Influence of Triphenylphosphonium Pendant Groups on the Rheological and Morphological Properties of New Quaternized Polysulfone

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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 (nonsolvent) systems, were evaluated by rheological investigations. The polyelectrolyte effect, induced by enhanced dissociation of the ionizable groups and by mixed solvents' quality, modify the rheological functions, that is, dynamic viscosity, elastic shear modulus, and viscous shear modulus, as well as the thermodynamic parameters obtained from the rheological properties, such as apparent activation energy. These results were correlated with the morphological properties of the films obtained from solutions in solvent/nonsolvent mixtures and compared with other quaternized polysulfones, having different hydrophobic characteristics. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1752–1762, 2013

INTRODUCTION

Polymeric membranes have been developed for a wide variety of applications in separation technology, biological processes, medical devices, and blood purification. Systems generally composed of polymer, solvent, and nonsolvent are usually used to make asymmetric membranes, the process being 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 system.[1,2] Owing to some emerging problems, such as fouling, either blending with an additional polymer or other modification of membrane polymers became necessary.[3,4]

Also, the studies have been carried out on the miscibility behavior of polymers with different polarities.[5–7] In this context, it is known that polysulfones, possessing superior properties, such as chemical, mechanical, and thermal resistance represent the ideal candidates in the membrane industry. The use of these polymers for the aqueous phase is restricted by their hydrophobicity and may be improved by their modification through different processes. Thereby, desirable combination between polysulfones' properties and their availability makes them attractive materials for the manufacture of commercial membranes and biomedical applications, such as gas separation, pervaporation, hemodialysis, nano and ultrafiltration, cell culture, biological processes, or blood purification.[8–10]

Several reviews on the chemical 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,[11] for facilitating aggregation[12] or as an aid in matrix reinforcement of ionomers.[13,14] Owing 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, and water filtration membranes.[15] In this context, the search for alternative proton-conducting membranes capable of operating at high temperatures has extended the focus of the research area, and increased the interest for investigating alternative phosphonic "protogenic" groups, having ability to facilitate proton conductivity under low-humidity conditions.[16–19] Moreover, phosphonated model compounds have been recently shown to possess an attractive combination of properties that motivates the investigation of phosphonated polymers as proton conductors under low-humidity conditions.[16] Thus, polymers carrying these groups have properties quite different from those of polysulfones. For example, phosphonated polymers generally show a higher degree of hydrogen bonding and a lower water uptake, comparatively with their sulfonated compounds. As this is a relatively new topic, some key characteristics of the phosphonic
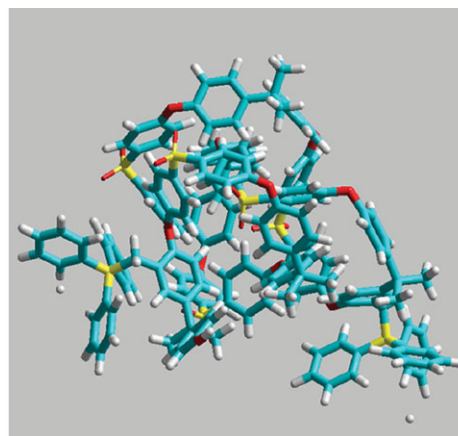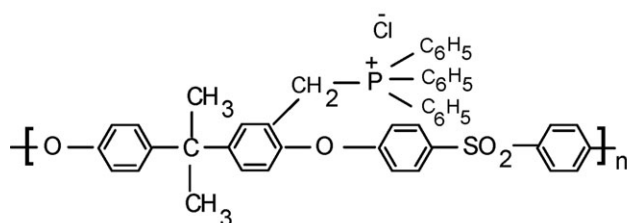
Scheme 1. Chemical and conformational structures with minimized energies, considering five repeating units of PSFP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

units should be underlined as compared to the sulfonic units. In a previous article of ours, synthesis of a new quaternized polysulfone obtained by the quaternization reaction of chloromethylated polysulfone with triphenylphosphine and its opto-electronic properties has been presented.[20] Theoretical evaluation of the refractive index showed that the molar refraction-to-molar volume ratio for different atoms present in the studied samples is reflected in the variation of the refractive index, and also that such values of the refractive index correspond to transparent materials. Theoretical data of the dielectric constants at visible wavelength also confirmed the low polarizability of this sample. At the same time, dielectric spectroscopy studies performed over a wide wavelength range showed that the dielectric constant decreases with frequency increasing and that the dielectric loss behavior exhibits two types of transition temperatures: γ—where a relatively broad distribution of the relaxation times and a symmetrical dielectric dispersion was evidenced; and β—at high frequencies.

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. For obtaining highly porous membranes, the corresponding films, obtained from solutions in a N,N-dimethylformamide (DMF)/water solvent mixture, were analyzed in correlation with morphological investigation.

EXPERIMENTAL

Materials

UDEL-1700 polysulfone (Union Carbide) (PSF) ($M_n = 39{,}000$ 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. A mixture of commercial paraformaldehyde with an equimolar amount of chlorotrimethylsilane (Me$_3$SiCl) as a chloromethylation agent, and stannic tetrachloride (SnCl$_4$) as a catalyst, was used for the chloromethylation reaction of polysulfone, at 50°C. 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 (chlorine content, 6.29%) with triphenylphosphine.[21] The quaternization reaction was performed by mixing CMPSF (chlorine, 6.29%) with triphenylphosphine (PPh$_3$), in the presence of dioxane. 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, Cl$_i$, and total chlorine, Cl$_t$, were determined by potentiometric titration (Titrator TTT1C Copenhagen), with 0.02N 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 46%.

The general chemical structure of PSFP is shown in Scheme 1. In addition, Scheme 1 shows the PSFP conformational structures with minimized energies, for a general visualization of chain flexibility. This structure was obtained using the HyperChem 8.0.7 professional program (Demo version) with Amber 99 force field approximation and Polak-Ribiere conjugate gradient in vacuum, at a temperature of 0 K (a graphic professional program that allows for rapid structure building, geometry optimization, and molecular display), considering five structural units of PSFP.

