

Sulfonation of Polysulfones: Suitability of the Sulfonated Materials for Asymmetric Membrane Preparation

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Received 15 February 2001; accepted 13 July 2001

ABSTRACT: The effect of the starting polymer on the reaction of sulfonation of polysulfones was investigated. When concentrated sulfuric acid is used as the sulfonation reagent in an organic solvent-free reaction, a polymer degradation equally occurs, leading to a decrease in the yield of product recovery. Poly(ether sulfone) Cardo appears to be the most resistant to chain scission in the medium and a control of the sulfonation degree can be performed via the reaction condition control. The reaction can be monitored by UV–Visible spectrophotometry. Phase inversion by immersion of a *N*-methyl-2-pyrrolidone–polymer dope in water led to asymmetric membranes with an average pore size in the range of that of ultrafiltration and that of nanofiltration membranes. The latter membranes can only be obtained at high polymer concentrations and at moderate sulfonation degrees. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2461–2473, 2002

Key words: sulfonation; sulfuric acid; degradation; nanofiltration; hydrophilic

INTRODUCTION

Polysulfones belong to a class of high glass transition temperature polymers of high mechanical, thermal, and chemical resistances. They are widely used in the manufacture of asymmetric membranes with different pore sizes in the active (skin) layer.^{1–3} These asymmetric membranes find various applications as ultrafiltration membranes in different industries, where separations of solvent and small solutes from bacteria, viruses, or soluble macromolecules (synthetic or natural polymers) are required.^{4–7} Asymmetric polysulfone membranes are also used as a sup-

port layer for a thin film of crosslinked polyamide made by interfacial polycondensation in the preparation of reverse osmosis and nanofiltration membranes.⁸ However, the polysulfones are hydrophobic and sensitive to many organic solvents. Therefore, they cannot be used as asymmetric support films for the pervaporation membranes, which are generally designed to work in organic solvents. Even for the applications in aqueous media, the hydrophobic nature of the membrane surface leads to an easy deposition of macromolecular solutes or particles, which have hydrophobic regions. In addition to the fouling due to deposition of large-size species on the membrane surface, the hydrophobic nature of the materials leads to a bad wetting of the pores and low water flux through the membrane pores. The lower the pore size, the larger the pressure required to induce the solvent transport.

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Contract grant sponsor: Réseau MPP Normandie.

Journal of Applied Polymer Science, Vol. 84, 2461–2473 (2002)
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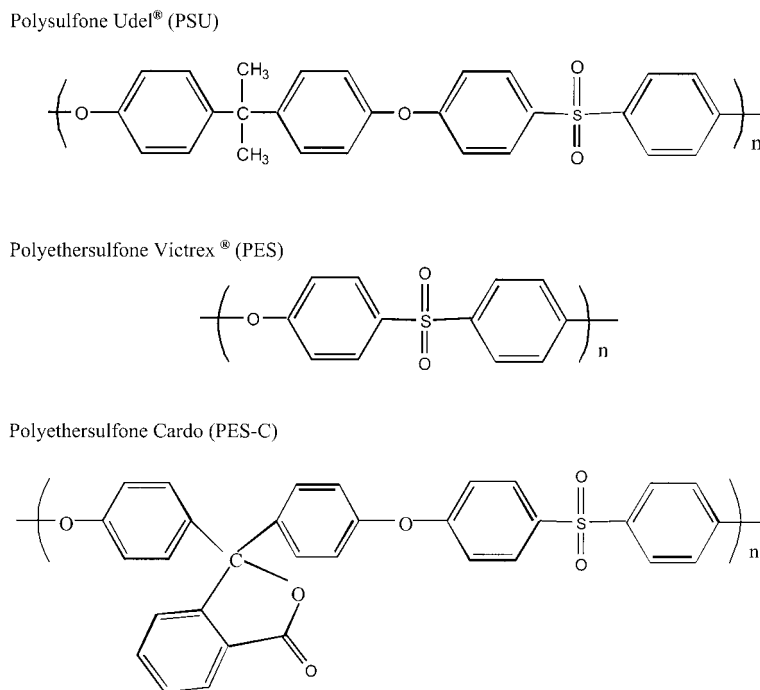


Figure 1 Chem structures of polysulfone units.

An increase in the membrane hydrophilicity appears to be a good way to improve the membrane resistance to solvent alteration and to fouling as well. Different methods to impart a better hydrophilic character to polysulfone membranes were investigated: addition of hydrophilic polymers to the membrane materials dope,^{9–10} immobilization of polymers with hydrophilic segments by photopolymerization, or adsorption.¹¹

Introduction of ionic groups into membranes may impart not only the hydrophilicity¹² but also new functions. The fixed charges are expected to exclude solutes or colloids bearing the same sign of charge as these fixed charges. One can thus expect to obtain asymmetric nanofiltration membranes by the one-step coagulation method.

Three different polysulfones are commercially available: polysulfone Udel® (PSU), initially marketed by General Electric Corp., but now produced by BP/Amoco (Alpharetta, GA) or BASF Corp. (Frankfurt, Germany); poly(ether sulfone) Victrex® (PES), first produced by ICI but presently manufactured by Victrex Ltd. (Lancashire, UK); and poly(ether sulfone) Cardo (PES-C). The latter is only available in China from Engineering Plastics of Jiangsu (Suzhou, China). Although all of these polysulfones are aromatic polysulfones containing an ether link in the backbone, they differ in the nature of aliphatic carbon situated between the two *p*-phenolate rings. In the Udel

type, the aliphatic carbon atom bears two methyl groups, whereas in the Cardo type, this is a carbon atom involved in a five-member lactone ring of a phenolphthalein moiety (Fig. 1). In the Victrex type, aliphatic carbons are absent in the backbone.

