

*Dedicated to the memory of
Professor Cristofor I. Simionescu (1920–2007)*

INFLUENCE OF NON-SOLVENT ON THE GELATION PHENOMENON OF POLYMER SOLUTIONS

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The effect of water (as non-solvent) on the dynamic behaviour of polyacrylonitrile solution in dimethylformamide was investigated. At low temperatures ($< 0^{\circ}\text{C}$), the gelation becomes faster in presence of small content of water (up to 3%). The sol-gel transition was investigated at -5°C in function of water concentration through the evolution of the viscoelastic parameters as a function of time. The frequency sweep tests evidenced different behaviours in the sol (at 25°C) and in the gel (at -5°C) states. An increase of the water content ($> 3\%$) determines a phase separation due to the decrease of the polymer-solvent miscibility.

INTRODUCTION

The interest in the physical gelation of synthetic polymers has been receiving more attention during the last years,¹⁻⁵ although the phenomenon has been reported several decades ago.⁶⁻⁸ In dilute solutions, due to physical interactions between the macromolecular chains, many natural or synthetic polymers can form clusters or thermoreversible physical aggregates.⁹⁻¹¹ If the concentration increases, in semidilute or moderately concentrated solutions, gel-like structures can be formed in certain solvents.¹²⁻¹⁵

The physical gelation is ascribed as being the formation of a tridimensional network, with junctions of physical nature. This was explained as being due to rapid crystallization,¹³ liquid-liquid phase separation when macroseparation is hindered by kinetic impediments,¹⁶ increasing the polymer concentration or molecular weight of the polymer^{6,14,15} or worsening solvency.^{6,13} A two step mechanism of gelation was also discussed for natural and synthetic polymers in solutions: first the conformation of macromolecules changes from random coil state to a partially helical state, and then the helical parts aggregates to form network

junctions.¹⁷ Thus, a fast intramolecular conformational change is followed by an intermolecular association, leading eventually to gelation.

Among the several physical properties, viscoelastic properties change dramatically during the gelation process of a polymer solution: the system is liquid-like before crosslinking and after the gelation point its behaviour becomes a solid-like.^{18,19} A network is formed and, beyond the gel point, it continuously develops with increasing the crosslinking density.

Polyacrylonitrile (PAN) is insoluble in non-polar solvents at any temperature and it dissolves in organic polar solvents, such as dimethylformamide (DMF), dimethylacetamide or dimethylsulfoxide.²⁰ PAN solutions in good solvents mentioned above can form gels by a variety of mechanisms.^{1,13,21} If cooled, the solvent itself crystallizes before PAN does. In fact, according to literature data,²¹ propylene carbonate is the only one solvent from which PAN crystallizes.

In some previous papers,^{22,23} we investigated the gelation phenomena occurring in semidilute and concentrated solutions of PAN in dimethylformamide in different conditions: by freezing and thawing method or by changing

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temperature or polymer concentration. The gelation time is shorter for longer freezing time or for higher PAN concentrations (or molecular weights), whereas the gel strength increases with increasing the aging time.^{1,14,22} In the present paper dynamic oscillatory measurements at small strains are carried out to investigate the gelation of a semidilute PAN solutions (3% wt.) in dimethylformamide (DMF) in the presence of a certain quantity of water as non-solvent.

RESULTS AND DISCUSSION

Generally, in oscillatory tests a sinusoidal stress (or strain) was applied to the upper plate of the rheometer. The resulting strain (or stress) can be resolved into components that are in phase with the input (elastic response) and $\pi/2$ out of phase with the input (viscous response). From these data a complex modulus, G^* , is determined as a function of frequency:

$$G^* = G' + iG'' \quad (1)$$

where G' is the storage modulus and G'' is the loss modulus, giving information on energy storage and energy dissipation during the flow, respectively. For a perfectly elastic solid, $G'' = 0$ and according to eq. (1) $G^* = G'$. For a Newtonian fluid, $G' = 0$ and $\eta^* = G''/\omega$, where ω is the oscillation frequency.

The loss tangent, $\tan \delta$, is a measure of the ratio lost to stored energy in a cyclic deformation:

$$\tan \delta = \frac{G''}{G'} \quad (2)$$

A low value in $\tan \delta$ indicates a high degree of elasticity (more solid-like). This is characteristic to structured macromolecular solutions (clusters, aggregates) or gels. For viscous solutions, $\tan \delta$ is very high because both solvent and polymer contribute to G'' but only the polymer contribution is incorporated into the G' value.

