

## MORPHOLOGICAL AND RHEOLOGICAL PROPERTIES OF NEW QUATERNIZED POLYSULFONE WITH TRIPHENYLPHOSPHONIUM PENDANT GROUPS

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### ABSTRACT

A new quaternized polysulfone with triphenylphosphonium pendant groups was synthesized by reacting chloromethylated polysulfone with triphenylphosphine. The molecular restructurations, generated by hydrogen bonding, electrostatic interactions and association phenomena in ternary quaternized polysulfone/N,N-dimethylformamide (solvent) / water (non-solvent) systems, were evaluated by rheological investigations. The results were correlated with the morphological properties of the films prepared from solutions in solvent/nonsolvent mixtures.

### INTRODUCTION

Polysulfonic membranes have been developed for a wide variety of applications in separation technology, biological processes, medical devices, and blood purification. Generally, solvent/nonsolvent mixtures are used to make asymmetric membranes, in which the processes are governed by diffusion of the various low molecular weight components. The introduction of nonsolvents plays an important role in membrane formation through the occurrence of specific interactions in the three component systems [1].

Several reviews on the modification of polysulfones by different chemical mechanisms have reported the introduction of reactive groups onto the polysulfone backbone. Among them, phosphonium cations may improve the thermal stability of polymers, being preferred for long-term use applications [2], for facilitating aggregation [3] or as an aid in matrix reinforcement of ionomers [4, 5]. Due to the enhanced thermal stability of phosphonium versus ammonium cations, phosphonium-containing polymers have a significant technological importance as phase-transfer catalysts, antistatic agents, biocides, humidity sensors, water filtration membranes [6].

In the present work, for obtaining highly porous membranes, the films prepared from solutions in a N,N-

dimethylformamide (DMF)/water solvent/nonsolvent mixture were analyzed by rheological method, in correlation with morphological investigation. Results show the influence of quaternized polysulfone chemical structure - containing triphenylphosphonium pendant groups (PSFP), for establishing its processing/property relationships.

### NOMENCLATURE

$E_a$	[kJ/mol]	activation energy
$E_{ass}$	[kJ/mol]	negative contribution of the associated formations at activation energy
$E_{dis}$	[kJ/mol]	positive contribution of disengagement at activation energy
$f$	[Hz]	oscillation frequency
$K$	[Pa s <sup>n</sup> ]	consistency index
$n$	[-]	flow index
$R$	[J/molK]	universal gas constant
$\Delta S$	[J/molK]	flow activation entropy
$T$	[K]	absolute temperature

#### Special characters

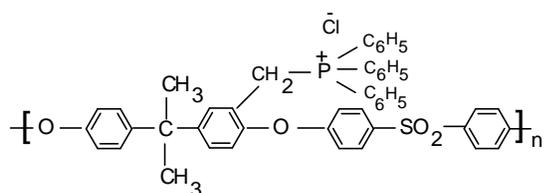
$\dot{\gamma}$	[1/s]	shear rate
$\eta$	[Pa s]	dynamic viscosity
$\eta_0$	[Pa s]	zero-shear viscosity
$\sigma$	[Pa]	shear stress

### EXPERIMENTAL

UDEL-1700 polysulfone (Union Carbide) ( $M_n = 39000$  g/mol;  $M_w/M_n = 1.625$ ), a commercial product, was purified by repeated reprecipitations from chloroform and dried for 24 h in vacuum, at 40°C, before being used in the synthesis of chloromethylated polysulfone.

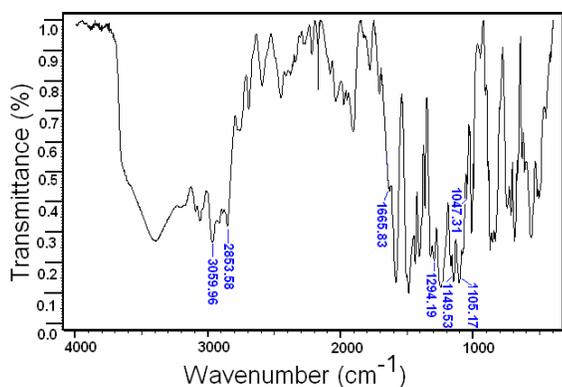
Polysulfone with triphenylphosphonium pendant groups, PSFP, was synthesized by reacting chloromethylated polysulfone (CMPSF) with triphenylphosphine [7]. Ratios between the ionic chlorine and total chlorine contents show that

the quaternization reaction of CMPSF occurs at a transformation degree around 46%. Chemical structure of PSFP was illustrated in scheme 1:



**Scheme 1** General structure of quaternized polysulfone with triphenylphosphonium pendant group

Figure 1 presents ATR-FT-IR spectrum - recorded on film using a Nicolet-6700 ATR-FT-IR spectrometer (Thermo Electro Corporation), in the range 400 to 4000  $\text{cm}^{-1}$  - which confirms the structure of PSFP.



**Figure 1** ATR-FT-IR spectra for PSFP in 4000-400  $\text{cm}^{-1}$  spectral regions

The infrared spectrum shows two characteristic absorption peaks at 3060-3200  $\text{cm}^{-1}$  and 1665-2000  $\text{cm}^{-1}$ , which refers to bands characteristic to aromatic rings. In addition, the band at 1294  $\text{cm}^{-1}$  is attributed to  $\text{SO}_2$  group and the vibrational band observed at 2854-2965  $\text{cm}^{-1}$  is associated with C-H stretching from alkyl groups (-CH, - $\text{CH}_2$ , - $\text{CH}_3$ ). The band at 1150-1169  $\text{cm}^{-1}$  is assigned for -P- $\text{CH}_2$ - bond, while the absorption corresponding to P-Aryl stretching occurs at 1047-1082  $\text{cm}^{-1}$ . A band characteristic to triphenylphosphonium salts can be observed at 1105  $\text{cm}^{-1}$ .

## METHODS

PSFP films were prepared from solutions at 6 g/dL concentration, in 100/0, 95/5, 85/15 and 75/25 v/v DMF/water solvent mixtures.

Atomic force microscopy (AFM) images were obtained on a SPM SOLVER Pro-M instrument that operated in semi-contact mode, at  $30 \times 30 \mu\text{m}^2$  scan area. A cantilever - NSG10/Au silicon type - with a 10 nm curvature radius and 286 kHz oscillation mean frequency was used to investigate the influence of

DMF/water solvent mixtures on the morphological properties of PSFP films.

The flow properties of PSFP in DMF/water solvent mixtures were determined on a Bohlin CS50 rheometer, manufactured by Malvern Instruments. The measuring system presents cone-plate geometry with a cone angle of  $4^\circ$  and 40 mm diameter. Shear viscosities were registered over the 0.7-1000  $\text{s}^{-1}$  shear rate domain, at several temperatures (25 - 40°C). According to the amplitude sweep test performed at a frequency of 1 Hz, in the linear viscoelastic regime for shear stresses between 0.5 and 30 Pa, a shear stress of 3 Pa was selected for all samples. During the oscillatory shear tests, frequency was varied between 0.01-15 Hz.

## TRENDS AND RESULTS

Polysulfone is an amorphous aromatic main-chain polymer formed by alternation of bisphenol A and biphenyl sulfone segments. The electron-donating effect of the ether linkages of the main chain activates the phenylene rings of the bisphenol A part toward nucleophilic attack, so that may be used for obtaining some modified polysulfones by chlorometilation, followed by quaternization process. In addition, triphenylphosphine was used in the synthesis of quaternized polysulfones to diversify specific applications, such as antibacterial activity. In this context, knowledge on the correlations between morphological properties of quaternized polysulfone with triphenylphosphonium pendant groups and rheological characteristics in solvent/nonsolvent mixtures is important.