Rheological Measurements

The flow properties of quaternary polysulfone with triphenylphosphonium pendant groups in DMF and DMF/water solvent mixtures were determined on a Bohlin CS50 rheometer, manufactured by Malvern Instruments (Worcestershire, United Kingdom). The measuring system presents cone-plate geometry with a cone angle of 4° and 40 mm diameter. Shear viscosities were registered in the range of 0.7–1000 s^{-1} shear rate domain, at several temperatures (25–40°C) and concentrations in semidilute domain ($c \gg c^* \cong 0.5-1.0$ g/dL—calculated from intrinsic viscosity, according to Rao's equation[22,23]). According to the amplitude sweep test performed at a frequency of 1 Hz, in the linear viscoelastic regime for shear stresses between 0.15 and 30 Pa, a shear stress of 0.3 Pa was selected for all samples. During the oscillatory shear tests, frequency was varied between 0.01–15 Hz.
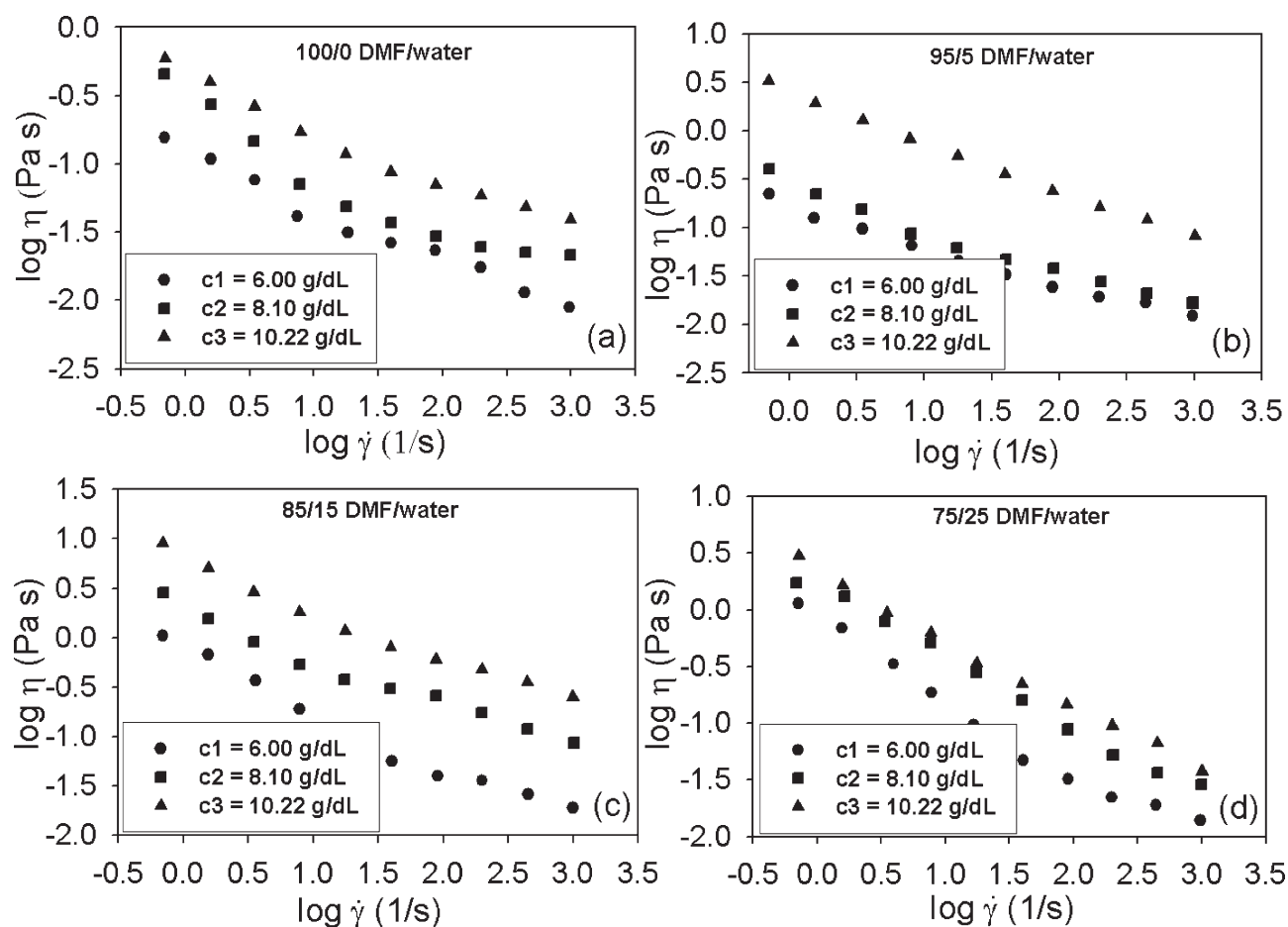
Figure 1. Log–log plots of viscosity as a function of shear rate for PSFP at different concentrations, at 25°C, in different solvent mixtures: (a) 100/0 DMF/water, (b) 95/5 DMF/water, (c) 85/15 DMF/water, and (d) 75/25 DMF/water.

Atomic Force Microscopy

A standard procedure for PSFP film preparation from casting solutions in DMF and 95/5, 85/15, and 75/25 v/v DMF/water solvent mixtures at 6 g/dL concentrations was applied. The polymer solutions were cast on glass plates and initially solidified by slow drying in a saturated atmosphere of the used solvent for 72 h and finally under vacuum, at 30°C for 24 h. Thus, the prepared films were subjected to morphological analysis.

Atomic force microscopy (AFM) images were taken in air, on SPM SOLVER Pro-M platform, having a NSG 10 cantilever with a 10 nm tip radius. The setup was operated in the tapping mode with 286 kHz cantilever oscillating frequency, in $10 \times 10 \ \mu m^2$ scan area, 256×256 scan point size images being thus obtained.

RESULTS AND DISCUSSION

Polysulfone is an amorphous aromatic main-chain polymer formed of alternating bisphenol A and biphenyl sulfone segments. The strong electron-withdrawing effect of the sulfone units gives a slightly acidic character to the ortho-to-sulfone aromatic hydrogens. On the other hand, 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 it may be used for obtaining some modified polysulfones, through chloro-

methylation, followed by quaternization process. In addition, triphenylphosphine was used in the synthesis of quaternized polysulfones to diversifiy specific applications, for example antibacterial activity. Thus, the electrostatic interaction between the positive charge of the quaternary phosphonium groups and the negatively charged species from the cellular membrane plays an important role in stopping the growth of some bacterial cells.[21,24] In this context, knowledge on the correlations between the rheological characteristics in solvent/nonsolvent mixtures and the morphological properties of quaternized polysulfone with triphenylphosphonium pendant groups is especially important.

