



*Dedicated to the memory of
Professor Victor-Emanuel Sahini (1927–2017)*

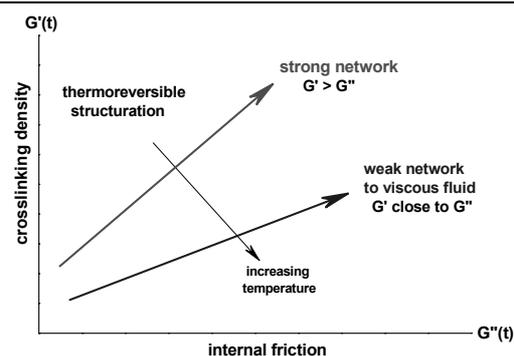
VISCOELASTIC BEHAVIOUR OF THERMOREVERSIBLE POLYACRYLONITRILE GEL ELECTROLYTE

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Electroactive gel based on polyacrylonitrile (PAN) dissolved in ethylene carbonate (EC)/LiClO₄ mixture was prepared and the viscoelastic properties were investigated at different temperatures. Between 5 °C and 25 °C the formed network presents high elasticity and stability. The network strength slowly decreases below 5 °C and this tendency is more pronounced above 60 °C. The gel structure fails for high temperatures (around 100 °C). In the Cole–Cole plot, the data obtained for PAN/EC/LiClO₄ at low or high temperatures showed small deviations in the master curve. The elasticity, the absence of the thermal history and the thermoreversible behaviour of the PAN/EC/LiClO₄ gel electrolyte make it a promising material for Li based batteries or actuators.



INTRODUCTION

The increasing requirements concerning the performances of batteries used for electronic devices determine a continuous exploration of new materials which are suitable for high capacity electrochemical cells. In this context, the use of polymers in the presence of lithium salts appears to be a promising solution.¹ Lithium ions possess a small ionic radius and they require a minimum solubility in low dielectric media. LiClO₄ has the advantage of relative low hygroscopicity and is stable to ambient moisture. This salt is frequently used as electrolyte solute due to its satisfactory solubility, high conductivity (~9 mS/cm in ethylene carbonate/dimethyl carbonate mixture at

20 °C) and high anodic stability (up to 5.1 V on a spinel cathode surface in ethylene carbonate/dimethyl carbonate).²

Ethylene carbonate (EC) is considered a cosolvent electrolyte with high dielectric constant and low viscosity in melt state. In an electrolyte solution, it improves the ion conductivity.¹

During the last period, the concept of polymer electrolytes has been more and more used to develop new materials which combine the high conductivity of liquid electrolytes with the solid-like properties of polymer gels.³⁻⁷ By immobilizing the electrolyte solution into the polymer matrix with mechanical stability, a gel electrolyte with a high ionic conductivity at room temperature and high mechanical strength is formed.

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Poly(acrylonitrile) (PAN) is a versatile polymer due to its unusual properties in dilute⁸⁻¹⁰ and concentrated^{11,12} solutions, being able to form associates,^{8,9} clusters and aggregates,^{11,12} thermoreversible physical gels^{13,14} or irreversible gels.^{14,15} In the presence of an electrical field, the orientation of CN groups occurs due to their high polarity, unusual for other vinyl polymers, this aspect being of interest for the actuators design. According to literature data, the gel electrolytes prepared from PAN and EC/LiClO₄ present ionic conductivity of about 10⁻⁶ S/cm at room temperature, value accepted for commercial applications.³⁻⁵

In this paper an electroactive PAN gel in EC/LiClO₄ mixture was prepared in order to investigate the rheological behaviour at different temperatures.

RESULTS AND DISCUSSION

Temperature influence on the viscoelastic behaviour of PAN electrolyte gel

The viscoelastic behaviour was followed in frequency sweep tests at different temperatures. For the present discussion, we have chosen the plots obtained at 3 reference temperatures (Figures 1-3): room temperature (25 °C), a very low temperature that can be reached during the winter (-20 °C) and a limiting temperature of 100 °C, above which the

ethylene carbonate evaporates and this can determine a network collapse.

