



Physical ageing and molecular mobilities of sulfonated polysulfone for proton exchange membranes

C. Lixon Buquet^{a,b}, F. Hamonic^a, A. Saiter^a, E. Dargent^{a,*}, D. Langevin^b, Q.T. Nguyen^b

^a LECAP EA 4528, Institute for Materials Research FED 4114, Université de Rouen, Avenue de l'Université BP 12, 76801 Saint Etienne du Rouvray, France

^b PBS Department, UMR 6270 CNRS, MPBM, FR 3038, Université de Rouen, Boulevard Maurice de Broglie, 76821 Mont Saint Aignan Cedex, France

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ABSTRACT

The thermal behaviour, the physical ageing and the amorphous phase dynamics of polysulfone (PSU) and sulfonated polysulfone (SPSU) are characterized by thermogravimetric analysis and temperature modulated differential scanning calorimetry. The sulfonic group introduction (the sulfonation degree is 70%) in the polymer implies a drastic decrease of the thermal decomposition temperature (220 and 517 °C for SPSU and PSU respectively) and a modification of calorimetric parameters (for SPSU, the heat capacity in the glassy state is lower and the glass transition temperature T_g is higher than for PSU). In terms of molecular dynamics, the amorphous phase heterogeneities are greater and the cooperative rearranging region size at the glass transition temperature is smaller for SPSU than for PSU. Moreover, after a physical ageing process, the enthalpy recovery kinetic has slowed down by sulfonation. These results can be explained from the existence of sulfonic domains confining the amorphous phase domains.

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1. Introduction

The proton exchange membrane (PEM) is the core part of the Proton Exchange Membrane Fuel Cell. Nafion[®], manufactured by Dupont de Nemours, is the membrane commonly used as electrolyte for its good chemical and thermal resistance and high proton conductivity [1]. However this conventional polymer electrolyte membrane is expensive, mechanically unstable at temperature above 100 °C and conductive only under wet conditions in other words for a temperature lower than 80 °C [2].

Eventually, a lot of researches have carried to find new membranes, more successful, to replace the fuel cell's reference. Some thermoplastic such as polysulfone (PSU) [3], polyethersulfone [4], polyetherketone [5], polyimide [6], polybenzimidazole [7] were proposed to be the possible replacements of Nafion[®] provided that sulfonic groups are introduced into their structural units. Among the quoted polymers, the polysulfone (aromatic amorphous thermostable polymer, see Fig. 1) is considered as one of the most interesting for its low price and its commercial availability [8], as well as for its high glass transition temperature and its good mechanical properties [9]. To replace the fuel cell reference membrane, the conductivity of the new membrane must be known but also its mechanical, chemical and physical properties. In this work we propose to study the thermal behaviour, the physical ageing

and the amorphous phase dynamic of sulfonated polysulfone (SPSU).

The glassy state of an amorphous polymer exists at temperature below the glass transition temperature T_g and is characterized by an excess of free volume, an excess of enthalpy and an excess of entropy, when comparison is made with the thermodynamic equilibrium state. As a direct consequence, a glass kept at $T < T_g$ will lose its excess of enthalpy and entropy by molecular relaxation to reach the thermodynamic equilibrium state. This process is generally called structural relaxation or physical ageing [10]. After an infinite ageing duration performed on a glass maintained at a temperature $T_a < T_g$, but closed to T_g , the expected enthalpy loss ΔH_∞ can be estimated by means of the following relationship:

$$\Delta H_\infty = (C_{p_l} - C_{p_g})(T_g - T_a) \quad (1)$$

where C_{p_l} and C_{p_g} are the specific heat capacity of the equilibrium liquid and of the glass respectively. In polymer amorphous phases, main α relaxation processes are known to be cooperative phenomena and the molecule motions depend on neighbor's concerted motions [11]: the rearranging movement of one structural unit is only possible if a certain number of neighboring structural units is also moved within a polymer chain or in different chains in the vicinity. In this work, the sulfonation effects on the structural relaxation phenomena occurring at the glass transition in PSU samples are also investigated.

