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RESEARCH PROJECTS FOR ENCOURAGING ESTABLISHMENT OF YOUNG INDEPENDENT RESEARCH TEAMS

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HIGH PERFORMANCE POLYMERIC BIOMATERIALS BASED ON FUNCTIONALIZED POLYSULFONES WITH MEDICAL APPLICATIONS

- 2013 -

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BRIEF REPORT

concerning the results obtained by the project team between May 1st, 2013 – December 15th, 2013

Objectives and activities proposed for Stage I - 2013:

Objectiv 1. *Synthesis of some new functionalized polysulfones containing quaternary ammonium groups*

Activities: 1.1. Scientific documentation concerning using functionalized polysulfones in biomedicine;

1.2. Purification of the monomers and solvents;

1.3. Synthesis of functionalized polysulfones with dimethyl-alkylamine;

1.4. Confirmation of quaternized polysulfones structures by elemental analysis, IR and ^{1}H-NMR spectroscopy;

1.5. Solubility testes, GPC.

Objectiv 2. *Achievement of composites/blends based on functionalized polysulfones with optimal properties in bio-applications*

Activities: 2.1. Scientific documentation concerning the properties, utilization and importance of composites/blends for obtaining semipermeable biomembranes;

2.2. Obtaining functionalized polysulfones/derivatives cellulose composites/blends;

2.3. Obtaining functionalized polysulfones/ polyvinyl alcohol composites/blends.

Objectiv 3. C*onformational characteristics of composites/blends based on functionalized polysulfones*

Activity: 3.1. Studies concerning conformational modifications of ionic polymers in ternary system: viscometry, rheology.

Objectives and activities performed.

All activities proposed for this stage were performed and are briefly presented in this report.

The research project developed in May-December 2013 period includes two main directions:

1. *Synthesis of new functionalized polysulfones containing quaternary ammonium groups and development of the composites based on functionalized polysulfone with optimal properties for bioaplications (***Objectives 1 and 2***).*
2. *Studies on the conformational changes of ionic polymers in ternary mixtures (evaluated experimentally by viscometry and rheology), under the influence of the structural characteristics of the polymers from the mixture, concentration and composition (***Objective 3 - partially***).*

Objectiv 1. *Synthesis of some new functionalized polysulfones containing quaternary ammonium groups*

1.1. Scientific documentation concerning using functionalized polysulfones in biomedicine

At the international level, the dynamics of the scientific research within the proposed investigation field is generated by the improvement of life quality. In the near future can be anticipated the development of the biomaterials based on synthetic polymers (*polysulfones, modified polysulfones, polyvinyl alcohol*, etc.), natural polymers (*cellulose, cellulose derivatives*, etc.) and their composites/blends, in order to confer enhanced *biocompatibility, biofunctionality* and *biodurability*[1,2].

The scientific research from the last years in the biomaterial field highlighted interesting classes of synthetic polymers, mentioning here the importance of the *polysulfones, polyvinylic alcohol (PVA)*, as well as natural polymers, such as *cellulose derivative*. In the last decade of the twentieth century, *polysulfones* (PSF) - high performance polymers – containing sulfone groups and aromatic nuclei, have come into attention because of their interesting properties that make them useful in a wide range of applications, as high performance engineering plastics, ion exchange membranes, biomembranes, materials compatible with blood, antiviral agents[3-6]. It is well known that, due to optical properties, mechanical and chemical properties, and also, the film-forming properties, *polysulfones* are included in the category of *membrane materials*, and, by their functional properties, represent some of the best materials used in many areas of everyday life[7-9].

Research in physical chemistry and technology of macromolecular compounds were focused in recent years mainly on preparation of *new porous materials* with application in the various forms: *films, membranes, tubes, micro*- and *nanoparticles, gels*, etc., being used as immobilization of active principles (drugs, enzymes, food additives, cosmetics, microorganisms, cells), media for tissue regeneration, prostheses obtaining, dialysis membranes, filter media, ion exchange, etc.[10-15]. Macromolecular compounds (*polysulfone, cellulose, PVA,* etc.) are frequently use to obtain such materials.

Currently, there are some disadvantages in applicability of *polysulfones* in the biomedical field, due to the hydrophobic nature of polymer chain[16-18]. To resolve this problem, it was following to improve the properties of biomaterials by surface modification[19,20]. In this context, the scientific researches concerning chemical modification of *polysulfones*, especially by *chloromethylation*, represent an interesting subject from both theoretical and practical points of view[9,21]. On the other hand, addition of functional groups (*e.g., ammonium quaternary groups*) to polysulfone backbone represent a useful way to change some properties of the material, such as solubility characteristics[22,23], hydrophilicity, antimicrobial properties[4-6]. Therefore, these polymers have multiple applications, such as *biomaterials* and *semipermeable membranes* used in biotechnology, medicine, food industry, etc.[24-29].

For this reason, one of the project goals is to bring new contributions to this field, by employing some fundamental research concerning characterization of new performed polymeric materials.

1.2. Purification of the monomers and solvents

Synthesis of functionalized polysulfones (proposed for these researches) was performed using a series of materials that have been purified by different methods and are displayed in Table 1.

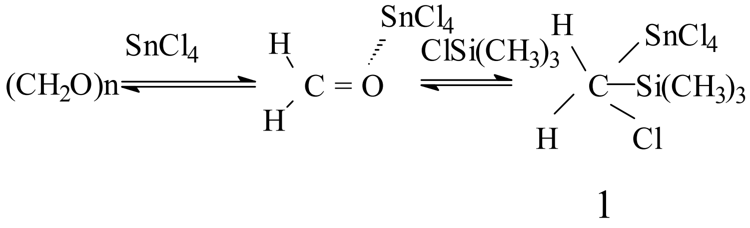
Table 1. Materials used for obtaining functionalized polysulfones and purification methods