The complex viscosity, η^* , is given by:

$$|\eta^*| = \sqrt{(\eta')^2 + (\eta'')^2} \quad (3)$$

where η' is the real part of the complex viscosity, which stands for the viscous behaviour, while η'' is the imaginary part of the complex viscosity, which stands for the elastic behaviour.

In some recent papers,^{22,23} we showed that by freezing semidilute (5%) and concentrated (more than 7%) PAN solutions in DMF a thermoreversible

gelation occurs. In the present study, we investigate a solution of 3 % PAN in DMF in different experimental conditions. Firstly, we followed the dynamic behaviour of this solution as a function of time at low temperature, *i.e.*, -5°C . We monitored the time necessary to attain the thermal equilibrium and this was around 450 seconds. After this period of time, the evolution of the dynamic parameters (G' , G'' , $\tan \delta$ and η^*) was followed.

In a second step, the solution of PAN in DMF was mixed with different quantities of water (1%, 3%, 5% and 7%) at 25°C by using a magnetic stirrer for 100 seconds. Each sample was introduced into the rheometer measuring device and then cooled at -5°C . The evolution of the complex viscosity for all systems (after waiting 450 seconds for the thermal equilibrium) is given in Fig. 1. After a short period of time, depending on the water content, the complex viscosity starts to sharply increase, suggesting the occurrence of a sol-gel transition phenomenon. During this process, the macromolecules loss their individuality due to the formation of crosslinked structures. Finally, the viscosity tends to attain a constant value, showing the end of the supramolecular structure formation.

As we can see in Fig. 1, a maximum η^* value is attained for 3% water, whereas for 7% water a demixing induced by the shear was observed at the end of the experimental test. Increasing the water content above 3%, the PAN gels do not have any definite supramolecular structure and the observed behaviour can be due to some side-processes accompanying gelation (molecular aggregation, crystallization of the solvent⁸) or due to the increase of DMF – water interactions, determining a decrease of PAN-DMF interactions.

The evolution of the viscoelastic parameters (as well as the loss tangent) for the two limiting behaviours, *i.e.* 3% PAN solution without water and the same solution with 3% water, are given in Figs. 2 and 3, respectively.

In absence of water (Fig. 2), at the beginning of the experiment the sample shows a preponderant viscous behaviour ($G'' > G'$; $\tan \delta$ is high); after 930 seconds the elastic and loss moduli increase and after more 670 seconds they attain very closed values, the loss tangent decreases and becomes nearly unity. This is characteristic to a critical gel state^{18,19} when the system combines the liquid and the solid behaviour. In this state, there is no intrinsic size and the molecular motions are correlated over large distances and material properties are considered independent on the structural details of the materials.¹⁸

