



Fundamental perspectives on development of conductive blends based on quaternized polysulfone: Optical and dielectric response

Anca Filimon and Adina Maria Dobos

*“Petru Poni” Institute of Macromolecular Chemistry, Iasi,
700487, Romania*

OBJECTIVES

Analysis and understanding of the polarization and conductivity mechanisms exhibited in new blends based on quaternized polysulfones (i.e., quaternized polysulfone/cellulose acetate phthalate – PSFQ/CAP).



Improvement of the ionic conductivity and also optimization of optical and dielectric properties of films based on quaternized polysulfone blend for better electrical performances required by the ionic exchange membranes.

Chemical and conformational structures (with minimized energies, considering four repeating units) of quaternized polysulfone (PSFQ) and cellulose acetate phthalate (CAP)

Sample	Chemical structure	Conformational structure	M_n (g/mol)
PSFQ			28,000
CAP			2,534

Optical and Dielectric Measurements

Transmittance:

- SPECORD 200 Analytik-Jena spectrophotometer
- 200-1100 nm wavelengths.

Dielectric spectroscopy:

- Novocontrol Concept 40 broadband dielectric spectrometer;
- temperature was controlled with a 0.1 °C device by the Novocontrol Quatro Cryosystem, in dry nitrogen atmosphere;
- samples were sandwiched between two gold-coated brass electrodes and tested by sweeping the frequency between 10-10⁶ Hz, over a temperature domain between -120 and +120 °C.

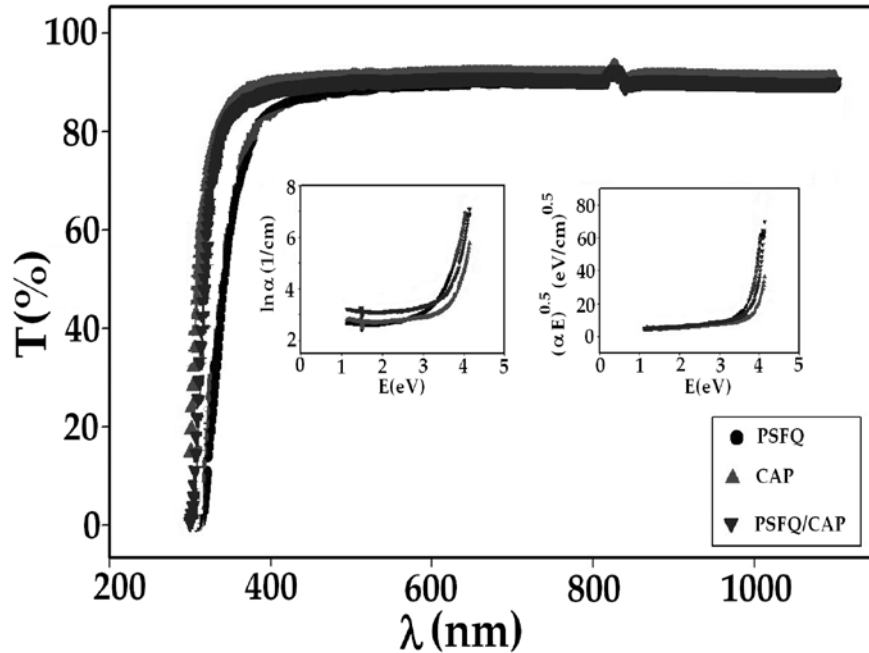
Optical parameters:

E_{gap} - optical gap energy

E_{urbach} - Urbach edge energy

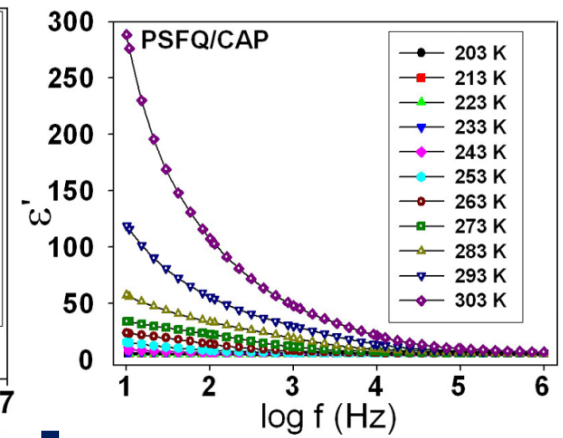
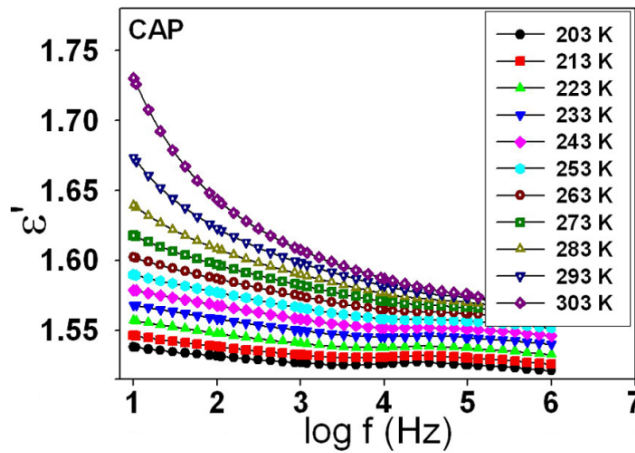
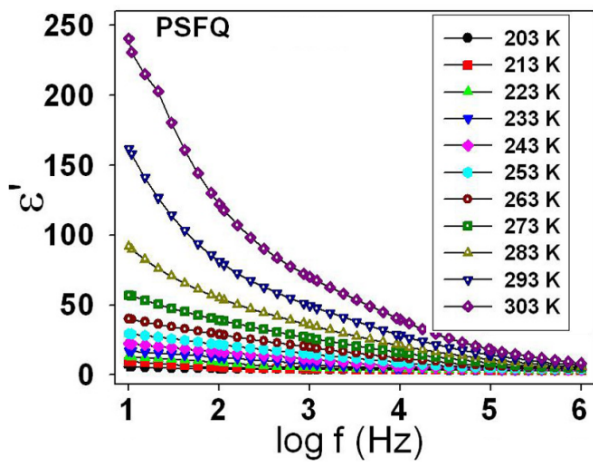
E_{tail} - Urbach tail