* Corresponding author. Tel.: +33 2 32 95 50 83; fax: +33 2 32 95 50 82.
E-mail address: eric.dargent@univ-rouen.fr (E. Dargent).

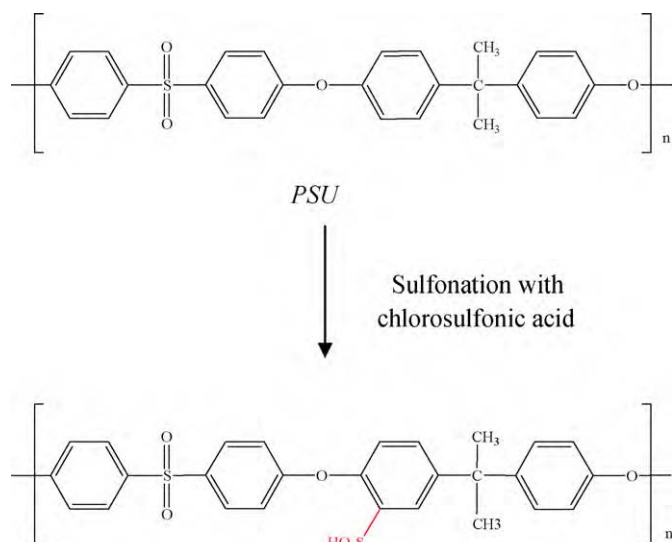


Fig. 1. Synthesis of sulfonated polysulfone (SPSU).

2. Experimental

2.1. Material

Polysulfone Udel 3500 or PSU used in this study is supplied by Solvay Advanced Polymer. Udel P-3500 is an amorphous polymer with a very high molecular weight grade ($M_w = 79,000 \text{ g mol}^{-1}$), and a tough, rigid, and transparent high-strength thermoplastic. The glass transition temperature of the dry material is $T_g = 185^\circ\text{C}$. In order to obtain a membrane, PSU is dissolved into N-methylpyrrolidone (NMP) (30% in weight), the solution is then poured on a glass support and the membrane is dried in a vacuum at 80°C over the night, then at 130°C during 4 h.

Sulfonated polysulfone (SPSU) is prepared following the procedure described by Quentin [12]. PSU (43.2 g) is dissolved in 1,2-dichloroethane (DCE) (450 ml) by stirring at 80 rpm at 60°C to obtain a homogeneous solution. A solution containing the chlorosulfonic acid (6.6 ml) dissolved in DCE (90 ml) is slowly added drop by drop during 1 h at 60°C and 80 rpm. The reaction mixture is stirred for 3 h. Afterwards, the precipitate polymer is isolated and washed with water and sodium hydroxide until neutral washing. Then SPSU is dried at 80°C over the night. To realize sulfonated polysulfone membranes, the sulfonated polymer is dissolved into N-methylpyrrolidone (NMP) (30% in weight), the solution is then poured on a glass support and dried in a vacuum at 80°C over the night, then at 130°C during 4 h. The sulfonation reaction is not total so the grafting rate is not reached one sulfonic group by monomer (SPSU is composed of sulfonated and non-sulfonated monomers, shown together in Fig. 1). In order to know the degree of sulfonation (DS) which is defined by the average number of sulfonic groups present in the sulfonated polymer, it is necessary to calculate the ion exchange capacity (IEC). The IEC indicates the number of milliequivalents of ions in 1 g of the dry polymer. A piece of membrane is exchanged with H^+ by immersing the sample in hydrochloric acid (HCl) 1 M for 24 h. The membrane is washed with distilled water until neutral washing to remove any excess of H^+ ions. Then, the sample is dried at 80°C over the night in a vacuum and weighted (W_{dry}). Afterwards, the membrane is immersed in 25 ml of sodium chloride (NaCl) 2 M during 24 h to exchange the H^+ with Na^+ . The resultant solution is then titrated by an aqueous solution of sodium hydroxide 0.02 M (C_{NaOH}) (equivalent volume = V_{NaOH}). The

ion exchange capacity is defined by the following relation:

$$\text{IEC} = \frac{C_{\text{NaOH}} \times V_{\text{NaOH}}}{W_{\text{dry}}} \quad (2)$$

From the IEC, the DS is calculated with the equation:

$$\text{DS} = \frac{M_0 \times \text{IEC}}{1 - 81 \times \text{IEC}} \quad (3)$$

With M_0 , the molar mass of the repetition unit of PSU (442 g mol^{-1}) and 81, the molar mass of the added sulfonic group (SO_3H). In this work, the degree of sulfonation DS is 70%.