Chemical designation	Company	Acronym	Purification method
UDEL-3500* polysulfone	Union Carbide	PSF	Was purified by repeated reprecipitation from chloroform and dried for 24 h in vacuum at 40 °C, before being used in the synthesis of chloromethylated polysulfone.
Paraformaldehyde	Fluka		-
Chlorotrimethylsilane	Fluka	Me_3SiCl	Was used without further purification.
Stannic tetrachloride	Fluka	$SnCl_4$	Was used without further purification.
Chloroform p.a.	Fluka	$CHCl_3$	Was washed with distilled water in a separating funnel, dried over anhydrous Na_2SO4, and subsequently distilled.
Chloromethylated polysulfone	Synthesized in laboratory.	CMPSF	Was purified by repeated reprecipitation from chloroform and dried for 24 h in vacuum at 40 °C.
N,N-dimethylformamide	Fluka	DMF	Was distilled at vacuum over P_2O_5 to remove water and to make an approximately neutral pH.
Dimethylbutylamine	Fluka	DMBA	Was used without further purification.
Methyl alcohol p.a.	Chemical Company		Was used without further purification.
Ethylic ether p.a.	Chemical Company		Was used without further purification.
Polysulfone with quaternary ammonium groups	Synthesized in laboratory.	PSFQ	Was purified by dissolution in N,N-dimethylformamide and precipitated in ethylic ether.

*IUPAC name: poly[oxy-1,4-phenylsulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4 phenylene] aromatic polysulfone

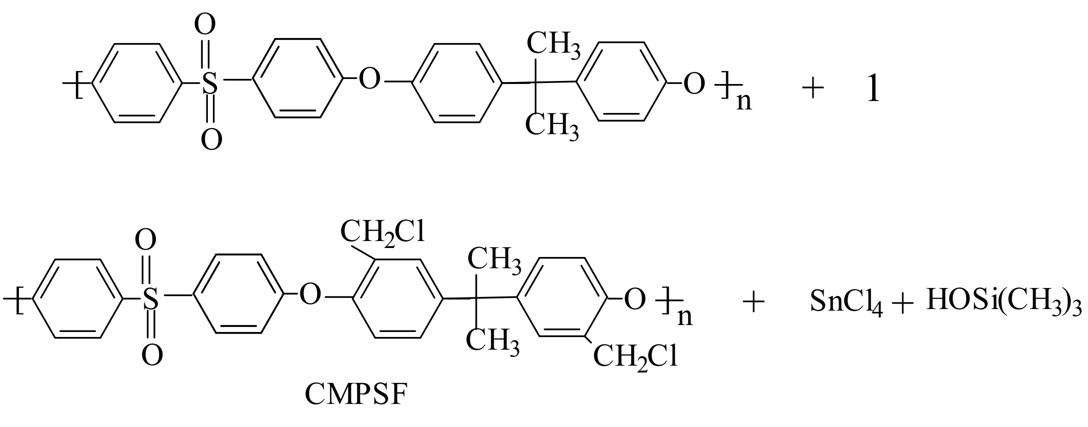
1.3. Synthesis of functionalized polysulfones with dimethyl-alkylamine

Strategy of synthesis involves the control of chain flexibility and mobility of the segments by incorporating of reactive functional groups. Polysulfone with aromatic heterocyclic (PSF)[30,31] has been functionalized by chloromethylation reaction (the reaction temperature 50-52 °C, reaction time predetermined 74 hours), when have been introduced chloromethylene groups, $-CH_2Cl$, at aromatic nucleus of the macromolecular chain, obtaining the functional groups with increased reactivity, therefore, a intermediate polymer for the synthesis of other functional groups in the side chain of polysulfone. A mixture of commercial paraformaldehyde with an equimolar amount of chlorotrimethylsilane as a chloromethylation agent, and stannic tetrachloride as a Lewis catalyst, were used for the chloromethylation reaction of PSF (Scheme 1 and 2).



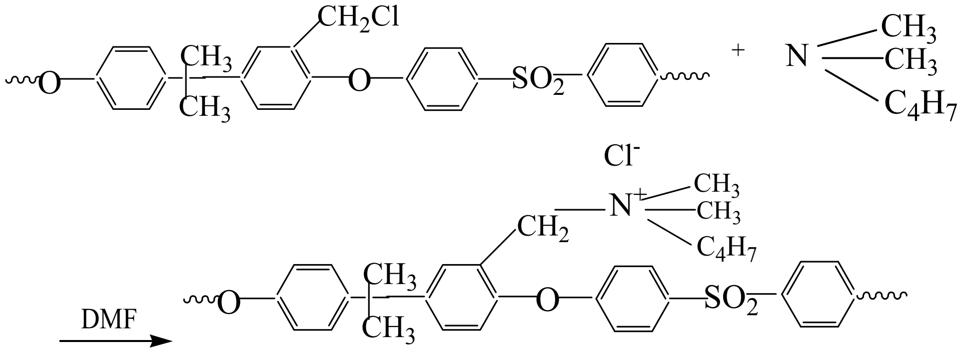
Scheme 1. Training reactive specie in the chlomethylation reaction

Under the action of stannic tetrachloride, paraformaldehyde generates active formaldehyde, which reacts with the trimethylchlorosylane forming chloromethyltrimethyl silyl ether with a similar structure as that of monochloromethyl methyl ether. This is the chloromethylation agent and it has the advantage of being formed “in situ”, so that the toxicity of the entire process is greatly reduced and the degradation products are less toxic than those of a conventional chloromethylation agent.



Scheme 2. Chloromethylation reaction of polysulfones

Polysulfones with alkyl side groups (PSFQ) were synthesized by reacting CMPSF with tertiary amine, N, N-dimethylbutylamine. The quaternization reaction was performed in N, N- dimethylformamide (DMF), at a CMPSF/ tertiary amine molar ratio of 1:1.2, for 10 h, at 60 °C (Scheme 3).



Scheme 3. The reaction of chloromethylated polysulfone with N,N- dimethylbutylamine

1.4. Confirmation of quaternized polysulfones structures by elemental analysis, IR and ^{1}H-NMR spectroscopy

1.5. Solubility testes, GPC

The characteristic absorption bands are identified by the FTIR spectra for CMPSF and PSFQ structures. The absorption bands at approximately 2990–2950 cm^{-1} and 2894–2850 cm^{-1} are assigned to the –CH$_3$ and –CH$_2$ vibrations of aliphatic units, respectively. The aromatic structure is confirmed by the appearance absorption bands at approximately 1590 to 1410 cm^{-1}; the absorption bands characteristic of –SO$_2$ asymmetric stretching appear at 1330 and 1300 cm^{-1}, which are a pair of split peaks, while the strong absorption band around 1150 cm^{-1} corresponds to –SO$_2$ symmetric stretching. The chloromethyl units (−CH$_2$Cl) from CMPSF are confirmed by the specific band at 1260 cm^{-1}. Also, in the FTIR spectra of CMPSF there is an absorption band at 669 cm^{-1}, characteristic to the C-Cl link.