Shear Viscosity Measurements for Polysulfone with Triphenylphosphonium Pendant Groups

Figure 1(a–d) shows the logarithmic plots of dynamic viscosity as a function of shear rate for PSFP in DMF and DMF/water, at 25°C. Different concentrations of solutions exhibit the shear thinning profile as a function of viscosity versus shear rates. In this context, one can conclude that this modified quaternized polysulfone is a pseudoplastic material characterized by a reduced entanglement density, and an enhancing number of oriented segments, as a result of the increasing shear rates.[25,26] The higher orientation of the polymer chains is the major cause of the non-Newtonian behavior. On the other hand, the
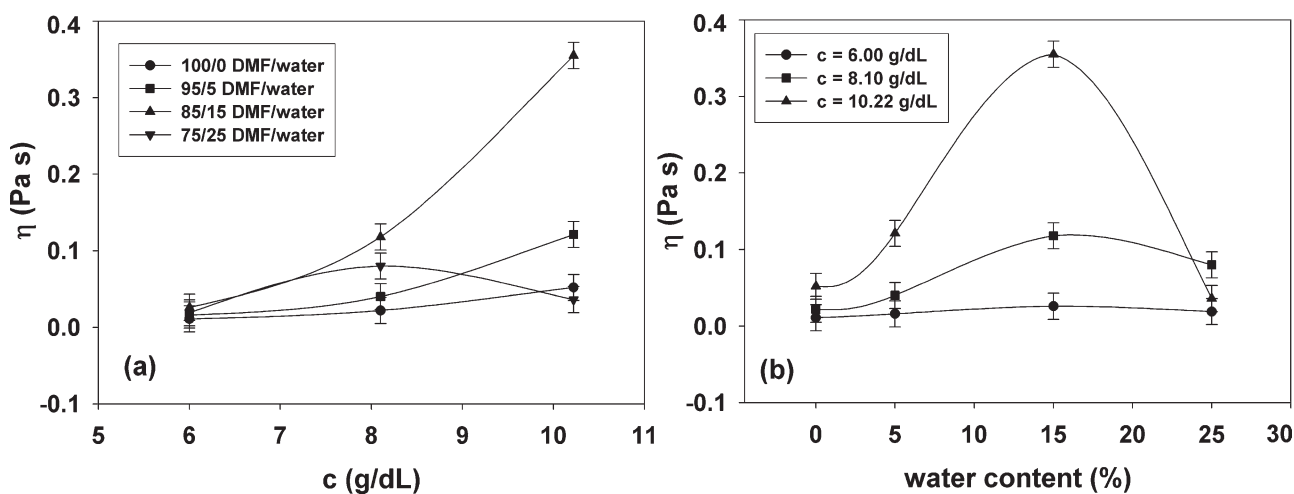
Figure 2. Dependence of viscosity, with average errors of ± 0.017, as a function (a) of concentration at different DMF/water contents and (b) of water content at different concentrations, for a shear rate of 440 s^{-1}.

interactions between the PSFP and the mixed solvent decrease with increasing the water content, which modifies the PSFP structure and the rheological behavior in solution. It must be mentioned that this modified polysulfone in DMF/water solvent mixtures contains a charged atom at two unquaternized structural units. Consequently, the viscoelastic behavior of PSFP can differ from that of neutral polymers. In particular, the occurrence of a relationship between zero shear viscosity and concentration, and an enhanced shear thinning[27] should be expected. Thus, the polyelectrolyte effect of this modified polysulfone in semidilute domain is owing to the expansion of the polyionic chain (even the charge density is low, where $Cl_i = 2.06\%$)—caused by a progressively enhanced dissociation of the ionizable groups as concentration decreases—to the intensification of the intramolecular repulsive interactions between the ionized groups (i.e., triphenylphosphonium), and to a more expanded hydrodynamic volume spread all along the chain.[23] From this reason, at lower concentration, higher values of dynamic viscosity can be expected. In addition, the affinity of either DMF or DMF/water for the quaternized sample depends on the neutral segment and on the charged groups. Figures 1 and 2 show the influence of the ionized groups and solvent mixtures compositions. At 6.0 and 8.10 g/dL concentrations, the viscosity of PSFP in 75/25 DMF/water is higher than in 95/5 DMF/water, and for 10.22 g/dL, the viscosity in 75/25 DMF/water is lower than in 95/5 DMF/water. Generally, the polyelectrolyte effect induced by an enhanced dissociation of the ionizable groups determines both the modification of the swelling degree of the polymer coil and the difference in composition of the mixed solvent inside and outside the coil. Also, in DMF/water system can appear association phenomenon.[28] Addition of nonsolvent (water) increases the thermodynamic quality of the mixed solvent for PSFP until 15% water content, evidencing an increasing of dynamic viscosity. These results are related to the Gibbs free energy of mixing solvents, quantifying the polymer–binary solvent interaction by dynamic viscosity. Above this water composition, dynamic viscosity decreases. This behavior was observed for all studied concentrations. In addition, interactions from system including association phenomena can introduce small differences in the values of

dynamic viscosity versus concentration, in experimental error limits as shown in Figure 2.

The shear thinning behavior obeys the power-law relationship between shear stress, σ, and shear rate, $\dot{\gamma}$, expressed in eq. (1):

$$\sigma = K \cdot \dot{\gamma}^n \tag{1}$$

where n and K stand for flow behavior index and consistency index, respectively.

Thus, as shown in Figure 3(a), the PSFP in DMF reveals that the flow behavior indices are lower than the unit, 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.

In 95/5, 85/15, and 75/25 v/v DMF/water solvent mixtures [Figure 3(b–d)], one can observe that the flow behavior index is <1, and that, generally, they decrease with increasing the water content. Moreover, Figure 3 points out higher values for the flow behavior indices, once concentration is increasing, according to the rheological behavior observed in Figure 1 for DMF. The solution consistency—induced by the water nonsolvent component from solvent mixtures—takes higher values than in a pure DMF solvent, as a result of the modification of interactions from the system, generated by the composition of solvent mixtures 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, can be described by an apparent activation energy, E_a, using Arrhenius equation [eq. (2)]:[29,30]