2.2. Analysis techniques

2.2.1. Thermogravimetric analysis

The thermal stability of the polymer membranes is analyzed by thermogravimetric measurements, using a Netzsch TGA 209 balance. The measurements are carried out in nitrogen atmosphere from 20 to 700°C at a heating rate of $10^\circ\text{C}/\text{min}$. Before measurement, membranes are dried at 200°C for several hours in order to eliminate trapped water and solvents in the membrane structure. The samples are subjected to thermogravimetric analysis both before and after sulfonation to determine the decomposition temperature.

2.2.2. Temperature modulated differential scanning calorimetry

Temperature modulated DSC (TMDSC) is performed on the TA apparatus (DSC 2920). Calibration in temperature and energy is carried out using standard values of indium and zinc.

The specific heat capacities for each sample with different ageing time are measured using sapphire as a reference. The sample mass are chosen to be similar to the sapphire sample mass, i.e. approximately 20 mg. The TMDSC experiments are performed with oscillation amplitude of $\pm 0.318^\circ\text{C}$, an oscillation period of 60 s and with a heating rate of $2^\circ\text{C}/\text{min}$. In this study, the apparent complex heat capacity C^* with the in-phase component noted C' and the out-of-phase component noted C'' have been analyzed.

More details concerning the determination of the complex heat capacity, especially the correction of the measured phase angle for contributions originating from heat transfer, are given in Ref. [13]. The temperature cycle carried out before the measurements in TGA is also applied before the measurements in TMDSC to dry the samples. The glass transition temperature T_g of PSU and SPSU are detected as 185 and 190°C respectively, and physical ageing are performed at $T_a = T_g - 15^\circ\text{C}$ in the TMDSC oven for different ageing times t_a included between zero (unaged samples) and 237 h. After that, ageing samples are analyzed by TMDSC and a second run is immediately performed. This second run (after rejuvenation) is compared to the TMDSC curve of the unaged sample to be sure that no chemical modification occurs during the different steps of the thermal procedure.

3. Results and discussion

3.1. Thermogravimetry analysis

TGA analysis of PSU and SPSU are reported in Fig. 2. One weight loss stage is distinguished about 517°C (67%) for the thermostable PSU (Fig. 2a), which can be attributed to the main chain decomposition of the polymer [14,15]. For SPSU, the mass vs. temperature curve is more complex and two weight loss stages could be observed (Fig. 2b): the first mass loss occurs between $T = 220^\circ\text{C}$ and $T = 370^\circ\text{C}$ (onset = 244°C , 14.5%) and the second occurs between $T = 370^\circ\text{C}$ and $T = 700^\circ\text{C}$ (onset = 454°C , 41%). Park et al. [16], who realized thermogravimetric analysis/mass spectrometer measurements, have attributed these mass losses respectively to the

