

**STRUCTURE–RHEOLOGY RELATIONSHIP IN POLYSULFONES WITH  
TRIPHENYLPHOSPHONIUM PENDANT  
GROUPS SYSTEMS FOR ENGINEERING APPLICATIONS**

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**Abstract**

Ionic polysulfones have received widespread attention for their promising roles in order to create new materials that can modulate the membrane properties. In this context, understanding of mechanisms developed in quaternized polysulfones with triphenylphosphonium pendant groups solutions, considering their specific interactions and the way in which these interactions affect their physical properties were evaluated by rheological investigations. Rheological behavior of this system, described by the non-linear flow curve, indicates the effect of the chemical structure of quaternized polysulfone, in order to facilitate the subsequently preparation of the active membranes. Thus, this study analyzes the processing-property relationship of solutions based on quaternized polysulfones and possibility of using it's, with expected future developments in the engineering fields.

**Introduction**

Polymeric materials are used for a wide range of industrial products making them more valuable to their users, namely, in separation technology, food processing, biological processes, medical devices and blood purification or hemodialysis [1,2]. In this context, it is known that polysulfones (PSFs), possessing superior properties, such as chemical, mechanical, and thermal resistance, represent the ideal candidates in the membrane industry. However, the use of these polymers is restricted by their hydrophobicity and may be improved by their modification through different processes [3-5]. Therefore, the introduction of reactive groups (e.g., ammonium, phosphonium) onto the polysulfone backbone affords the possibility to obtain polysulfones with improved properties. Thus, polymers carrying these groups have properties quite different from those of polysulfones and have a significant technological importance for the manufacture of commercial membranes with expanding the application area of the polysulfones, such as gas separation, pervaporation, hemodialysis, nano and ultrafiltration, cell culture, biological processes, or blood purification [6-8].

Particularly, functionalized polysulfones with triphenylphosphonium pendant groups, PSFPs, indicate some key characteristics generated by the phosphonium units, which should be underlined as compared to the ammonium or sulfonic units. Generally, PSFP shows a higher degree of hydrogen bonding and a lower water uptake, comparatively with their sulfonated compounds. Owing to the enhanced thermal stability of phosphonium versus ammonium cations, PSFPs have a greater technological importance as phase transfer catalysts, antistatic agents, biocides, humidity sensors, and water filtration membranes [9]. Consequently, the phosphonium cations may improve the thermal stability of polymers, being preferred for long-term use applications [10], for facilitating aggregation [11] or as an aid in matrix reinforcement of ionomers [12].

This study evaluates the effect of the chemical structure of quaternized polysulfone with triphenylphosphonium pendant groups (PSFP) on the rheological data for establishing its

processing-property relationships. The knowledge of the rheological parameters of PSFP solutions is very important for development of flow models for engineering applications, formulation of commercial production, design and process evaluation, quality control and storage stability. Therefore, these results are useful in future investigations concerning utilization of these polymers as semipermeable membranes in biomedical or industrial field.

### Experimental

Commercial aromatic polysulfone (PSF, UDEL-3500) was used in the synthesis of chloromethylated polysulfones (CMPSFs) and subsequently, of polysulfones containing triphenylphosphonium pendant groups (PSFPs) [3,4,13]. Thus, a mixture of commercial paraformaldehyde with an equimolar amount of chlorotrimethylsilane ( $\text{Me}_3\text{SiCl}$ ) as a chloromethylation agent, and stannic tetrachloride ( $\text{SnCl}_4$ ) as a catalyst, was used for the chloromethylation reaction of polysulfone, at 50 °C [3,4]. The reaction time necessary to obtain chloromethylated polysulfones (CMPSF) was 72 h. Finally, the samples were dried under vacuum at 40 °C.

Polysulfone with triphenylphosphonium pendant groups, PSFP was synthesized by reacting chloromethylated polysulfone with triphenylphosphine ( $\text{PPh}_3$ ) in the presence of dioxane [13]. The mixture was maintained under stirring, in nitrogen atmosphere, for 15 h at 90 °C. The viscous product thus obtained was filtered, washed with dioxane and ethyl ether, and finally dried.

The contents of ionic chlorine,  $\text{Cl}_i$ , and total chlorine,  $\text{Cl}_t$ , were determined by potentiometric titration (Titrator TTT1C Copenhagen), with 0.02N  $\text{AgNO}_3$  aqueous solutions. The ratios between the ionic chlorine and the total chlorine contents show that the quaternization reaction of CMPSF occurs at a transformation degree around 72 %. The characteristics of the synthesized polysulfones are presented in Table 1.

**Table 1.** Total chlorine, ionic chlorine, and phosphorus contents, substitution and functionalization degrees and number-average molecular weights,  $\bar{M}_n$ , of polysulfone and functionalized polysulfones

Properties	PSF	CMPSF	PSFP
Cl (%)	-	8.68	5.85
$\text{Cl}_i$ (%)	-	-	4.23
P (%)	-	-	3.11
Substitution degree (%)	-	98	72
Functionalization degree (mmol/g)	-	-	1.001
$\bar{M}_n$ (g/mol)	39,000	29,000	28,000

Rheological properties of quaternary polysulfone with triphenylphosphonium pendant groups in N,N-dimethylformamide (DMF) were determined on a Bohlin CS50 rheometer, manufactured by Malvern Instruments (Worcestershire, United Kingdom). The measurements were performed by using a system presents cone-plate geometry with a cone angle of 4° and 40 mm diameter. Shear viscosities were registered in the range of 0.07–150 1/s shear rate domain, at several temperatures (25–45 °C) and concentrations in semi-dilute domain ranging from 5–12.5 g/dL. According to the amplitude sweep test performed at a frequency of 1 Hz, in the linear viscoelastic regime for shear stresses between 2 and 10 Pa, a shear stress of 2 Pa

was selected for all samples. Rheological tests were obtained with an accuracy of  $\pm 5\%$ , for different measurements.

