

Proton Conducting PAMPS Networks: From Flexible to Rigid Materials

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ABSTRACT: To elaborate tailor-made proton conducting materials showing an interesting range of flexibility, a series of conetworks combining poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) and poly(ethylene oxide) dimethacrylate (PEGDM) with various chain lengths was synthesized. The homogeneity of these conetworks was checked by differential scanning calorimetry and dynamic mechanical thermal analysis. The swelling behavior of these materials is strongly influenced by the amount of sulfonic acid groups and the endothermal peak temperature, characteristic of the presence of bound water in the

conetwork, increases from 65 to 120°C when AMPS amount increases from 10 to 75 wt %. In addition, the proton conductivity of these materials varies from 10^{-3} to 10^{-1} S cm⁻¹, depending on the AMPS amount. The storage moduli were found to be affected by both the AMPS content in the conetwork and its crosslinking density. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3672–3680, 2008

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INTRODUCTION

Ionic conducting polymer electrolytes find numerous applications in electrochemical devices in which high ionic conductivity is required, such as fuel cells, electrochromic devices, or sensors.^{1–4} Among ionic conducting polymers, proton conducting polymers have been the subject of greatest attention. Thus, polyelectrolytes containing sulfonic acid groups are particularly interesting because of their high conductivity resulting from the high dissociation constant value of the sulfonic acid group, both in polar organic solvents and in water.⁵ The water swelling extent is also a key consideration for proton conducting polymer electrolyte materials. Indeed, extreme water swelling causes a loss of dimensional stability, while low water swelling reduces proton conductivity. Crosslinking is an efficient means to control swelling, also yielding the dimensional and thermal stability of the obtained materials.^{6–10}

Most materials made from poly(2-acrylamido-2-methyl-propanesulfonic acid) (PAMPS) appear as hydrogels showing a particularly high proton conductivity.¹¹ A major challenge in the elaboration of electrochemical devices is to include PAMPS in

materials exhibiting no cold flow while maintaining the PAMPS hydrogel high proton conductivity (1.24 S cm⁻¹ as 80 wt % in water).¹² To achieve this, PAMPS must be crosslinked or combined into a copolymer^{2,13} to obtain a material that can be conveniently handled. This pathway is particularly interesting due to the fact that crosslinking prevents dissolution of the polymer and should also reduce undesirable swelling. However, it appears that this synthetic route is not always efficient enough and that many of the described PAMPS-based crosslinked materials still behave as hydrogels. For example, PAMPS crosslinked with *N,N*-methylene-bisacrylamide (BAA) yields a hydrogel, the swelling and conductivity of which depend on the crosslinking density and the nature of the solvent. The highest conductivity values for PAMPS hydrogels (about 1 S cm⁻¹) are obtained with networks containing 60–80 wt % water and 1–2 wt % BAA.¹² However, light scattering measurements studies carried out on these hydrogels reveal a nonhomogeneous distribution of PAMPS and BAA in the systems.¹⁴ Hydrogels were also obtained when crosslinking copolymers of PAMPS with acrylamide,^{15,16} *N*-*tert*-butylacrylamide,¹ or 2-hydroxyethyl methacrylate.^{2,17}

On the other hand, PEO-based solid polymer electrolytes (SPEs) have been extensively investigated as ionic conducting materials mainly in the presence of lithium salts.^{18,19} The metal coordination process through lone electronic pairs of PEO oxygen atoms

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improves ion-pair separation, which in turn can favour increased ionic conductivity. However, one of the main drawbacks of PEO-based SPEs is the significant degree of crystallization of the PEO segments at ambient temperature which occurs as soon as the PEO molecular weight exceeds 2000 g mol^{-1} . Indeed ion migration mainly takes place in the amorphous parts of the polymer and the crystalline regions drastically decrease ion mobility. A variety of approaches has been used to decrease the PEO crystallinity among which the preparation of networks with relatively short PEO segments.^{19,20} However, due to the network architecture the polymer flexibility decreases compared with the linear polymer and, consequently, the ionic conductivity decreases accordingly. All the expected improvements through network controlled synthesis nevertheless do not lead to conductivity values higher than $10^{-4} \text{ S cm}^{-1}$ for PEO-based SPEs.

The design of materials, which are proton conducting and exhibit a large flexibility range, is achieved by combining moderately low water swelling PEO components with PAMPS into conetwork architectures. To reach this particular configuration, a series of α,ω -dimethacrylate poly(ethylene oxide)s (PEGDMs) with different molecular weights ($M_n = 875, 550, \text{ and } 330 \text{ g mol}^{-1}$) were chosen as crosslinkers for PAMPS. Each of these PEGDM crosslinkers will lead to a conetwork showing a given crosslinking density, i.e. a conetwork for which a different degree of swelling can be expected. In addition each conetwork should exhibit particular mechanical properties while the chemical nature of the partners remains unchanged. Thus a large range of proton conducting materials, from rigid to flexible materials, could be elaborated both changing the partner respective amounts in the material and the crosslinking density. The properties of the conetworks were quantified by means of differential scanning calorimetry (DSC), conductivity measurements, and dynamic mechanical thermal analysis (DMTA).

EXPERIMENTAL

Materials

The 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (Aldrich, 99% purity) was used without further purification. α,ω -dimethacrylate poly(ethylene oxide) (PEGDM) oligomers with various molecular weights ($M_n = 875, 550, \text{ and } 330 \text{ g mol}^{-1}$) were provided by Acros. The 2,2'-azobisisobutyronitrile (AIBN, Acros Organics) was recrystallized in methanol and DMSO (Merck, puro grade) was distilled before use.