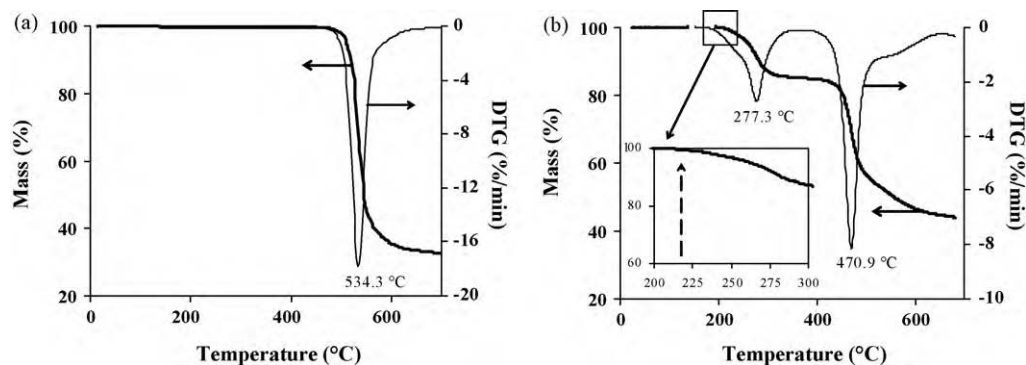


Fig. 2. Thermogravimetric (mass%) (—) and derivative thermogravimetric (DTG %/min) (---) curves under nitrogen atmosphere obtained for (a) polysulfone (PSU) and (b) sulfonated polysulfone (SPSU).

thermal activated decomposition of sulfonic acid groups in the polymer chains and to the splitting of the main chains [17]. Generally the sulfonic acid groups act as initiators for the degradation of SPSU membrane, it's the reason for which the main chain degradation starts earlier than for the PSU [18]. Moreover, Lufano et al. [8] have explained that the lower decomposition temperature of the SPSU with respect to PSU is an enhanced asymmetry in the polysulfone structure due to the introduction of SO₃ groups that renders it less regular, and therefore, less stable. The thermogravimetric curves show that no weight loss is observed below 220 °C: this confirms that water and solvent are removed efficiently with the temperature cycle carried out before the measurement. So, to avoid any degradation or variation of the DS in SPSU samples, we limit the TMDSC thermal analysis to a maximum temperature of 215 °C.

3.2. Temperature modulated differential scanning calorimetry

Heat flow curves for PSU and SPSU are reported in Figs. 3 and 4. For PSU, the usual variation of the glass transition phenomena observed for amorphous thermoplastic occurs: (i) appearance of an endothermic peak due to the structural relaxation phenomena superimposed to the glass transition heat flow step and (ii) the more important the ageing time, the more intensive the relaxation peak (involving a higher enthalpy loss) and the higher the temperature of the maximum of the peak. No variation of the heat capacity step ΔC_p is observable with ageing and the second runs corresponding to rejuvenated samples (not shown here) are all perfectly superimposed to the one of unaged sample. Thus, only physical ageing occurs during the thermal procedure. For SPSU, an endothermic

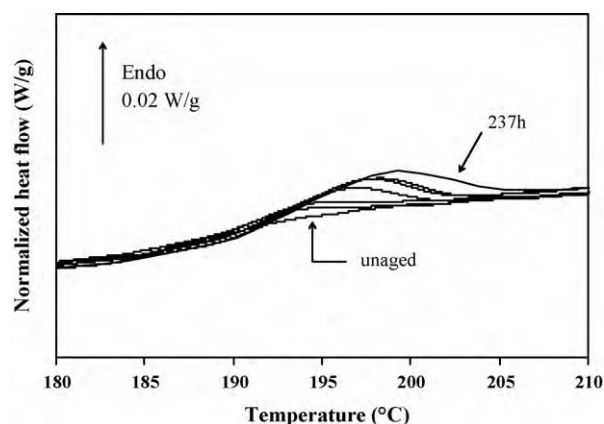


Fig. 4. Normalized heat flow curves for sulfonated polysulfone (SPSU) at different ageing times ranging from $T_a = 0$ h to $T_a = 237$ h.

peak also appears but the magnitude seems lower than for PSU and the shift of the glass transition temperature looks weaker than for PSU. Moreover, no variation of ΔC_p is measured between PSU and SPSU ($\Delta C_p = 0.20 \pm 0.01 \text{ J g}^{-1} \text{ K}^{-1}$) while the glass transition is 5 °C higher for the SPSU. These results are no surprising because introduction of ionic or polar groups is known to be detected in DSC by an increase of T_g .

