

## INFLUENCE OF TEMPERATURE ON DYNAMIC BEHAVIOR OF POLYACRYLONITRILE IN DIMETHYLFORMAMIDE

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The dynamic behavior of polyacrylonitrile solutions in dimethylformamide was investigated at different temperatures. For low polymer concentrations, the viscoelastic parameters as a function of the oscillation frequency at different temperatures have a typical behavior of the most polymer solutions. With increasing of polymer concentration, two types of gelation processes were evidenced: a reversible gelation in the region of low temperatures, whereas at high temperatures an irreversible gelation occurs.

### INTRODUCTION

The properties of polyacrylonitrile (PAN) in solutions of dimethylformamide (DMF) have been investigated in different concentration regimes: extremely dilute, dilute and moderately concentrated solutions.<sup>1-3</sup> In moderately concentrated solutions, gel-like structures were evidenced.<sup>4-7</sup> The 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 behavior becomes a solid-like.<sup>8</sup> A network is formed and, beyond the gel point, its firmness continues to increase with increasing the crosslinking density. The whole phenomenon can be followed by the evolution of rheological properties of the system.

The viscoelastic properties of the PAN gels prepared by freezing and thawing method were investigated by following the power law dependence of the dynamic viscoelasticity,<sup>7</sup> as proposed by Winter and Chambon,<sup>8</sup> *i.e.*,  $G'(\omega) \propto G''(\omega) \propto \omega^n$ . 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.<sup>7</sup> In a previous paper,<sup>9</sup> it was shown that also the freezing time strongly influences the viscoelastic properties of the resulted gel. The

response of the macromolecules to an external load depends on the rate of deformation compared with the rate of spontaneous structural reorganization at the molecular level.

In the present paper dynamic oscillation measurements at small strains are carried out and the temperature effect on the dynamic behavior of semidilute solutions of polyacrylonitrile in dimethylformamide was investigated.

### RESULTS AND DISCUSSION

Generally, the behavior of the polymer systems submitted to an external stress is strongly influenced by the characteristics of the macromolecular chains, such as: size, shape and spatial arrangement, degree of branching, etc. but also by the thermal history of the sample.<sup>7,9</sup> The oscillatory tests involve the application of a sinusoidal stress (or strain) 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  $G'$  (storage or elastic modulus) and  $G''$  (loss or viscous modulus) give information on

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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  $\eta^*$  is the complex viscosity and  $\omega$  represents the frequency of oscillation.

The phase angle,  $\delta$ , is a dimensionless parameter associated with the degree of viscoelasticity of the sample. 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  $\tan \delta$  or  $\delta$  indicates a high degree of elasticity (more solid-like). For dilute solutions  $\tan \delta$  is very high because both solvent

and polymer contribute to  $G''$ , but only the polymer contributes to  $G'$  value.

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. From Fig. 1 it is clear that there is no significant change in viscoelastic parameters as long as the stress is less than 20 Pa. For this study, the experimental investigations were carried out at a constant shear stress of 1 Pa. Also, there is no time dependence of  $G'$ ,  $G''$ ,  $\delta$  and  $\eta^*$  (Fig. 2).

The complex viscosity decreases ten times when the temperature increases from 0°C to 120°C (Fig. 3), but for the whole domain of temperature the solution exhibits a Newtonian behavior.