Conetwork synthesis

The overall composition of the conetworks was varied from 90 to 10 wt % of each partner amount. When the PEGDM reacts, it forms a PEO network thus all investigated conetworks are reported as PEO_{*x*}/PAMPS (*y/z*), the number *x* following PEO corresponding to the molecular weight of the PEGDM oligomer used for the conetwork synthesis. The numbers between brackets (*y/z*) correspond to the PEGDM and AMPS weight proportions, respectively. Thus, a conetwork obtained from a mixture of 1 g α,ω -dimethacrylate poly(ethylene oxide) ($M_n = 875 \text{ g mol}^{-1}$) and 0.34 g AMPS will be noted PEO₈₇₅/AMPS (75/25).

All conetworks were synthesized according to the same pathway. For example, PEO₃₃₀/AMPS (25/75) conetwork was prepared as follows: 3 g AMPS (14.49 mmol), 200 mg AIBN (1.22 mmol, 5 wt % by weight with respect to the sum of AMPS and PEGDM), and 1 g PEGDM (3.03 mmol— $M_n = 330 \text{ g mol}^{-1}$) were dissolved in 4.5 mL DMSO. All conetworks were synthesized keeping the same weight ratio between the sum of AMPS and PEGDM monomers and AIBN. DMSO volumes were set at 1.5 mL per AMPS gram. The mixture was degassed under nitrogen and then poured into a mould made from two glass plates clamped together and sealed with a 0.5-mm-thick Teflon[®] gasket. The mould was then kept at 60°C for 3 h and a post cure was carried out at 120°C for 1 h. The sample was then immersed in a large volume of water (twice 1 L per 4 g conetwork) for 24 h in order to exchange DMSO with water. Samples were then dried for 12 h at 60°C under vacuum (under a 0.1 mmHg vacuum). All samples are transparent.

Linear AMPS homopolymer (PAMPS) was synthesized by dissolving 0.4 g AMPS and 20 mg AIBN in 0.6 mL DMSO. The mixture was heated at 60°C for 3 h and at 120°C for 1 h under nitrogen. PAMPS was then precipitated in acetone and dried for 12 h at 60°C under vacuum.

Characterizations

Soluble fraction in the final material

The amount of unreacted starting material contained in the conetwork is quantified from a known weight of conetwork extraction in a Soxhlet with dichloromethane or methanol for 48 h. After extraction, the sample was dried under vacuum at 50°C until constant weight and then weighted. The extracted content (EC) is given as a weight percentage $EC(\%) = \frac{(W_0 - W_E)}{W_0} \times 100$ where W_0 and W_E are the weights of samples before and after extraction, respectively.

Swelling behavior

The swelling behavior of the materials was determined by water uptake measurements after immersing the different conetworks in deionised water for 12 h (which was shown to be largely sufficient to reach the maximum swelling value). After 12 h, the wetted conetworks were blotted dry with absorbent paper before weighing again. The water swelling ratio was calculated as $SR(\%) = \frac{W-W_0}{W_0} \times 100$ where W_0 and W were the sample weights before and after soaking in water, respectively.

T_g and water boiling point determination

For DSC measurements, the samples stored in the laboratory environment (about 20°C and 50 to 70% RH) were placed in an aluminium cell. The heating thermograms were recorded at 5°C min⁻¹ heating rate between -75 and 175°C after standard cooling to -75°C (20°C min⁻¹) on a DSC Q100 model (TA Instruments) calibrated with Indium standards. Boiling water endotherms were only detected on the first heating curves while the glass transition temperature (T_g) values were measured on the second scan.

Thermogravimetry analysis

Thermogravimetry measurements were performed using a TGA Q50 model (TA Instruments). Samples were heated at 20°C min⁻¹ from ambient temperature to 500°C, under argon atmosphere (60 mL min⁻¹).

Conductivity measurements

The proton conductivity σ was calculated from the impedance data, using the relation $\sigma = \frac{l}{R \times S}$ where l and S denote the thickness and the crosssectional area of the conetwork. The resistance value (R) associated with the sample conductivity was determined from the high-frequency intercept of the impedance with the real axis. The conductivity activation energy (E_a) was measured from temperature-conductivity curves according to the standard law. Conetworks were immersed for 12 h in water prior to conductivity measurements. Swollen conetworks were then cut into 1 cm² and were pressed between two single gold electrodes. To measure the temperature dependence of the conductivity, the cell was placed in a tempered, double-walled vessel and the temperature recorded in close proximity to the membrane with a K -type thermocouple. Measurements were carried out at temperatures ranging from 20 to 60°C. AC impedance spectra were recorded from 50,000 to 0.1 Hz with amplitude of 10 mV using an Autolab PGSTAT 30 Instrument.

Mechanical properties

Dynamic mechanical thermal analysis (DMTA) measurements were carried out on film samples with a Q800 model (TA Instruments) operating in tension mode. Experiments were performed at a 1-Hz frequency and a heating rate of 3°C min⁻¹ from -75 to 75°C. Typical dimensions of the samples were 5 mm × 25 mm × 0.5 mm. The set-up provides the storage and loss moduli (E' and E'') and the damping parameter or loss factor ($\tan \delta$). The E' evolution was analyzed after normalization of all storage moduli at 3000 MPa at -75°C.