The three polysulfones would not have the same ability to react with different sulfonation agents. Sulfur trioxide was reported to be an efficient sulfonation agent,¹³ especially when the gas is soluble in the solvent used for the polymer. However, the ready-to-use liquid reagent for sulfonation is expensive. The reaction can be carried out in a chlorinated solvent in which the polysulfone is dissolved.¹⁴ A more complex method of sulfonation via metalation-sulfination oxidation steps was proposed by Kerres et al.^{15–16}

The cheapest reagent for sulfonation would be oleum (SO₃ dissolved in pure sulfuric acid) or sulfuric acid (98 wt %), which could be used as both reactant and solvent. As far as we know, there has been very few works reported in the literature on the sulfonation by the latter reagents.¹⁷

The aim of the present work was to compare the suitability of the three different polysulfones for their sulfonation by sulfuric acid, in particular, from the viewpoint of polymer degradation. The sulfonated polymer must be capable of forming asymmetric membranes with required me-

Table I Main Characteristics for Polysulfone PSU and Polyethersulfones PES and PES-C

Samples	M_0 (g/mol)	M_w (g/mol)	Degradation Temperature (°C)	T_g (°C)	Intrinsic Viscosity (dl/g)	Solvent	References
PSU, P 3500	442	84,000	523	190	0.62	NMP, DCM, DCE, DMF, DMAc, dioxane, THF, DMSO	18,19,20
PES, 5200 P	232	58,000	540	227	0.32	DMF, DMSO, DCM, NMP, DMAc	14,19,21,22,23
PES-C	532	—	—	260	0.74	DMF, DMAc, DMSO, NMP, DCE, CHCL ₃	1

DCE, 1,2-dichloroethane; DCM, dichloromethane; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO; dimethylsulfoxide; NMP, *N*-methyl-2-pyrrolidone; THF, tetrahydrofuran.

chanical, thermal, chemical, and separation properties. Asymmetric membranes were thus prepared with the sulfonated polysulfones to evaluate their suitability for membrane preparation and tested in nanofiltration of salt solutions.

EXPERIMENTAL

Materials

Polysulfone Udel® (P3500), poly(ether sulfone) Cardo, and poly(ether sulfone) Victrex® (5200 P) were obtained from their respective manufacturers. The main characteristics of the polymers reported in the literature are collected in Table I.

Chlorosulfonic acid, oleum, sulfuric acid of 98 wt % content, and the other solvents (*N*-methyl-2-pyrrolidone, 99%; 1,2-dichloroethane, HPLC grade) were used as received from Aldrich-Sigma.

Synthesis Procedure

The polymer powder was dissolved in sulfuric acid in a glass reactor equipped with a mechanical stirrer. The temperature for polymer dissolution was the same as the reaction temperature. The reported reaction time was the total time for polymer dissolution and reaction. After a fixed reaction time, the reaction medium was poured in a large volume of cold water under strong stirring. A cooling bath was used to remove the heat generated by the dilution of concentrated sulfuric acid in water. The sulfonated polymer was precipitated under the acid form. However, a fraction of the modified polymer could dissolve in cold water if the sulfonation extent was high enough

or if the polymer chains were sufficiently hydrolyzed. The yield shown in this article is the yield in weight of the polymer recovered by precipitation compared with the weight of the initial sample.

For the reaction based on chlorosulfonic acid reagent, the polymer was first dissolved in dichloroethane (DCE) to obtain a 7.5 wt % solution. Similarly, a solution of chlorosulfonic acid diluted in DCE (10 wt %) was prepared. Then, chlorosulfonic acid solution was added drop-wise to the solution. After the reaction at fixed temperature and time, the modified polymer was recovered by precipitation in an appropriate coagulation bath.

Ion-Exchange Capacity (IEC) Determination

Ion-exchange capacity (IEC) determination was carried out by back-titration of the sulfonated polymer film put under the acid form. Care was taken to ensure the absence of water in the hygroscopic polymer, the total exchange of the accessible sulfonic groups of the solid film, and the absence of dissolved carbon dioxide in the aqueous media. A film of a sulfonated sample in *N*-methyl-2-pyrrolidone (NMP) was carefully dried at 100°C and then at 150°C under vacuum for 48 h. The dry film was then equilibrated twice with a large volume of 0.1M hydrochloric acid solution and then thoroughly washed. The film in the acid form was next equilibrated with an excess of 0.01N NaOH solution, and this solution was back-titrated with a 0.01N HCl solution. The IEC is defined as the ratio of the number of exchanged H⁺ (in equivalent gram) to the weight of the dried film (in kilograms).²⁴ The value used in

the calculation was the weight of dried film after IEC determination, under the Na^+ form. If we assume that all the sulfonic groups in the film are accessible (i.e., ion-exchangeable), the average sulfonation degree D_s can be calculated from the IEC. D_s is the fraction of monomer unit which is sulfonated (ion-exchangeable) after the reaction. Thus, the mass of a monomer unit bearing an averaged number D_s of ion-exchangeable groups is equal to the ratio of D_s to IEC:

$$M_0 + 103D_s = D_s/\text{IEC}$$

where $M_0 = 532$ g/mol is the mass of the unit of the initial polymer (PES-C) and 103 is the molar mass of the SO_3Na group. It approaches

$$D_s = \frac{M_0\text{IEC}}{1000 - 103\text{IEC}} \quad (1)$$

The IEC determination is also a way to show the presence of fixed acid groups in the modified polymers. For instance, the IEC values of 0.90 and 1.47 equiv H^+ /kg correspond to the D_s values of 0.53 and 0.92, respectively.

FTIR Spectrophotometry

FTIR spectra of dried 15- μm -thick films were recorded with a Perkin–Elmer Spectrum 2000. Because of the influence of the counterion nature of the sulfonated group on the residual water amount and on the maxima of some IR bands,²⁵ all sulfonated films were put in the sodium form and were dried under vacuum for 48 h.

UV–Visible Spectrophotometry

The spectra of the polymer sample in an appropriate solvent were recorded with a Perkin–Elmer Spectra AA. The reaction monitoring was carried out in a stirred quartz cell at a constant temperature of 25°C. The polymer concentration in the sulfonation medium was adjusted to obtain a correct absorbance for the main peaks throughout the reaction. The spectrum of the sulfonation medium without the polymer was taken as a reference.

Differential Scanning Calorimetry (DSC)

Thermal properties of the polymer samples in sodium form were measured with a Perkin–Elmer DSC 7. Typically, a sample of ~ 10 mg is placed in a pan and its thermogram is recorded as a second

run at a scanning rate of 10 K min^{-1} under nitrogen atmosphere from 293 to 673 K.