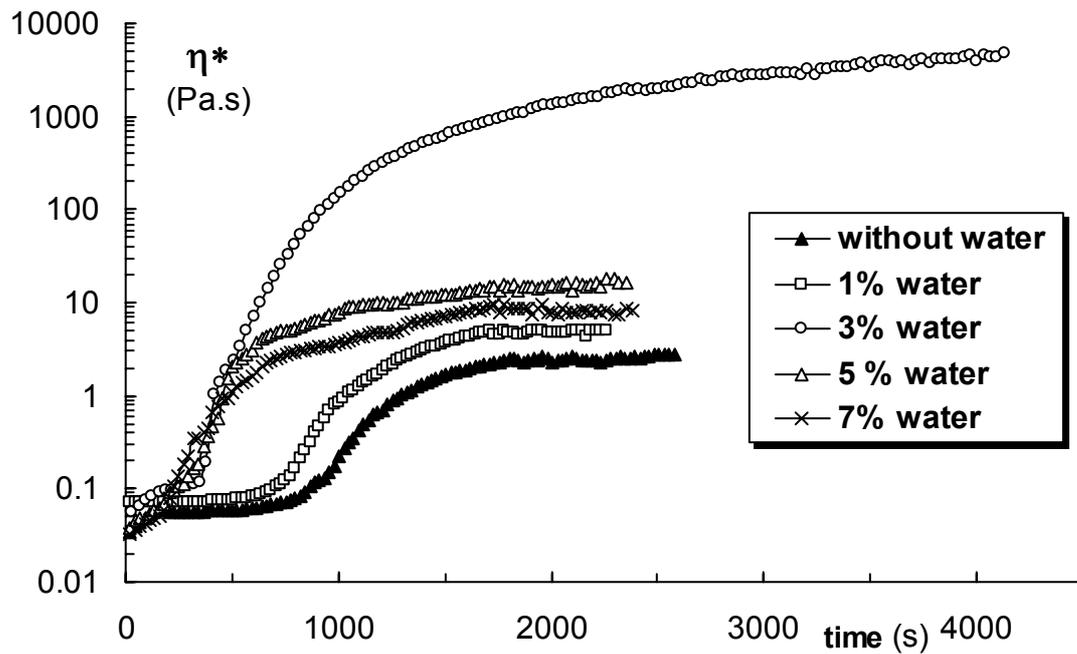


Fig. 1 – Dependence of the viscosity as a function of time for 3% PAN solution in DMF in the presence of different contents of water (at constant temperature of -5°C).

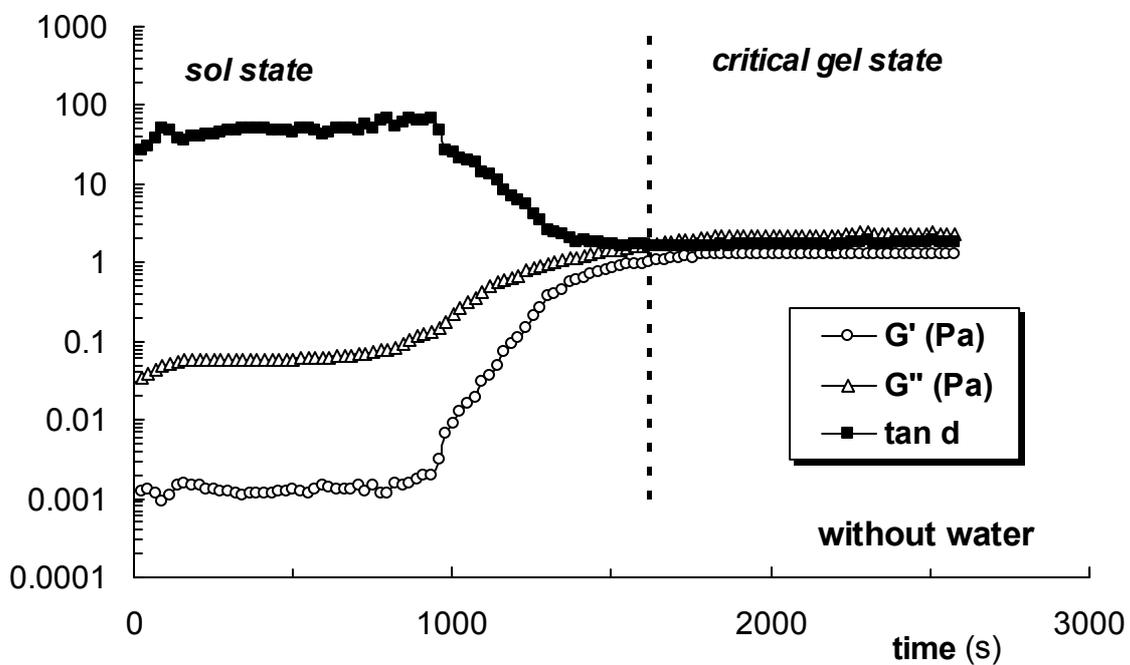


Fig. 2 – Evolution of the viscoelastic parameters as a function of time for 3% PAN solution in DMF in absence of water (at constant temperature of -5°C).