RESULTS AND DISCUSSION

PEO-AMPS conetworks were synthesized by free-radical copolymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) with α,ω -dimethacrylate poly(ethylene oxide) (PEGDM) oligomers as crosslinker with various molecular weights ($M_n = 875, 550, \text{ and } 330 \text{ g mol}^{-1}$). The copolymerization was initiated by radicals generated at 60°C by 2,2'-azobisisobutyronitrile (AIBN) as thermal initiator ($[AIBN]/[C=C] = 0.043$). The strong incompatibility of the starting materials namely AMPS and PEGDM was overcome by copolymerisation/crosslinking reactions carried out in DMSO as common solvent (1.5 mL per gram of AMPS). Indeed, water cannot be used because, contrary to AMPS, PEGDMs (875, 550, and 330 g mol⁻¹) are not soluble enough in water. The overall PEO/AMPS composition of the conetworks was varied from 10 to 90 wt % of each partner amount. Thus the quantity of DMSO in the starting reaction mixture varies from 20 to 59 wt % with respect to the total amount of products in the reaction mixture when the AMPS content varies from 10 to 90 wt % with respect to the total amount of compounds.

To check that AMPS and PEGDM are quantitatively copolymerized and crosslinked, the extractible products contained in the conetworks were measured systematically with methanol on the one hand, and dichloromethane, on the other hand. Crude conetworks directly issued from the synthesis reaction yield from about 20 to 60 wt % soluble fraction whatever the extraction solvent and the conetwork composition. This amount corresponds very closely to the DMSO weight proportion introduced in the starting mixture. ¹H NMR analyses of the methanol solution fraction confirm the presence of the introduced amount of DMSO and show that a small quantity of AMPS monomer and/or oligomers is also present (never more than 4 wt % as determined by conductivity measurements on samples extracted with water). On the other hand, ¹H NMR analyses of the products extracted with dichloromethane only evidence the presence of DMSO (to the exclusion of

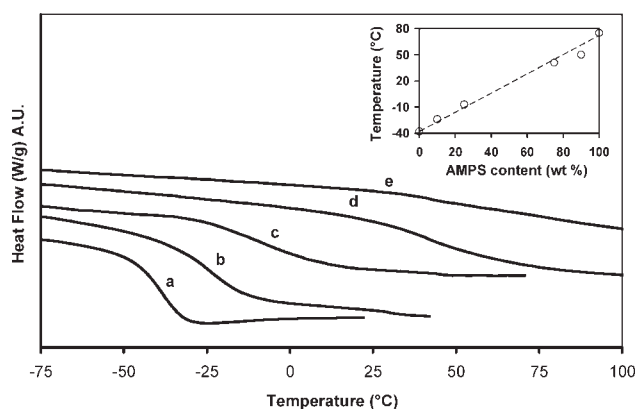


Figure 1 DSC traces of (a) PEO₈₇₅ single network and PEO₈₇₅/AMPS (b) (90/10), (c) (75/25), (d) (25/75), (e) (10/90) conetworks—second scan—heating rate: 5°C min⁻¹—insert: experimental values (○) and values calculated from additivity rule (- -) of T_g as function AMPS content.

PEGDM). The different PEO/AMPS conetworks should thus be considered as correctly crosslinked. Considering the difficulty to remove DMSO from conetwork by heating or/and under vacuum, DMSO was exchanged with water and samples were then dried before further characterizations.

Thermal behavior

Having established that the crosslinking is completed enough such that no more than 4 wt % AMPS remains unreacted, the homogeneity of distribution of AMPS and PEGDM in the conetworks was then studied. As the reactivity ratios of the AMPS and PEGDM monomer pair are not published to our knowledge, one can reasonably assume that they should be close to those of AMPS and methacrylate polyethylene oxide methyl ether (PEGM - $M_n = 1068 \text{ g mol}^{-1}$) measured in DMSO at 70°C by Fineman-Ross method.²¹ The reactivity ratio values i.e. $r_{\text{AMPS}} = 0.57$ and $r_{\text{PEGM}} = 3.05$ suggest as a first approximation that PEGDM methacrylate functions rather react in the early reaction stages leading to a more or less inhomogeneous material. Thus, to investigate the conetwork homogeneity, glass transition temperatures (T_g) of the conetwork series were measured by DSC. Indeed, two glass transitions, each corresponding to a different phase (PEO and PAMPS), would be detected in case the material was inhomogeneous. The T_g of linear PAMPS is measured at +72°C. It should be noted that the T_g values of linear PAMPS reported in the literature vary from 75°C²² to 124°C²³ according to the experimental synthesis conditions. Thus the +72°C T_g value of linear PAMPS reported here is in agreement with those reported in the literature. On the other hand the T_g of PEO single networks are equal to +3 and -38°C for samples prepared from PEGDM with $M_n = 550$

and 875 g mol⁻¹, respectively. Thus the particular PEO₈₇₅/AMPS conetwork series was chosen as a test series because PEO₈₇₅ and PAMPS show the largest gap in T_g values i.e. -38°C compared with +72°C.

The DSC thermograms of the conetworks are shown in Figure 1. Whatever the conetwork composition, a single T_g value is detected witnessing the absence of PEO or AMPS enriched cluster formation during the conetwork synthesis. In addition, the T_g value depends on the conetwork composition according to the additivity rule equation (insert Fig. 1). For example, PEO₈₇₅/AMPS (90/10) and (10/90) conetworks show one T_g at -25 (b) and 48°C (d), respectively. However no clear glass transition temperature could be detected on the PEO₈₇₅/AMPS (50/50) sample (the same observation was reported on a *N,N*-methylene-bis-acrylamide/AMPS hydrogel.¹²) On the other hand, the homogeneity of a conetwork can also be derived from dynamic mechanical thermal analysis (DMTA) which is often a more sensitive technique than DSC as far as the detection of the occurrence of phase separation is concerned. The $\tan \delta$ peak of the α -relaxation is associated with segmental chain motions and is also among others greatly influenced by the conetwork weight composition.