At 25 °C, the storage (G') and loss (G'') moduli are independent on the oscillation frequency (ω), $G' \gg G''$ and the loss tangent ($\tan\delta = G''/G'$) is below 0.1 (Figure 1). At lower temperatures, the PAN gel presents a higher G' value, but G'' is more sensitive to the decrease of the temperature due to a rise in chain friction. A higher increase of G'' as compared with G' at -20 °C observed in Figure 2 (when the loss tangent also increases) can be taken as an indicative of the decrease of the network strength. The plot obtained at 100 °C (Figure 3) suggests a *critical state of matter* between viscous liquid and solid-like behaviour ($\tan\delta$ is constant and close to unity). Such behaviour was associated with *critical gel* structure.^{15,16}

The thermoreversible behaviour of PAN electrolyte gel was tested at different heating rates in temperature sweep tests and it was observed that the sample characteristics are not influenced by the thermal history. In Figure 4, the results obtained for a heating rate of 1 °C/min are shown. Up to 60 °C, only a small decrease in viscoelastic moduli and complex viscosity (η^*) can be observed, the loss tangent being nearly constant. By heating the sample above 60 °C, the interaction forces in the network structure become weaker and practically above 90 °C the sample loses the three-dimensional structure.

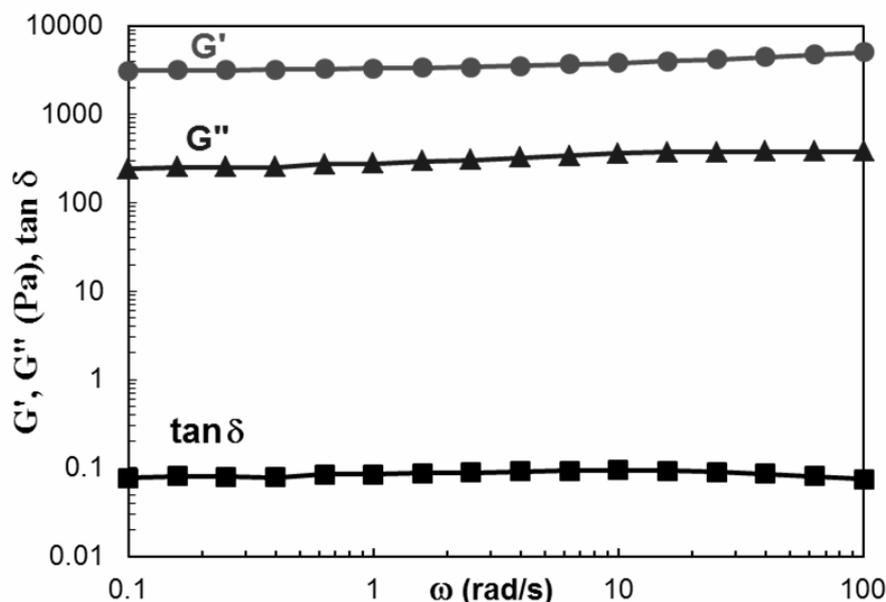


Fig. 1 – The typical gel-like behaviour observed for PAN/EC/LiClO₄ sample at different temperatures up to 70 °C. The results from this figure were obtained at 25 °C.

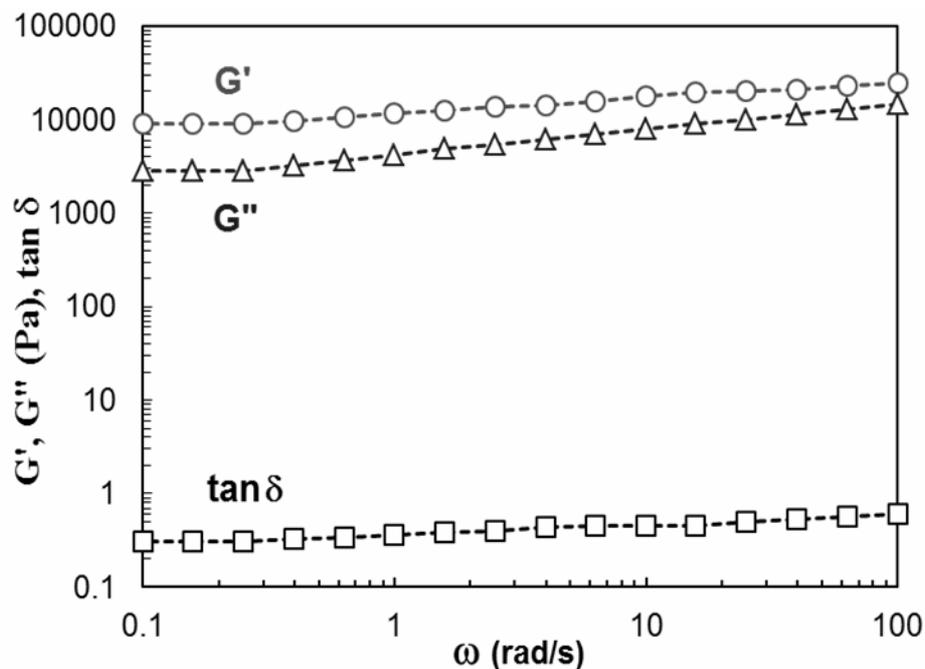


Fig. 2 – The viscoelastic behaviour of PAN/EC/LiClO₄ sample at -20 °C.

