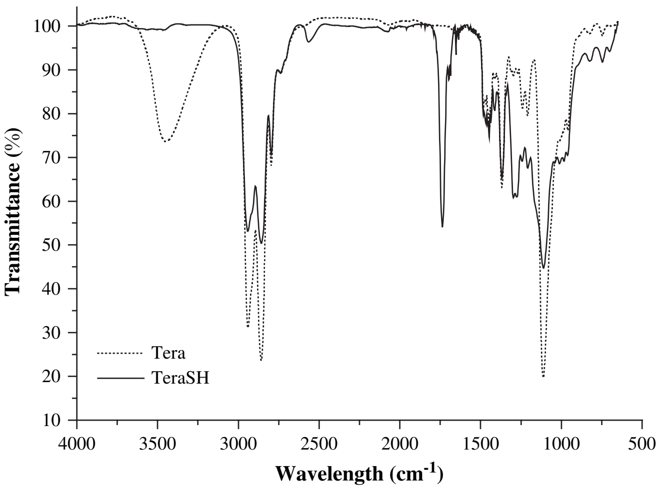


Fig. 2. IR monitoring of the thiolation of Tera compound.

Resulting TeraSH was characterized by ^{1}H NMR (Fig. 1). Disappearance of peaks corresponding to the hydroxyl group at 2.4 ppm and to the CH_2 in the α position of the hydroxyl groups at 3.6 ppm was observed. ^{1}H NMR spectrum of TeraSH also showed a peak at 4.1 ppm (ester protons CH_2–COOC), confirming the transformation of the hydroxyl groups into ester ones, as well as a peak at 3.15 ppm for the CH_2 in the α position of the sulfur atom. Finally, a triplet at 1.99 ppm was observed and attributed to the SH group. Reaction appeared to be quantitative.

In the second step, TeraSH reacted with vinyl phosphonic acid and AIBN in refluxing acetonitrile to reach diphosphonic acid TeraSP. The latter was characterized by ^{1}H NMR analysis (Fig. 1) which confirmed the chemical structure with the presence of methylene groups close to the phosphorus atom (2 ppm) and with the signals corresponding to both methylene groups on each side of the sulfur atom (2.8 and 3.2 ppm). In addition, the presence of the acid proton was identified at 7.5 ppm and no remaining vinyl protons (around 5.7 and 6.2 ppm) were observed. ^{1}H NMR study revealed that the addition of the α,ω-dimercaptan oligomer onto vinyl phosphonic acid occurred. As described in the literature, transfer constant C_T of SH groups onto vinyl phosphonic acid is high (close to 7). As a consequence, the monoaddition (only one monomer added per mercaptan group) is largely favoured [45] leading to the α,ω-diphosphonic acid oligomer. The ^{31}P NMR spectrum showed the presence of only one peak at

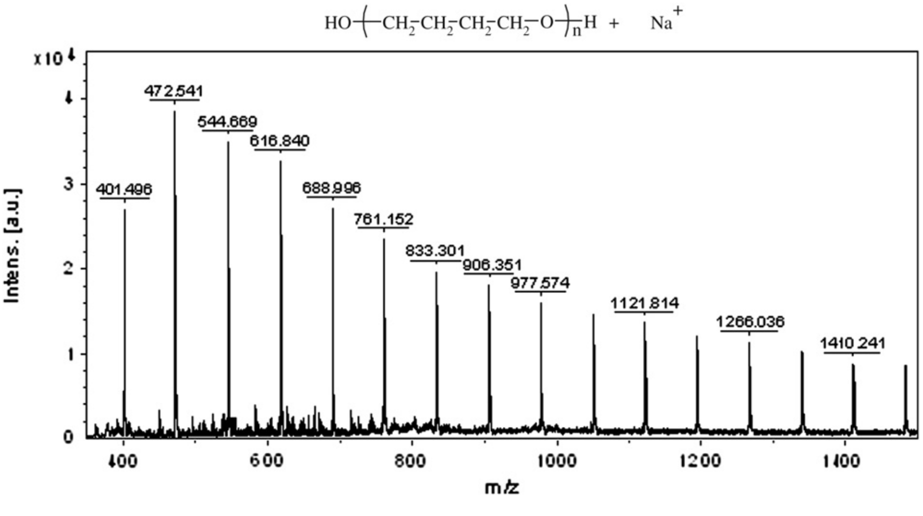


Fig. 3. MALDI-TOF spectrum of Tera compound.