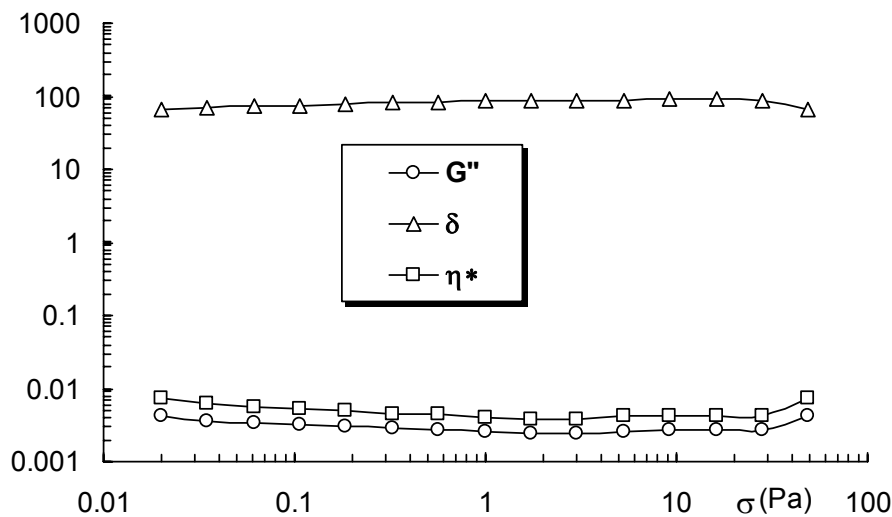


Fig. 1 – The evolution of the viscoelastic parameters as a function of shear stress for 1% PAN in DMF at 20°C ( $\omega = 1$  rad/s).

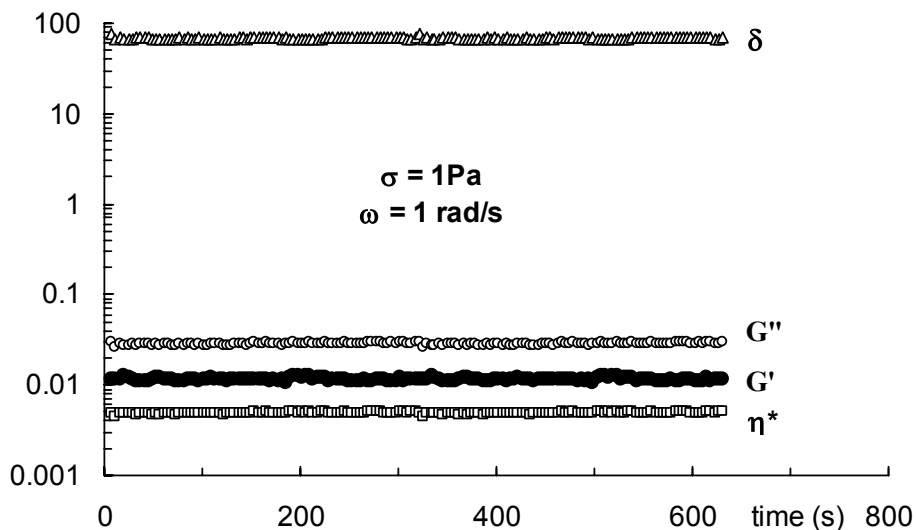


Fig. 2 – The evolution of the viscoelastic parameters as a function of time for 1% PAN in DMF at 20°C at the shear stress of 1 Pa.