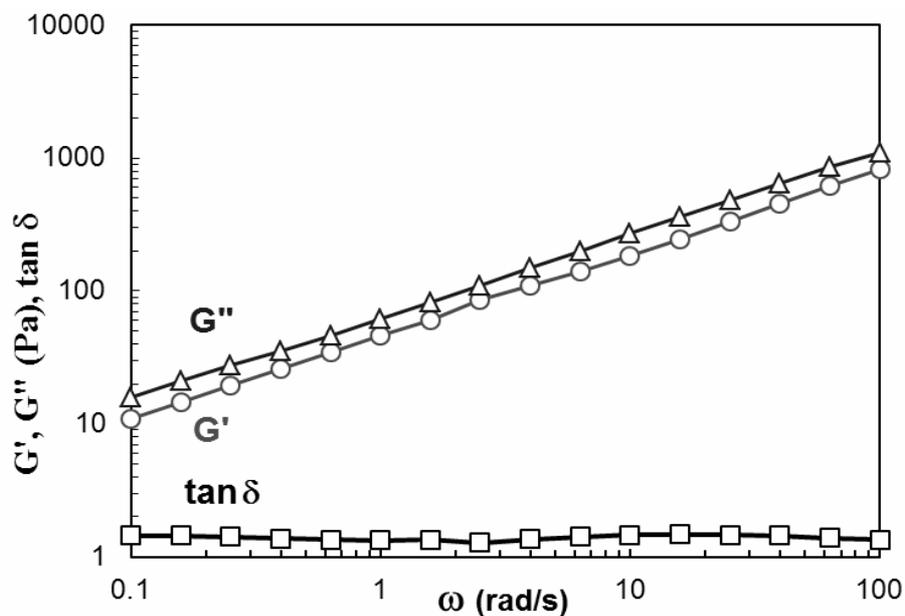


Fig. 3 – The viscoelastic behaviour of PAN/EC/LiClO₄ sample registered at 100 °C.

The heating rate influences only the behaviour at high temperatures, the starting temperature for the decrease in the viscoelastic parameters is shifted to higher values. Some tests made with the same sample at increasing and decreasing temperature show no influence of the thermal history on the viscoelastic parameters. This confirms the observation concerning the sample stability.

The curves of the complex viscosity in oscillatory shear conditions at different temperatures are given in Figure 5. The slope of 0.83 observed at low temperatures decreases progressively as the temperature increases and the changes in the sample structure determines a change in the slope at low oscillation frequency. The intra- and intermolecular interactions between nitrile groups by means of Li⁺ ions are influenced by the temperature change.