The usual procedure is used to calculate the enthalpy loss as illustrated in Fig. 5: the hatched area (observable only for PSU) is subtracted from the dotted one in order to taken into account only the enthalpy loss due to the ageing phenomenon. As shown in Fig. 6,

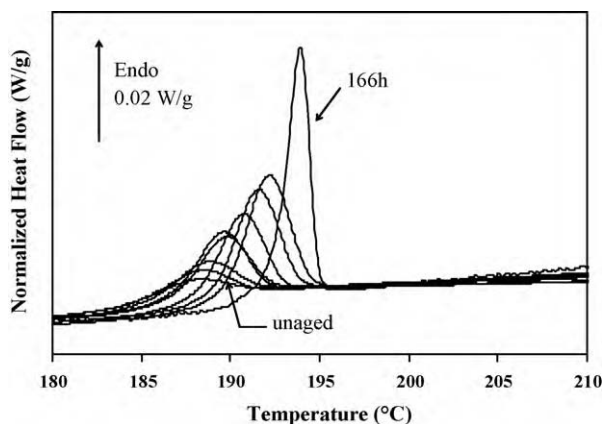


Fig. 3. Normalized heat flow curves for polysulfone (PSU) at different ageing times ranging from $T_a = 0$ h to $T_a = 166$ h.

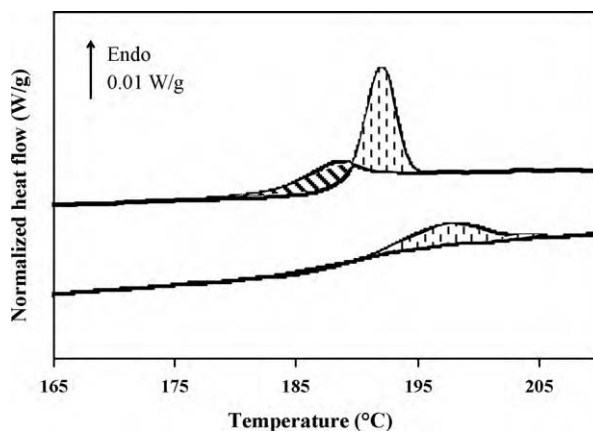


Fig. 5. Calculation method of enthalpy loss: the area under the aged sample curve is subtracted from the area under the unaged sample curve ($\Delta H = \int_{T_a}^{T_b} \dot{Q} dt - \int_{T_a}^{T_b} \dot{Q} dt$).

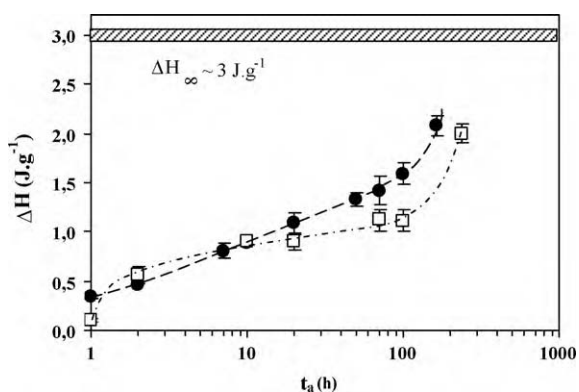


Fig. 6. Enthalpy loss ΔH (J g^{-1}) in function of the ageing time t_a (h) for polysulfone (PSU) and sulfonated polysulfone (SPSU) samples.

we observe that the enthalpy loss increases as a function of the ageing time for PSU and SPSU. No significant difference is observable between PSU and SPSU variations for times lower than 10 h. For higher ageing times, kinetic of enthalpy is lower for SPSU than for PSU. The theoretical value of ΔH_∞ (which is equal to 3 J g^{-1} for PSU and SPSU samples) is reported in Fig. 6. We can see that after an ageing duration of 100 h, the experimental values of enthalpy losses represent 52 and 37% of the theoretical value, for PSU and SPSU respectively. In order to discuss our results, we have reported in Table 1, the values of $\% \Delta H_{(\text{after } 100 \text{ h})}$ (corresponding to the ratio between the enthalpy loss reached after an ageing duration of 100 h and ΔH_∞ at $T_a = (T_g - 15^\circ\text{C})$) for different polymeric systems. The enthalpy loss being strongly linked to the experimental conditions, we have chosen to give in this table, only the results obtained in our laboratory with exactly the same experimental protocol. We can observe that the PSU samples have a classical behaviour in terms of structural relaxation processes: the enthalpy losses reached after an ageing duration of 100 h are in the same range than those obtained for the other systems: $\% \Delta H_{(\text{after } 100 \text{ h})} = 58 \pm 18$. For SPSU, the enthalpy loss for and above 100 h is weaker. So, enthalpic recovery seems to be reduced by the polymer sulfonation.