In the FTIR spectrum of the polysulfone with quaternary ammonium groups the absorption bands around 1260 cm^{-1} and 669 cm^{-1} disappear; this is confirmation of the substitution the chlorine atom with the tertiary nitrogen. Generally, in the range 3100-3500 cm^{-1} appears a wide absorption band which is generated by the valence vibrations of −OH from alcohol molecules that associate through hydrogen bonds.

Furthermore, the success in substituting the chlorine from ─CH$_2$Cl group with DMBA was demonstrated by ^{1}H-NMR analysis. The characteristic peaks associated to the protons of ─CH$_2$Cl group situated at 4.45 ppm in the CMPSF spectrum disappeared in the PSFQ spectrum.

The total chlorine content of CMPSFs was determined by the modified Schöninger method and the degree of substitution (DS) was calculated using the following equation:

$$GS = \frac{M_{PSF} \times m_{Cl}}{(M_{Cl} \times 100) - (M_{CH_2Cl} \times m_{Cl})} \tag{1}$$

unde: M_{PSF} is the molecular weight of the PSF structural unit , M_{Cl} si M_{CH_2Cl} are the atomic weight of chlorine and the molecular weight of $–CH_2Cl$ group, respectively, m_{Cl} - is the chlorine amount, analytically determined.

Table 2. Characteristics of the chloromethylated (CMPSF) and quaternized (PSFQ) polysulfones

Sample	CMPSF	PSFQ
Total chlorine content, Cl (%)	7.42	-
Ionic chlorine content, Cl_i (%)	-	5.44
Nitrogen content, N (%)	-	2.48
Substitution degree, DS	1.03	-
Quaternization (transformation) degree	-	≈1 (η = 98 %)
Number average molecular weight, $\overline{M}_n$	29 000	28 000
Polydispersity, $\overline{M}_w / \overline{M}_n$	2.311	2.64
Solubility	Chloroform, DMF, DMSO, NMP	Chloroform, DMF, DMSO, NMP, DMF+methanol, DMF +water
FTIR spectra, (KBr, cm^{-1})	2990, 2950, 2895 ($-CH_3$, $-CH_2$); 1590, 1510, 1495, 1480, 1410 (aromatic); 1330, 1300 ($-SO_2$ asim.); **1260** (C–O–C; **CH_2Cl)**; 1150 ($-SO_2$ sim.); 1015 (aromatic); 875, 855, 840 (1,4-phenyl ring)	2990, 2950, 2895 ($-CH_3$, $-CH_2$); 1590, 1510, 1495, 1480, 1410 (aromatic); 1330, 1300 ($-SO_2$ asim.); **1250** (C–O–C;**$-CH_2Cl$);** 1150 ($-SO_2$ sim.); 1015 (aromatic); 875, 855, 840 (1,4- phenyl ring)
^{1}H-NMR spectra, ($CDCl_3$, δ - ppm)	7,80–7,65 (m, 4H, aromatic, orto at SO_2–); 7,40–6,50 (m, 11H, aromatic); **4,45** (s, 2H, **CH_2Cl)**; 1,65 (s, 6H, $(CH_3)2C<$)	**4,45** (s, 2H, **$-CH_2$** adjacent to quaternary nitrogen, N^+; **2,91** (3H from methyl group to quaternary nitrogen)

The contents of ionic chlorine, Cl_i, and total chlorine were determined by potentiometric titration (Titrator TTT1C Copenhagen), with 0.02 N $AgNO_3$ aqueous solutions. The ratios between the ionic chlorine and total chlorine contents show that the quaternization reaction of CMPSF occurs at a transformation degree close to 98 %. The chemical characteristics of the synthesized polysulfones are presented in Table 2.

The results show that, the proposed polymers were synthesized and the estimated structures, confirmed by IR and ^{1}H-NMR, are consistent with the corresponding activities of this project phase. The obtained polymers for biomedical applications exhibit increased reactivity, good solubility and ability to form films. Consequently, the complex structures are capable to achieve macromolecular composites that combine different specific properties favorable for the followed purpose.

Objectiv 2. *Achievement of composites/blends based on functionalized polysulfones with optimal properties in bio-applications*

2.1. Scientific documentation concerning the properties, utilization and importance of composites/blends for obtaining semipermeable biomembranes

Biomaterials prepared from functionalized polysulfones, cellulose derivatives, polyvinyl alcohol (PVA), as well as their composites/blends, contribute significantly at the quality and efficiency of the systems that address to human health. Therefore, the interest in this research field is justified both by theoretical approaches – fundamental research (study of interaction between polymer raw materials, or interactions between polymer matrix and low molecular weight compounds immobilized or filtered through porous material, performing chemical modifications on macromolecular compounds, allowing the change of the membrane transfer properties or the reaction with biologically active compounds), and especially from practical purposes, demanding a systematic approach and development[10,32-46].

A successful alternative for the development of new polymeric materials is blending of the already existing polymers, to obtain a balance among the desired properties exhibited by the individual components. The increasing need of materials for new applications requires polymers with diverse architectures, inducing specific properties[47,48]. Among such materials, cellulose acetate phthalate (CAP) has proven to be a remarkably versatile biomaterial and can be used in wide variety of application domains[49-53]. In this context, cellulose acetate phthalate (CAP) has been used for several decades as a pharmaceutical excipient; enteric coatings based on CAP are resistant to acidic gastric fluids, but easily soluble in the mildly basic medium of the intestine. Recently, its potential to inhibit infections by human immunodeficiency type 1 virus, several herpes viruses in vitro, and other sexually transmitted disease pathogens has been investigated.

Consequently, cellulose and its derivatives could function as a scaffold material for the regeneration of a wide variety of tissues, showing that it could eventually become an excellent platform technology for medicine. If cellulose can be successfully mass produced, it will eventually become a vital biomaterial and will be used in the creation of a wide variety of medical devices and consumer products.