Swelling Ratio (SW) in Water

The sample films in the sodium form were equilibrated for 72 h in water at 25°C. The swelling ratio was calculated from the weight gain of the sample after sorption equilibrium in water as the ratio of this weight gain to the weight of the dry film.

Size Exclusion Chromatography

The weight-averaged and number-averaged molecular weights were obtained with a size exclusion chromatograph (pL Gel mixed type C 5- μm column, Touzart and Matignon) calibrated with polystyrene molecular weight standards. Thus, the molecular weights shown in this article are only polystyrene-equivalent ones measured in specific conditions (i.e., in dichloromethane at 25°C). Because of the repulsion of ionic charges in the dissolved sulfonated polymer chains, the values obtained would be overestimated. They are used here for comparison purposes.

Scanning Electron Microscopy (SEM)

The scanning electron microscope (JEOL JSM 35CF) was widely used to study the structure of membranes. The samples were dried and then immersed in liquid nitrogen before their breaking. The samples were recovered with a thin gold layer and placed on a support in the SEM. The SEM analysis was carried out under high vacuum on the dried membranes. The cross sections of polymeric membranes and the top skin layer area topography were investigated in detail.

Nanofiltration Experiments

The nanofiltration operations were carried out with a process in batch. The salt concentrations were followed by conductivity measurements.

The transport phenomena in process-driven processes can be described by macroscopic parameters. The volume flux (J_v) and rejection (R) are supplied in the following equation:

$$J_v = K_p\Delta P \quad (2)$$

$$R = 1 - C_p/C_r \quad (3)$$

where K_p , ΔP , C_p , and C_r are the permeability coefficient, driving pressure, permeate concentration, and retentate concentration, respectively.

Table II Properties of Sulfonated Polyethersulfones Victrex® Obtained with Acid Sulfonation Methods

Samples	Sulfonation Medium	Time of Reaction	Temperature of Reaction(°C)	Recovery Yield (%)	Ion Exchange Capacity (equiv/Kg _{dry})	SW
SPES1	H ₂ SO ₄ , 98%	3 h	0	10	0.43	0.12
SPES2	H ₂ SO ₄ , 98%	40 min	22	80.1	0.23	0.14
SPES3	H ₂ SO ₄ , 98%/DCM	3 h	4	111.5	0.26	0.16
SPES4	HClSO ₃ /DCM ^a	3 h	24	28.8	0.64	1.59

^a Chlorosulfonic acid was first diluted in dichloromethane (DCM) to obtain a 10 wt % solution.

RESULTS AND DISCUSSION

Analysis of Sulfonation Behaviors

Polyethersulfone Victrex®

Reactions of PES with sulfuric acid could be carried out in solution because of a better solubility of PES, and that of its sulfonated form in sulfuric acid. Although the sulfonation degrees of room temperature reactions were low, fractions of the polymer were lost in the precipitation step (Table II). As before, these results suggest a partial degradation of the polymer backbone, resulting in shorter, more water-soluble chains. The low recovery yield for the reaction at 0°C was due to the nondissolution of a large fraction of PES in sulfuric acid at this temperature, but the fraction dissolved in the reactant was well sulfonated. We tried to increase the sulfonation degree by using dichloromethane to dissolve first the polymer be-

fore adding the sulfonation reactant. When sulfuric acid was used as the reactant, the polymer obtained after 3 h reaction at 4°C was totally recovered by precipitation, and the sulfonation efficiency was slightly improved (Table II). With chlorosulfonic acid, which is a stronger sulfonation agent, the sulfonation degree reached ~ 0.64 for a 3-h reaction at 24°C. However, the recovery yield decreased drastically because of the dissolution of a fraction of the modified polymer in the precipitation medium (Fig. 2). The dissolved polymer must consist of short chains of the sulfonated polymer, as the nondegraded chains of the sulfonated polymer is not soluble in water at such a low sulfonation degree. It appears from the UV spectra that the polymer fraction recovered as a precipitate, the polymer fraction made soluble by the precipitation bath (water), and the polymer fraction in the wash water have similar chemical structures. In other words, the

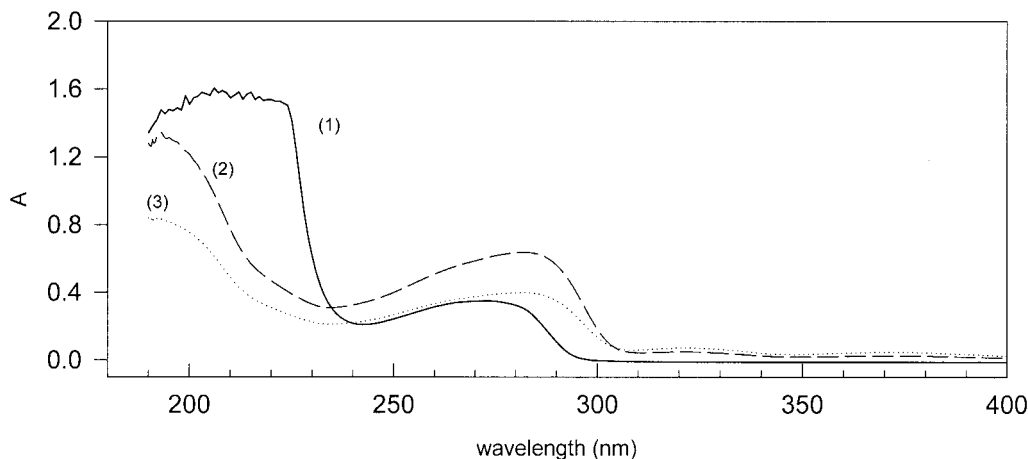


Figure 2 UV-visible spectra of (1) the polymer recovered by precipitation of the 3-h reaction batch (SPES4 sample) in cooled water bath; (2) the water-soluble fraction of the same batch; and (3) the water-soluble sulfonated PES fraction recovered in water in the washing step.