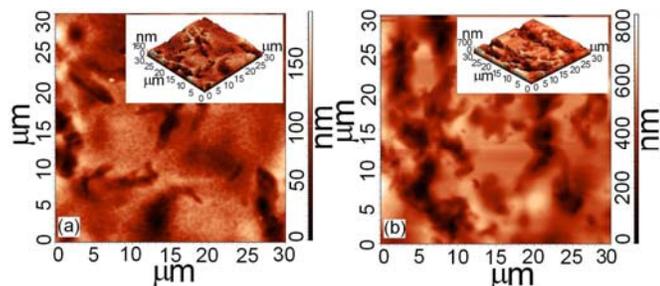
### Morphology of PSFP films

The AFM images of PSFP films prepared by casting solution in 100/0, 95/5, 85/15 and 75/25 v/v DMF/water solvent mixtures at 6 g/dL concentration, show that increasing of the water content leads to a decrease of pore number and an increase of both pore characteristics (area, depth, average length, mean width) and surface roughness parameters (including average roughness and root mean square roughness).

Thus, for water content, which corresponds to the solubility limit (75/25 v/v DMF/water), the depth value and roughness parameters are lower. Pore sizes enhancement is induced by the casting solutions properties, where the interactions due to hydrogen bonding enhance and different association phenomena occur.

One can mention that the small hydrophilic characteristics given by the triphenylphosphonium pendant groups, where the electron-donor interactions exceed the electron-acceptor ones, influence film morphology and rheological properties, as well.

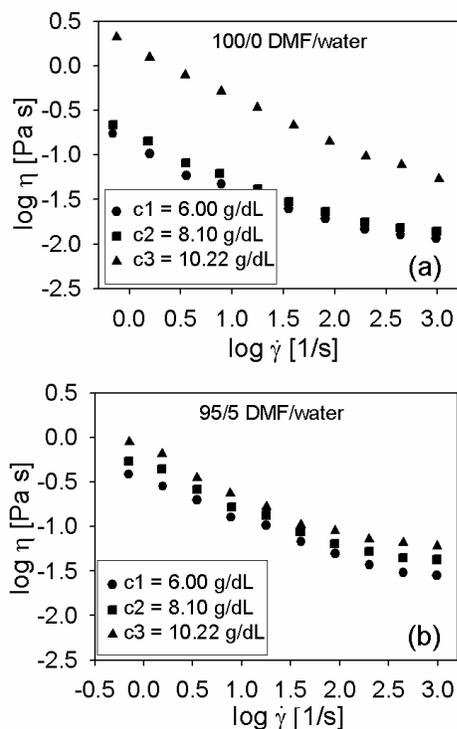
The molecular interactions in this type of structure should be reflected in a predictable performance of these materials. Consequently, surface morphology depends on the history of films preparation, including the characteristics of quaternized polysulfones and the thermodynamic quality of solvents.



**Figure 2** 2D AFM images for PSFP films in: (a) 100/0 and (b) 85/15 DMF/water solvent mixtures; small figures inserted correspond to 3D AFM images

### Shear viscosity measurements for PSFP

Figures 3 and 4 show the logarithmic plots of dynamic viscosity as a function of shear rate, for PSFP in DMF/water, at 30°C. Different concentrations of solutions exhibit the shear thinning profile as a function of viscosity versus shear rates.