On the other hand, the excellent physical properties of polyvinyl alcohol (PVA), including its high hydrophilicity, flexibility, film-forming, emulsifying, dispersing power, adhesive strength, tensile strength, and chemical stability, recommend him as being capable of improving the performance of polysulfone membranes[54-59]. Based on these versatile properties, PVA has been widely used, especially in fiber coating, adhesives, emulsion polymerization, films for packing and farming, and also as coating agent for tablets and capsules.

Therefore, the development of new composites - functionalized polysulfones/natural polymer (CAP) and synthetic polymer (PVA) - used in obtaining of semipermeable membranes with superior performance to those already known, suitable for biomedical applications, proper for biomedical applications, contribute to the development of knowledge in this area.

2.2. Obtaining functionalized polysulfones/derivatives cellulose composites/blends

2.3. Obtaining functionalized polysulfones/ polyvinyl alcohol composites/blends

Ternary complex systems consisting of functionalized polysulfones/natural polymer (CAP)/solvent and functionalized polysulfones/synthetic polymer (PVA)/solvent were realized and studied from the optimization perspective of conformational, thermodynamic and morphology under the influence of various factors (temperature, composition, concentration , etc.).

Homogeneous solutions of quaternized polysulfones (PSFQ) and CAP were prepared by dissolution in N-methyl-pyrrolidone (NMP) and kept for 24 h at room temperature. At the same time, PVA solutions were obtained by dissolution in NMP heated at 85 °C, followed by dissolution in a water bath with a constant temperature of 80 °C under continuous stirring for 7 h. Finally, all solutions were degassed.

Blends/Composites of PSFQ (1)/CAP (2) and PSFQ (1)/PVA (2) in NMP were prepared by mixing PSFQ with CAP and/or PVA solutions in different ratios, i.e., 100/0, 75/25, 50/50, 25/75, and 0/100.

Objectiv 3. *Conformational characteristics of composites/blends based on functionalized polysulfones*

3.1.Studies concerning conformational modifications of ionic polymers in ternary system: viscometry, rheology

For the systems proposed for analysis, consisting in pure polymers (PSFQ, CAP, PVA) and their mixtures in various compositions, in a first stage, were carried out studies on their properties in solution. Because the polymer processing often starts from the solution phase, the viscometer and rheological behavior of such systems was studied under the influence of composition, temperature and concentration, correlated with the structural characteristics of each polymer from the mixture. The study remark the influence of flexibility/hydrophilicity of the involved polymers and the cumulative effects of specific interactions developed by elecrostatice interactions, hidrogen bonds, and association phenomena that occur in the system. Additionally, the above-mentioned interactions indicate the compatibility of these polymers over a large composition range. This study investigates the hydrodynamic functions from the perspective of some newly-issued theories and analyzes the choice of optimal polymer mixtures compositions for specific applications in biomedical domains.

(A) Because of complexation polysulfone structure through chemical modifications and their specific characteristics, the experimental method by which have been discussed the conformational properties of the obtained composites is viscometry, the most widely used experimental method for multicomponent systems based on charged polymers. Indeed, the viscometric behavior is related to the polymer structural characteristics (nature of the polycation, its size and charge density), but also to environment properties, such as ionic strength, pH and addition of other solvent or salts[60].

Hydrodynamic volume of macromolecules in dilute solution, size and conformation of polymer chains have been described by intrinsic viscosity, $[\eta]$. In this context, Fig. 1a and b give indications on the electrolyte effect of quaternized polysulfone, by application of the Huggins equation (Eq. (2))[61].

$$\eta_{sp} / c = [\eta]_H + k_H [\eta]_H^2 c \tag{2}$$

where the parameters involved are: specific viscosity – η_{sp}, Huggins constant – k_H , concentration of polymer solution – c.

Examination of Huggins plots for pure components, PSFQ, CAP, PVA, and for their mixtures at different compositions, PSFQ/CAP and PSFQ/PVA, in NMP revealed the balance between the forces acting in polymeric complex systems over a large concentration domain. Generally, the increase in viscosity is due to electrostatic repulsions between charge groups and/or intermolecular interactions, while the decrease in viscosity is the result of intramolecular interactions. In addition, different characteristics of the polymers from the system, their mixing ratios and the solvent used influence the specific interactions established among the components of the complex polymeric systems and, therefore, the viscometric behavior.

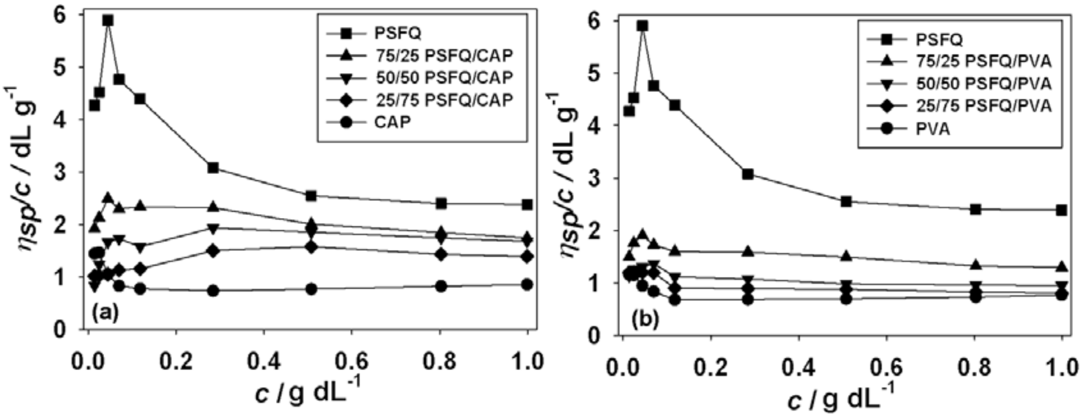


Figure 1. Huggins plots for: (a) PSFQ, CAP and PSFQ/CAP mixtures, and (b) PSFQ, PVA, and PSFQ/PVA mixtures in NMP at different mixing ratios and 25 °C

In accordance with all these remarks, a clear polyelectrolyte effect, namely a well-defined upward curvature, was noticed for PSFQ, caused by the progressively enhanced dissociation of the ionizable groups as concentration decreases, and therefore intensification of the intramolecular repulsive interactions between the ionized groups (*i.e.*, ammonium groups) spread all along the chain. Moreover, Fig. 1 illustrates the influence of polymer mixtures composition on η_{sp} / c, as depending on the neutral segment and on the charged groups. Thus, a higher content of quaternized units in the polymer mixtures has brought about an increase of viscosity, which means an increase of coil dimension in solution. This effect results from the higher electrostatic repulsions and cumulative steric hindrances, which caused a more expanded hydrodynamic volume and an increase of the long-range repulsive interactions.

