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Rheological Investigation of Thermal-Induced Gelation of Polyacrylonitrile Solutions

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Abstract In this article, thermal-induced gelation of polyacrylonitrile (PAN) solutions in dimethylformamide was studied through rheological measurements. The entangled and non-entangled states were delimited for an overlap parameter of macromolecular coils of 2.7. In temperature sweep experiments, two types of gelation processes were identified for PAN entangled solutions at: (1) a reversible gelation in the region of low temperatures (below 15 °C) due to the formation of a crosslinked structure with a small region of order that dissolves completely in an excess of solvent, and (2) an irreversible gelation at high temperatures (above 60 °C) and this gel is insoluble in an excess of solvent, due to the formation of a chemical three-dimensional network. Physical PAN gels with good elastic properties were also obtained by the freezing and thawing method. The gel properties depend on the thermal history of the solution (freezing time, aging time, and aging temperature), its composition (concentration and molar mass of the polymer), and gelation conditions (freezing rate). The gelation was attributed to the formation of junction zones via an aggregation process between a certain number of chain segments due to attractive dipole–dipole interactions.

Keywords Entangled solutions · Gel · Polyacrylonitrile (PAN) · Viscoelastic parameters

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1 Introduction

Polyacrylonitrile (PAN) possesses many outstanding properties, such as high specific strength, high specific module, etc. However, in many applications (such as fibers, PAN-based carbon fibers, etc.) [1,2], the quality of PAN-based materials is strongly dependent on the properties of a filature solution which have direct relationship with the structure and properties of fibers. This polymer is insoluble in non-polar solvents, and it dissolves at room temperature in organic polar solvents, such as dimethylformamide (DMF), dimethylacetamide (DMA), or dimethylsulfoxide (DMSO) [3]), or in some ionic aqueous media, but the polymer will not crystallize from these solvents [4,5]. Propylene carbonate is the only solvent from which PAN crystallizes [4].

The interest in PAN thermo-reversible gels has continuously increased over the past decade [6–9]. A thermo-reversible gel can be regarded as a three-dimensional network of flexible chains crosslinked by physical bonds. Contrary to chemical networks, the energy level of physical bonds is sufficiently low to dissolve them with an increase in temperature. Beckmann and Zenke [5] call this process “melting” of the thermo-reversible gel at “the gel melting temperature”. Also, the gel can be dissolved in an excess of solvent and a homogeneous solution can be obtained [10].

Reversible gelation was ascribed as being due to rapid crystallization [4], increasing the polymer concentration or molar mass of the polymer and cooling the solutions [7,11,12], or reduced solvency which could be realized by temperature changes or the addition of a poor solvent to a polymer dissolved in a good solvent [4,11]. Tanaka [7] investigated the parameters that govern the sol–gel transition of PAN in DMA by following the viscoelastic behavior for the gels prepared by the freezing and thawing method.

Different theoretical and experimental studies concerning the viscoelastic behavior near the sol–gel transition were reported [7–17]. Nevertheless, a systematic study of conditions in which the sol–gel or gel–sol transitions occur from PAN solutions was not yet undertaken.

The main objective of the present article is to prepare PAN gels which are responsive to environmental conditions. The discussion will be concentrated on the influence of the gelation conditions on the rheological parameters which are very sensitive to the sol–gel transition process. Dynamic rheology is a powerful tool to monitor crosslinking and microstructural changes in a material without disruption of the microstructure if the experimental investigations are carried out at low deformations. The experimental determination and prediction of gelation are important for the processing of crosslinking polymers, whereas the criticality of the phenomenon and the universality of the properties make gelation interesting from a fundamental point of view.

2 Experimental

PAN under study was synthesized by radical polymerization in benzene using 2,2′-azobisisobutyronitrile as an initiator at 60 °C. The resulting samples were filtered and purified by dissolution in DMF, followed by precipitation in methanol, then

Table 1 Weight average molar masses and polydispersity indices of PAN samples as well as the intrinsic viscosities and Huggins constants in DMF at 25 °C

Sample	$M_w \times 10^{-3}$ ($g \cdot mol^{-1}$)	M_w/M_n	$[\eta]_H$ ($dL \cdot g^{-1}$)	k_H
1	18	1.22	0.362	0.295
2	35	1.27	0.595	0.315
3	45	1.23	0.715	0.380
4	102	1.20	1.300	0.495
5	108	1.19	1.351	0.498

dried under reduced pressure at room temperature. The samples were submitted to fractionation by using DMF–methanol mixtures as solvent–precipitant systems.