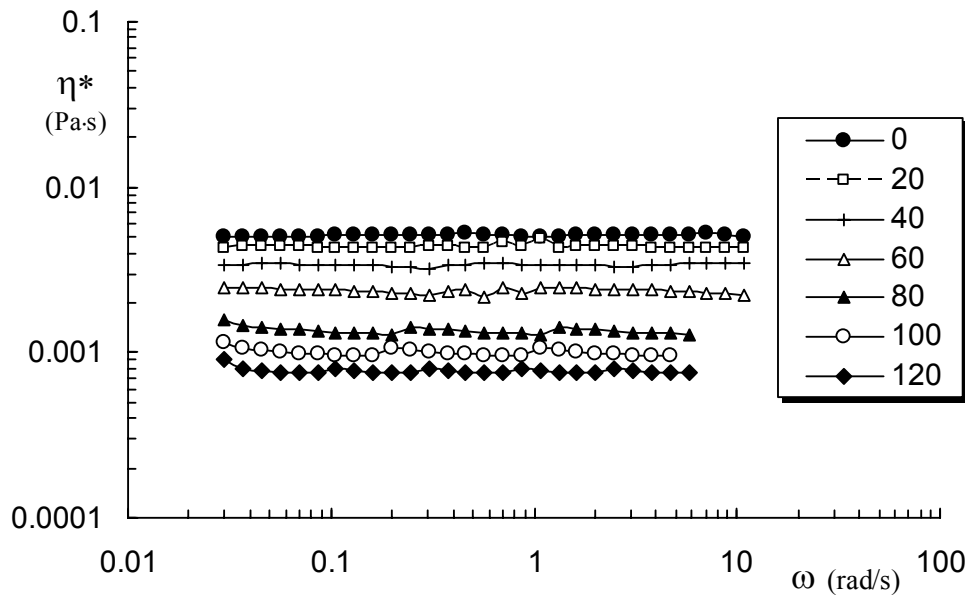


Fig. 3 – Complex viscosity as a function of frequency for 1% PAN in DMF at different temperatures.

The viscoelastic moduli increase with increasing frequency, the sample having a preponderant viscous character. In Figs. 4 and 5 the evolution of  $G''$  and  $\delta$  as a function of frequency ( $\omega$ ) for the solution 1% PAN in DMF at different temperatures is given. The moduli variation with frequency is

typical for viscoelastic Maxwellian fluids, that is,  $G''$  scales with  $\omega$  and  $G'$  with  $\omega^2$ . The ratio between the viscous and elastic components of the complex modulus remains almost unchanged with increasing temperature (Fig. 5).

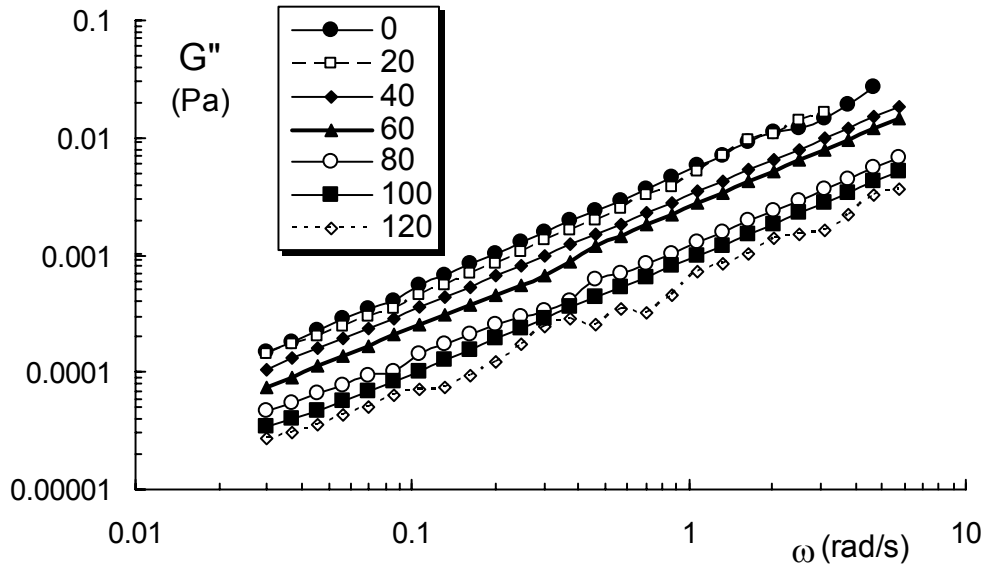


Fig. 4 –  $G''$  as a function of frequency for 1% PAN in DMF at different temperatures.

For 3% PAN in DMF we obtained a similar behavior as for 1% polymer concentration, but the dynamic behavior becomes more complicated if the polymer concentration increases. For example, for 5% PAN in DMF there is a certain range of temperature (between 20°C and 40°C) for which a similar behavior was observed (Figs. 6-8) but for

a given temperature, in our case 50°C, the viscoelastic parameters of PAN solutions ( $G'$ ,  $G''$  and the complex viscosity) start to increase. This is an irreversible process and after the experiment is realized, the sample is not completely soluble in DMF.