Sample	d (mm)	E_{tail} (meV)	E_{urbach} (meV)	E_{gap} (meV)
PSFQ	0.08	657	218	3.78
CAP	0.06	741	231	3.44
PSFQ/CAP	0.04	599	240	3.72



Transmission spectra, initiated in the ultraviolet domain, present a high transparency value of **about 90 %**

- Urbach energies obtained for studied polymeric films increase as the transparency of samples increase.
- For PSFQ film, which is less transparent, E_{urbach} value is smaller comparatively with the values of Urbach energies obtained for polymeric films with higher transparency (CAP and 70/30 wt./wt. PSFQ/CAP).
- E_{tail} energy of CAP sample presents a higher value than for PSFQ and for their blends.
- Variation of these parameters is related to the localized state induced by the atomic structures of the polymers.



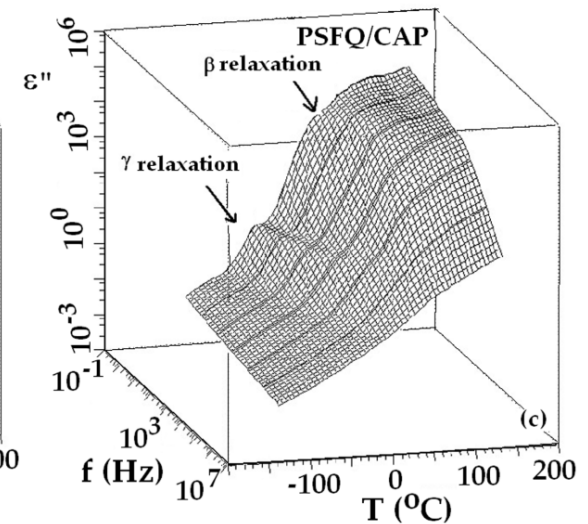
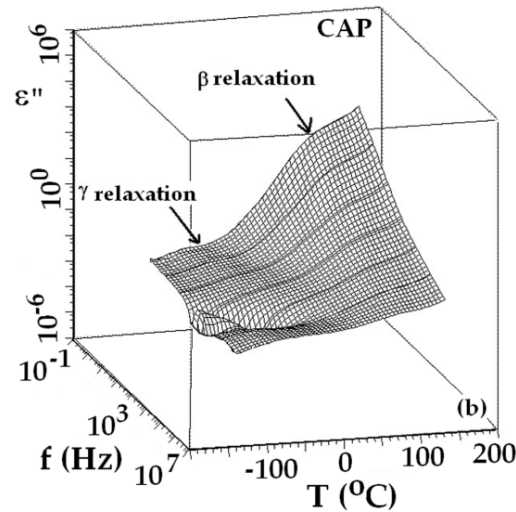
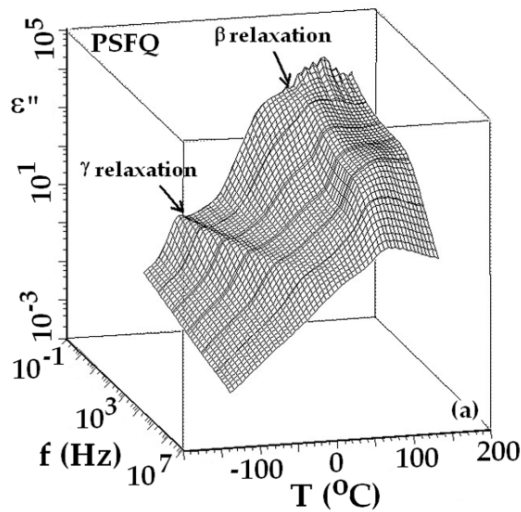
- **dielectric constant** increases with increasing of **temperature** due to the enhancement of total polarization, arising from dipoles orientation and trapped charge carriers
- **dielectric constant** decreases with increasing of **frequency** due to dielectric dispersion as a result of molecules lagging behind the alternation of the electric field, at higher frequencies.