$$\ln \eta = \ln \eta_0 + \frac{E_a}{RT} \tag{2}$$

where η_0 represents a pre-exponential constant, R is the universal gas constant, and T is the absolute temperature. Distribution
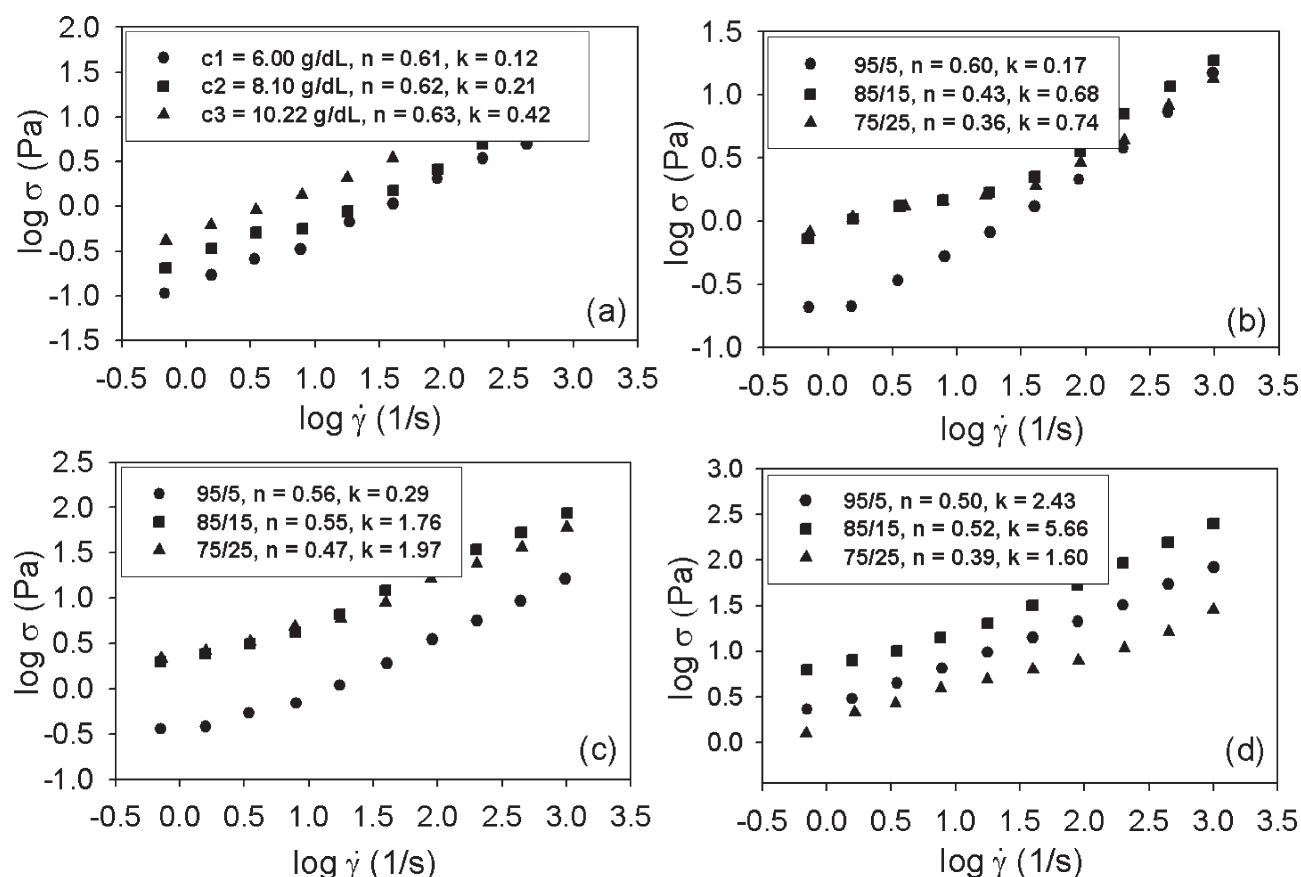
Figure 3. Log–log plots between shear stress and shear rate for PSFP at 250°C: (a) in 100/0 DMF/water at different concentrations, (b) at 6.00 g/dL and different DMF/water contents, (c) at 8.10 g/dL and different DMF/water contents and (d) at 10.22 g/dL and different DMF/water contents.

of the hydrophobic structures involved a wide temperature range for the association process, with the association thinning effect developed only for extended association. The apparent activation energy was discussed at lowest measured shear rate ($\dot{\gamma} \approx 0.7$ s^{-1}), because of the non-Newtonian flow in all domain of shear rates. 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 apparent activation energy involves two processes [eq. (3)]:

$$E = E_{dis} + E_{ass} \qquad (3)$$

where E_{dis} is the positive contribution of disengagement and E_{ass} is the negative contribution of the associated formations. The dependencies between dynamic viscosity and reverse temperature for 0.7 s^{-1} shear rate, of the Arrhenius plot type, are shown in Figure 4, in the temperature range of 25–40°C. These plots lead to different values of the apparent 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 being 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 preponderant, compared with the negative contribution of the associated formations, E_{ass}, leads to positive

values of E_a, whereas the negative value is generated by the preponderantly negative contribution of E_{ass}, comparatively with E_{dis}. Thus, water contributes to the specific molecular rearrangement of the system with temperature modification, favoring the formation of associated molecules at high concentration and high water content. Thus, it is relevant that the rheological
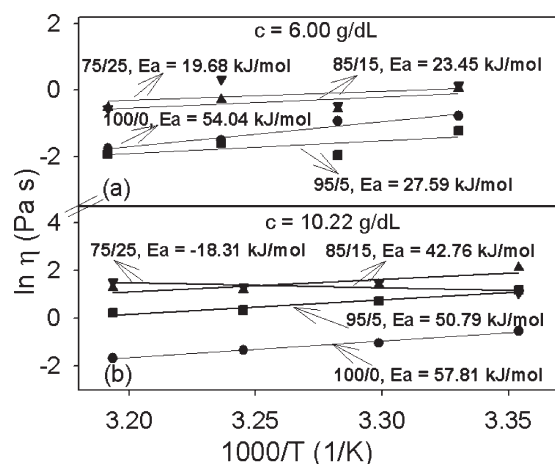