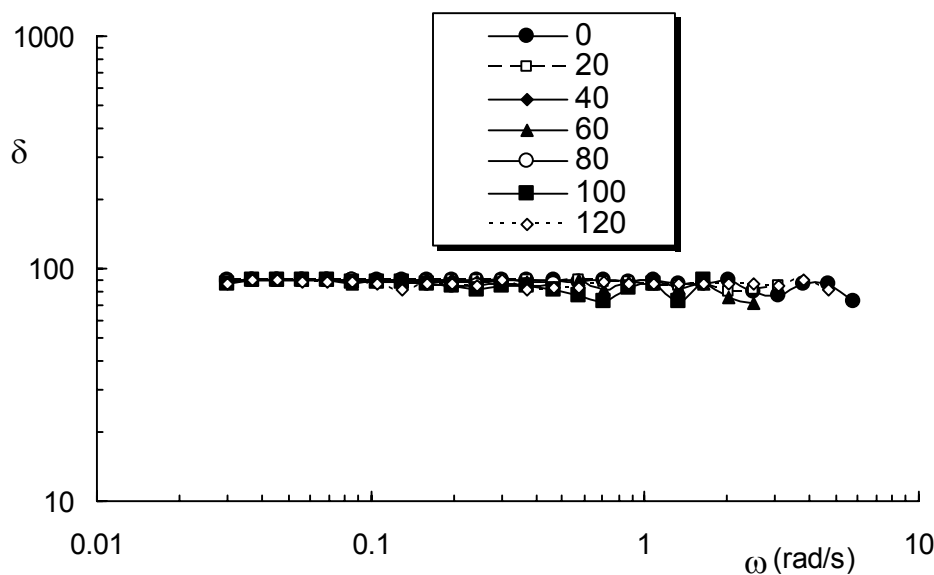


Fig. 5 –  $\delta$  as a function of frequency for 1% PAN in DMF at different temperatures.

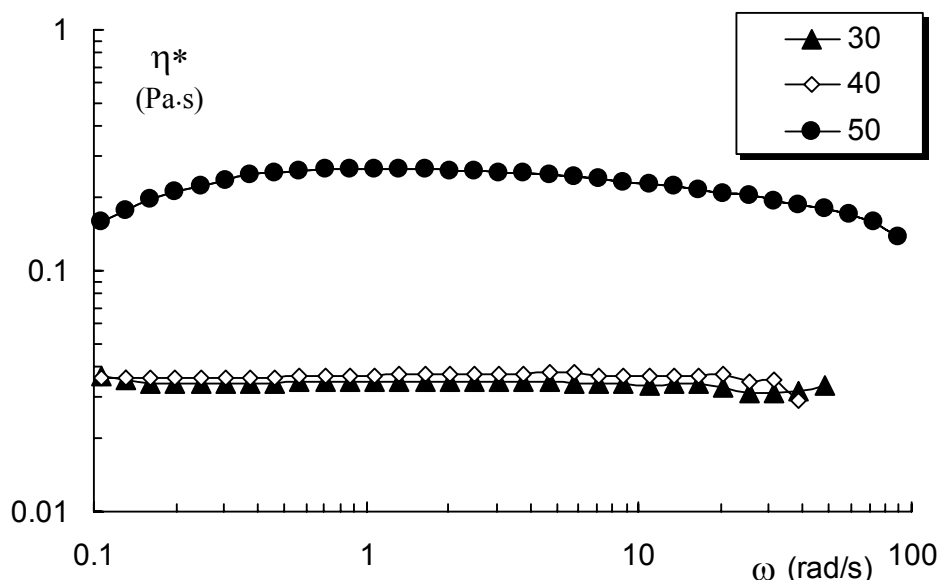


Fig. 6 –  $\eta^*$  as a function of frequency for 5% PAN in DMF at different temperatures.