Thermomechanical properties of PEO₈₇₅-AMPS conetwork series are reported in Figure 2. PEO₈₇₅ single network shows a mechanical relaxation characterized by a maximum $\tan \delta$ value located at -20°C ($\tan \delta_{(\text{PEO}_{875})} = 0.7$) [Fig. 2(a)]. On the other hand, thermomechanical characteristics of the PAMPS homopolymer cannot be obtained since linear PAMPS is a powder.

A single α mechanical relaxation is detected for PEO/AMPS (90/10) and (75/25) conetworks located at -15 and 0°C, respectively. For higher AMPS contents in the conetwork, $\tan \delta$ -temperature curves are quite different. For example, PEO₈₇₅/AMPS (50/50) conetwork shows a very broad relaxation ranging over 130°C, the maximum $\tan \delta$ value appearing at

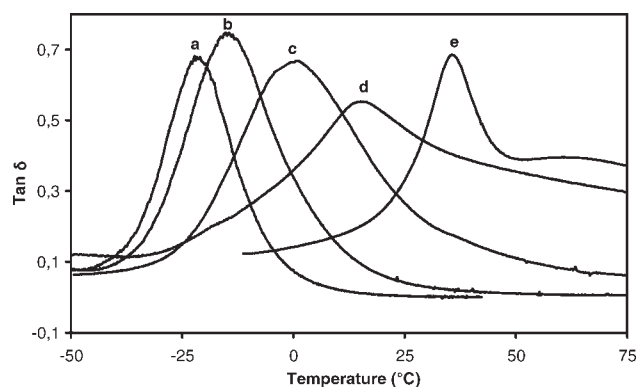


Figure 2 Loss tangent vs. temperature curves of (a) PEO₈₇₅ single network, PEO₈₇₅/AMPS (b) (90/10), (c) (75/25), (d) (50/50), and (e) (25/75) conetworks.

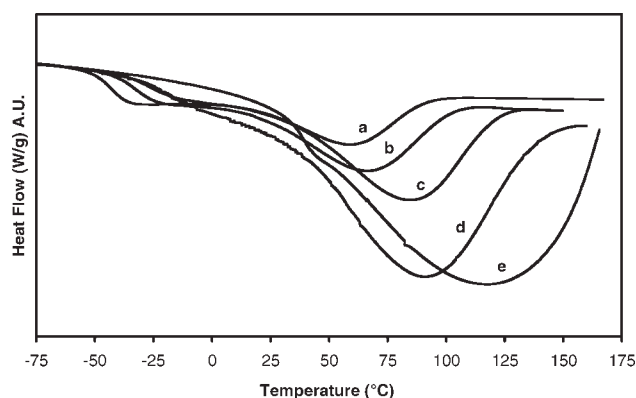


Figure 3 DSC measurements on (a) PEO₈₇₅ single network, PEO₈₇₅/AMPS (b) (90/10), (c) (75/25), (d) (50/50), and (e) (25/75) conetworks—first scan—heating rate: 5 K min⁻¹.

+15°C. The PEO₈₇₅/AMPS (25/75) conetwork shows two superimposed peaks: a narrow one the maximum of which is centered at 35°C and a very broad one at higher temperature ($T_{\alpha} = \sim 60^{\circ}\text{C}$). Thus, these two peaks might be assigned to two domains with different compositions: one would be composed of a rich PEO₈₇₅ phase containing AMPS ($T_{\alpha} = +35^{\circ}\text{C}$) and the other of a rich AMPS one containing PEO₈₇₅ ($T_{\alpha} = \sim 60^{\circ}\text{C}$ being spread out on a few 10°). Furthermore, the width of these $\tan \delta$ peaks increase with AMPS content (for example the half-height width of $\tan \delta$ peak is equal to about 20°C and to 40°C for the PEO₈₇₅ single network and PEO₈₇₅/AMPS (75/25) conetwork, respectively). Knowing that the broader the $\tan \delta$ peak, the less homogeneous the composition of the material, this increasing width of the conetwork relaxation peaks might be assigned to a nonhomogeneous crosslinking density throughout the sample.

In addition, the mechanical relaxation of the PEO₈₇₅ single network at -20°C disappears in the whole conetwork series. Thus although the crosslinking density is not homogeneous (broad transitions), a true phase separation which would lead to two well separated peaks does not take place during the conetwork synthesis or at least is considerably limited.

Water contained in a polymer material usually shows a different behavior compared with bulk water. When a small amount of water is inserted in a material, the water molecules strongly associate with the polar and ionic groups present on the polymer chain and cannot be detected by calorimetric analysis (nonfreezing-bound water).^{1,12,24} On the other hand, water which has a lower degree of interaction with the polymer can be detected by calorimetric analysis (freezing-bound water). Generally, it freezes and boils at temperatures lower and higher, respectively, than that of bulk water.

To characterize the water state in the conetwork series, DSC measurements were carried out on PEO₈₇₅/AMPS conetworks containing from 10 to 75 AMPS wt %

(Fig. 3). Only the first scan is represented. No ice melting endotherm is detected whatever the conetwork composition when samples are cooled from room temperature to -90°C and then heated back to room temperature. The water contained in the conetworks is thus in strong interaction with polymer chains.

A broad endothermic peak was detected from 40 to 90°C on the thermogram recorded on PEO₈₇₅ single network. This phenomenon has often been observed on material containing ethylene oxide units and was assigned to absorbed water.²⁵⁻²⁷ As far as the conetworks are concerned the endothermic peak temperature is strongly affected by AMPS weight content. Indeed, the peak temperature increases from 65 to 120°C when AMPS amount increases from 10 to 75 wt %. Because of the slow heating rate (5°C min⁻¹), the shift in the temperature position cannot be assigned to a kinetic effect. In addition the peak intensity strongly increases with the AMPS content showing that the bound water amount in the conetworks increases accordingly. This water is associated to ionic and polar sites since no melting peak is detected. Similar results were obtained on PEO₅₅₀/AMPS and PEO₃₃₀/AMPS conetworks.