For the polymers mentioned in Table 1, it is clear that an ageing duration of 100 h is not enough to attempt the equilibrium state. Usually, a sigmoidal behaviour is expected for the variation of enthalpy loss as function of ageing duration. Our data correspond surely to the beginning of the sigmoidal shape. Moreover, from the entropic model proposed by J. L. Gomez Ribelles, it has been shown that ΔH_∞ is not always reached even if the sample is maintained at an ageing temperature close to T_g during an infinite duration [24,25]. So, duration necessary to reach the complete structural

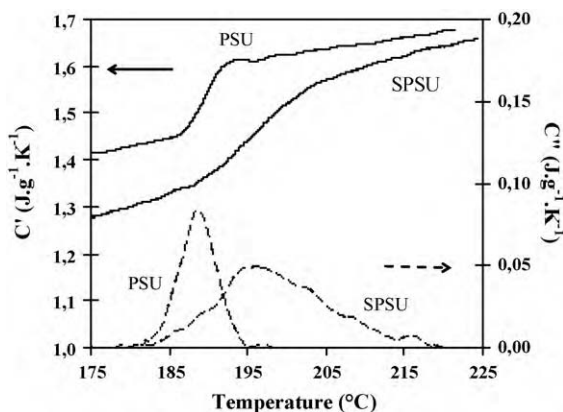


Fig. 7. C' and C'' curves obtained by TMDSC during heating on an unaged polysulfone (PSU) sample and an unaged sulfonated polysulfone (SPSU) sample.

relaxation, i.e. the time to reach the extrapolated curve of the liquid like-state cannot be given from these results.

It is well known that TMDSC not only allows to obtain the heat flow signal, but also the complex heat capacity C^* , the in-phase C' component and the out-of-phase C'' component as described in the experimental section. The C' heat capacity accounts for a seeming storage part, where heat is transferred in the given time interval in-phase with the temperature change (in analogy to the storage modulus of DMA) [26]. At a given time and corresponding temperature, heat flows into the sample to equilibrate temperature between sample and surroundings (ideally without temperature gradient, so that there is no change in entropy). Any slow kinetics, as for example in the glass transition region, limit the heat transfer. If after a given time interval, the sample could be kept adiabatically, the temperature would slowly decrease as the kinetics allow approach to internal equilibrium. As temperature and time change in the modulation experiment, the heat needed to reach internal equilibrium contributes to the heat flow at a higher temperature, accounting for the out-of-phase heat flow. Wunderlich explains that the heat capacity of polymers is the sum of the heat capacity due to skeletal vibration (with inter- and intramolecular contributions) and groups vibrations (originate from the relatively isolated groupings of atoms along the backbone chain) [21]. In the glassy state of PSU and SPSU, the C' component is null and the C'' component is representative of the heat capacity of the materials. Fig. 7 shows that C'' is significantly lower for SPSU than for PSU. So, for a given temperature, the vibration of the glassy SPSU is lower than for PSU. We can suppose that sulfonation leads to a modification of the sulfonated aromatic group vibration and/or appearance of an additional group vibration due to sulfonated group. At temperature higher than T_g , the difference between C' values for SPSU and PSU progressively decreases. The heat capacities of liquids are linked to vibrations, and also large-amplitude rotations, internal rotations (conformational motion) and translations. Influence of the sulfonic group presence progressively vanishes with temperature. The C'' peak of the SPSU sample is significantly wider than those of PSU. It shows that sulfonation leads to a wider glass transition phenomenon. The cooperative motions which occur in the glassy state of materials could be described in terms of Cooperative Rearranging Regions (CRR). The main idea of Donth and other workers [27–29] was to relate statistical thermodynamic relations to the width of relaxation time distribution of the so-called cooperative α process. Each subvolume (called also CRR) with a specific size equal to $V_{SV} = \xi_{T\alpha}^3$ can be then considered as a thermodynamic system in metastable equilibrium with fluctuating variables having a Gaussian distribution. Each subvolume has its own glass transition temperature T_{α} and its own relaxation time τ . In Donth's approach [30–32], the characteristic volume of cooperativity at T_{α} noted $\xi_{T\alpha}^3$, and the number of monomer units in the CRR noted N_{α} , can be estimated from the two following equations for a glass former at its equilibrium state:

$$\xi_{T\alpha}^3 = \frac{\Delta(1/C_V)}{\rho(\delta T)^2} k_B T_{\alpha}^2 \quad (4)$$

$$N_{\alpha} = \frac{\rho N_A \xi_{T\alpha}^3}{M_0} \quad (5)$$

with N_A the Avogadro number, δT the mean temperature fluctuation related to the dynamic glass transition of one CRR, T_{α} the glass transition temperature, k_B the Boltzmann constant, ρ the polymer density ($\rho = 1.24 \text{ g cm}^{-3}$), C_V the heat capacity at constant volume and M_0 the molar mass of one monomer unit ($M_0 = 442 \text{ g mol}^{-1}$ for PSU and $M_0 = 498.2 \text{ g mol}^{-1}$ for SPSU). In this study, we assume that the CRR size can be estimated from this approach despite the presence of sulfonic groups. Indeed, we assume that the sulfonic groups play the rule of static structural heterogeneities like nanoclays [33].

Table 1
 Values of % $\Delta H_{\text{after } 100\text{h}}$ (corresponding to the ratio between the enthalpy loss reached after an ageing duration of 100 h and ΔH_{∞} at $T_a = (T_g - 15^\circ\text{C})$) for different polymeric systems: polysulfone PSU, sulfonated polysulfone SPSU, poly-L-lactide acid PLLA, polycarbonate PC, polycyclohexane-1,4-dimethanol terephthalate PCT, poly(2,2-dialkylpropane-1,3-diyl) carboxylbisphenyl-4,4 dicarbonyl DP1.1, poly-methyl (α -3-alkyl) acrylate C3.

		T_g ($^\circ\text{C}$)	$(\Delta H_{100\text{h}}/\Delta H_{\infty})^*100$	Références
PSU		185	52	This work
SPSU		190	37	This work
PLLA		58	56	[19]
PC		145	58	[20]
PCT		86	40	[21]
DP1.1		101	69	[22]
C3		57	75	[23]

The approximation for the calculation of the characteristic cooperativity volume $\xi_{T\alpha}^3$ from Eq. (4) neglects the difference between the heat capacity step at constant pressure and at constant volume, and the step of reciprocal specific heat capacity can be estimated from:

$$\Delta\left(\frac{1}{C_v}\right) \approx \Delta\left(\frac{1}{C_p}\right) = \left(\frac{1}{C_p}\right)_{\text{glass}} - \left(\frac{1}{C_p}\right)_{\text{liquid}} \quad (6)$$

The CRR size $\xi_{T\alpha}$ and the monomer unit average number per CRR N_{α} , can be estimated from temperature modulated DSC (TMDSC) data. Indeed, the parameters given in Eq. (4) can be extracted from C' and C'' signals as shown in Fig. 7, corresponding respectively to the in-phase and the out-of-phase components obtained for an unaged PSU sample. $\Delta(1/C_p)$ values are obtained from the C' values for the glassy and the liquid state at T_{α} . δT and T_{α} values are extracted of C'' curves: T_{α} is the maximum and δT is the standard deviation obtained from the best Gaussian fit of each C'' signal: T_{α} is equal to 188.6 and 198.9 $^\circ\text{C}$ for PSU and SPSU respectively; δT is equal to 3.0 and 7.4 K for PSU and SPSU respectively.