Figure 4. Arrhenius plots of dynamic viscosity at low shear rate for PSFP in DMF/water solvent mixtures at different concentration: (a) 6.00 g/dL and (b) 10.22 g/dL.
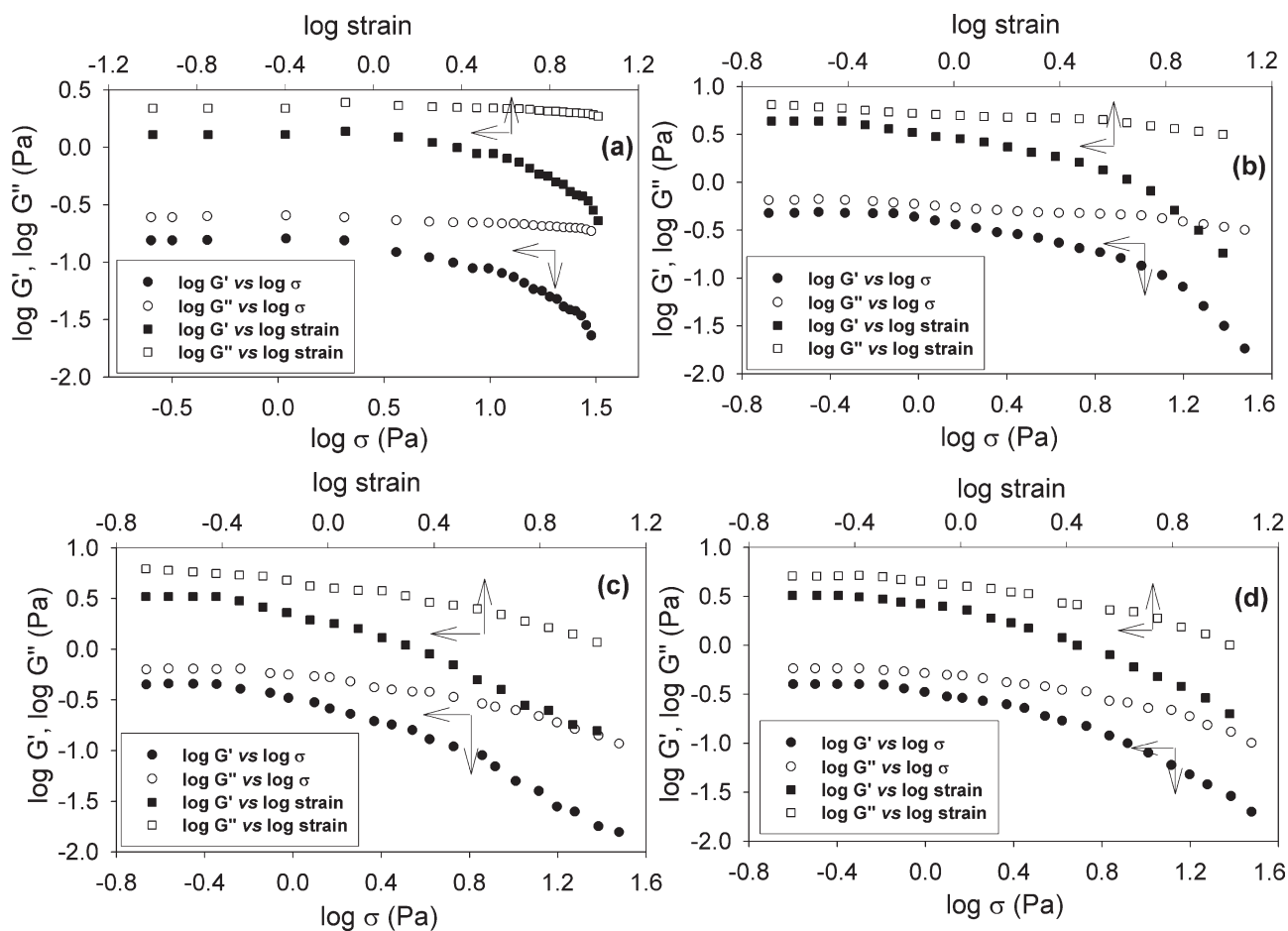
Figure 5. Log–log of storage and loss moduli versus shear stress and strain amplitude, respectively, for PSFP at 8.10 g/dL concentration, in (a) 100/0 v/v, (b) 95/5 v/v, (c) 85/15 v/v, and (d) 75/25 v/v DMF/water solvent mixtures. Double logarithmic plot of storage and loss moduli versus strain amplitude are shifted upward to 1 for a better visualization.

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. 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. These influences can generate different flow behaviors, such as Newtonian, shear thinning, or shear thickening flow. Previous studies on the PSFQ, PSF-DMEA, and PSF-DMOA quaternized polysulfones obtained by quaternized reactions of chloromethylated polysulfones with *N,N*-dimethylethanolamine,[31] *N,N*-dimethylethylamine,[32] and *N,N*-dimethyloctylamine,[32] respectively, show these aspects, and also that the activation energy, including disengagement and association phenomena, is modified in correlation with the hydrophobic characteristics of the modified polysulfones, which decrease in the following order: PSFP > PSF-DMOA > PSF-DMEA > PSFQ. Thus, for a more hydrophobic character of polymers, the association phenomena become predominant.

Dynamic Modulus

Viscoelastic measurements can significantly contribute to the knowledge and differentiation of polymer systems, completing