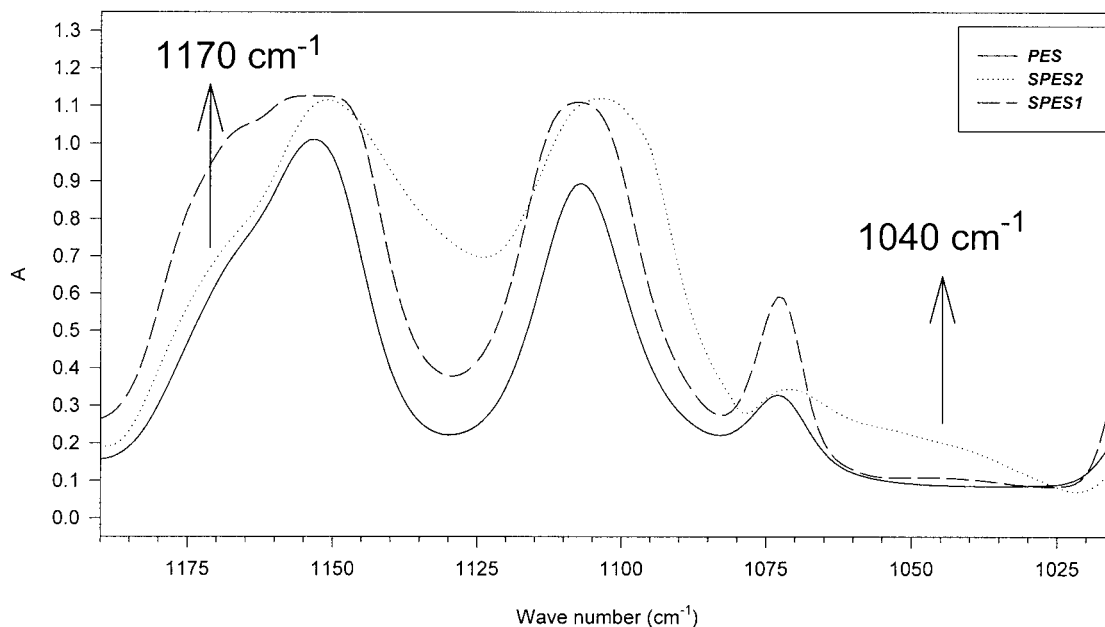


Figure 3 FTIR spectra of PES and PES sulfonated by sulfuric acid.

water-soluble fractions would possess the same chemical groups as the precipitated polymer (although the average molecular weight may be different). The presence of substituted sulfonic acid groups in the recovered polymer was checked by IR spectroscopy (Fig. 3). IR spectroscopy did not show any alteration of the polymer structure. Nevertheless, this does not mean that there was no polymer degradation, as the new chemical groups formed by the polymer alteration may be at low concentration in the polymer or may have low IR-absorption coefficients.

Polysulfone Udel®

PSU did not give rise to sulfonated polymers when sulfuric acid was used as the sulfonation medium. The polymer pellets were not swollen nor dissolved by the acid. Attempts to increase

solid/liquid interface by grinding the beads or by precipitation of the dissolved polymer in a nonsolvent did not lead to significant improvement of the sulfonation efficiency. The use of SO_3 -sulfuric acid reagent did not improve the sulfonation either.

The PSU sulfonation with chlorosulfonic acid in dichloroethane patented by Quentin²⁶ was repeated in various conditions to evaluate the suitability of the procedure. Although the sulfonation was successful (SO_3 bands detected at the same wave number as Fig. 3, and determinable IEC, Table III), the D_s remained low compared with the SPSU3 sample prepared under optimized conditions by Rhodia Corp., according to Quentin's patent. The decrease in the polymer recovery yield by precipitation with the temperature increase suggests that there was a polymer degra-

Table III Properties of Sulfonated Polysulfones Udel® Obtained with Chlorosulfonic Acid in Dichloroethane

Samples	Sulfonation Medium	Reaction Time	Reaction Temperature (°C)	Recovery Yield (%)	IEC (equiv/Kg _{dry})	SW
SPSU1	$\text{HClSO}_3/\text{DCE}$	3 h	2	63.2	0.16	0.04
SPSU2	$\text{HClSO}_3/\text{DCE}$	3 h	24	26.5	0.35	0.04
SPSU3 ^a	—	—	—	—	0.80	1.91

^a Sample from Rhodia; undisclosed sulfonation conditions.

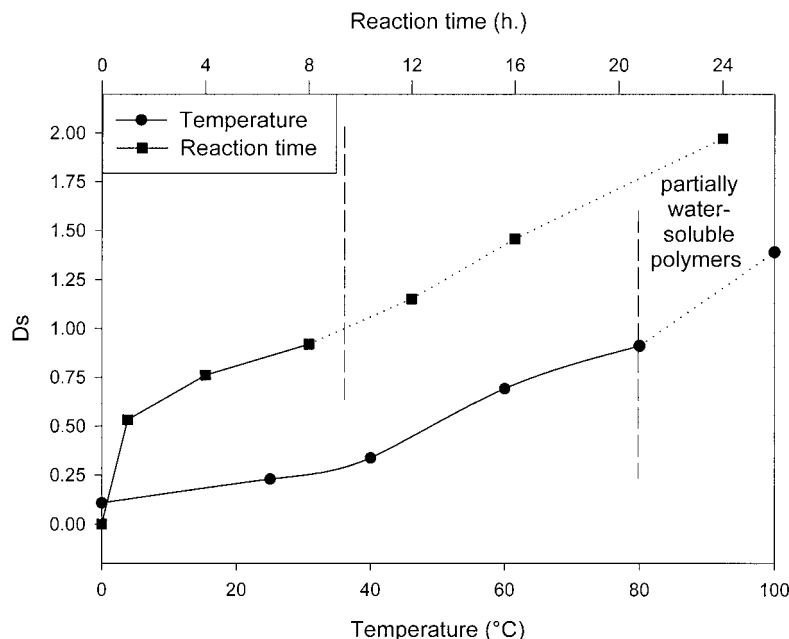


Figure 4 Influence of reaction temperature and time on the sulfonation degree (D_s) of PES-C sulfonated at a polymer/acid ratio of 10 wt/vol %. Sulfonation conditions: 4 h for the reaction temperature influence and 60°C for the reaction time effect.

dation which led to a better solubility of the modified polymer, whatever the solvent nature.