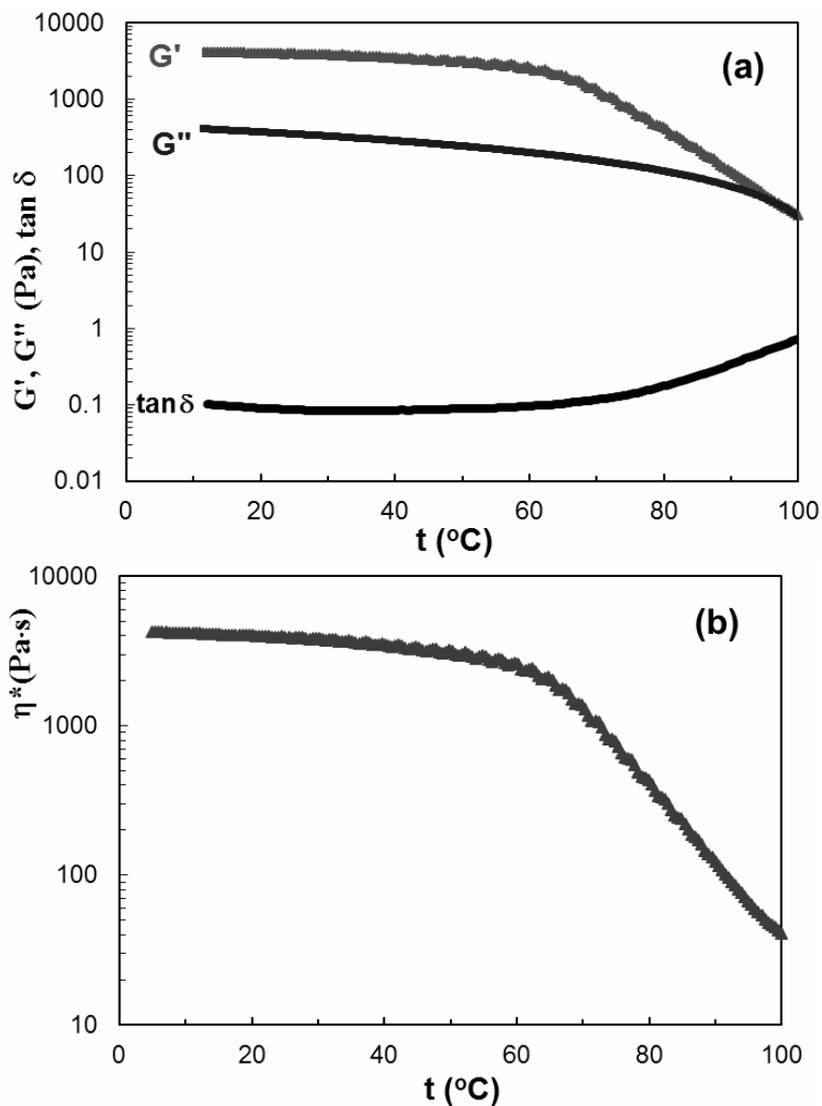


Fig. 4 – The temperature dependence of (a) viscoelastic moduli and loss tangent and (b) complex viscosity, for a heating rate of 1 °C/min.

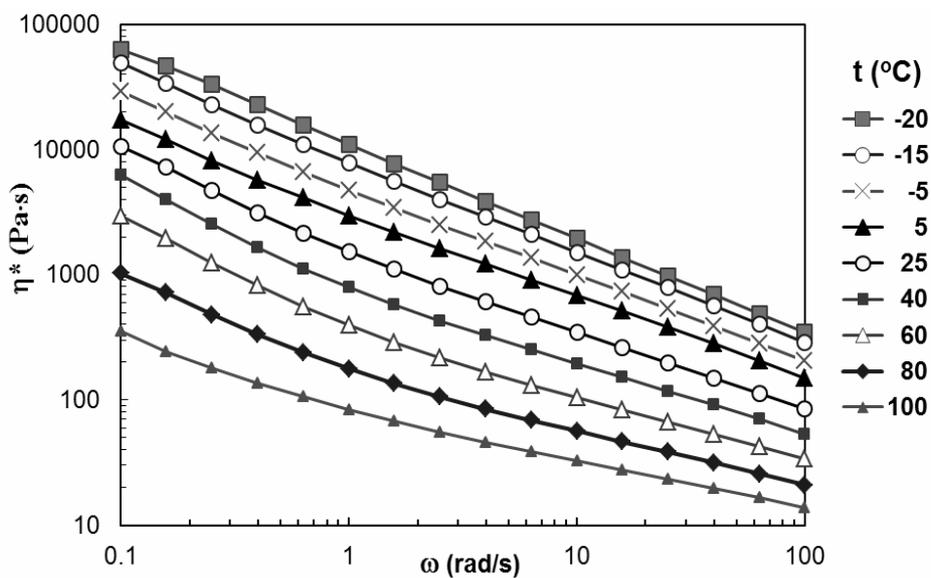


Fig. 5 – Complex viscosity as a function of the oscillation frequency at different temperatures.