Over the dilute concentration domain where condition $1.25 < \eta_{rel} < 1.9$ is obeyed, CAP and PVA have exhibited a neutral behavior, and for PSFQ/CAP and PSFQ/PVA mixtures with low PSFQ content the polyelectrolyte effect is diminished. On the contrary, it is knowledge that, in the region of low polymer concentrations, for which the values of relative viscosity are lower that 1.2, the reduced viscosity deviates upwards or downwards from the linear dependence given by Huggins equation which made more difficult the evaluation of intrinsic viscosity through extrapolation to zero polymer concentration.

According to literature, it should be emphasized that the viscosity abnormality observed over an extremely dilute concentration regime is due to the adsorption phenomena produced on the viscometer wall surface, an important effect for polymers with polar groups[62,63]. The effect of solvent-solvent or polymer-polymer intramolecular interactions could determine adsorption of the polymer molecules on the viscometer capillary walls, which agrees with some recent results obtained for polyvinyl alcohol solutions in water[64].

The interactions between chains at very low polymer concentrations can be explained by chains motion, due to the flow of the solution or to Brownian motion. In addition, the sharp discontinuity observed could be attributed to changes in macromolecular conformation.

Deviations from linearity reported in the dilute concentration domain are eliminated by Rao approximation (Eq. (3) – slightly sensitive to the possible errors occurring in relative viscosity data, η_{rel}, according to Fig. 2.

$$\frac{1}{2\left(\eta_{rel}^{1/2}-1\right)}=\frac{1}{[\eta]_R c}-\frac{(a-1)}{2.5} \tag{3}$$

where $a = 1/\Phi_m$ and the maximum volume fraction to which the particles can pack – Φ_m, expressed as $\Phi_m = \frac{[\eta]}{2.5} c_m$.

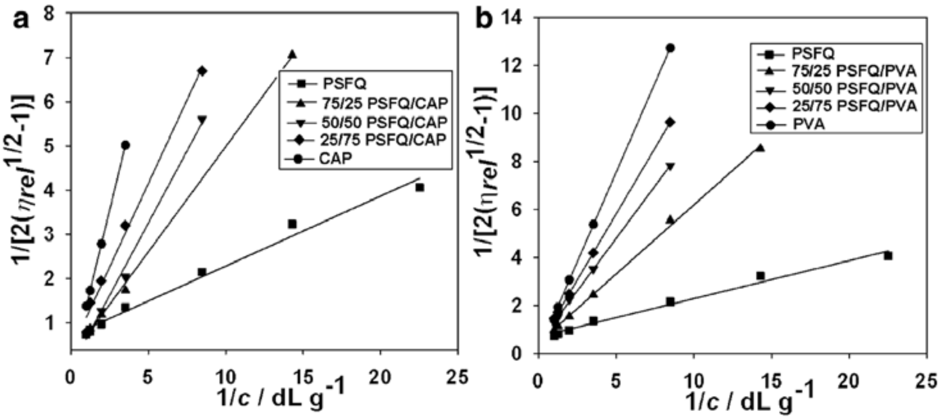


Figure 2. Rao plots for: (a) PSFQ, CAP and PSFQ/CAP mixtures, and (b) PSFQ, PVA, and PSFQ/PVA mixtures in NMP at different mixing ratios and 25 ° C[61]

In addition, Wolf equation (Eq. (4)), applicable to both charged and uncharged polymer solutions at sufficiently low polymer solution concentrations, was used:

$$\ln \eta_{rel} = \frac{c[\eta]_{Wolf} + Bc^2[\eta]_{Wolf}[\eta]^{\bullet}}{1 + Bc[\eta]_{Wolf}} \tag{4}$$

where *B* represents hydrodynamic interaction parameter and $[\eta]^{\bullet}$ is the characteristic specific hydrodynamic volume.

The experimental data were well fitted according to Wolf equation (Fig. 3), and besides the intrinsic viscosity, $[\eta]_{Wolf}$, the $[\eta]^{\bullet}$ and *B* parameters were evaluated (Table 3)[61].

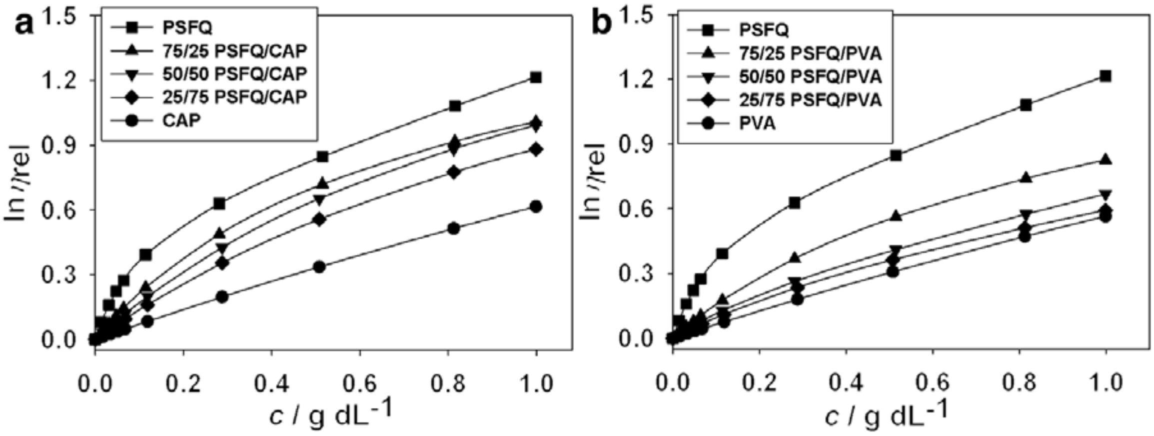


Figure 3. Plots of $\ln \eta_{rel}$ as a function of concentration for: (a) PSFQ, CAP and PSFQ/CAP mixtures, and (b) PSFQ, PVA, and PSFQ/PVA mixtures in NMP at different mixing ratios and 25 °C