The molar masses were determined by gel permeation chromatography using a PL-EMD 950 evaporative mass detector equipped with 2xPLgel 5 μm Mixed-C, 300 × 7.5 mm columns. The columns system was thermostated at 25 °C. Calibration was carried out using standard polystyrene with narrow polydispersity. The samples were eluted with DMF and the flow rate was 0.7 $mL \cdot min^{-1}$. The volume of the injected polymer solutions was always 20 μL. The polymer solutions were prepared and kept at room temperature for several days.

The viscometric measurements were carried out in DMF at 25 °C, with an Ubbelohde suspended-level viscometer. The kinetic energy corrections were found to be negligible. The flow time for the solvent was 166.25 s. The flow volume of the viscometer was greater than 5 mL, making drainage errors unimportant. Flow times were obtained with an uncertainty of 0.02 %.

Table 1 presents the characteristic data for PAN samples used in this study.

For rheological measurements, the PAN solutions were prepared by heating the PAN and DMF mixture at 40 °C, waiting 2 days for reaching thermodynamic equilibrium. A homogeneous PAN solution in DMF was cooled in a liquid nitrogen bath, then heated at 25 °C and poured into the measurement unit. Before the experimental investigations, the solution was kept at 25 °C for a period of time. The freezing time was denoted by t_F and the time passed after the sample was heated at a certain temperature (aging temperature) was denoted as aging time, t_A.

The rheological measurements were performed using a stress controlled CVO rheometer with parallel plate geometry (60 mm diameter and 500 μm gap) and thermal control by the Peltier effect. Prior to rheological measurements of PAN solutions, a 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 a constant shear stress of 1 Pa and an oscillation frequency of 1 $rad \cdot s^{-1}$, in frequency sweep tests (in the frequency range from 0.01 $rad \cdot s^{-1}$ to 100 $rad \cdot s^{-1}$) at a constant shear stress of 1 Pa and in temperature sweep tests (shear stress of 1 Pa and oscillation frequency of 1 $rad \cdot s^{-1}$). Also, steady shear measurements were performed at different temperatures.

The rheological investigations were carried out from −10 °C to 80 °C, covering the temperature range encountered in different applications. The physical gelation

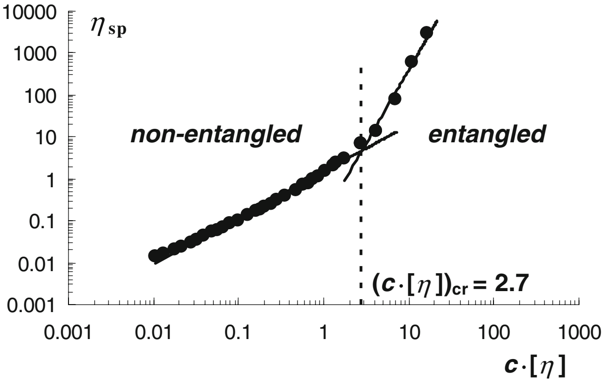

Fig. 1 Specific viscosity as a function of the overlap parameter, $c \cdot [\eta]$, for PAN solutions in DMF at 25 °C

was observed for entangled polymer solutions above −10 °C. For temperatures higher than 80 °C, the polymer solutions become brown and very viscous, this being due to chemical interactions between the –C≡N groups and the formation of chemical crosslinks.

3 Results and Discussion

3.1 States of PAN Solutions

Previously [18] it was shown that the limit between semidilute and concentrated regimes for PAN solutions in DMF at 25 °C is around $6\,\mathrm{g \cdot dL^{-1}}$, and this value is independent of the molar mass. In this work, viscoelastic behavior was investigated for semidilute ($1\,\mathrm{g \cdot dL^{-1}}$, $3\,\mathrm{g \cdot dL^{-1}}$, and $5\,\mathrm{g \cdot dL^{-1}}$) and concentrated ($8\,\mathrm{g \cdot dL^{-1}}$, $10\,\mathrm{g \cdot dL^{-1}}$, and $14\,\mathrm{g \cdot dL^{-1}}$) PAN solutions.