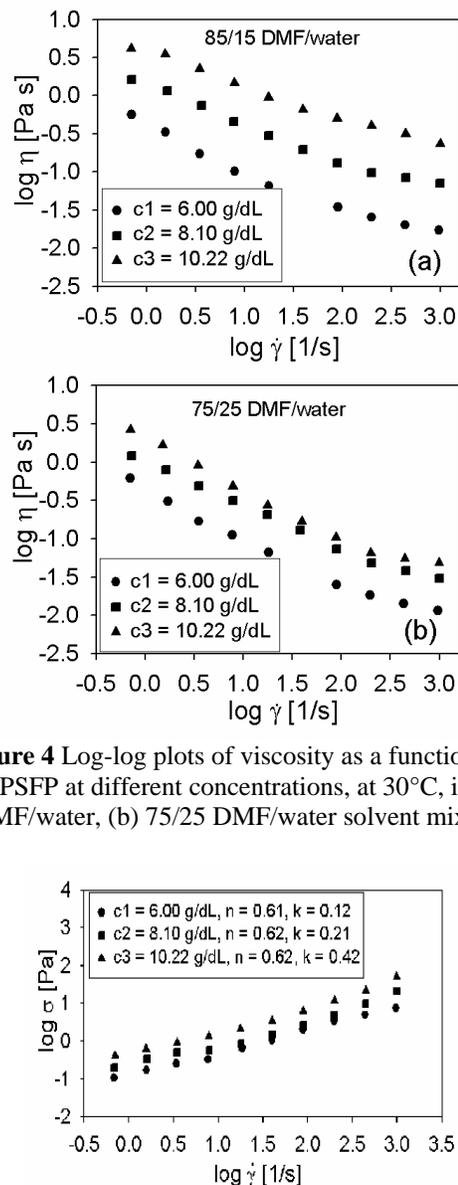


**Figure 3** Log-log plots of viscosity as a function of shear rate for PSFP at different concentrations, at 30°C, in (a) 100/0 DMF/water, (b) 95/5 DMF/water solvent mixtures

The shear thinning behavior obeys the power-law relationship between shear stress,  $\sigma$ , and shear rate,  $\dot{\gamma}$ , expressed in the equation 1:

$$\sigma = K \cdot \dot{\gamma}^n \quad (1)$$

Thus, according to Figure 5, the PSFP in DMF reveals that the flow behavior indices are lower than the unity, indicating a shear thinning behavior, along with their increase with increasing concentration. On the other hand, solution consistency in the DMF solvent also increases with increasing concentration; these results can be explained by the modification of polymer interactions in the system, generated by solutions' concentration.



**Figure 4** Log-log plots of viscosity as a function of shear rate for PSFP at different concentrations, at 30°C, in (a) 85/15 DMF/water, (b) 75/25 DMF/water solvent mixtures

**Figure 5** Log-log plots between shear stress and shear rate for PSFP at 25°C, in DMF at different concentrations

In 95/5, 85/15 and 75/25 v/v DMF/water solvent mixtures, could be observed that the flow behavior indices are also lower than the unit, and that, generally, they decrease with increasing the water content. Moreover, Table 1 illustrates higher values for the flow behavior indices, once concentration is increasing, according to the rheological behavior. The solution consistency

- induced by the water nonsolvent component from solvent mixtures - takes higher values than in a pure DMF solvent; thus, these results show that modification of interactions from the system is generated by the solvent mixtures composition and by solution concentrations.

The interactions between the chain segments, which imply the size of the energy barrier for the movement of an element of the fluid, were described by the activation energy, evaluated from Arrhenius equation [8, 9]:

$$\ln \eta = \ln \eta_0 + \frac{E_a}{RT} \quad (2)$$

**Table 1** Flow behavior and consistency indices of PSFP for different concentrations and solvent mixtures

PSFP in solvent mixtures [v/v]	<i>n</i>	<i>K</i>
6.00 g/dL		
95/5 DMF/water	0.60	0.17
85/15 DMF/water	0.43	0.68
75/25 DMF/water	0.36	0.74
8.10 g/dL		
95/5 DMF/water	0.56	0.29
85/15 DMF/water	0.55	1.76
75/25 DMF/water	0.47	1.97
10.22 g/dL		
95/5 DMF/water	0.50	2.43
85/15 DMF/water	0.52	5.66
75/25 DMF/water	0.39	1.60

Distribution of the hydrophobic structures involved a wide temperature range for the association process, with the association thinning effect developed only for extended associations. The activation energy for PSFP solutions evidenced no associated chain formation, where the positive contribution of the disengagement process is higher than the negative contribution of the associated chain formation. Consequently, the overall activation energy involves two processes (equation 3):