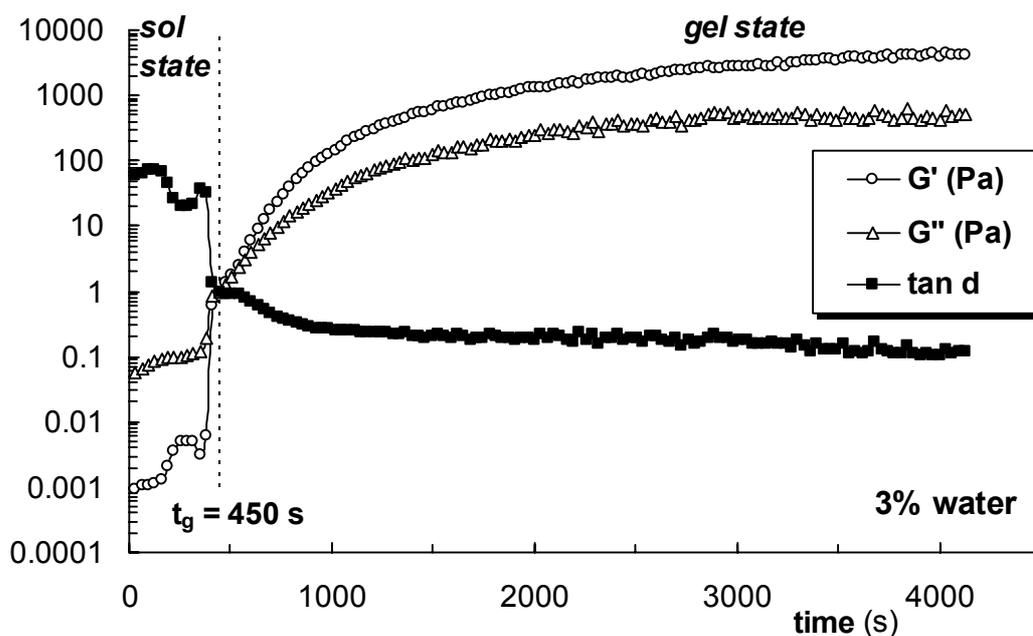


Fig. 3 – Evolution of the viscoelastic parameters as a function of time for 3% PAN solution in DMF in presence of 3% water (at constant temperature of -5°C).

The presence of water induces in the first moments an increase of the dynamic moduli, more evident for the loss modulus (Fig. 3). After 380 seconds, a sharp increase of both moduli is observed, the storage modulus becomes rapidly higher than the loss modulus and the loss tangent attains very fast a value lower than unity. After 2000 seconds, the network structure evaluated to an equilibrium state for which G' is nearly ten times higher than G'' .

For a better understanding of the gelation process, frequency sweep tests were carried out for all samples in sol state (at 25°C) and in gel state (at -5°C , after waiting for the sol-gel transition). Fig. 4 shows the evolution of G' , G'' and η^* as a function of the oscillation frequency for a constant shear stress of 1 Pa. A typical behaviour for a polymer solution is observed: $G' \sim \omega^2$ and $G'' \sim \omega$. The crossover frequency at which $G' = G''$ is a measure of the longest relaxation time (τ_1) which is given by the reciprocal value of the frequency (expressed in radians per second). The sample shows a Newtonian behaviour at 25° , the complex viscosity is independent on the shear oscillation frequency.

At -5°C (Fig. 5), the viscoelastic behaviour is completely changed due to the structural changes in the sample. Firstly, G' is higher than G'' and for oscillation frequency higher than 1 rad/s the curves recorded for both moduli are nearly parallel, characteristic to critical gel state.¹⁸ In the other hand, the complex viscosity is very high at low

oscillation frequency (10^5 times higher than its value at 25°C) and around 0.1 rad/s it starts to decrease, varying as $\omega^{-0.81}$, typical dependence for the polymers in the entangled state.²⁴

By introducing 3% water in the solution of 3% PAN in DMF, all parameters are slowly changed at 25°C , showing higher values (Fig. 6). The viscous behaviour is qualitatively similar with the sample without water, *i.e.* a Newtonian viscosity over the investigated range of frequency. Also, the $G'' - \omega$ dependence is not altered. Nevertheless, the storage modulus changes its behaviour and it scales as $G' \sim \omega^{1.8}$. This can be due to the increase of polymer-polymer interactions due to the non-solvent presence in the system. This determines a shift of the crossover point to lower values and to an increase of the longest relaxation times (τ_1).

More qualitatively changes occur by cooling this solution at -5°C (Fig. 7). After waiting 2000 seconds for the occurring of the transition from the sol to the gel state, all parameters: G' , G'' and η^* are considerably higher than at 25°C and their values are also higher than for the sample free of water. The exponents of $G' - \omega$ and $G'' - \omega$ dependences are very low are closed each other (around 0.1) and $G' > G''$. The complex viscosity shows a narrow range of Newtonian behaviour below 0.04 rad/s. The pseudoplastic behaviour starts to a lower oscillation frequency as compared with a sample without water and it is characterized by $\eta^* \sim \omega^{-0.886}$.