Polyethersulfone Cardo

Both the starting PES-C and sulfonated polymer were well soluble in sulfuric acid. Contrary to the two former polysulfones, PES-C shows a good ability for a controlled sulfonation by sulfuric acid (Fig. 4): the longer the reaction time (or temperature), the higher the D_s value. High sulfonation degrees can be obtained at moderate reaction temperature and time (e.g., 60°C, 8 h, Table IV). The recovery yield values, which exceed 100% for reaction times shorter than 10 h, correspond to a quantitative precipitation, from the reactions medium, of the polymer whose unit molecular weight

is higher than the initial one. However, as the polymer solubility in water increases with its sulfonation degree, the sulfonated polymer cannot be recovered by precipitation in water when its D_s exceeds 0.9–1.0. The high ability of PES-C to be sulfonated is probably due to its better solvation by sulfuric acid and to its specific chemical structure. The glass transition temperature of the sodium salt of the sulfonated polymers was measured by DSC: it increases rapidly with the sulfonation degree (Fig. 5) to reach high values (e.g., 277°C for the sulfonated PES-C of $D_s = 0.92$).

The sulfonation degree of water-soluble sulfonated polymers cannot be determined by IEC measurements. We showed that it can be obtained from the polymer glass transition temper-

Table IV Properties of Sulfonated Polyethersulfones Cardo Obtained with Sulfonic Acid (Sulfonation conditions: 60°C; polymer/acid ratio of 10 wt/vol%)

Samples	Sulfonation Medium	Reaction Time (h)	Reaction Temperature (°C)	Recovery Yield (%)	IEC (equiv/ Kg_{dry})	SW
SPES-C1h	H ₂ SO ₄ , 98%	1	60	113	0.91	2.09
SPES-C4h	H ₂ SO ₄ , 98%	4	60	118	1.25	2.52
SPES-C8h	H ₂ SO ₄ , 98%	8	60	121	1.47	9.25
SPES-C24h	H ₂ SO ₄ , 98%	24	60	3	2.06	Water-soluble

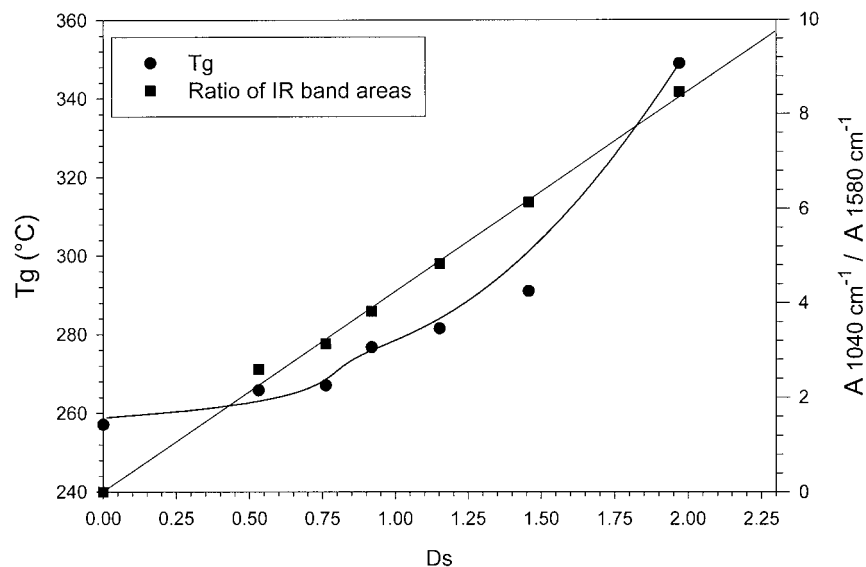


Figure 5 Calibration curves for the sulfonation degree from the glass transition temperature (DSC data) and from FTIR spectra (using the ratio of the areas of the band at 1040 cm^{-1} to that at 1580 cm^{-1}).

ature or from the ratio of IR characteristic band areas using preestablished calibration curves (Fig. 5). The highest sulfonation degree reached in the present study was 1.98.

Evidence of the Backbone Degradation by Size Exclusion Chromatography

A breaking of bonds in the polymer backbone leads to a decrease in the polymer molecular weight and a widening of the molecular weight distribution. Thus, a backbone degradation can be evidenced by a study of the molecular weight distribution by means of size exclusion chromatography. Figure 6 shows a shift of the molecular weight distribution of the PES samples toward a lower value (approximately half of the molecular weight of the initial sample) after a 3-h sulfonation reaction; a similar decrease in the polymer molecular weight was observed for PES-C after a 24-h reaction time at 60°C (Table V). This result suggests that sulfuric acid degrades PES-C much more slowly than PES.

The PES-C sample having halved polymer molecular weight after a 24-h reaction had a high D_s and was water-soluble; it had to be recovered from the precipitation medium by water evaporation and purified by dialysis. It seems that a high reaction temperature and a long reaction time favor the degradation of PES-C.

When the reaction time increases, the sulfonation degree increases first rapidly and then more

slowly (Fig. 4). Apparently, the rate of the reaction batches tends to slow down. However, the reaction rate pattern (without leveling off for long-time reactions) is not reminiscent of that of a reaction which approaches an equilibrium (Fig. 4). We speculate that the change in the reaction rate is due to a change in the reaction mechanism: the sulfonic groups, once fixed on the aromatic rings, deplete the aromatic rings of their electrons by attractive and resonance effects and reduce the rate of subsequent electrophilic substitutions on the rings.

As the reaction batches seem to be kinetically controlled, the sulfonation degree of the samples modified at different temperatures represents the observed reaction rate constant. When the Arrhenius relationship is used to correlate the sulfonation degree with the reaction temperature, a linear Arrhenius plot was obtained. The activation energy derived from this plot is $\sim 21\text{ kJ/mol}$.