Cole-Cole master curve

Conventionally, the dynamic mechanical spectrum is given in a plot of the viscoelastic moduli $G'(\omega)$ and $G''(\omega)$ as a function of the oscillation frequency (as shown in Figures 1-3). In the Cole–Cole plot the components of the complex dynamic response are plotted against one another. Such plots could give qualitative information concerning the macromolecular structure and architecture as well as the formation of supramolecular structures, such as three-dimensional networks. G' provides a measure of crosslink density, and thus the slope of the $G'(t)$ vs. $G''(t)$ reflects the changes in internal friction as the crosslinking advances.¹⁷⁻¹⁹

The Cole–Cole plots for PAN electrolyte gel at different temperatures are given in Figure 6. The slopes of the $G'(t)$ vs. $G''(t)$ curves obtained at different temperatures are close to unity. The deviation of the slope from 2, typical to homogeneous polymer solutions, is a measure of the changes in overall structure and supramolecular structuration of the sample into a three-dimensional network.

The chain mobility decreases at low temperature determining to some extent an alteration of the network strength which might result from weak polymer–polymer interaction. However, this

constraint could be collapsed by applying a higher oscillatory deformation (increasing the oscillation frequency). This hypothesis is verified by the fact that Cole–Cole plot (Figure 6) gave a single master curve with little scattering of data points regardless of the temperature change.

A schematical representation of the experimental observations concerning the thermoreversible gelation is given in Figure 7. The interactions between the components of PAN/EC/LiClO₄ system were evidenced by Raman and IR spectroscopy.²⁰ In EC/LiClO₄ solvent, there exist strong interactions between the Li⁺ ions and the EC molecules (C=O group of the EC molecule). In the presence of PAN, a complex is formed between EC and polymer chains due to the dipole-dipole interactions of EC and -CN groups of PAN. It was also shown that Li⁺ ions are located near the nitrogen atoms of the -CN groups inside the PAN macromolecules dissolved in the electrolyte solution.

A strong network structure is formed between 5 °C and 60 °C. At low temperatures, the chains and ions mobility decreases,²¹ but the internal friction increases, as a result G'' increases faster than G' . Above 60 °C, the complex formed by between Li⁺ and -CN polar groups is slowly destroyed and the network structure fails above 90 °C.

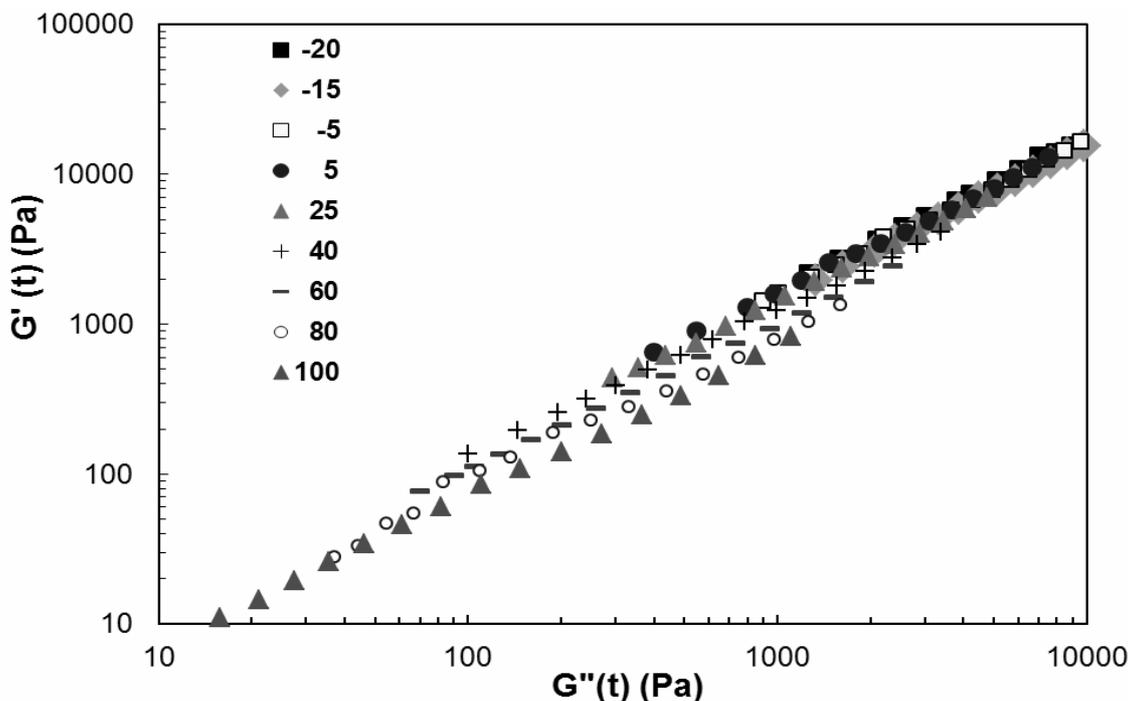


Fig. 6 – $G'(t)$ as a function of $G''(t)$ for PAN/ EC/LiClO₄ at different temperatures.