The specific hydrodynamic volume, $[\eta]^{\bullet}$, which reflect the influence of the charged density, records maximum value for PSFQ and thereafter decreases, as an uncharged polymer is added into the system. Therefore, with increasing of CAP or PVA content to the solution of PSFQ, specific hydrodynamic volume becomes zero. Moreover, for mixtures with a higher PVA content (over 0.5 volume fraction of PVA), $[\eta]^{\bullet}$ was found to be equal to zero, because the molecular weights of the PSFQ and PVA have close values, so that, their effect on specific hydrodynamic volume was considered as minimum.

Table 3. Viscometric parameters of Wolf equation for PSFQ/CAP and PSFQ/PVA polymer mixtures in NMP at 25 °C

System	ϕ_1	$[\eta]_W$ **(dL g^{-1})**	$[\eta]^{\bullet}$ **(dL g^{-1})**	***B***
PSFQ/CAP/NMP	1	6.496	0.671	1.490
	0.75	2.473	0.204	0.655
	0.5	1.720	0.92	-1.049
	0.25	1.418	0.140	-0.138
	0	0.715	0	0,225
PSFQ/PVA/NMP	0.75	1.758	0.141	0.774
	0.5	1.205	0.040	0.658
	0.25	0.961	0	0.611
	0	0.653	0	0.236

For multicomponent systems polymer/polymer/solvent, the dependence of intrinsic viscosity on composition is complex, being influenced by the conformational changes of each type of polymer within mixing, as well as by the thermodynamic or hydrodynamic interactions among polymers. Accordingly, the intrinsic viscosity values are affected by the charge density of the alkyl radical of the studied quaternized sample, composition of the polymer mixtures, and also by the used solvent. Moreover, viscometric properties are influenced by polymers characteristics, which permit limitation of compatibility and a well-established compatibility domain. Consequently, according to these affirmations based on viscometric data, PSFQ/CAP and PSFQ/PVA mixtures in NMP have a low miscibility over the whole composition domain, as a result of the competition among different thermodynamic interactions (Fig. 4a).

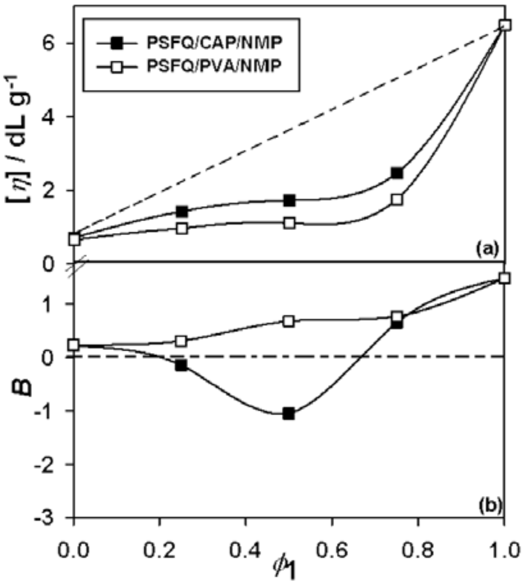


Figure 4. Dependence of intrinsic viscosity (a) and of *B* parameter (b) on the volume fraction of PSFQ. Dotted line from part (a) indicates additive rule ($[\eta]_m^{id} = \Sigma[\eta]_i\varphi_i$)

In Fig. 4b some differences appear between both studied systems PSFQ/CAP/NMP and PSFQ/PVA/NMP. It is observed from variation of *B* parameter with PSFQ composition a maximum positive value for PSFQ, followed by decrease at addition of uncharged polymers, CAP and PVA. A poor interaction between polymer coils and the solvent appears for 50/50 and 25/75 (v/v) PSFQ/CAP mixtures, where *B* corresponds to negative values. This condition suggests an aggregation tendency as a result of hydrogen bonding formation.

(B) The results obtained by the flow behavior study and viscoelastic properties reveals the structural processes that influence the dynamic viscosity and viscoelasticity of studied polymer systems , with different specific characteristics hydrophilic/hydrophobic and flexibility/rigidity. Therefore, the type of interactions and structural peculiarity of polymers in the blends, as well as the composition of polymer mixtures modify the rheological functions, evidencing the orientation or mobility of chain segments in the shear field.

Rheological investigations of pure components (PSFQ, CAP, and PVA) and of their blends in NMP, where a complex behaviour appears under specific conditions of blend composition, were evaluated in terms of the dynamic viscosity–shear rate dependence (Figs. 5 and 6)[65].

- PSFQ presents a non-Newtonian behavior (thinning), that occurs over the entire shear rate domain. Instead, for CAP occurring two regions, namely, the region corresponding to thinning phenomenon present at low shear rates and then, the Newtonian plateau at high shear rates. Exception displays of the PVA solutions which exhibit a Newtonian behavior over the applied shear rate domain (Fig. 5);

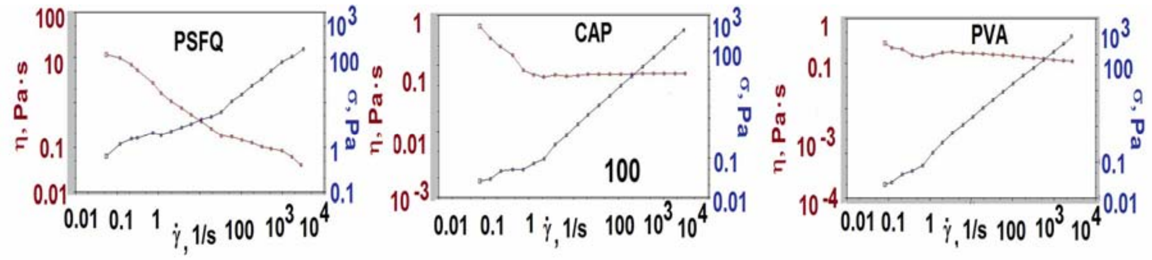


Figure 5. Flow curves created by dynamic viscosity *versus* shear rate for pure components: PSFQ, CAP, and PVA at 25 °C