the rheological studies developed in shear regime. Prior to the measurements of these PSFP solutions, a suitable strain amplitude test was performed, involving measurement of the strain dependence of moduli, to ensure the linearity of viscoelasticity. Also, the stress sweep experiment was performed to establish the sample resistance to deformation, at a constant frequency of 1 Hz. Figure 5 exemplifies the variation of the storage and loss modulus, respectively, versus strain amplitude and shear stress, for PSFP, in 100/0, 95/5, 85/15, and 75/25 v/v DMF/water solvent mixtures, at a concentration of 8.10 g/dL. At low deformation, G' is constant and lower than G'', showing viscoelastic fluid properties, both moduli decreasing at higher deformation, which is the typical behavior, as evidenced by strain sweep results for most polymer solutions. Also, as the polymer solutions' chain is in a state of entanglement at small strain, both moduli remain constant in the linear region. It can be concluded that, in good solvent, the plateau region for both moduli is larger, decreasing with the presence of a nonsolvent in the system. Increasing of the shear stress may induce disruption of the initial polymer structure outside the equilibrium state. This behavior also appears for 6.00 g/dL concentration in all solvent mixtures and for 10.22 g/dL—only in a pure solvent, DMF. Figure 6 shows the appearance of structured polymer
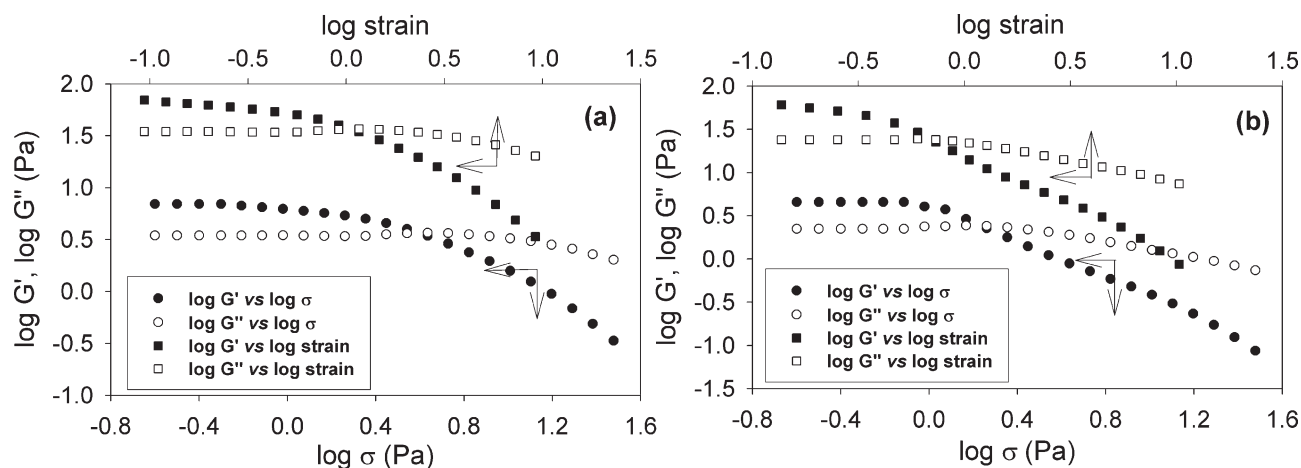
Figure 6. Log–log of storage and loss moduli versus shear stress and strain amplitude, respectively, for PSFP at 10.22 g/dL concentration, in (a) 95/5 v/v and (b) 75/25 v/v DMF/water solvent mixtures. Double logarithmic plot of storage and loss moduli versus strain amplitude are shifted upward to 1 for a better visualization.

characteristic at lower deformation, for a concentration of 10.22 g/dL in all solvent mixtures, when $G' > G''$; the linear region decreases with increasing of nonsolvent content, and a intersection of G' and G'' arises at the end of the linear-viscoelastic region. Thereby, the aspect of the curves for both moduli could be related to polymer topological entanglements.[33]

Figures 5 and 6 have allowed the selection of shear stress on 0.3 Pa for viscoelastic measurements. Thus, the storage and loss moduli are plotted as a function of frequency for PSFP

solutions in DMF/water at different concentrations and 25°C (Figures 7 and 8). At lower concentration of 6.00 and 8.10 g/dL and low frequency, the storage modulus, G', and the loss modulus, G'', are approximately proportional to f^2 and f^1, respectively, and, in this frequency range, G'' is always higher than G', a characteristic behavior of the viscoelastic fluid.[34] In addition, at higher values of frequency, G' becomes higher than G'', and their crossover increases with decreasing water content. For a 10.22 g/dL concentration of PSFP in mixed solvents, lower
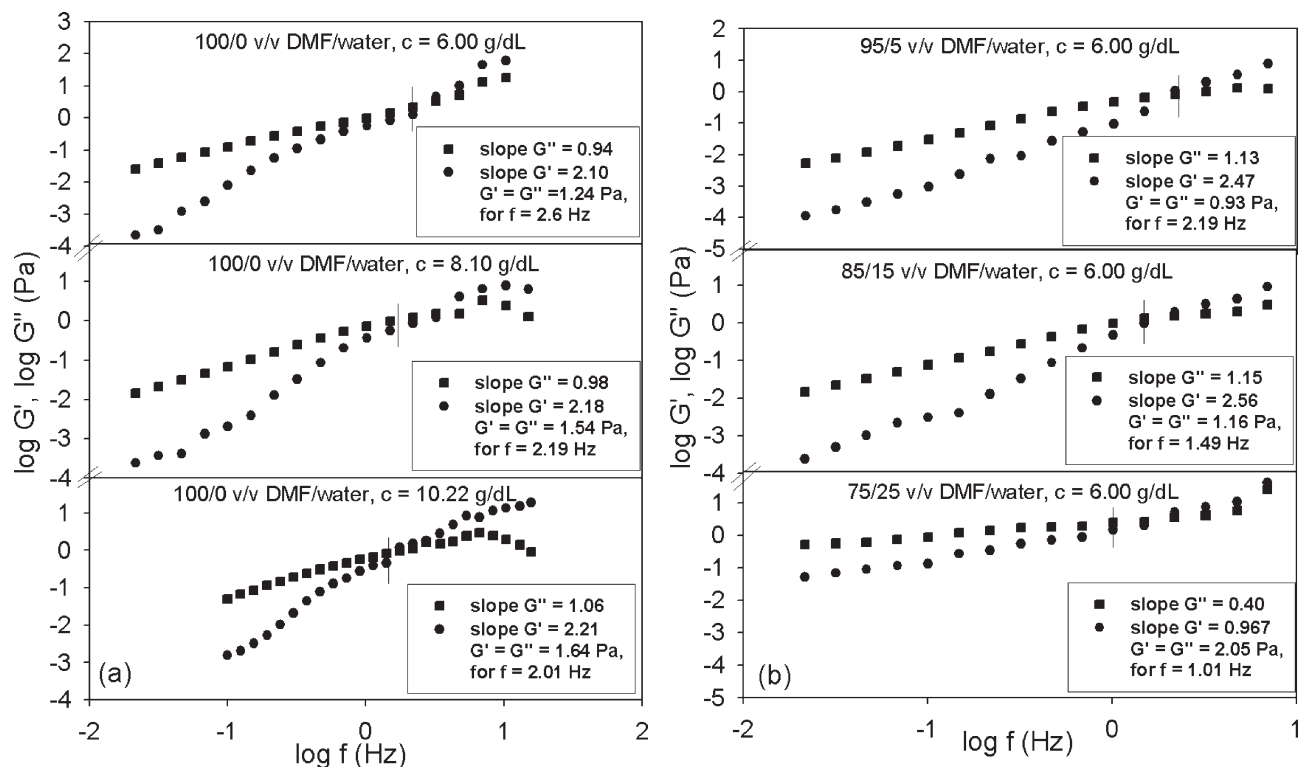