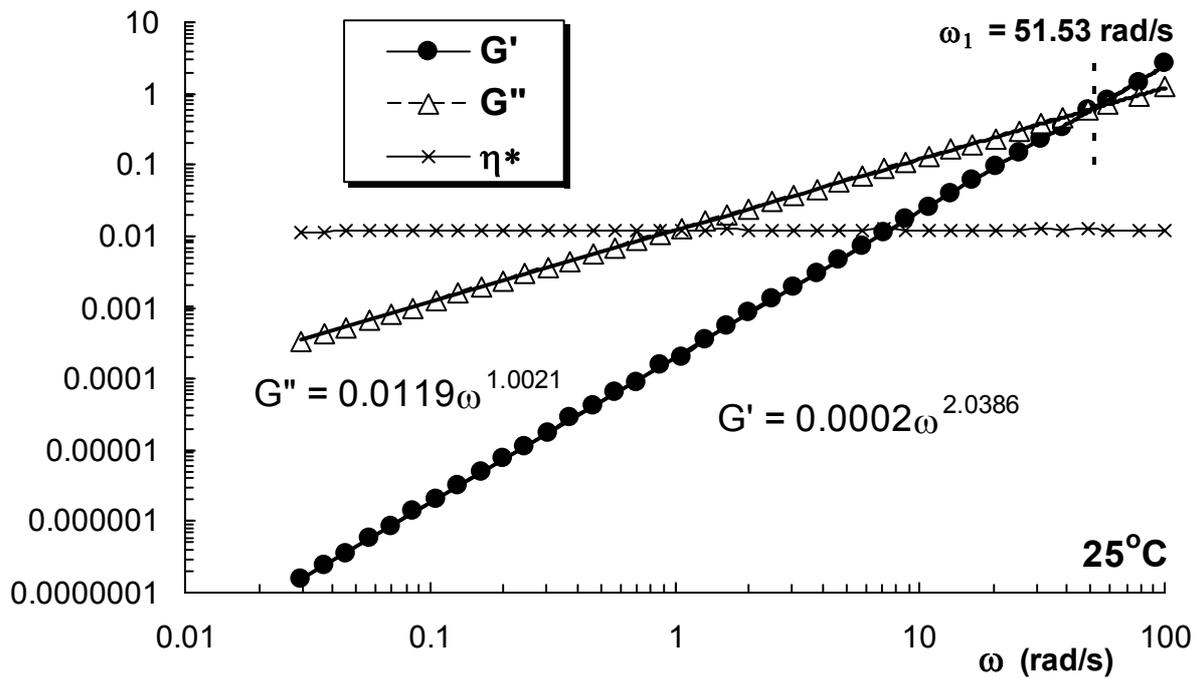


Fig. 4 – Variation of G' (Pa), G'' (Pa) and η^* (Pa·s) as a function of oscillation frequency for 3% PAN solution in DMF in absence of water (at constant temperature of 25°C).