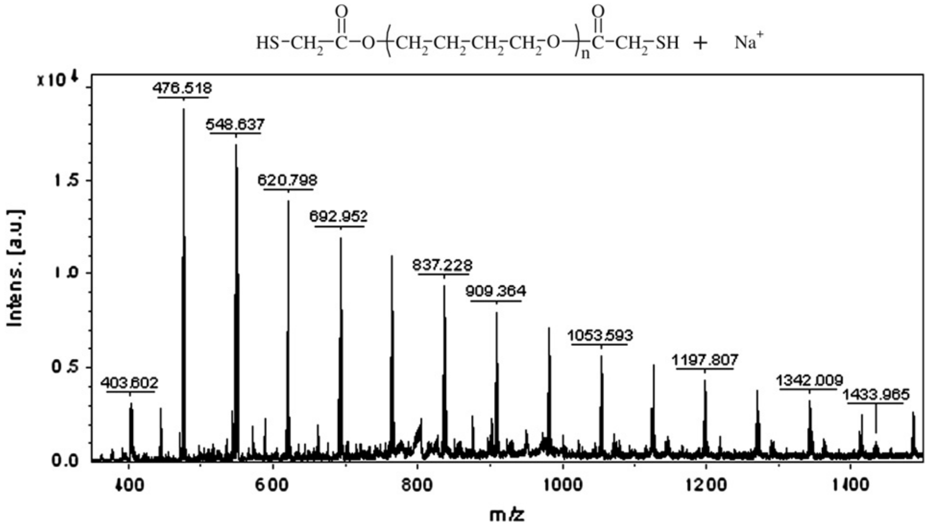


Fig. 4. MALDI-TOF spectrum of TeraSH compound.

30.5 ppm attributed to the phosphonic acid functions indicating that no free vinyl phosphonic acid (VPA) remained in the product since no signal of phosphorus from VPA was observed.

Infrared spectroscopy on TeraSH (Fig. 2) showed the disappearance of the hydroxyl absorption band (3500 cm^{-1}), the appearance of the SH band at 2600 cm^{-1} and of the carbonyl groups of the obtained thioglycolic esters at 1700 cm^{-1}.

Size exclusion chromatography (SEC) analyses were not achieved as phosphonic acid based polymers adsorbed quite a lot on the different columns making this analysis impossible and causing damages on the apparatus and devices. On the other hand, MALDI-TOF mass spectroscopic analyses permitted to determine molar mass of the synthesized products. Fig. 3 shows masses distant from 72 Da for Tera compound, corresponding to the $(C_4H_8O)/Na^+$ species with n varying from 5 ($M = 401.496$ Da) to 19 ($M = 1410.241$ Da).

In the case of compound TeraSH, the mass peaks (Fig. 4) represent the pairs TeraSH/Na^+ which are also distant from 72 Da. The different peaks observed previously in Fig. 3 are now shifted, due to the functionalization of Terathane® 650 with thioglycolic acid.

Spectrum of TeraSP (Fig. 5) was more complicated than TeraSH one. Masses distant from 72 Da were observed with n varying from 3 ($M = 620.664$ Da) to 15 ($M = 1486.001$ Da) corresponding to compounds functionalized by one phosphonic group on each extremity (α,ω-diphosphonic acid oligomers). If these awaited peaks were observed, some supplementary peaks were also present. These ones were attributed to oligomers bearing more than two phosphonic acid groups per chain. Even if the transfer constant C_T of SH groups onto vinyl phosphonic acid is high, the addition of two monomers per SH was also possible, and few oligomers could bear more than two phosphonic acids per chain. As an example, compounds with three phosphonic acid groups (one on one side and two on the other side) were observed at 800.9, 873.0, 945.1. At last, oligomers with two phosphonic acid functions on each extremity were identified at 909.2, 981.3, 1053.4, etc. Nevertheless, these compounds with more than two phosphonic acid groups per chain were present in a very minor quantity as proved by the acid titration (see Section 2.4.3) which confirmed the obtaining of the α,ω-diphosphonic acid oligomers.