## Results and discussion

Dynamic rheology is one of the most effective tools to investigate the flow behavior and microstructural changes in the polymer materials. Thus, the flow behavior of PSFP in DMF at different concentrations, where a complex behavior appears under specific conditions, was evaluated from the dynamic viscosity - shear rate dependence (Figure 1a).

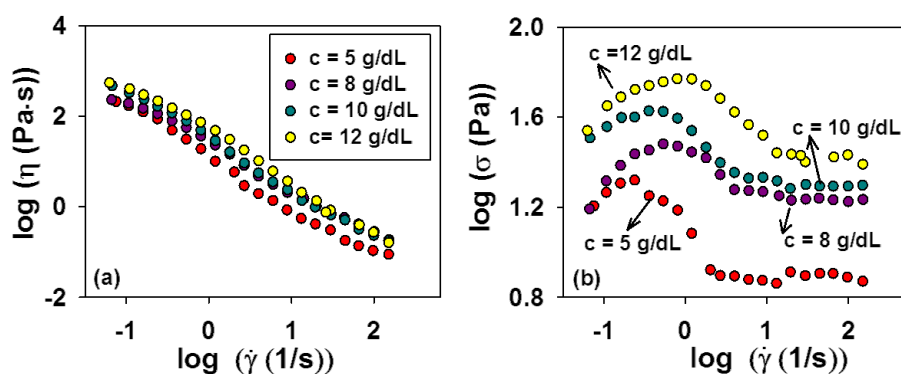


Figure 1. Variation of rheological parameters for solutions of PSFP in DMF at different concentrations and 25 °C: (a) Double logarithmic plot of dynamic viscosity ( $\eta$ ) versus shear rate ( $\dot{\gamma}$ ); (b) Logarithmic plot of shear stress ( $\sigma$ ) as a function of shear rate ( $\dot{\gamma}$ ).

According to literature data [14], examination of flow curves (Figure 1a) reveal that, the dynamic viscosity - shear rate dependence for PSFP solutions exhibit a shear thinning behavior in the shear rate range studied. Therefore, the investigated solutions present a dynamic viscosity that decreases with increasing of shear rate due to the destruction of the solutions microstructure at high shear, showing a pseudoplastic flow (“shear thinning”). In addition, increase of concentration led to an increase of dynamic viscosity on the shear rates domain. At the same time, it is observed that, as shear rate increases, the slope of curves decreases, and a Newtonian plateau tends to appears. In this context, one can conclude that these solutions possess properties of pseudoplastic materials, characterized by reduced entanglement density and enhanced number of oriented segments, as a result of increasing shear rates [15].

In our study, rheological tests were performed by increasing the shear rate at the different state of movement, in order to quantify flow behavior. Thus, this behavior illustrated in Figure 1a is also reflected in the variation of shear stress ( $\sigma$ ) with shear rate ( $\dot{\gamma}$ ) (Figure 1b). Concentrated solutions studied reveal a maximum on upward curve at very low shear rate, explained by Burgentzle et al. [16] as a consequence of the fact that a large shear stress must be applied to break the strongly network between polymer particles and to orient in the flow direction.

The solutions exhibit peculiar properties, namely they stop to flow abruptly below a critical stress and start to flow at a high velocity beyond a critical stress [17]. In accordance with literature [17], the rheological behavior of concentrated PSFP solutions is the result of the competition between the two processes which occur in these systems:

- “aging phenomena” which consists of a viscosity increase at rest due to the build-up of the microstructure and
- “shear rejuvenation” process associated with the decrease of the viscosity in time under shear due to the destruction of the microstructure.

Flow behavior illustrated in Figure 1a is also reflected in the values obtained for the flow behavior ( $n$ ) and consistency ( $k$ ) indices, evaluated from variation of shear stress ( $\sigma$ ) with shear rate ( $\dot{\gamma}$ ) according to the Ostwald-de Waele model [2]. The values of these parameters are indicative which can be explained by modification of the specific interactions from the system PSFP/DMF.

Consequence, this behavior can be explained by the balance between macromolecular mobility and specific interactions, reflecting the significant contribution of electrostatic interactions and, also suggesting the manifestation of an aggregation tendency as results of the long-range interactions between polymer chains.

### Conclusion

Influence of the structural characteristics of polysulfone with triphenylphosphonium pendant groups, PSFP is reflected on the rheological properties, through dynamic viscosity and consistency indices. Therefore, the quantified results of parameters which describe the conformation properties of PSFP solutions determine a lower packing efficiency conducting to a shear thinning behavior in the shear rate range studied. Additionally, the rheological behavior of PSFP solutions is affected by specific interactions, including hydrogen-bonding and association phenomena.

The results of this study have demonstrated that PSFP solutions may provide some important advantages concerning to their specific applications. Thus, these results are useful in future investigations on engineering applications, and utilization of these polysulfones as membranes in this field.

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