Furthermore, Figure 4(A) shows the thermogravimetric analysis spectra of PEO₈₇₅/AMPS conetworks

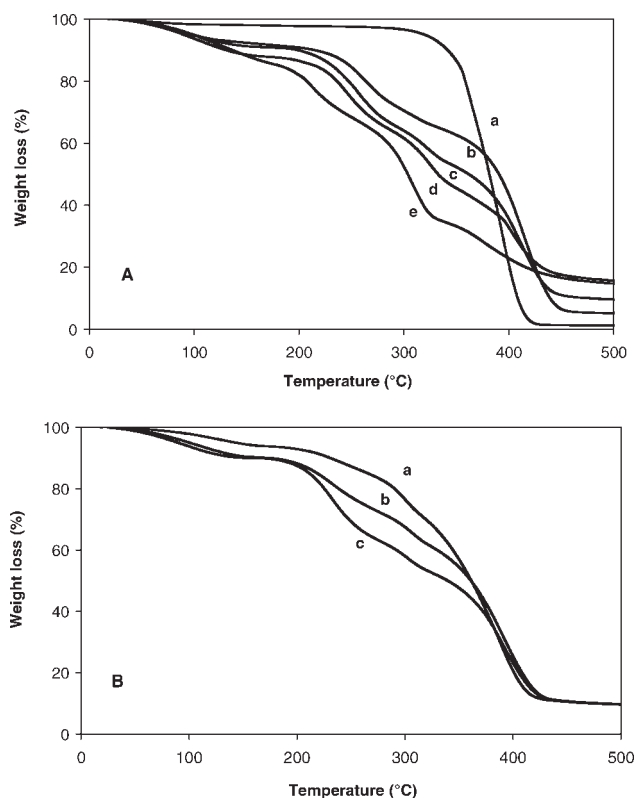


Figure 4 TGA curves of (A): (a) PEO₈₇₅ single network and PEO₈₇₅/AMPS (b) (90/10), (c) (75/25), (d) (50/50), (e) (25/75) conetworks—(B): PEO/AMPS (75/25) co-networks synthesized starting from (a) PEGDM₃₃₀, (b) PEGDM₅₅₀, and (c) PEGDM₈₇₅.

containing from 10 to 75 AMPS wt %. Single PEO₈₇₅ network is stable at temperature up to 325°C, and its decomposition proceeds in a single step whereas PEO₈₇₅/AMPS conetworks are characterized by different thermogravimetric profiles. A first weight loss is detected between 80 and 150°C and it is assigned to the evaporation of water contained in the materials. When the amount of AMPS in the conetwork increases from 10 to 75 wt %, the absorbed water amount increases from 8 to 13 wt %, confirming the results previously obtained by DSC (Fig. 3): the higher the AMPS content in the conetwork, the more the amount of water adsorbed by the material. A second decomposition region, beginning at 200–225°C and ending at about 325°C, is noticeable and due to the decomposition of PAMPS domains.²⁸ Earlier onset of the decomposition temperature is noted for the conetworks with a higher amount of AMPS. Thus the temperatures corresponding to 20% weight loss decreased from 264 to 207°C with the increase of AMPS content from 10 to 75%. Therefore improvement of thermal stability of the materials is achieved by decreasing AMPS content in the conetwork. A third weight loss from 325 to 425°C is attributed to the decomposition of the PEGDM segments. Beyond 425°C, one observes the presence of a residue the proportion of which increases from 5 to 16% (as measured at 500°C) when the AMPS content increases from 10 to 75 wt %. This is typical of the presence of an inorganic residue. Jiang et al.²⁹ studied the thermal degradation of poly(vinylsulfonic acid) and identified the residue by infrared analysis as sulfate ions formed during the decomposition of the polymer. Thus one can suppose the same decomposition process occurs in the PEO/AMPS conetworks.

In addition, the influence of the crosslinking density on the thermal stability of the materials is presented in Figure 4(B), for PEO/AMPS (75/25) conetworks. Earlier decomposition is observed for the longer PEGDM chain length ($M_n = 875 \text{ g mol}^{-1}$): a decrease in the crosslinking density leads to a decrease of the decomposition temperature. Thus the crosslinking density affects the thermal stability of the material (the best thermal stability is obtained when PEGDM₃₃₀ is used as a crosslinker).

Swelling behavior

The water content of a hydrophilic material strongly affects its mechanical properties, dimensional stability, and proton conductivity. The proton conductivity of the present conetworks is ensured by sulfonic acid groups. The conetwork ability to absorb and to maintain significant amounts of water should thus favour the ionic conductivity. Unfortunately, materials with high sulfonate group content generally

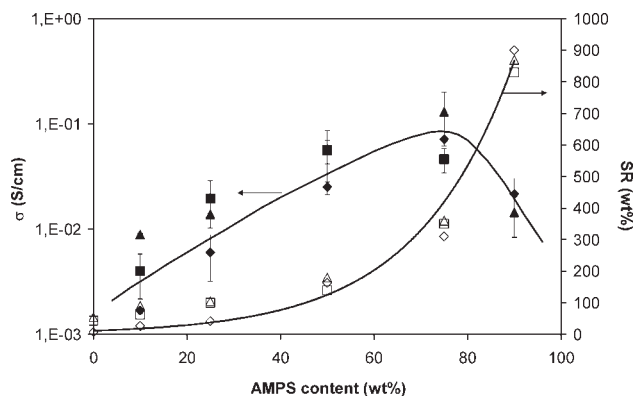


Figure 5 Swelling ratio (empty symbol) and proton conductivity (full symbol) versus AMPS contents for (\diamond , \blacklozenge) PEO₃₃₀/AMPS, (\square , \blacksquare) PEO₅₅₀/AMPS, and (\triangle , \blacktriangle) PEO₈₇₅/AMPS conetworks.

absorb excessive amounts of water, leading to very poor tearing strength. The water swelling ratios were measured on the three conetwork series with different weight compositions (Fig. 5).