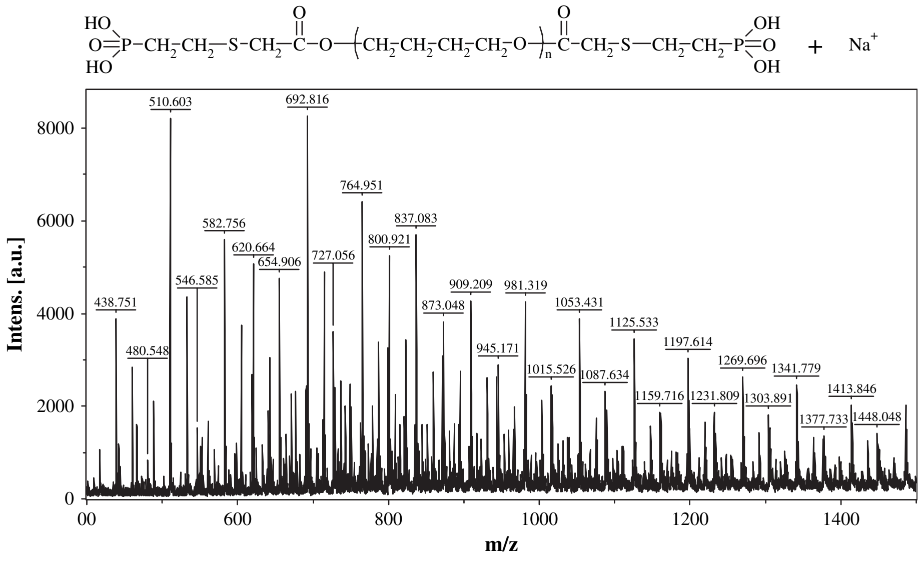
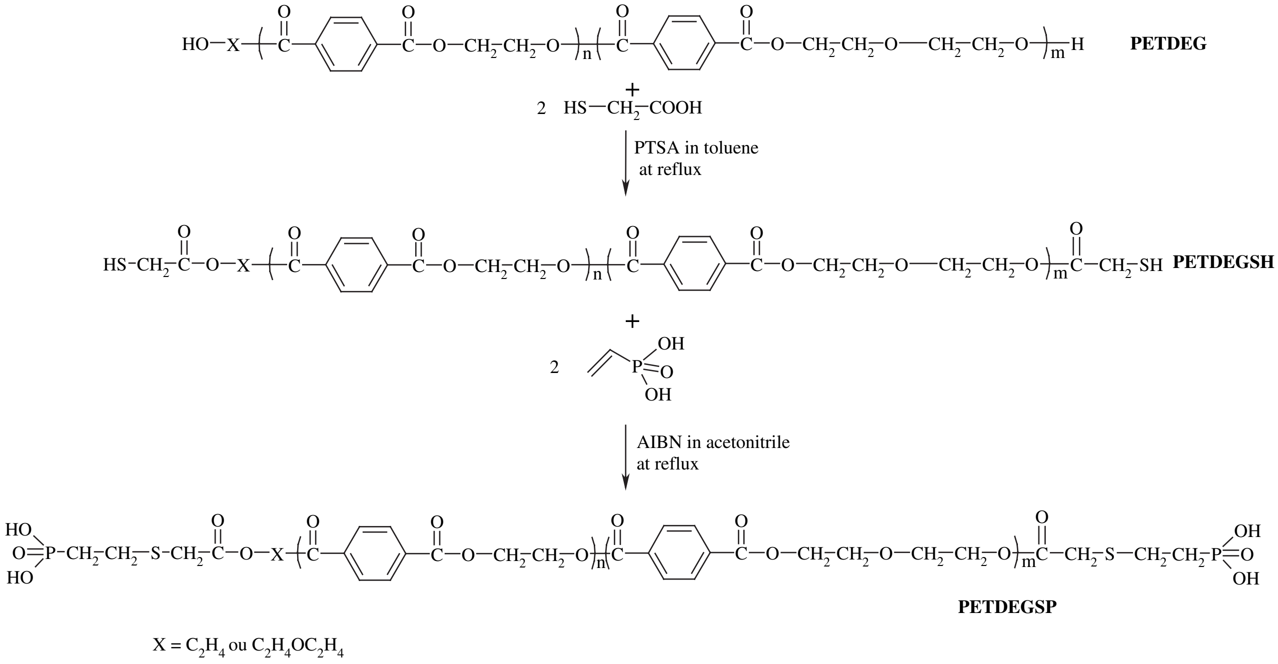


Fig. 5. MALDI-TOF spectrum of TeraSP compound.