On the Polysulfone Degradation Mechanism

A time monitoring of UV-Visible spectra of the polymer dissolved in sulfuric acid confirmed that the degradation of the PES-C chain appeared in a late period (Fig. 7). The intensity of the 323-nm band, which is assigned to the $\Pi \rightarrow \Pi^*$ electron transition of aromatic rings substituted with a sulfonic group, was very low in the early period of the reaction and then increased largely in the later period (Fig. 7). The appearance of the phenol

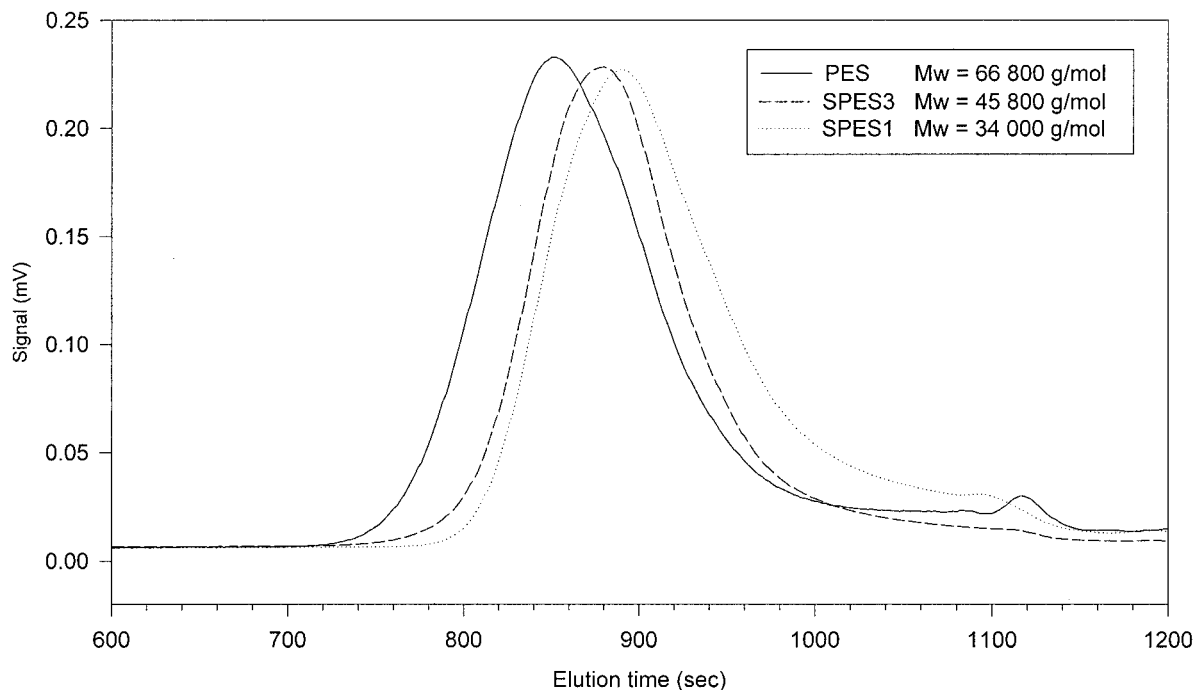


Figure 6 Molecular weight distributions of the initial PES and the sulfonated ones (SPES1 and SPES3) from size exclusion chromatography.

group in the sulfuric acid medium can be explained by the hydrolysis of the ether link in the main chain according to the mechanism described in Figure 8.

The similar increase in the intensity at 323 nm (Fig. 9) in a late period observed for a sample of sulfonated PSU suggests that the decrease in the sulfonated PSU recovery yield was due to the hydrolysis of the ether link in the acid medium according to the same mechanism.

Unlike PSU and PES, PES-C has a hydrolyzable lactone ring on the side chain. Nevertheless, these lactone rings seem to be at least as stable as

the ether link in the backbone. At very long reaction time (100 h), the decrease in the visible band at 523 nm, which can be assigned to the $n \rightarrow \pi^*$ electron transition of a carbonyl group conjugated with an aromatic ring, can be explained by the opening of a fraction of lactone rings.²⁷

A chain scission at the aliphatic carbon in the main chain was reported for PSU and PES submitted to irradiation.^{28–29} Such a possibility of main chain degradation is not envisaged in the sulfonation by a strong acid in a polar solvent, where heterolytic bond rupture prevails.

Suitability of the Polymer for the Preparation of Asymmetric Nanofiltration Membranes

Nanofiltration membranes were successfully prepared from a polymer dope containing 40 wt % of the SPSU3 sample (Table VI). It showed reasonable flux at 5 bar, the lowest pressure used in nanofiltration, and exhibited partial rejections of 35 and 17% for Ca^{2+} and Na^+ , respectively (operation conditions: $5 \times 10^{-4} \text{ mol L}^{-1}$, 25°C, and 5 bar).

The sulfonated PES-C of highest sulfonation degree led to an asymmetric membrane having the best salt rejection and flux (Table VI). It thus appears that both the membrane salt rejection and the permeation flux are improved by an in-

Table V Average Molecular Weights M_n and M_w and Polydispersity Index of PES and PES-C Before and After Sulfonation

Samples	M_w (g/mol)	M_n (g/mol)	Polydispersity Index
PES	66,800	17,900	3.73
SPES3	45,800	19,600	2.33
SPES1	34,800	12,300	2.80
PES-C	117,000	65,200	1.81
SPES-C24h ^a	60,000	31,000	1.93

^a Values obtained by light of scattering (solvent: LiNO_3 0.1M).

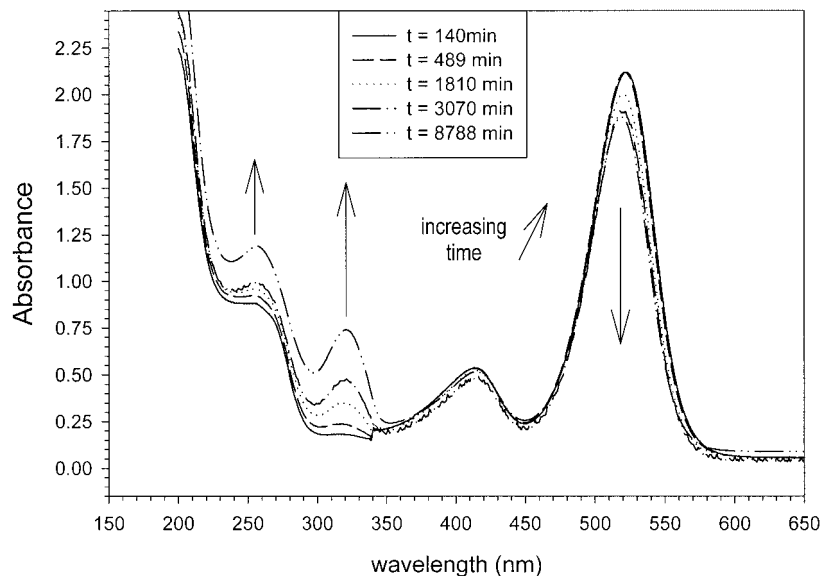


Figure 7 Influence of the reaction time on the UV-visible spectra of PES-C in the reaction medium. Sulfonation conditions, 60°C; polymer/acid ratio, 10 wt/vol %.

crease in the sulfonation degree. The hydrophilic sulfonic groups would enhance the water flow through the nanopores by making them more wettable and improve the salt rejection by a com-

plex salt retention mechanism which would include the Donnan effect. However, other phenomena (steric exclusion, electrokinetic phenomena, etc.) may affect the membrane properties as well.