In a previous study, we observed that a gel-like structure is formed by freezing the concentrated PAN solution.<sup>9</sup> To see if such structures are formed in the range of temperature closer to room temperature, we followed the evolution of the viscoelastic parameters in a temperature sweep test at increasing and decreasing temperature, by considering 25°C as starting temperature and a heating rate of 2°C/min (Figs. 9-10).

From 5°C to 70°C, both  $G'$  and  $\eta^*$  dependences on temperature have a linear evolution. A strong increase of  $G'$  and  $\eta^*$  is observed when the temperature decreases below 5°C due to the gelation phenomenon that takes place due to the

formation of a structure with small region of order. We observed that  $G'$  and  $\eta^*$  follow the same pattern by increasing the temperature until the room temperature is reached. At 25°C the sample dissolves completely in excess of solvent.

A very sharp increase of the viscoelastic parameters was also obtained if the temperature increases above 70°C. By decreasing the temperature at 25°C, the parameters maintain this behavior with fluctuations around a certain value ( $10^4$  Pa·s for the complex viscosity and  $8 \cdot 10^3$  Pa for the elastic modulus). The sample is no more soluble in an excess of solvent.

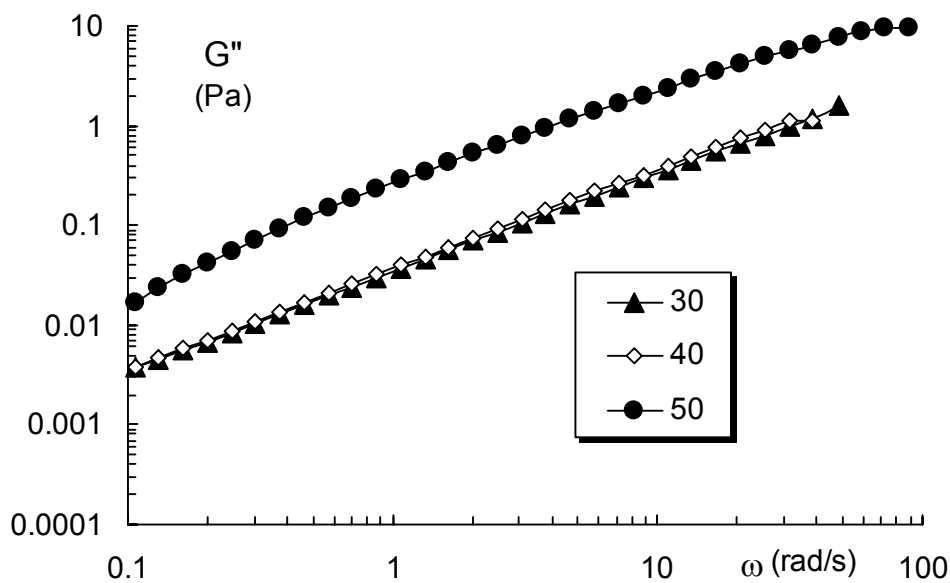


Fig. 7 –  $G''$  as a function of frequency for 5% PAN in DMF at different temperatures.