Figure 7. Log–log plot of storage and loss moduli as a function of frequency at 25°C for PSFP: (a) in 100/0 DMF/water, at different concentrations, (b) at different ratios of DMF/water solvent mixtures, at 6.00 g/dL.
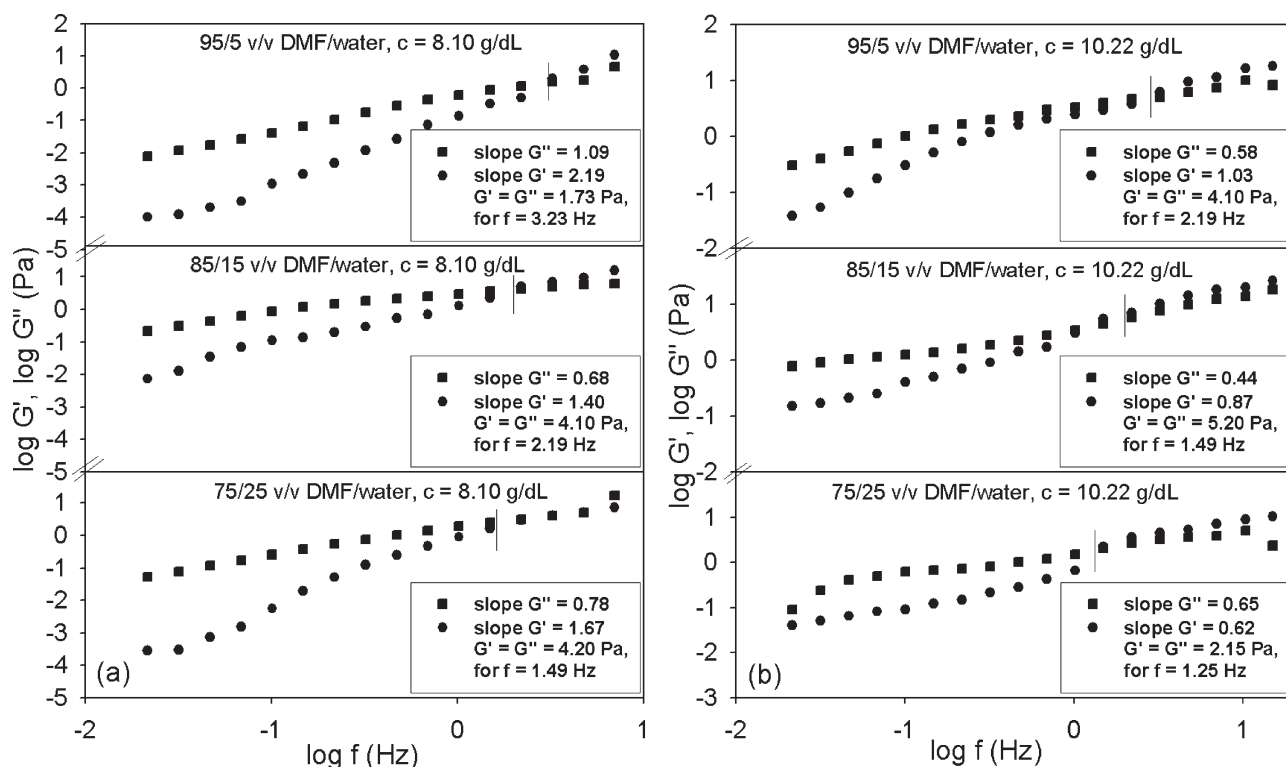
Figure 8. Log–log plot of storage and loss moduli as a function of frequency, at 25°C, for PSFP at different ratios of DMF/water solvent mixtures: (a) at 8.10 g/dL concentration and (b) at 10.22 g/dL concentration.

values of proportionality exponents between both moduli and frequency are obtained, owing to association and structured phenomena, a behavior evidenced by oscillatory tests.

Modification in polymer mobility for different compositions of solvent mixtures and concentrations is reflected in the G', G'', and $G' = G''$ values. Thus, the loss modulus shows smaller values, the storage modulus takes higher values, whereas with increasing the water content, the frequency corresponding to the crossover point, which delimits the limits of the viscous flow from the elastic one, takes lower values. On the other hand,

according to the previous assertions, when concentration increases, expansion of the polyionic chain decreases at the same time with dissociation of the ionizable groups from the modified polysulfone, generating a higher $G' = G''$ value. However, at a high concentration of 10.22 g/dL, the corresponding $G' = G''$ value decreases, which could be owing to some association phenomena generated by nonsolvent's presence in the system.

The complex viscosity evaluated from viscoelastic measurements decreases when angular frequency increases, and enhances when concentration increases, which indicates a pseudoplastic behavior,
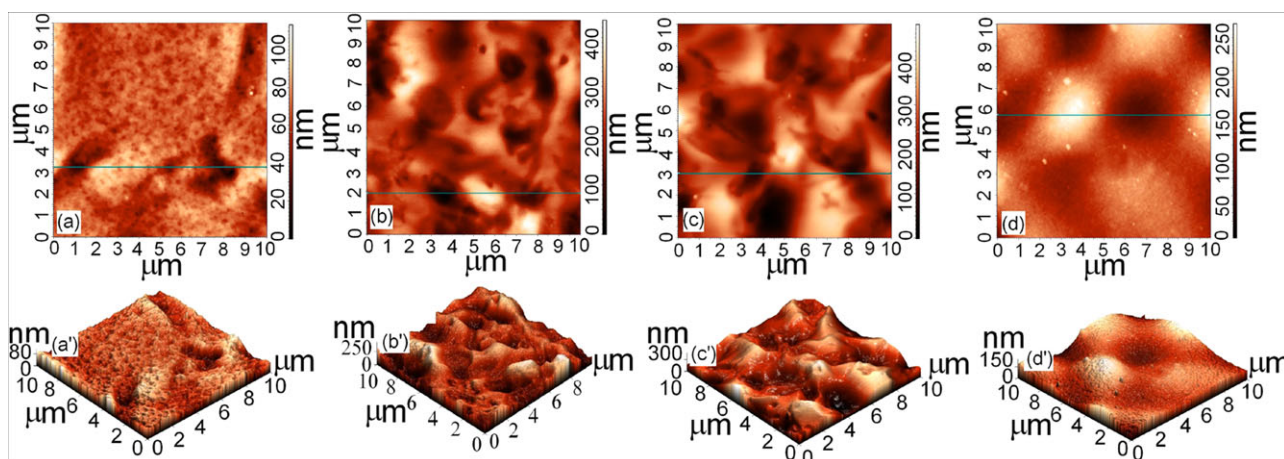