The PEO₃₃₀, PEO₅₅₀, and PEO₈₇₅ single networks show 10, 45, and 55% swelling ratio, respectively when soaked in water for 12 h. The swelling ratios increase exponentially with AMPS weight content in the conetwork series and is equal to 40, 160, and 350% for PEO₃₃₀/AMPS (75/25), (50/50), and (25/75) conetworks, respectively under the same conditions. PEO/AMPS (10/90) conetwork behaves as a hydrogel since its initial weight is multiplied by 10. However this swelling ratio is about twice lower than that of an AMPS/*N,N*-methylene-bis-acrylamide (93/7) hydrogel (2400%).¹²

In addition if one looks at the effect of the PEO chain length on the swelling ratio for a given AMPS amount, it is hardly noticeable. Thus, the swelling ratio is mainly governed by the AMPS content especially when it is higher than 50 wt %.

Proton conductivity

In a fully hydrated material, mobile protons of AMPS may dissociate from immobilized sulfonic acid groups and diffuse throughout the conetwork. One can assume that the crosslinked copolymer acts as a matrix which undergoes only very slow movements. The conetwork conductivity is thus mainly determined by two parameters: the mobility of the proton which depends on the amount and the structure of the bound water and the charge density which depends on the AMPS content. The proton conductivity may be also affected by the cross-linking density.

First, the proton conductivities of the three PEO/AMPS conetwork series synthesized from different molecular weight PEGDM were measured at 20°C.

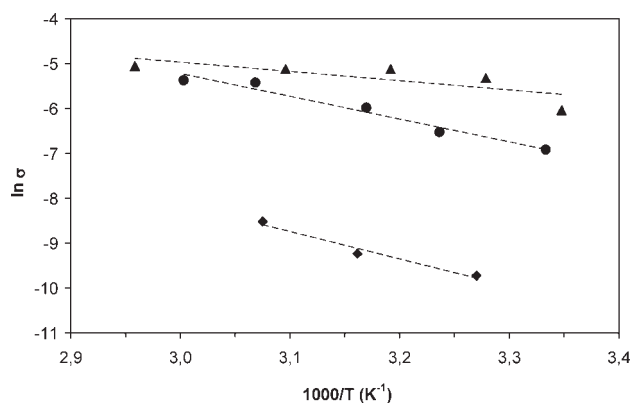


Figure 6 Arrhenius plot of conductivity as a function of temperature for PEO₃₃₀/AMPS (◆) (90/10), (●) (50/50), and (▲) (10/90) conetworks.

For a given AMPS content, the conductivity hardly depends on the PEGDM molecular weight (Fig. 5). Conductivities are similar for conetworks containing PEO₅₅₀ or PEO₈₇₅, and slightly lower for PEO₃₃₀. For example, PEO/AMPS (75/25) conetworks show a conductivity of 6.10^{-3} and 2.10^{-2} S cm⁻¹ when PEGDM₃₃₀ and PEGDM₈₇₅, are respectively chosen as crosslinker.

On the other hand, the proton conductivity increases with AMPS content up to 75 wt % in the conetwork. For example, the PEO/AMPS (90/10) to (25/75) conetwork conductivities vary from 2×10^{-3} to 7×10^{-2} S cm⁻¹ at 20°C which is comparable with results reported in the literature.^{30,31} These values of conductivity are comparable with those measured on AMPS/*N,N*-methylene-bis-acrylamide (93/7) hydrogel containing 80 wt %¹² water or linear poly(*N*-tert-butylacrylamide-*co*-AMPS) at 98% RH.¹ On the other hand for PEO /AMPS (10/90) conetworks, a significant decrease in the conductivities is observed compared with PEO/AMPS (25/75). This has been assigned to a predominant effect of the dilution of the charge carriers, due to excessive swelling, similarly to an observation reported by Qiao et al. on similar materials.³¹ It is believed the same effect is observed here. Thus, the highest proton conductivity ($\sigma = 0.1$ S cm⁻¹, $T = 20^\circ\text{C}$) was obtained for PEO₈₇₅/AMPS (25/75) conetwork.

Proton transport might occur through two mechanisms. The first transport mechanism, called a “vehicle” mechanism, assumes a proton combines with the solvent molecules (leading to H₃O⁺ in this case) and then diffuses as such.³² The second of these is a “jump” mechanism, which can be idealized as the proton being passed down the chain of water molecules. For such a mechanism, the activation energy for proton conductivity should be around 14–40 kJ mol⁻¹.³³ The particular value of the activation energy is therefore an indication on the proton transport mechanism.

Finally, proton conductivities of the PEO/AMPS conetworks were measured as a function of temperature from 20 to 60°C (Fig. 6). The variation of the conductivity follows the Arrhenius law in the studied temperature range. All conetworks exhibited positive temperature–conductivity dependencies whether they were prepared with different compositions or with different PEGDM lengths.

The conetwork conductivity E_a values were derived from the slope of Ln versus $1/T$ plots. All activation energy values obtained here are between 10 and 50 kJ mol⁻¹. For a PEO/AMPS conetwork series, E_a decreases when AMPS content increases. For example, PEO₃₃₀/AMPS (90/10) and (10/90) show E_a equal to 50 and 17 kJ mol⁻¹, respectively. These values are similar to E_a s measured on material containing AMPS.^{31,34} Hence, it can be concluded from the Arrhenius plot that the proton transport occurs predominantly by the “jump” mechanism.