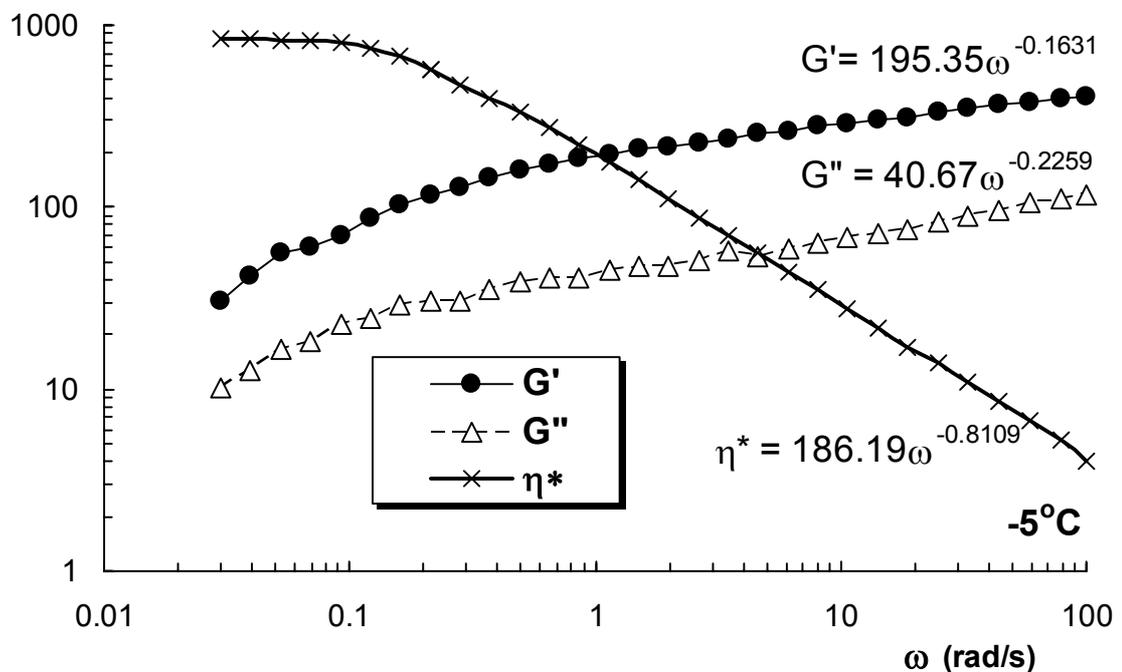


Fig. 5 – Variation of G' (Pa), G'' (Pa) and η^* (Pa·s) as a function of oscillation frequency for 3% PAN solution in DMF in absence of water (at constant temperature of -5°C).

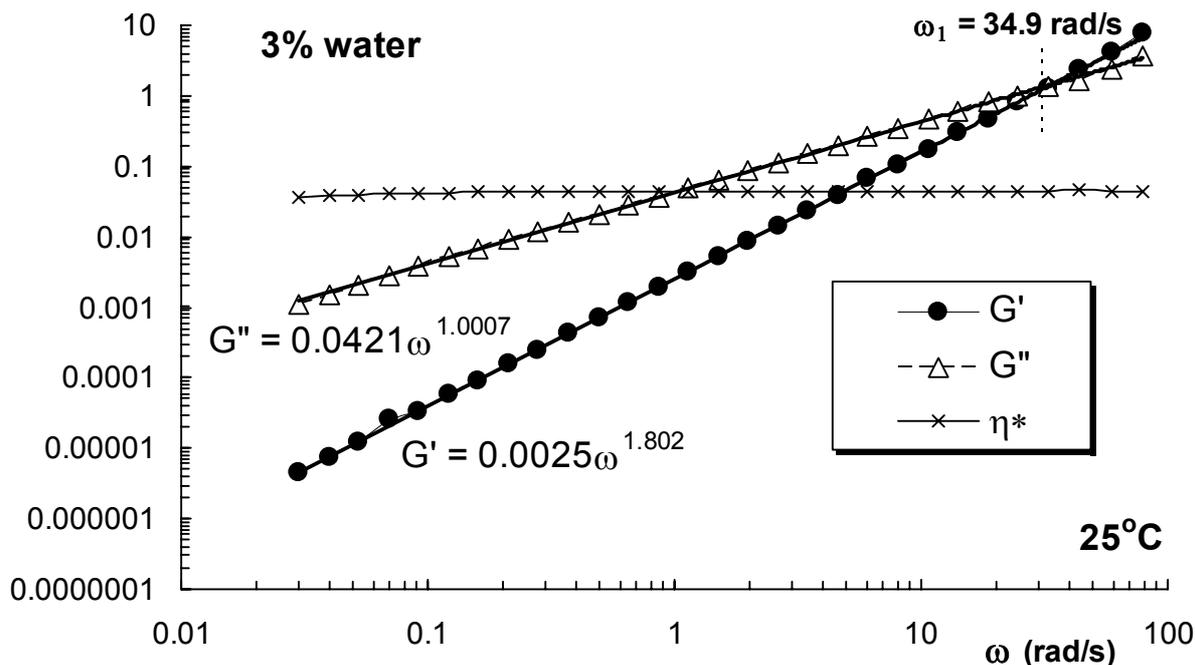


Fig. 6 – Variation of G' (Pa), G'' (Pa) and η^* (Pa·s) as a function of oscillation frequency for 3% PAN solution in DMF in presence of 3% water (at constant temperature of 25°C).