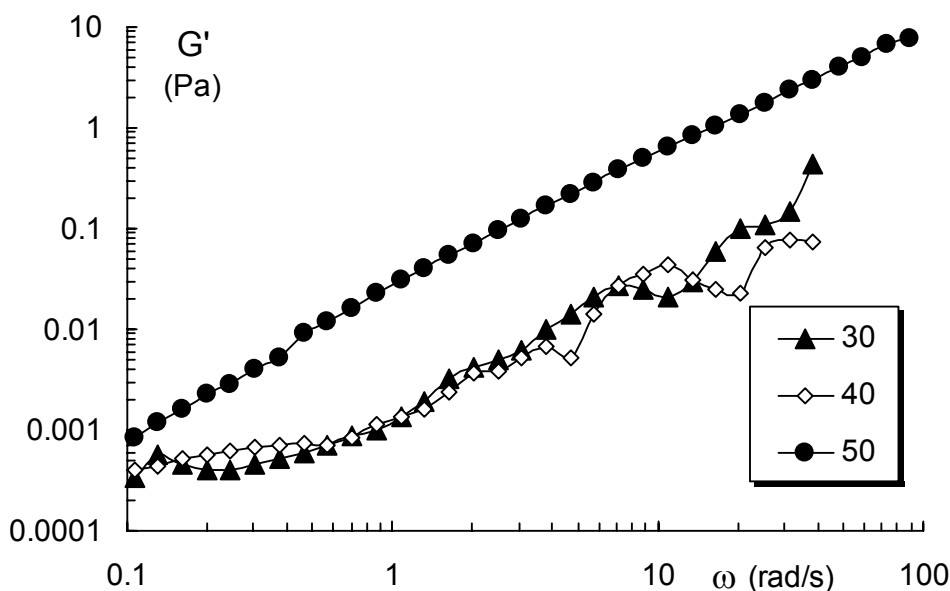


Fig. 8 –  $G'$  as a function of frequency for 5% PAN in DMF at different temperatures.

We suppose that a network is formed in both cases, but the evolution of the gelation phenomena is dependent on temperature: a reversible gelation takes place in the range of low temperatures (below  $5^{\circ}\text{C}$ ) and the gels melt upon heating and dissolve in an excess of solvent (physical crosslinking) and an irreversible one at high temperatures (above  $70^{\circ}\text{C}$ ) when it is possible to eliminate HCN from the polymer chains, which leaves double bonds in the macromolecules which may react each other and form a three-dimensional network (chemical crosslinking). Generally, a polymer gel consists of a polymer-solvent network with junctions of a no-fluctuating nature,<sup>10</sup> in

contrast with the junctions existing in an entangled polymer which are fluctuational in nature.<sup>11</sup> The junction points are permanent chemical crosslinks when the gel is irreversible, or temporary bonds, continuously breaking or re-forming by changing the temperature, polymer concentration or shear conditions in this case the gel is reversible. For PAN solutions in DMF the network structure depends on the thermal history, polymer concentration and external conditions; as a consequence the gelation point is not a constant for this system, being identified in well established conditions.

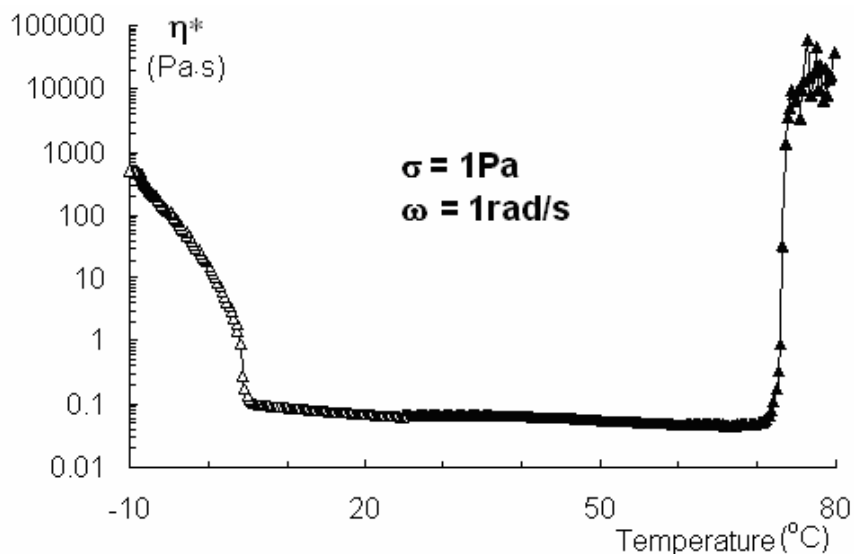


Fig. 9 –  $\eta^*$  as a function of temperature for 5% PAN in DMF for a heating rate of 2°C/min.