$$E_a = E_{dis} + E_{ass} \quad (3)$$

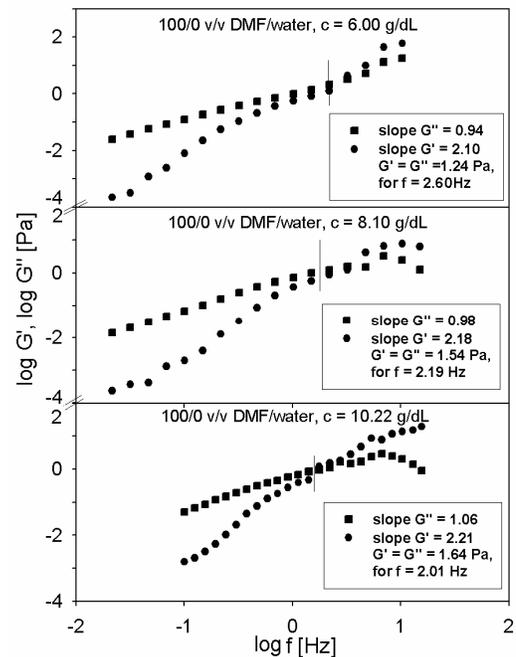
The Arrhenius plot for zero-shear viscosity ( $\dot{\gamma} \approx 0.7s^{-1}$ ) is presented in Table 2, over the 25 - 40°C temperature range. The linear dependencies between viscosity and reverse temperatures lead to different values of the activation energy, depending on solvent/nonsolvent composition; positive values of  $E_a$  were obtained for all DMF/water compositions at the studied concentrations. An exception was observed for 10.22 g/dL concentration at a higher water content, 75/25 v/v DMF/water. The positive contribution of the disengagement,  $E_{dis}$ , which becomes predominant in comparison with the negative contribution of the associated formations,  $E_{ass}$ , leads to positive values of  $E_a$ , while the negative value is generated by the preponderantly negative contribution of  $E_{ass}$ , comparatively with  $E_{dis}$ . Thus, water content contributes to the

specific molecular rearrangement of the system with temperature modification, favouring the formation of associated molecules at high concentration and high water content. Thus, it is relevant that the rheological properties are influenced by the small hydrophilic characteristics given by the triphenylphosphonium pendant groups, which permits some limitation of the water content in solvent mixtures, and a well established solubility domain.

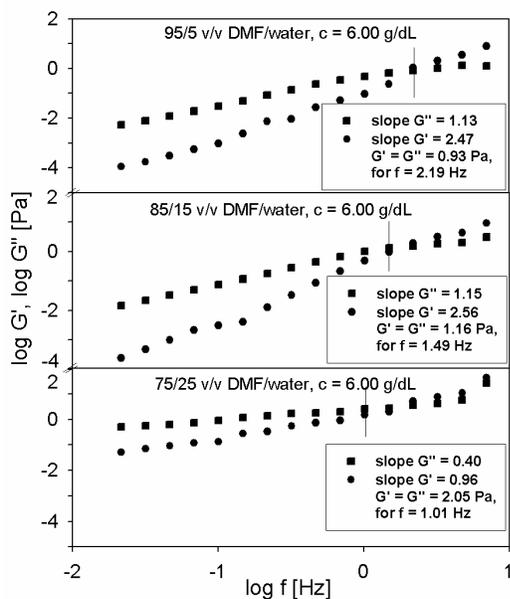
**Table 2** Activation energy for PSFP solutions for different solvent mixtures

Concentration of PSFP	DMF/water solvent mixtures [v/v]	$E_a$ [kJ/mol]
6.00 g/dL	100/0	54.04
	95/5	27.59
	85/15	23.45
	75/25	19.68
10.22 g/dL	100/0	57.81
	95/5	50.79
	85/15	42.76
	75/25	-18.31

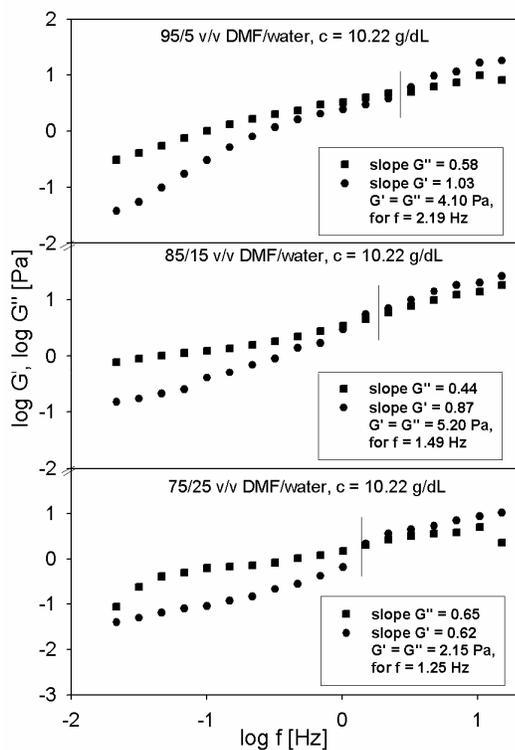
Moreover, the type of pendant groups from quaternized polysulfones influences the solubility process in DMF/water, generating molecular restructurations in solution, under the influence of hydrogen bonding, electrostatic interactions and association phenomena.