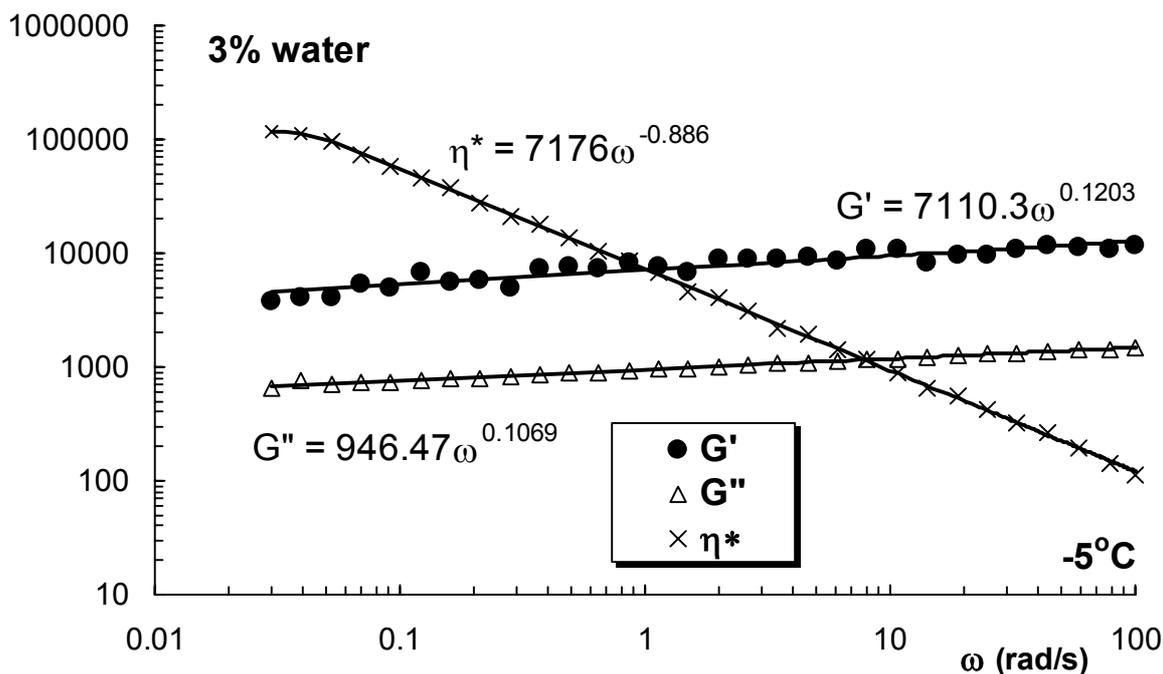


Fig. 7 – Variation of G' (Pa), G'' (Pa) and η^* (Pa·s) as a function of oscillation frequency for 3% PAN solution in DMF in presence of 3% water (at constant temperature of -5°C).

As we discussed above, the presence of the non-solvent affects the dynamic response even at 25°C. Thus, the addition of a low content of water determines an increase of τ_1 which attains a maximum value around 3% water (Fig. 8). A

further increase in non-solvent content determines an increase of the polymer-polymer interactions and the system undergoes a phase separation.

The addition of a non-solvent in a polymer – good solvent system determines the increase of

polymer-polymer interactions and the formation of intermolecular association with small ordered regions involving the neighboring segments belonging to one or more polymer chains (Fig. 9). These regions act as coupling points and they coexist with others parts of the macromolecular chains which cannot be separated each other.

We suppose that one of segments of the linear chain in solution can form crosslink with other segments either on the same chain or on other chains. In the former case, structures similar with intramolecular rings are formed. In the latter case, however, intermolecular interactions take place forming branched structures. As a consequence, the apparent molecular weight increases, determining a viscosity increase. As we observed in this study, the worse of the thermodynamic

quality of the solvent by addition of a non-solvent determines a faster increase of viscosity.

The rise in molecular weight is, in turn, accompanied by an increase in the number of future crosslinking sites. In this way, with time and as more and more such coupling points exists, the molecular weight increases faster and faster until it becomes "infinite". At this point, the so-called gel point, the largest individual molecule completely spans the container in which it sits. As already reported,¹⁸ when the molecular weight becomes infinite, the longest relaxation time is also infinite, so the sample no longer flows like a polymer solution. It has instead the properties of an equilibrium solid, and this corresponds to a gel state.