- the non-Newtonian domain becomes less pronounced with the increasing of CAP content in PSFQ/CAP blend (Fig. 6a) and PVA respectively, in the case of PSFQ/PVA blend (Fig. 6b);
- it is observed that the variation of PVA composition in the studied systems determines changes of the rheological properties of PSFQ/PVA blends, suggesting that the PVA acts as a plasticizer[66];
- the dynamic viscosity of the studied blends is expected to depend on blend chain packing efficiency and specific interactions which, in turn, are influenced by the rigidity of the molecular backbone.
- the hydrophilic or hydrophobic characteristics of the polymers influence the compatibility in NMP, generating molecular restructuring in solution, under the influence of hydrogen bonding and association phenomena. Thus, it is evident that the rheological properties are influenced by polymer characteristics, which limits compatibility and a well-established compatibility domain.

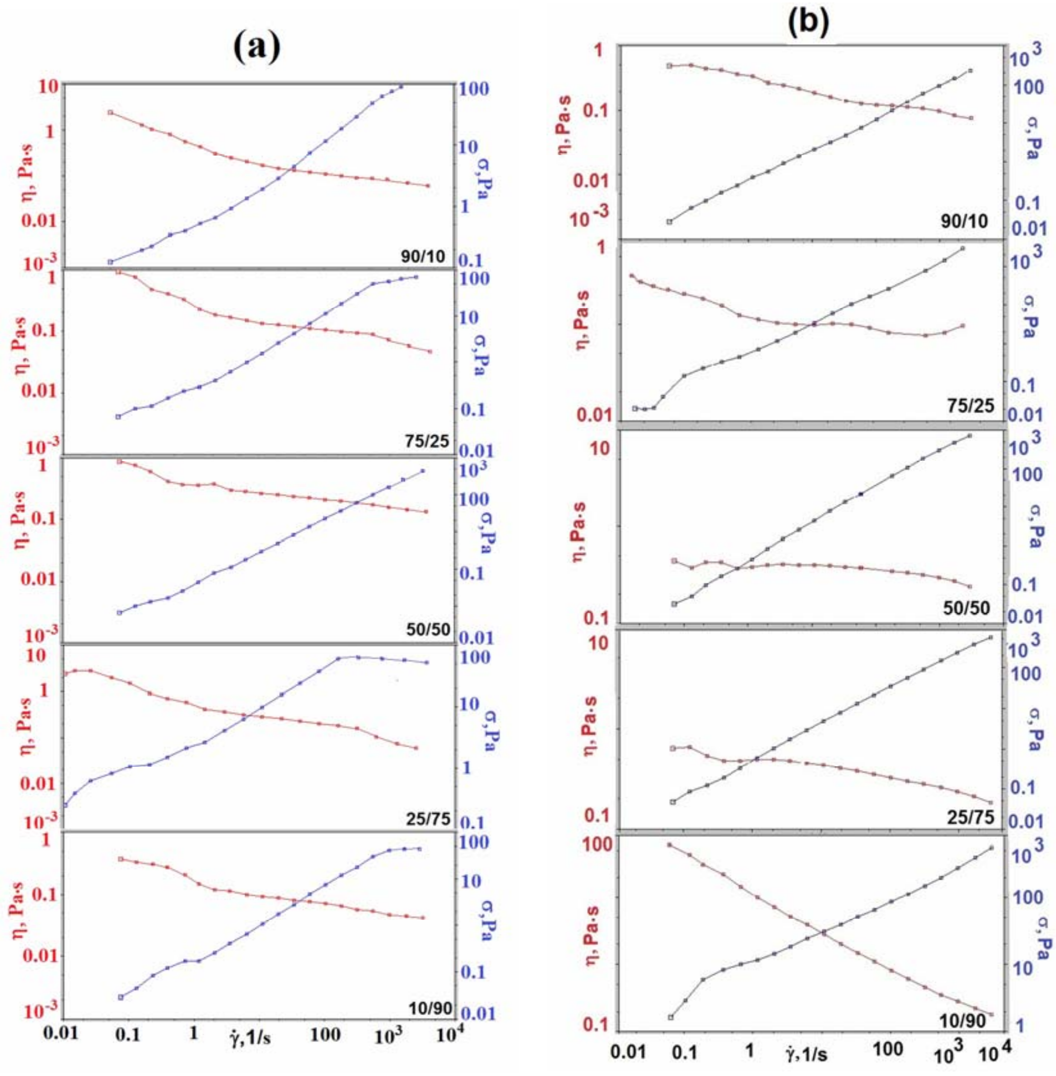


Figure 6. Flow curves created by dynamic viscosity *versus* shear rate for: (a) PSFQ/CAP and (b) PSFQ/PVA blends in different mixing ratios at 25 °C

The flow activation energy, E_a, (Eq. (5)) is influenced by the interactions between the chain segments of polymers in the presence of solvent.

$$\ln \eta = \ln \eta_0 + \frac{E_a}{RT} \tag{5}$$

where: $\eta_0 \sim e^{\Delta S / R}$ is a pre-exponential constant (in which ΔS is the flow activation entropy), R is the universal gas constant and T is the absolute temperature.

Similar to dynamic viscosity, activation energy gets modified, being affected by the nature of the functional groups of polymers from blend, solvent, composition of polymer blends, also by the competition between homogenous and heterogenous interactions. In particular, less flexibility of quaternized polysulfone determines the geometric constraints in macromolecular chains and thus, induces the stiffness chain, the characteristic reflected in the blends properties. The flow activation energies (23.16; 21.58; and, respectively, 17.01) follows this order: PSFQ <CAP <PVA, which coincides with the increased flexibility of pure polymers.

Viscoelastic measurements can significantly contribute to the knowledge and differentiation of polymer systems, completing the rheological studies developed for the shear regime. The effect of polymer structural characteristics and blend composition on the mobility of the segments from the shear field is reflected in the storage, G', and loss, G'', moduli. Figures 7 and 8 illustrate the variation of viscoelastic moduli *versus* oscillatory frequency (f) at 25 °C for the investigated blends.