Scheme 2. Synthesis of the diphosphonic compound (PETDEGSP) issued from PET glycolysate.

3.2. Compounds issued from PET glycolysates

The functionalization of PET oligomers was achieved according to the same reactional pathway than for Terathane® 650 (Scheme 2).

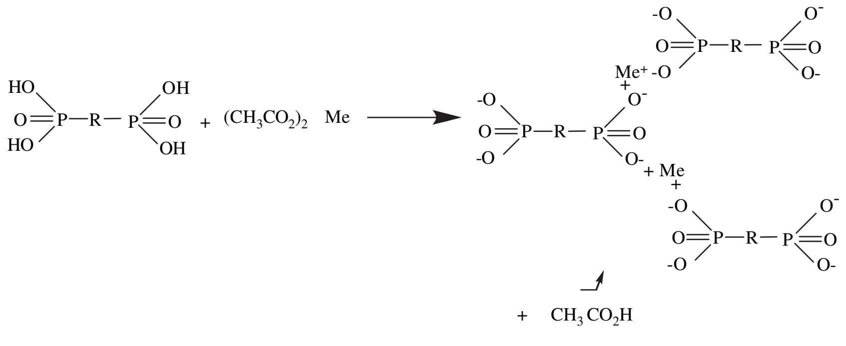
^{1}H NMR spectrum of PETDEG has previously been described by Auvergne et al. [46]. Spectrum of PETDEGSH showed that the CH_2 in α to hydroxyl groups of PETDEG (4 ppm) disappeared, as expected because of the functionalization. A peak was observed at 3.4 ppm for the CH_2 in the α position of the sulfur atom, as well as a peak at 2 ppm due to the SH group. Thiolation reaction with thioglycolic acid appeared to be quantitative.

Furthermore, in the case of PETDEGSP, the ^{1}H NMR analysis confirmed that vinyl phosphonic acid was added onto SH group, with the presence of methylene groups in the α position of the phosphonyl group (2.1 ppm) and by signals corresponding to two methylene groups on each side of the sulfur atom (2.8 and 3.2 ppm). The addition of only one VPA per SH group was also favoured, as in the case of TeraSP, in accordance with the literature [45]. In addition, the presence of the acid proton signal was observed at 9.4 ppm and no vinyl protons around 5.7 and 6.2 ppm coming from residual VPA were noticed. On the other hand, many peaks were observed by ^{31}P NMR in deuterated chloroform (δ: 33.23 (s); 31.05–30.51 (m); 28.00 (s)) and assigned to phosphonic groups with different environments. Indeed, previous studies [47–50] showed that PETDEG present a complex chemical structure as chain ends can be based either on ethylene glycol terephthalate moities or on diethylene glycol terephthalate ones. Moreover, free ethylene glycol and diethylene glycol were difficult to eliminate due to their high viscosity [48], leading to by-products (conversion of OH in SH and after, addition of VPA) exhibiting different ^{31}P NMR peaks.

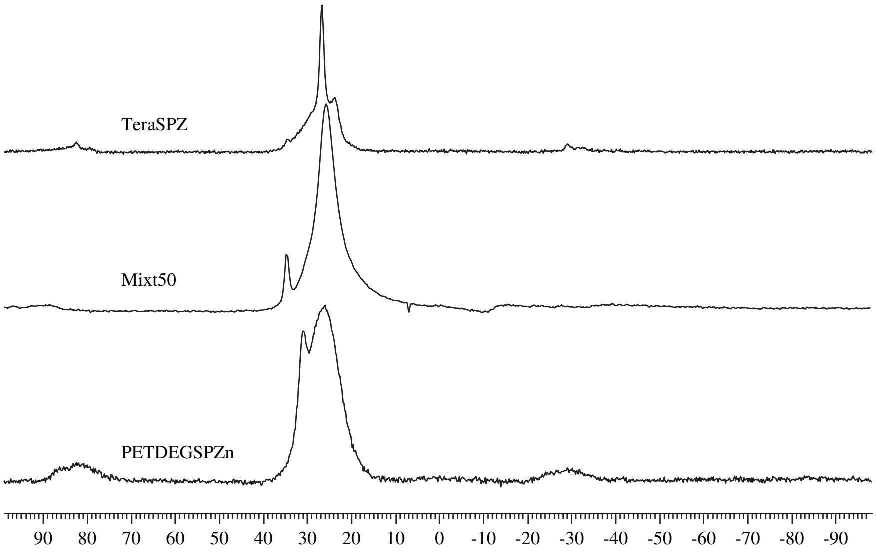
Infrared spectroscopy confirmed the disappearance of the hydroxyl band (3500 cm^{-1}), the appearance of the SH band (2600 cm^{-1}) and pointed out the complete thiolation of PETDEG. The tiny peak observed close to the hydroxyl band for PETDEGSH may be explained by the presence of small amounts of terminal carboxylic groups (1% of the extremities) in the glycolysate used [48]. MALDI-TOF mass spectroscopy analysis of the starting PETDEG has already been described in the literature [47]. Spectra were very complex and the functionalization of glycolysates by thioglycolic acid and then vinyl phosphonic acid made them more complicated to be solved.