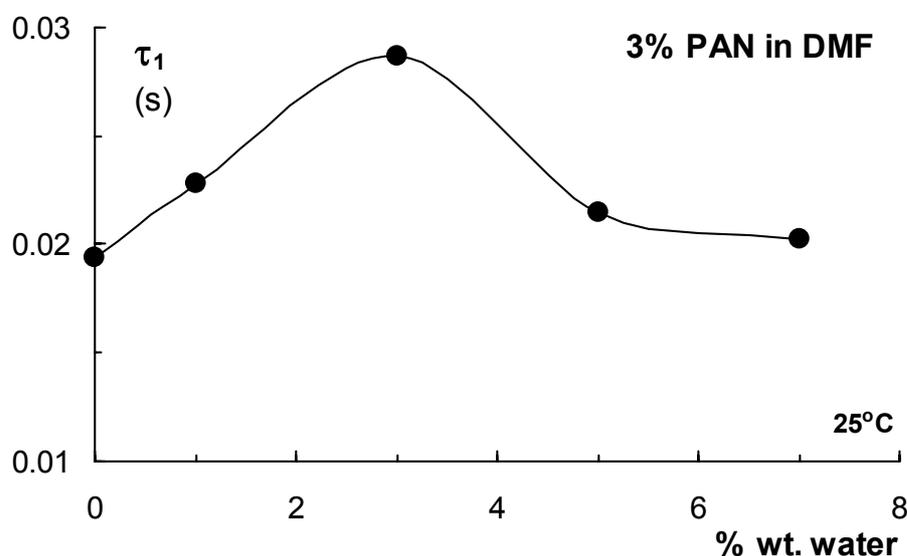


Fig. 8 – Dependence of the relaxation time as a function of water content for a solution of 3% PAN in DMF (at constant temperature of 25°C).

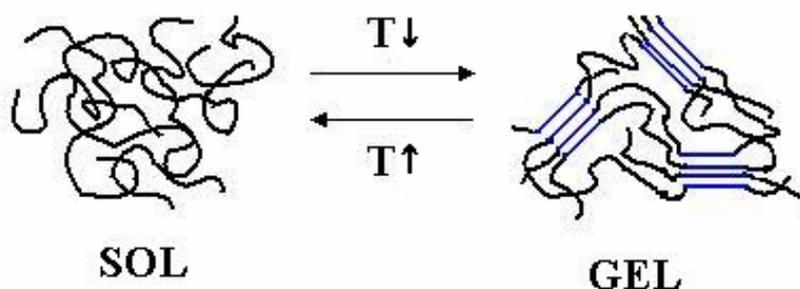


Fig. 9 – Schematic representation of the sol and gel states obtained for PAN in solution through the temperature change.

EXPERIMENTAL PART

Polyacrylonitrile (PAN) under study was synthesized by radical polymerization in benzene using 2,2'-azobisisobutyronitrile as initiator at 60°C. The resulting samples were filtered and purified by dissolution in dimethylformamide (DMF), followed by precipitation in methanol, then dried under reduced pressure at room temperature. The samples were submitted to fractionation by using DMF-methanol mixtures as solvent-precipitant systems.

The molecular weights were determined by gel permeation chromatography (GPC) using a PL-EMD 950 Evaporative Mass Detector equipped with 2xPLgel 5 μ m MIXED-C, 300x7.5mm columns. For this study, a PAN sample with $M_w = 5 \times 10^4$ and $M_w/M_n = 1.2$ was selected.

The PAN solutions were prepared by heating the PAN and DMF mixture at 40°C, waiting 2 days for reaching the thermodynamic equilibrium. Before the rheological investigations, the non-solvent (water) was added in droplets under continuously stirring until a homogeneous system is resulted. For this study, samples with 1%, 3%, 5% and 7% water were prepared and investigated. In addition, a sample without water was investigated in the same experimental conditions.

The rheological measurements were performed at 25°C and -5°C using a CVO Rheometer with parallel plate geometry (60 mm diameter and 500 μ m gap) and thermal control by Peltier effect. Prior to rheological measurements of PAN solutions, suitable shear amplitude was determined by measuring the shear stress dependence of moduli to ensure the linearity of dynamic viscoelasticity.

The dynamic properties were followed as a function of time at constant shear stress of 1Pa and oscillation frequency of 1 rad/s and in frequency sweep tests (in the frequency range 0.01 – 100 rad/s) at constant shear stress of 1Pa.

CONCLUSIONS

By cooling PAN-DMF solutions, a sol-gel phase transition occurs due to the formation of intermolecular association with small ordered regions involving the neighboring segments belonging to one or more polymer chains. The gel properties depend on the thermal history of the solution, its composition and gelation conditions. As a consequence, the gelation point is not a constant for this system, being identified in well established conditions.

The worsening of the solvent quality by adding a non-solvent involves a change of polymer-solvent interaction involving a faster gelation

because the polymer-polymer intermolecular bonds are favored over intramolecular ones (which in turn depends upon non-solvent concentration). The possible interactions between water and DMF will determine the segregation of polymer chains and macroseparation of the phases.

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