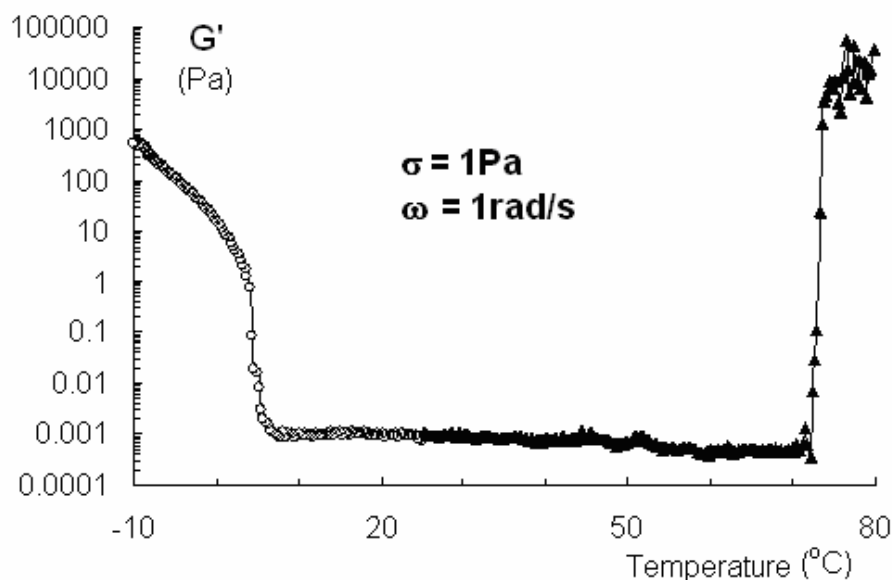


Fig. 10 –  $G'$  as a function of temperature for 5% PAN in DMF for a heating rate of 2°C/min.

## 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 $\mu$ m MIXED-C, 300x7.5mm columns. For this study, a PAN sample with  $M_w = 1.24 \times 10^5$  and  $M_w/M_n = 1.2$  was selected. The polymer solutions were prepared and kept at room temperature for several days.

The rheological measurements were performed at different temperatures between -10°C and 80°C using a stress controlled CVO Rheometer with parallel plate geometry (60 mm diameter and 500 $\mu$ m gap) and thermal control by Peltier effect.

The dynamic properties were determined in the frequency range of 0.01 - 100 rad/s at constant shear stress of 1 Pa. The temperature sweep tests were carried out at constant frequency (1 rad/s) and shear stress (1 Pa).

## CONCLUSIONS

Low concentration solutions (up to 3% PAN) exhibit a viscoelastic behavior, the rheological parameters being influenced by temperature and polymer concentration. The same behavior was

observed for 5% PAN solutions in the temperature range 20°C to 40°C. An anomalous behavior was observed above 50°C, the viscoelastic parameters of PAN solutions strongly increasing.

In a temperature sweep experiment, two types of gelation processes were identified for a solution of 5% PAN at low and high temperatures: a reversible gelation in the region of low temperatures (below 5°C) due to the formation of a crosslinked structure with small region of order that dissolves completely in an excess of solvent and an irreversible one at high temperatures (after 70°C) and this gel is insoluble in an excess of solvent, the –CN groups reacting with each other and forming a three-dimensional network. In frequency sweep tests the system attains a thermal equilibrium, whereas in conditions of continuous increase of temperature the gelation process is induced at higher temperature. Thus, the gelation is influenced by the thermal history of the solution, polymer concentration and shear conditions. A monitoring of the gelation phenomena can be

realized by following the viscoelastic parameters as a function of temperature.

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