3.3. Synthesis of ionomers

Halato ionomers are most often obtained by reaction of polymers bearing acid functions with metallic acetate to form acetic acid and ionic bonds between metallic ions and the neutralized acid functions (Scheme 3). Diacid compounds which were synthesized



Scheme 3. Synthesis of halato-telechelic ionomers based on phosphonic acids.



TeraSPZn: solid ^{31}P NMR δ: 26.55(s); 23.66(s)
PETDEGSPZn: solid ^{31}P NMR δ: 30.58(s); 25.91(s)

Fig. 6. Solid ^{31}P NMR of ionomers.

were viscous resins soluble in solvents while the ionomers precipitated in methanol as soon as they were formed. Ionomers based on Zn or Ca cations appeared as very viscous resins insoluble in common solvent whereas ionomers with Na were white powders soluble in common organic polar solvents.

The ^{31}P solid NMR spectra of the different solid ionomers TeraSPZn and PETDEGSPZn are reported in Fig. 6. Signals were downfield shifted from about 5 ppm compared to the ^{31}P NMR spectra of TeraSP and PETDEGSP in solution. This shift showed that the phosphonic acid P–OH groups of both compounds have been converted into P–O$^-$ groups in compounds TeraSPZn and PETDEGSPZn [51]. This observation partly confirmed the presence of ionic species (ionomers). It should be pointed out that peaks at 80 and −30 ppm were due to spinning bands.

The SAXS technique permitted to study the distance between scattering domains [11,16,17,42–44,52]. Peaks observed for $q < 0.5$ in Fig. 7 represented the distance between two ionic domains. Table 1 gathers the Bragg distances of the different compounds where q values were determined at the top of the peaks. The calculated distance had the same magnitude than that found by other authors in the case of halatotelechelic polybutadiene [53,54]. This distance was similar to the root mean square end to end distance of 60 Å for poly(oxytetramethylene) [55]. As proposed by Jerome et al. [53], the distance between two neighbouring ionic domains resulting from SAXS data gives only an indication of the chain configuration since some chains can form loops. Finally, we also noticed that the peak corresponding to PETDEGSPZn was much wider than for homologous TeraSPZn, confirming the wide molecular weight distribution inherent to the starting glycolysates [47].

The observed wide peak showed that both TeraSP and PETDEGSP segments were uniformly distributed in the final Mixt50 ionomer. The distance value d was precisely intermediate between PETDEGSPZn and TeraSPZn pure ionomer ones (composition of the mixture was 50/50 mol/mol%).

The EDX analysis permitted to confirm the presence of P, S and Zn elements in the material. Since zinc acetate was soluble in methanol and as obtained compounds were carefully washed for a long time with methanol, it might be stated that Zn ions which were observed were those associated by ionic bonds with phosphonic groups. Compounds Mixt50 and PETDEGSPZn showed identical spectra.