Thermomechanical properties

For one weight proportion, the conetwork macroscopic behavior varies from flexible to brittle film when the PEGDM molecular weight decreases from 875 to 330 g mol⁻¹. For a given PEGDM molecular weight, conetworks become more and more brittle with increasing AMPS content. These properties can be accurately quantified by DMTA.

First, storage modulus (E') versus temperature curves were recorded on a series of PEO₈₇₅/AMPS conetworks (Fig. 7). This crosslinker length (PEGDM₈₇₅) was chosen because its T_g (-28°C) shows the largest difference with the T_g of linear PAMPS ($+72^\circ\text{C}$). All E' –temperature curves show the same shape whatever the PEO₈₇₅/AMPS conetwork composition. Below the mechanical relaxation temperature, T_α , the storage modulus decreases slightly with the temperature. When the temperature increases, the storage modulus decreases rapidly at a

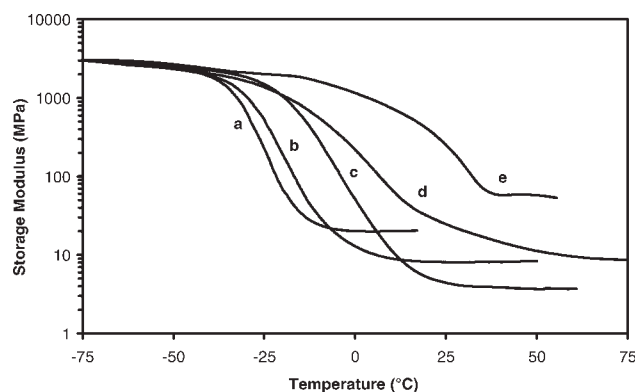


Figure 7 Storage modulus of PEO₈₇₅ single network (a) and PEO₈₇₅/AMPS (b) (90/10), (c) (75/25), (d) (50/50), and (e) (25/75) conetworks vs. temperature curves.

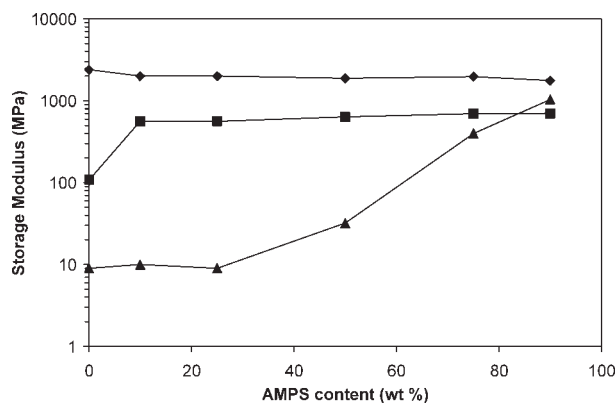


Figure 8 Storage moduli versus AMPS content for PEO/AMPS (◆) PEO₃₃₀/AMPS, (■) PEO₅₅₀/AMPS, and (▲) PEO₈₇₅/AMPS conetworks. $T = 20^{\circ}\text{C}$.

temperature around T_{α} the position of which depends on the conetwork composition (Fig. 2). Thus, T_{α} increases from -15 to $+60^{\circ}\text{C}$ when AMPS amount increases from 10 to 75 wt %. Above T_{α} , the storage modulus reaches the rubbery plateau, the modulus value of which depends on the AMPS content. Thus the rubbery plateau show storage moduli of about 6 and 80 MPa for PEO₈₇₅/AMPS (90/10) and (25/75) conetworks, respectively. Thus, the DMTA measurements show that it is possible to obtain proton conducting materials, whose behavior can be modified from a rigid device to a flexible one, and this only by changing the PEO/AMPS conetwork composition. Indeed, at 20°C , the storage modulus decreases from 1700 to 10 MPa, i.e. the material behavior is modified from rigid to flexible, when the AMPS content decreases from 75 to 10 wt %.

Another possibility for modifying the behavior of these conetwork series is to change the crosslinking density, i.e. the PEGDM crosslinker chain length. A decrease in the crosslinking density generally leads to a decrease in the material storage modulus. Thus, storage modulus of the three series of conetworks containing 0 to 90 wt % AMPS were recorded as a function of temperature and the particular values at 20°C for each sample were plotted as a function of temperature (Fig. 8). A large difference between the storage modulus of the PEO₈₇₅/AMPS series and the two others is observed. This can be explained by the difference of the storage modulus of PEO₈₇₅, PEO₅₅₀, and PEO₃₃₀ single networks which are equal to 10, 110, and 2400 MPa, respectively. Thus at 20°C PEO₈₇₅ single network shows a low storage modulus (10 MPa) that explains its flexibility. When the amount of AMPS increases in the conetwork, the storage modulus increases accordingly (T_g of linear PAMPS is equal to $+72^{\circ}\text{C}$). This clearly shows that the storage moduli of the PEO/AMPS conetworks are mainly influenced by the choice of the crosslinker particularly for the

proportions of AMPS lower than 50 wt %. For example, the storage modulus at 20°C of PEO/AMPS (90/10) conetworks increases from 10 to 2000 MPa when the PEGDM molecular weight decreases from 875 to 330 g mol^{-1} . Furthermore, storage moduli of different PEO/AMPS (10/90) conetworks reach almost 1000 MPa showing the low influence of the crosslinker at this composition.