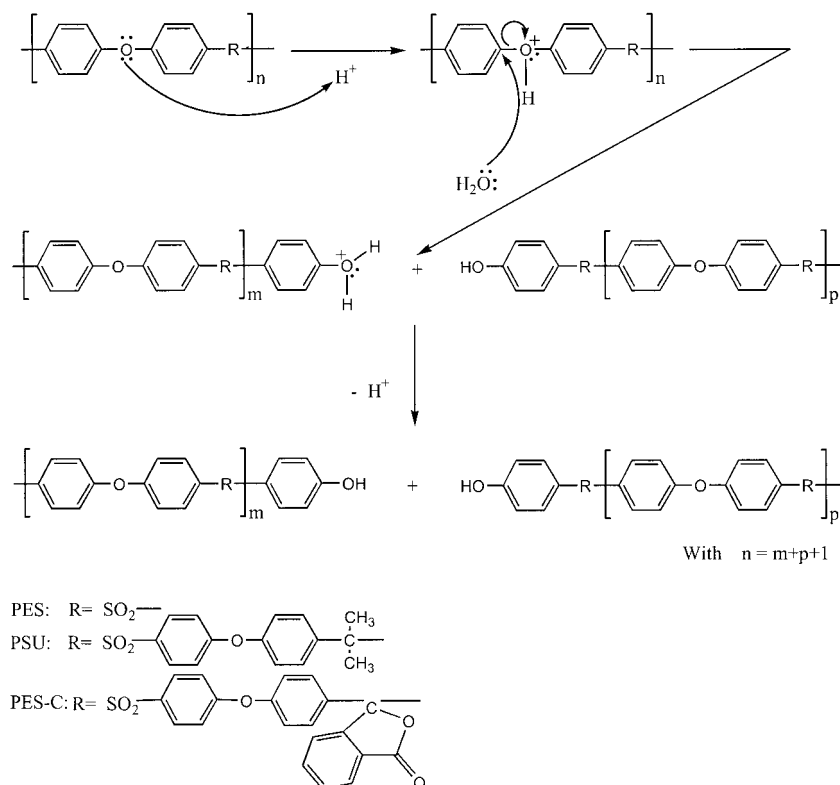


Figure 8 Hydrolysis mechanism of ether bond in acid medium.

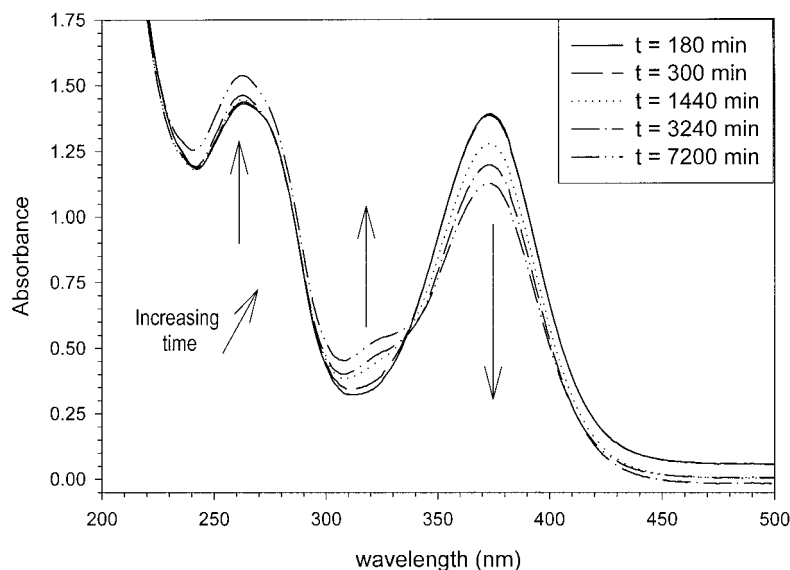


Figure 9 Influence of the reaction time on the UV-visible spectra of PSU in the reaction medium. Sulfonation conditions, 25°C; polymer/acid ratio, 10 wt/vol %.

Because of its higher swelling degree, the membrane made of sulfonated PES-C of 1.65 equiv/kg had apparently lower mechanical resistance, but was still resistant enough for a nanofiltration process. The samples of higher sulfonic contents were not suitable because of the membrane sensitivity to swelling in water.

The SEM micrographs (Fig. 10) show that the membranes which are effective in ultrafiltration have a spongelike structure. The nanofiltration membranes with large fractions of macrovoid (fingerlike) pores showed fairly good steady-state fluxes in nanofiltration (Table VI).

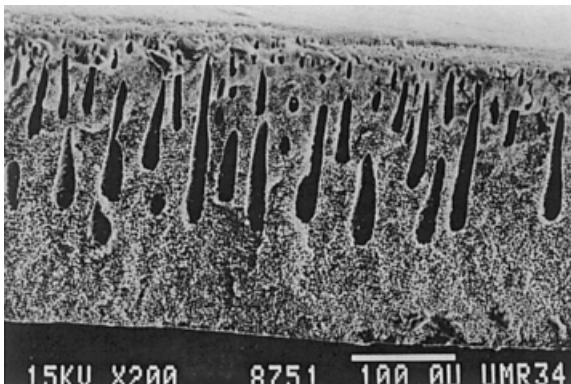
The PES-based membranes prepared according to the same procedure as the others exhibited negligible flux. This was probably due to unadapted membrane preparation conditions: the PES-based membranes show a structure quite different from that of the other membranes, with much lower porosity in the sublayer.