Differential Scanning Calorimetry (DSC) analyses revealed that compounds issued from Tera and PETDEG exhibited well different thermal behaviours that changed with the different functionalizations. Terathane® 650 (Tera) tends to easily crystallize (Fig. 8). Observed melting peaks can be explained by the high polydispersity of this commercial product. The crystallization decreased for the different modified polymers showing that the esterification of alcohol function disturbed the crystallization of the compound as only some chain segments could crystallize in that case. This crystalline organization was totally absent for TeraSPZn as ionic bonds drastically limited chain mobility. This decrease in chain mobility has been extensively studied by Eisenberg et al. [56] and Vanhoorne et al. [57] who pointed out this restriction in mobility, leading to higher T_g. They showed that in the case of polymers with higher molecular weights (>5000 g mol^{-1}), two T_gs could be observed: the first one due to polymer chains engaged in multiplets, and the second one to polymer chains without any interactions with ionic region. The behaviour of this type of ionomer was similar to what was also observed for phase segregated system [56,58,59]. In our study, ionomers were oligomers and this phase segregation was not detected. In some cases, a second transition was observed with negative temperature which tends to increase from TeraSH to TeraSPZn (Table 2). This increase in temperature was quite normal since adding polar or ionic groups at the chain ends results in a raise of glass transition. We have to note that, in the case of TeraSPZn, two heat capacity jumps were observed, the first one close to that of initial Tera and the second one, close to 20 °C. Polymer chains engaged in ionic domains had reduced mobility in comparison with that of in non-ionic ones. These temperatures were measured several times on different samples and same values were observed.

Similarly, no crystalline domains were observed for calcium ions and T_g values were in the same order of magnitude. The particular case of sodium must be noted since only one T_g was measured. This product remained soluble in methanol whereas ionomers from divalent ions were insoluble. At last, no influence of the quantity of the added cation on the thermal properties was noticed.

For compounds issued from PETDEG, behaviours were quite different (Fig. 9). They were strongly rigid compounds due to the presence of terephthalic rings. PETDEG was weakly crystalline ($T_m = 25$ °C) as already reported in the literature [60]. The glass

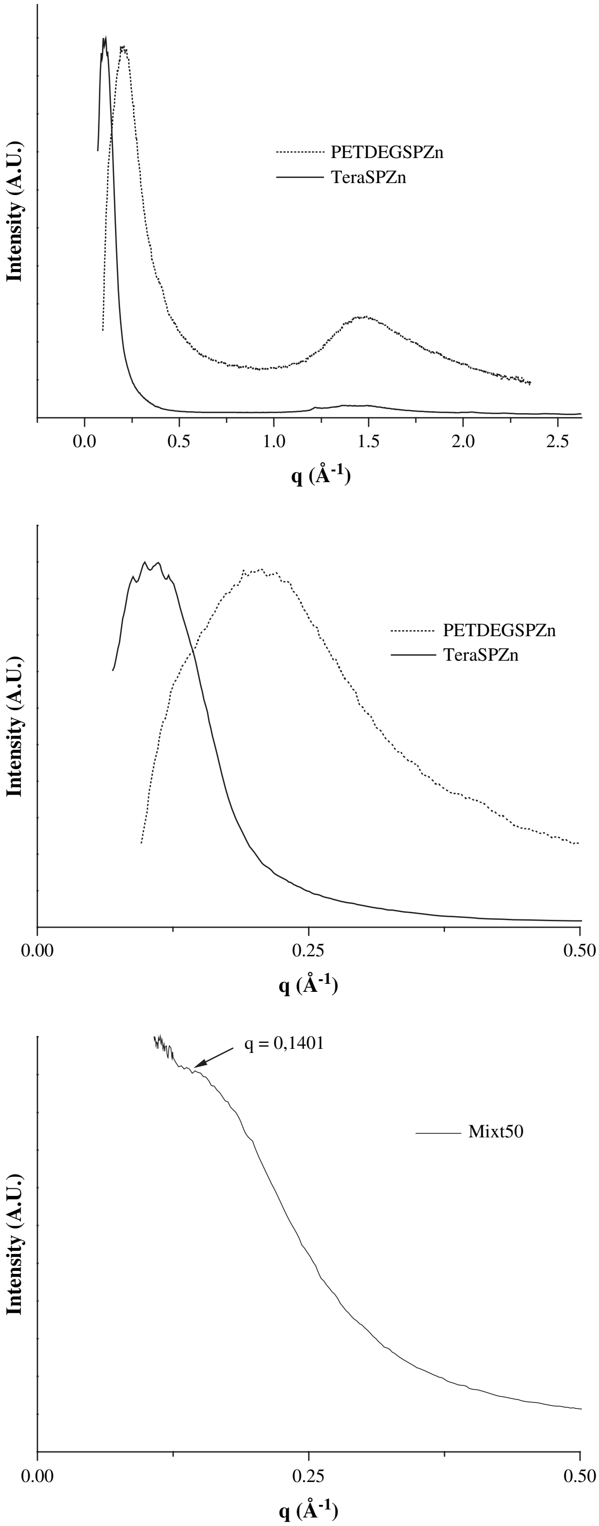


Fig. 7. SAXS spectrum of ionomers synthesized from Zn.