- at low oscillation frequency, all investigated blends behave as viscous liquids (the loss modulus being always higher than the elastic one, ($G'' > G'$), as a result of unrecoverable viscous loss - characteristic behavior of viscoelastic fluids.

- at high frequencies, the storage (elastic) modulus becomes higher than the loss (viscous) modulus. The solid-like character becomes predominant and determines the reversibility of the energy stored in the sample as a result of the number and strength of interactions of the system[66].

- the storage and loss moduli exhibit a power-law dependence on frequency, where $G' \sim f^2$ and $G'' \sim f^1$, are characteristics of viscoelastic fluids.

- the overlap frequencies, $f_{G'=G''}$, which delimits the viscous flow from the elastic one, occur at high frequencies, reflecting the influence of polymer chain flexibility, according to the following order: PVA > CAP > PSFQ (Fig. 7);

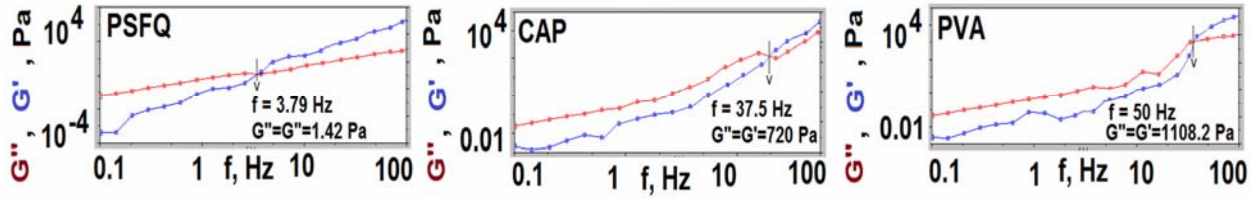


Figure 7. Double-logarithmic plots of shear moduli (G' and G'') *versus* oscillatory frequency (f) for pure polymers, PSFQ, CAP, and PVA at 25 °C

- one can remark that the overlap frequencies ($G' = G''$) are higher for PSF and CMPSF in NMP, which become higher when the CAP (Fig.8a) and PVA content, respectively in the polymer blends increases; consequently, structural particularities of polymers blend influence viscoelastic transition. These results are due to the specific interactions and to association and structural phenomena.

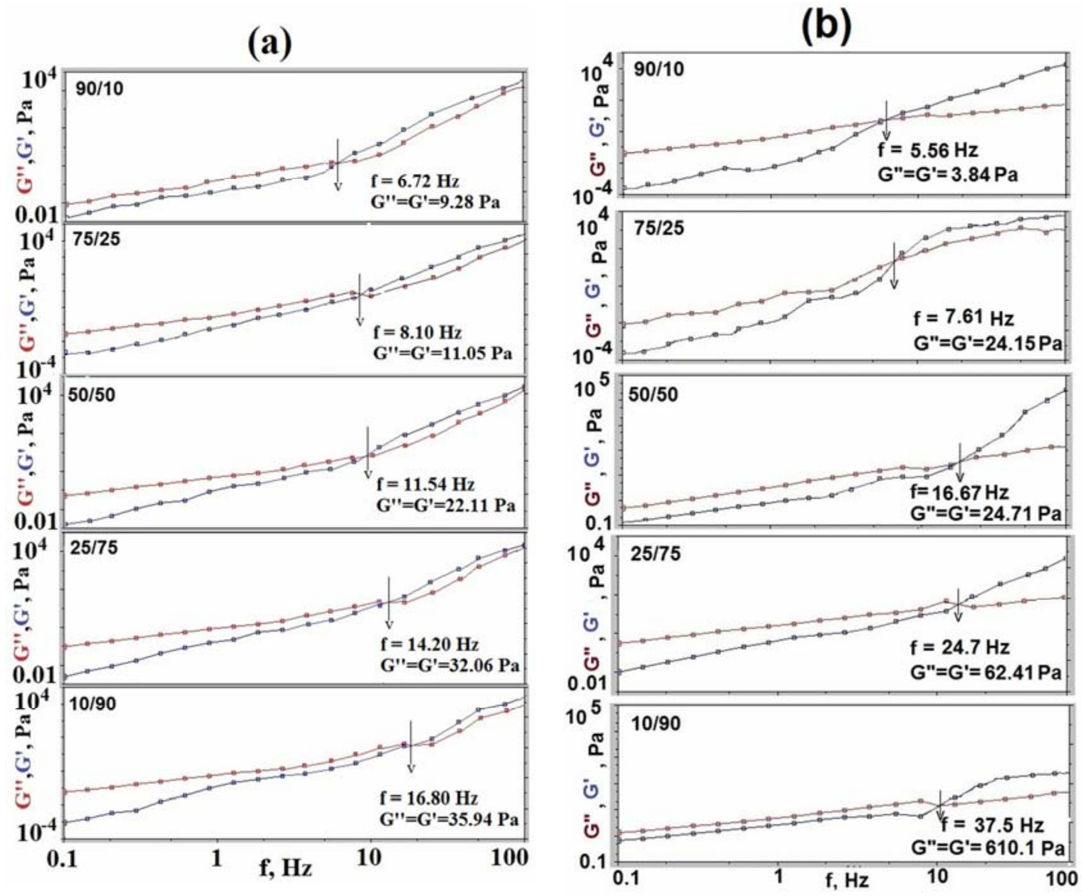


Figure 8. Double-logarithmic plots of shear moduli (G' and G'') *versus* oscillatory frequency (f) for: (a) PSFQ/CAP and (b) PSFQ/PVA blends at various mixing ratios at 25 °C

In conclusion, the results obtained in solution (dilute-concentrate domain) demonstrate that investigated blends/composites form the basis for future research on the obtaining the performance membranes with specific properties (specific morphology, controlled hydrophilicity and porosity, and biocompatibility, etc.). Therefore, knowledge of the structural parameters, as well as of the physical, chemical, and biological properties is essential for establishing the most appropriate compositions of these cationic polysulfones in polymer blends for specific biomedical applications.

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Director proiect,

A Filimon