CONCLUSION

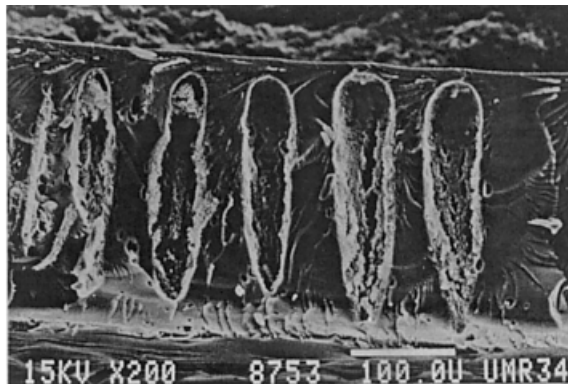
The PES and PES-C sulfonation involves an inexpensive reagent, sulfuric acid, in a one-step process. The sulfonation procedure shows key advantages: simplicity and absence of toxic organic solvent. However, there was a certain extent in chain degradation during the reaction, especially for PES. The main chain degradation of PES-C appears to be negligible for the sulfonation by sulfuric acid under controlled conditions. The easy control of the sulfonation degree makes it a convenient technique for the preparation of PES-C-based hydrophilic materials for asymmetric membranes by the simple phase-inversion technique. The sulfonated polysulfone membranes prepared from a dope containing high polymer contents (35–40 wt %) are of nanofiltration type. High-performance membranes can be obtained with the water-insoluble samples of high sulfon-

Table VI Salt Rejection and Permeation Flux for CaCl_2 $5 \times 10^{-4} \text{ mol L}^{-1}$ Solution, and for Pure Water in Nanofiltration ($T = 25^\circ\text{C}$)

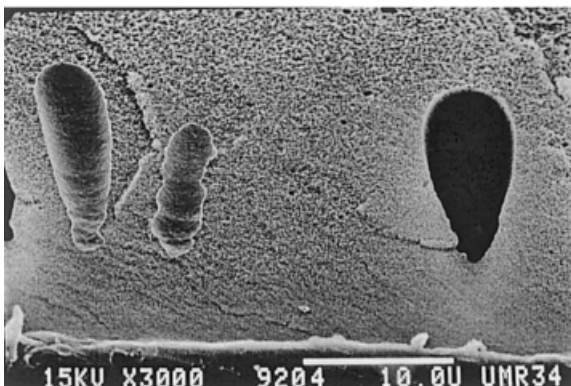
Samples	Pure Water Flux ($\text{L/m}^2 \text{ h}$)	Salt Permeation Flux ($\text{L/m}^2\text{h}$)	Salt Rejection (%)
PSU (under 5 bar)	74	69	8
SPSU3 (under 5 bar)	10	8.1	35
PES-C (under 3 bar)	540	525	5
SPES-C4h (under 12 bar)	69	30	63
SPES-C8h (under 12 bar)	63	20	89



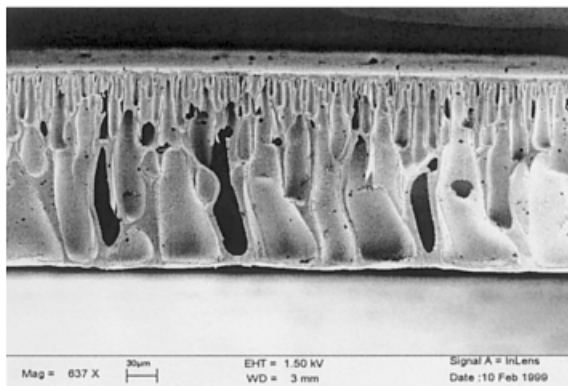
SEM micrograph 1



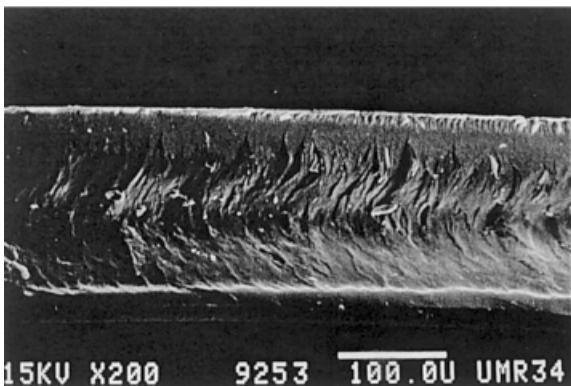
SEM micrograph 2



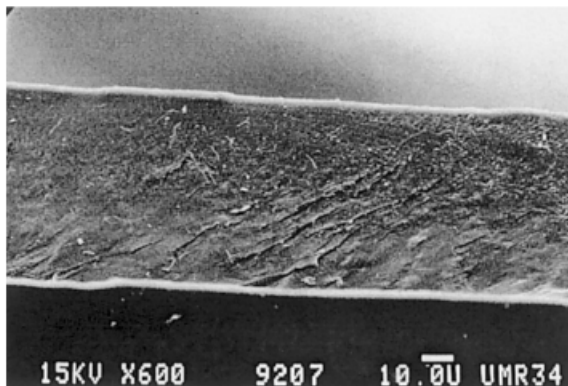
SEM micrograph 3



SEM micrograph 4



SEM micrograph 5



SEM micrograph 6

Figure 10 SEM micrographs of asymmetric membrane made of (1) PSU, polymer in 40 wt % NMP dope; (2) SPSU3, polymer in 40 wt % NMP dope; (3) PES-C, polymer in 30 wt % NMP dope; (4) SPES-C8h, polymer in 40 wt % NMP dope; (5) PES, polymer in 30 wt % NMP dope; (6) SPES3, polymer in 30 wt % NMP dope. Coagulation bath, pure water at 6°C.

ation degrees. The sulfonated PES-C allies well-known qualities of polysulfones with the hydrophilicity of its pores when the polymer is put in asymmetric membrane form. The sulfonated PES-C would be suitable for industrial manufactures of membranes which require stable hydrophilic surface/pores such as nanofiltration membranes, tight ultrafiltration membranes, and fouling-resistant ultrafiltration membranes. Water-soluble sulfonated PES-C may also find applications in the areas where a controlled hydrophilic–hydrophobic balance is required (e.g., as an additive for a polymer dopes in ultra- or nanofiltration membrane preparation). The high glass transition temperature of the sulfonated polysulfones, together with its hydrophilic nature, suggests that the polymers may be good candidates for water vapor/gas separation membranes.

We thank the Réseau MPP Normandie for financial support.

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