Table 1
Characteristic sizes determined by SAXS for Zn ionomers

Ionomers	Scattering vector, q (Å^{-1})	Bragg distance d (Å)
TeraSPZn	0.105	60
PETDEGSPZn	0.208	30
Mixt50	0.140	45

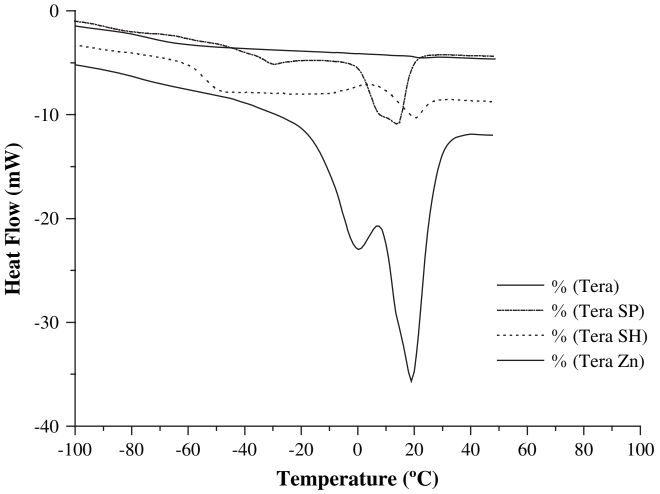


Fig. 8. DSC curves for compounds issued from Tera.

Table 2
Glass transitions observed for the different compounds

Compounds	T_g (°C)	T_m (°C)
Tera	−75	−1 and +18
TeraSH	−58	+20
TeraSP	−38	+5 and +15
TeraSPZn1	−70 and +20	–
TeraSPZn2	−68 and +18	–
TeraSPCa1	−61 and 5	–
TeraSPCa2	−59 and 3	–
TeraSPNa	−6	–
PETDEG	−51	–
PETDEGSH	−49	–
PETDEGSP	−19	–
PETDEGSPZn	23	–
Mixt50	3	–

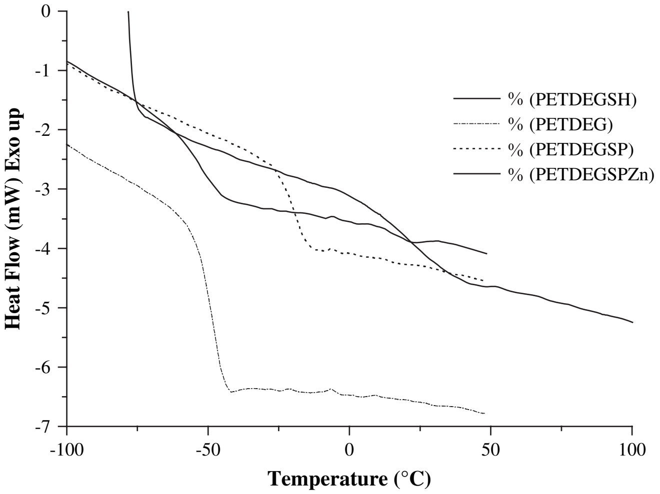


Fig. 9. DSC of compounds issued from PETDEG.

transition observed in PETDEGSH was close to the PETDEG one, showing that the functionalization by thioglycolic acid had only a low influence on the glass transition. The functionalization by phosphonic acids made the system more rigid and explained the increase of the glass transition temperature. This chain stiffness was enhanced during the association with Zn and thus, the temperature of the transition increased. The more the compounds were rigidified by functionalization, the more the temperature of the transition increased.

4. Conclusion

Telechelic halato ionomers based on phosphonic acid were synthesized according to a simple method using vinyl phosphonic acid like reagent. Nature of the starting telechelic compounds that were functionalized as well as nature of the used cation strongly influenced thermal properties of the final ionomers. Furthermore, crystallinity of the starting oligomers disappeared after cross-linking. Moreover, the mixture of two diphosphonic ionomers having different chemical structures allowed to afford an ionomer with intermediate properties. The use of this couple TeraSP/PET-DEGSP should permit to synthesize a range of ionomers with properties depending on the ratio of the different constituents.

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