The δT increase has been already observed for different polymeric systems [33,24], and this increase has often been attributed to a decrease of the characteristic cooperativity length. The CRR sizes for the PSU and SPSU unaged samples are calculated: $\xi_{T\alpha} = 2.5$ nm for PSU and $\xi_{T\alpha} = 1.6$ nm for SPSU. The monomer unit number in a CRR is $N_{\alpha} = 25$ for PSU and $N_{\alpha} = 7$ for SPSU. So, sulfonation leads to a decrease of the monomer unit number included in the same cooperative motion at the glass transition. It is interesting to compare these variations with literature. Indeed, many recent works on the determination of the CRR size from Donth's approach exist in the literature [34,35]. The decrease of the cooperativity length has been observed for polymeric systems in which the dynamic relaxation processes of the amorphous phase seem to be constrained by different ways: by the presence of crystalline phase [36–38] or by a pure geometric confinement in the case of polymers confined in nano-pores [39] or in confined syndiotactic poly(methyl methacrylate) system constrained by clay layers [33]. Prevosto et al. [40,41] have studied poly(ethylene-co-propylene) grafted diethylmaleate/montmorillonite nanocomposites from dielectric spectroscopy. They conclude on a cooperativity reduction when

the percentage of montmorillonite increases sufficiently, i.e. from 5%. From the same experimental technique, Fukao et al. [42] have shown confinement effects on the cooperativity in PVA and PMMA thin films prepared by spin coating: the cooperativity decreases when the film thickness decreases. By analogy, we can suppose that sulfonation leads to appearance of domains which decrease the size of the cooperative motion of the amorphous phase.

SPSU and PSU show different thermal behaviour and different amorphous phase properties. It is interesting to compare with other polymers for PEM. Numerous works [43,44], concerning the morphological characterization of Nafion® membranes, have been realized to determine the perfluorinated ionomer structure [45]. In a general way [46], these works have allowed to elaborate models which suggest a phase separation between hydrophilic and hydrophobic domains [5,47], i.e. between the side chains including the sulfonic acid groups and the main hydrophobic fluorinated carbon chain. For example, Gierke et al. [48,49] describe a model of ionic clusters that are approximately spherical in shape with an inverted micellar structure, and, Yeager and Steck [50] suggest a phase separation caused by a charge aggregation. In other words, these authors bring up the formation of ionic connected clusters responsible of the good transport of protons and water molecules. Moreover, after sulfonation of polyethersulfone (PES) with chlorosulfonic acid, Guan et al. [51] show, in atomic force microscopy (AFM), hydrophilic ionic domains connected to produce a co-continuous morphology at higher sulfonation degrees. Existence of ionic clusters is also well known in sulfonated poly(ether ether ketone) [52]. Thus, from these observations, we suppose that sulfonic clusters also exist after the sulfonation of polysulfone. The important degree of sulfonation of the studied SPSU (70%) leads to numerous domains which decrease the mobility of the polysulfone macromolecular chains. It is put in evidence by the lower heat capacity C' and the higher T_g of SPSU compare to PSU. The sulfonic domains increase the amorphous phase heterogeneities and act as crystals or nanoclays: they are responsible of the cooperativity length decrease and the slow enthalpy recovery kinetic.

4. Conclusion

Sulfonation of polysulfone is necessary to obtain a membrane with a good conductivity, but it leads a drastic decrease of the thermal degradation temperature for the final material. From this study, we show that the presence of ionic hydrophilic clusters implies thermal property modifications for polysulfone: an increase of the glass transition temperature and a decrease of the heat capacity in the glassy state. From the CRR concept, we show that the characteristic cooperativity length decreases. So the clusters act by confining the macromolecular chains. The ageing study of the samples allows to put in evidence that the enthalpy recovery kinetic has slowed down by sulfonation. These effects are not prejudicial for SPSU using as PEM, but must be known to predict ageing of such material.

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