Thus DMTA measurements quantify the macroscopic mechanical behavior of the conetworks and confirm that it is possible to elaborate tailor-made proton conducting materials displaying widely different storage moduli and therefore different flexibility. This behavior can be modulated not only at room temperature as described in this manuscript, but also for all other temperatures. In addition, all these materials show proton conductivity in the range 10^{-1} – 10^{-3} S cm^{-1} which is the same order of magnitude generally measured on AMPS hydrogels or copolymers.

CONCLUSION

Proton conducting conetworks combining a polyelectrolyte (PAMPS) and neutral polymer (PEO) were successfully developed. The choice of PEGDM as crosslinker allowed varying the crosslinking density without changing the chemical nature of the material precursors.

The amount of water absorbed by the conetworks mainly depends on the AMPS content. However the swelling ratio is lower than those reported for the AMPS hydrogels. Proton conductivities are quite comparable with those reported for the corresponding hydrogels. The highest proton conductivity equal to 10^{-1} S cm^{-1} at 20°C is obtained for PEO₈₇₅/AMPS (25/75) conetwork.

Thus, it is possible to elaborate tailor-made proton conducting materials showing different storage moduli and therefore different flexibility. This versatility is displayed in a large temperature range.

References

- Karlsson, L. E.; Wesslen, B.; Jannasch, P. *Electrochim Acta* 2002, 47, 3269.
- Walker, C. W. Jr. *J Power Sources* 2002, 110, 144.
- Barbosa, P. C.; Silva, M. M.; Smith, M. J.; Conçaves, A.; Fortunato, E. *Electrochim Acta* 2007, 52, 2938.
- Sakai, Y.; Matsuguchi, M.; Yonesato, N. *Electrochim Acta* 2001, 46, 1509.
- Hasa, J.; Ilavsky, M.; Dusek, K. *J Polym Sci Polym Phys Ed* 1975, 13, 253.
- Depre, L.; Ingram, M.; Poinsignon, C.; Popall, M. *Electrochim Acta* 2000, 45, 1377.
- Kerres, J. A. *J Membr Sci* 2001, 185, 3.
- Mikhailenko, S. D.; Wang, K.; Kaliaguine, S.; Xing, P.; Robertson, G. P.; Guiver, M. D. *J Membr Sci* 2004, 233, 93.

9. Lehtinen, T.; Sundholm, G.; Sundholm, F. *J Appl Electrochem* 1999, 29, 677.
10. Kang, M. S.; Choi, Y. J.; Moon, S. H. *J Membr Sci* 2002, 207, 157.
11. Randin, J. P. *J Electrochem Soc* 1982, 129, 1215.
12. Zygadlo-Monikowska, E.; Florjanczyk, Z.; Wielgus-Barry, E.; Hildebrand, E. *J Power Sources* 2006, 159, 392.
13. Karlsson, L. E.; Jannasch, P.; Wesslen, B. *Macromol Chem Phys* 2002, 203, 686.
14. Travas-Sejdic, J.; Easteal, A. J. *Polymer* 2000, 41, 2535.
15. Travas-Sejdic, J.; Easteal, A. J. *Polym Gels Networks* 1997, 5, 481.
16. Travas-Sejdic, J.; Easteal, A. J. *J Appl Polym Sci* 2000, 75, 619.
17. Zukowska, G.; Williams, J.; Stevens, J. R.; Jeffrey, K. R.; Lewara, A.; Kulesza, P. J. *Solid State Ionics* 2004, 167, 123.
18. Armand, M. B.; Chabagno, J. M.; Duclot, N. J. In *Fast Ion Transport in Solids*, Vashista, P., Eds., Elsevier: Amsterdam, 1979, p 131.
19. MacCallum, J. R.; Vincent, C. A.; Eds.; *Polymer Electrolyte Reviews I*, Elsevier: Amsterdam, 1987.
20. Carvalho, L. M.; Guegan, P.; Cheradame, H.; Gomes, A. S. *Eur Polym J* 2000, 36, 401.
21. Platel, D.; PhD of Paris VI University, 2005; p 45.
22. Huglin, M. B.; Rego, J. M.; Gooda, S. R. *Macromolecules* 1990, 23, 5359.
23. Coskun, R.; Soykan, C.; Delibas, A. *Eur Polym J* 2006, 42, 625.
24. Hatakeyama, H.; Hatakeyama, T. *Thermochim Acta* 1998, 308, 3.
25. Kotov, S. V.; Pedersen, S. D.; Qiu, W.; Qiu, Z. M.; Burton, D. J. *J Fluorine Chem* 1997, 82, 13.
26. Khalid, M. N.; Agnely, F.; Yagoubi, N.; Grossiord, J. L.; Couarraze, G. *Eur J Pharma Sci* 2002, 15, 425.
27. Kufact, M.; Bozkurt, A.; Tulu, M. *Solid State Ionics* 2006, 177, 1003.
28. Aggour, Y. A. *Polym Degrad Stab* 1998, 60, 317.
29. Jiang, D. D.; Yao, Q.; McKinney, M. A.; Wilkie, C. A. *Polym Degrad Stab* 1999, 63, 423.
30. Cho, K. Y.; Jung, H. Y.; Shin, S. S.; Choi, N. S.; Sung, S. J.; Park, J. K.; Choi, J. H.; Park, K. W.; Sung, Y. E. *Electrochim Acta* 2004, 50, 589.
31. Qiao, J.; Hamaya, T.; Okada, T. *Chem Mater* 2005, 17, 2413.
32. Smitha, B.; Sridhar, S.; Khan, A. A. *Macromolecules* 2004, 37, 2233.
33. Colombari, P.; Novak, A. In *Proton Conductors*, Colombari, P., Ed., Cambridge University Press: Cambridge, 1992, p 46.
34. Pei, H.; Hong, L.; Lee, J. Y. *J Power Sources* 2006, 160, 949.