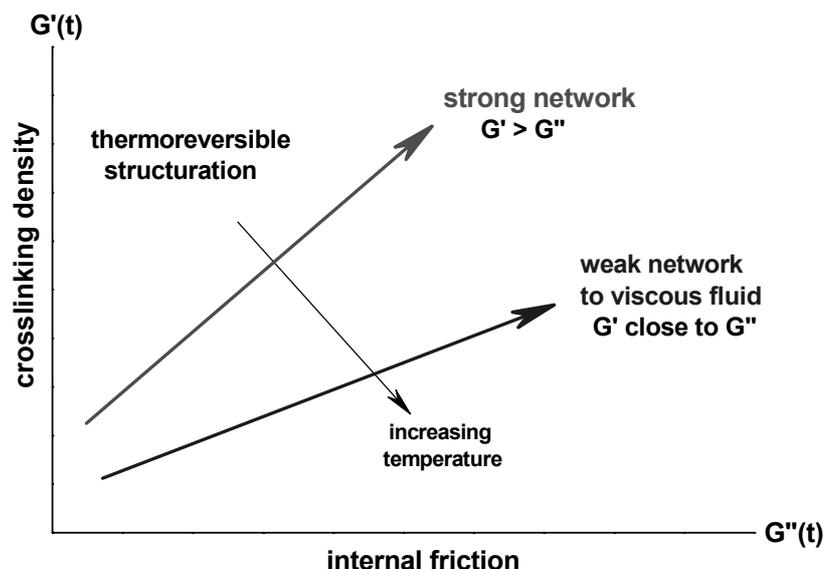


Fig. 7 – Schematical representation of the consequences of the temperature changes on the PAN/EC/LiClO₄ physical network formation.

EXPERIMENTAL

Materials and methods

Polyacrylonitrile was synthesized by radical polymerization in solution of benzene at 60 °C by using 2,2'-azobisisobutyronitrile as initiator, as reported previously.^{10,11,22} Briefly, the samples were purified and fractionated by dissolution in dimethylformamide (DMF) and precipitation in methanol and then dried at room temperature. The molecular weights were determined by gel permeation chromatography using a PL-EMD 950 Evaporative Mass Detector equipped with 2xPLgel 5 μm MIXED-C, 300x7.5 mm columns. The columns system was thermostated at 25 °C. The PAN samples were eluted with DMF and the flow rate was 0.7 mL/min. A sample of PAN with $M_w = 3.4 \times 10^4$ g/mol and $M_w/M_n = 1.2$ was selected for this study.

LiClO₄ salt was dissolved in EC by stirring at about 45 °C. The polymer was slowly added at room temperature to the solution electrolyte (90%EC/10%LiClO₄) and dissolved by a vigorous stirring for several hours until a homogeneous mixture of 20% PAN was obtained. After 24 h of storage at room temperature, the PAN/EC/LiClO₄ mixture was heated 60 minutes at 80 °C in order to ensure the complete homogenization. Then, the sample was stored for 3 days at room temperature for reaching the structural equilibrium before performing the rheological measurements.

Rheological tests

Rheological investigations were carried out with a MCR 302 Anton Paar rheometer equipped with a Peltier device for the temperature control. The measurements were performed by using parallel plate geometry, the upper plate having a radius of 25 mm (gap of 500 μm). Frequency sweep tests were carried out in the linear domain of viscoelasticity at different temperatures between -20 °C and 100 °C. The thermoreversible behaviour was followed in temperature sweep tests carried out between 5 °C to 100 °C for different heating rates at $\omega = 1$ rad/s and 1% deformation.

CONCLUSIONS

In this work, we studied the viscoelasticity of thermoreversible PAN gel formed in the presence of the EC/LiClO₄ electrolyte solution. The system behaves as a strong gel between 5 °C and 60 °C: $G' > G''$ and $\tan\delta$ is around 0.1, the network formation is ensured by the interactions between Li⁺ ions and -CN polar groups of PAN. The chain mobility decreases at low temperature (below 5 °C), determining to some extent an alteration of the network strength. Above 60 °C, the network structure becomes weaker and above 90 °C the sample loses the gel-like structure. This is completely recovered at further decreases of the temperature.

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