Figure 9. 2D and 3D AFM images for PSFP films in: (a, a′) 100/0; (b, b′) 95/5; (c, c′) 85/15; (d, d′) 75/25 DMF/water solvent mixtures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
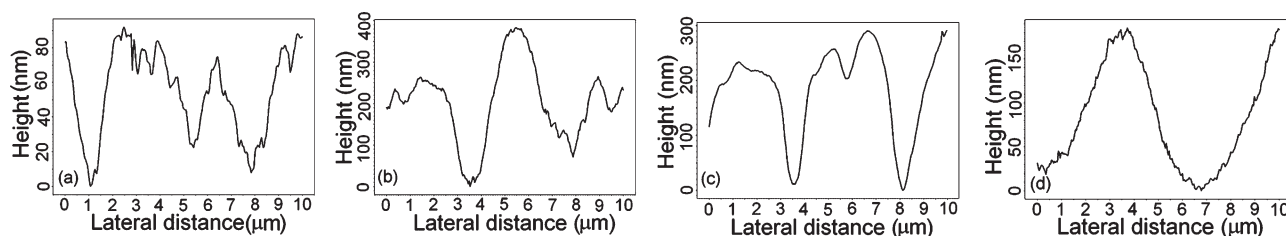
Figure 10. Surface profiles taking along the line from 2D AFM images of PSFP films in: (a) 100/0; (b) 95/5; (c) 85/15; and (d) 75/25 DMF/water solvent mixtures.

too. This non-Newtonian behavior is of special importance in the processing and fabrication of polymer materials. Literature mentions that decreased viscosity makes the polymer solution easier to process or squirt by small channels, such as through spinning, and that this decrease is associated with the development of elasticity in the polymer solution.[35] On the other hand, the electronegativity of the phosphorus atom on the triphenylphosphonium groups, generated by its electron-donor character, influences the dissolution of PSFP in DMF. Addition of water leads to the modification of solubility. It is known that water provides strong polar interactions. In this context, the DMF molecules may exhibit hydrogen bonding interactions with water and also mutual association phenomena, which disturbs dissolution. These interactions modify the flow properties, especially through enhancing the water content and concentration.

Morphology of PSFP Films

The AFM images of PSFP films prepared by solution in DMF/water solvent mixtures (Figures 9 and 10) 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, and mean width) and surface roughness parameters (including average roughness and root mean square roughness). For a water content value established at the solubility limit (DMF/water, 75/25 v/v), the depth value, and roughness parameters are lower. Pore sizes' enhancement is induced by the properties of the casting solutions, where the interactions owing to hydrogen bonding increase and different association phenomena occur.[36,37] Moreover, 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. On the other hand, according to the previous data, the type of pendant groups from quaternized polysulfones influences the morphological characteristics. Studies of the PSF-DMOA,[38] PSF-DMEA,[39] and PSFQ[24] quaternized polysulfones show that, as a nonsolvent, water determines different solubility limits in DMF/water (Table I). These limits can be correlated

Table 1. Pore Characteristics, Including Number of Pores Collected, Area (μm^2), Average Depth (nm), Average Length (μm), and Mean Width (μm), and Surface Roughness Parameters, Including Average Roughness, S_a (nm) and Root Mean Square Roughness, S_q (nm) for Films Prepared from Solutions in DMF/Water v/v, with 10×10 μm^2, 20×20 μm^2, 20×20 μm^2, and 60×60 μm^2 Scanned Areas for PSFP, PSF-DMEA, PSF-DMOA, and PSFQ, Respectively, Corresponding to 2D AFM Images

Solvent mixtures	Pores characteristics					Surface roughness	
	Number of pores	Area	Depth	Average length	Mean width	S_a	S_q
PSFP							
100/0	46	0.09	19.84	0.58	0.13	9.51	12.61
95/5	13	0.80	94.13	1.77	0.43	54.02	68.77
85/15	6	3.87	125.49	4.08	0.88	66.89	83.17
75/25	4	6.59	104.49	4.55	1.43	27.35	34.99
PSF-DMOA[38]							
75/25	–	3.12	13.65	3.26	0.96	1.59	2.34
50/50	–	2.09	5.55	2.63	0.64	1.52	2.17
PSF-DMEA[39]							
75/25	–	0.51	245.19	1.25	0.48	37.41	47.76
40/60	–	2.19	230.10	2.43	0.86	44.98	57.61
PSFQ[24]							
60/40	–	0.342	46.21	0.94	0.35	–	8.83
40/60	–	0.165	45.74	0.71	0.24	–	6.53

with the hydrophobic characteristics of the pendant groups. Moreover, according to the previous data concerning the surface tension properties of PSF-DMOA, PSF-DMEA, and PSFQ, the disperse contribution of the polar component to the total surface tension (%) has values of 3.4, 12.6, and 60.1, respectively, whereas the electron-donor and electron-acceptor components take low and slightly different values for PSF-DMOA and PSF-DMEA, and the electron-donor is higher than the electron-acceptor component for PSFQ. In this context, the higher hydrophobic characteristics of *N*-dimethyloctylammonium chloride, *N*-dimethylethylammonium chloride, and the higher hydrophilic characteristic of *N*-dimethyletanolammonium chloride pendant groups, respectively, influenced differently the solubility in DMF/water, as well as surface roughness and the pore parameters of the corresponding quaternized polysulfones.

CONCLUSIONS

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

The casting solutions of polymer show the influence of the nonsolvent content, temperature, and concentration on the rheological properties, through dynamic viscosity and viscoelastic properties. Recent studies reveal that PSFP is a pseudoplastic material with non-Newtonian behavior and shear thinning characteristic, which may be owing to the less entangled points observed at higher shear rates, resulting from a higher orientation of the polymer chains. In addition, the apparent 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, whereas the frequency corresponding to their overlapping decreases with increasing water content. In addition, the appearance of associations and structured phenomena is observed, generated by the increasing of intermolecular interactions in the systems with higher concentration and water content, both from strain amplitude or amplitude sweep tests and from viscoelastic measurements.

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:

1. The film prepared in DMF exhibits a larger number of pores and a low roughness.
2. Increasing of nonsolvent water content leads to a decrease of pore number, whereas their area, depth, average length, and mean width, and also surface roughness increase; at higher water content (DMF/water, 75/25 v/v), 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. Generally, it was found out that a higher hydrophobicity generates a higher surface roughness.

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. Thus, these results are useful in future investigations on specific biomedical applications, including the evaluation of bacterial adhesion to the surfaces, and utilization of modified polysulfones for semipermeable membranes in biomedical applications.

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