**Figure 6** Log-log plot of storage and loss moduli as a function of frequency at 25°C for PSFP in 100/0 DMF/water, at different concentrations



**Figure 7** Log-log plot of storage and loss moduli as a function of frequency, at 25°C, for PSFP at different ratios of DMF/water solvent mixtures at 6.00 g/dL concentration



**Figure 8** Log-log plot of storage and loss moduli as a function of frequency, at 25°C, for PSFP at different ratios of DMF/water solvent mixtures at 10.22 g/dL concentration

### Dynamic modulus

Prior to viscoelastic measurements, the suitable amplitude sweep test was performed by measuring shear stress

dependence on moduli at a certain frequency, to ensure the linearity of dynamic viscoelasticity for each sample. The storage and loss moduli are plotted as a function of frequency for PSFP solutions in DMF (Figure 6) and DMF/water (Figures 7 and 8) at different concentrations and 25°C.

At low frequency, the storage modulus,  $G'$ , and the loss modulus,  $G''$ , are proportional to  $f^2$  and  $f^1$ , respectively, and, over this frequency range,  $G''$  is always higher than  $G'$ , a characteristic behavior of the viscoelastic fluids [10]. In addition, at higher values of frequency,  $G'$  becomes higher than  $G''$ , and their crossover increases with decreasing concentration and water content. Still, for PSFP in DMF/water at a higher concentration of 10.22 g/dL, the corresponding exponents of frequency become smaller, due to the association phenomenon generated by water's adding in the system.

### CONCLUSION

New quaternized polysulfone, prepared by quaternization of chloromethylated polysulfone with triphenylphosphine, was investigated to obtain information on its rheological and morphological properties in DMF/water solvent/nonsolvent mixtures.

The polymer solutions measurements emphasize the influence of the nonsolvent content, temperature and concentration on the rheological properties, by dynamic viscosity and viscoelastic properties. These studies reveal that PSFP is a pseudoplastic material with non-Newtonian behavior and shear thinning characteristic that are generated by the less entangled points observed at higher shear rates, and which have as result a higher orientation of the polymer chains. In addition, the activation energy in PSFP/DMF/water solutions increases with concentration, having positive contributions of disengagement for lower water contents, and the negative contribution of the associated formations for higher water content.

On the other hand, shear moduli dependence on frequency follows a power law, where exponents are characteristic to viscoelastic fluids. Also,  $G'' > G'$  at lower frequencies and  $G' > G''$  at higher frequencies, while the frequency corresponding to their overlapping decreases with increasing concentration and the nonsolvent content.

The history of film preparation by a dry-cast process in DMF and DMF/water, illustrated by AFM images, showed that surface morphology is characterized by roughness and pores formation, depending on the thermodynamic quality of the solvent and on the solution properties established by rheological investigation:

- the film prepared in DMF exhibits a larger number of pores and a low roughness;
- increasing of nonsolvent water content leads to a decrease of pore number, while their area, depth, average length and mean width, and also surface roughness increase; at higher water content (75/25 v/v DMF/water), the hydrogen bonding interactions and association phenomena from the system

determine a lower roughness surface generated by a reduced depth and high width of pores.

The characteristics of quaternized polysulfones in solutions depend on the pendant groups linked to the main chain.

The findings of this study have demonstrated that quaternized polysulfone films with a proper macromolecular design may provide some important advantages in relation to specific applications.

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