Competition between the contributions of the main chain and the pendant groups is observed in:

$$\epsilon_{\text{PSFQ}} \gg \epsilon_{\text{CAP}}$$

- the electronic conjugations from the side chains of PSFQ contribute to the enhancement of ϵ' values
- the decrease in ϵ' values for CAP may be attributed to:
 - the ability of macromolecules dipoles to orient themselves in the direction of the applied field in the low frequency range;
 - dipoles will hardly be able to orient themselves in the direction of the applied field, in the high frequency range





Relaxation processes illustrated in tridimensional variation of dielectric loss, ϵ'' , with frequency and temperature \longrightarrow two types of relaxation, γ and β , appear.

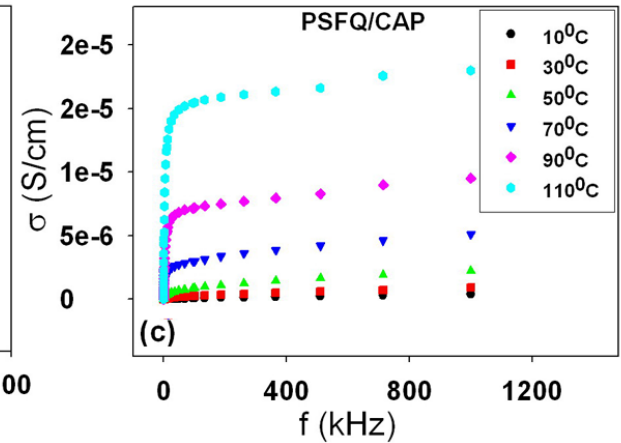
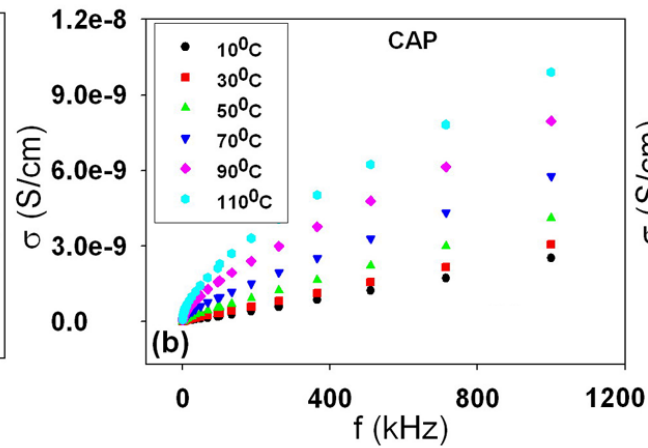
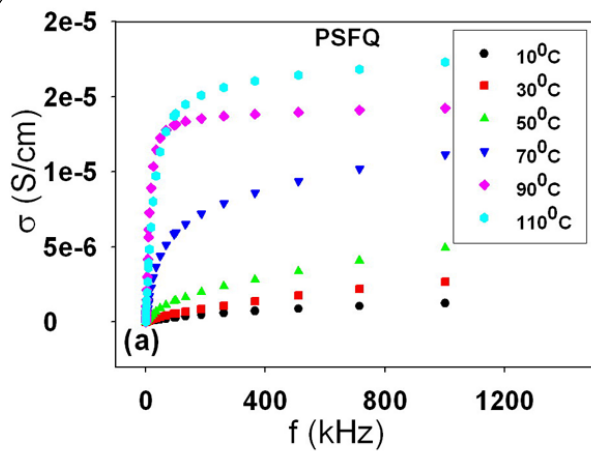
Polysulfone side chain produces:

- a decrease in the interchain attraction manifested in the starting chloromethylated polysulfone;
- imparts skeleton rigidity.

The main chain involves a localized and non-cooperative spectrum of motions.

Relaxation processes occur in polymers blend as result of the relaxations temperatures at which the two processes occur in the case of pure components.

In the used frequency range, the main contribution to dielectric relaxation appears only for the side groups motion, no contribution from the backbone of the main chain being noticed.



Variation of electrical conductivity, σ , with temperature and frequency is dependent on the structural parameters of the samples



The electrical conductivity, besides the electronic conduction is accompanied by an ionic conduction generated by the N,N-dimethylbutylamonium group from the quaternized polysulfone.

The linear dependence of conductivity on frequency around room temperature (30 °C) is due to electronic conduction via a hopping process.

Deviation from linearity at high frequencies may be due to the dispersion of the charge carriers produced by dipolar relaxation.

The electrical conductivity of the studied samples can be explained in terms of band conduction mechanisms, through band gap representation.

CONCLUSIONS

New blends of quaternized polysulfone/cellulose acetate phthalate provide a perspective for future approaches in industrial applications, due to the dielectric properties, conductivity, and implicitly electron interactions which represent fundamental features to enhance their electrical performance.



Findings of this study demonstrate that the blends based on quaternized polysulfones may offer important advantages for membrane applications, e.g., ionic exchange membranes.