Figure 1 shows the dependence of the specific viscosity for the PAN solutions in DMF at 25 °C as a function of a dimensionless parameter, $c \cdot [\eta]$, known as the coil overlap parameter, which provides an index of the total volume occupied by the polymer. Two linear dependences are obtained in a double logarithmic plot, delimiting the critical value $(c \cdot [\eta])_{cr} = 2.7$. As for example, by considering this value, $c_{overlap} = 2\,\mathrm{g \cdot dL^{-1}}$ is obtained for sample 5 (Table 1). The critical overlap concentration delimitates two states of PAN solutions: *non-entangled solution regime* where the scaling exponent is 1 for the dependence of η_{sp} as a function of $c \cdot [\eta]$ and *entangled (network) solution regime*, for which a value of 3.5 was obtained for the scaling exponent.

3.2 Viscoelastic Behavior of PAN Solutions as a Function of Temperature

In the oscillatory tests a sinusoidal stress (or strain) was applied to the upper plate of the rheometer and the resulting strain can be determined through the components of the complex modulus, G^*, which are in phase with the input (elastic response) and $\pi/2$ out of phase with the input (viscous response):

$$G^* = G' + \mathrm{i}G'' \tag{1}$$

where G' (storage or elastic modulus) and G'' (loss or viscous modulus) give 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 η^* is the complex viscosity and ω represents the frequency of oscillation.

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

$$\tan\delta = \frac{G''}{G'} \tag{2}$$

A low value in $\tan\delta$ 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 the G' value.

Solutions of PAN in DMF were submitted to frequency sweep tests before freezing. At 25 °C, the double logarithmic plots of dynamic moduli as a function of oscillation frequency give the following dependences: $G'(\omega) \propto \omega^2$, $G''(\omega) \propto \omega$ (Fig. 2).

At -5 °C (Fig. 3), the viscoelastic behavior is completely changed, suggesting some structural changes in the sample induced by the low temperature. Firstly, G' is higher than G'', and for an oscillation frequency higher than 1 $\mathrm{rad \cdot s^{-1}}$, the curves recorded for both moduli present very close values for the scaling exponent (0.18 and 0.21 for G' and G'', respectively), as predicted for the gel state: $G'(\omega) \propto G''(\omega) \propto \omega^n$ [15]. On the other hand, the complex viscosity is very high at a low oscillation frequency (10^5 times higher than its value at 25 °C) and around 0.1 $\mathrm{rad \cdot s^{-1}}$ it starts to decrease, varying as $\omega^{-0.81}$.

For PAN solutions, the evolution of the viscoelastic parameters in temperature sweep tests depends on the solution state. The experimental tests were realized by

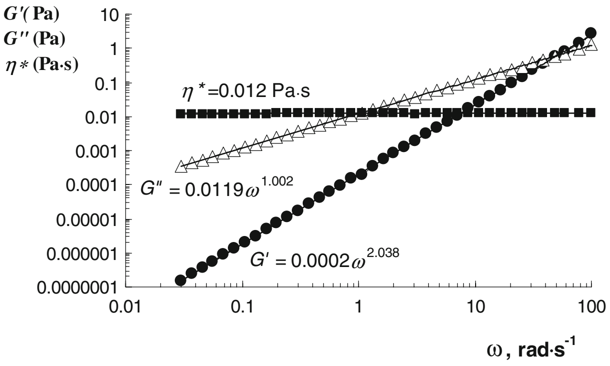

Fig. 2 Evolution of dynamic moduli and complex viscosity as a function of oscillation frequency for $3\ \mathrm{g \cdot dL^{-1}}$ solution of PAN (sample 5) at 25 °C

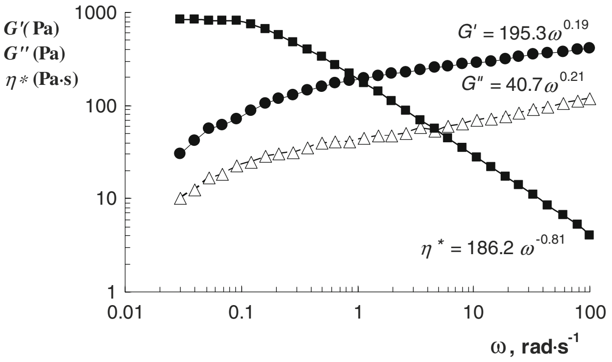

Fig. 3 Variation of G', G'', and η^* as a function of oscillation frequency for 3 g · dL^{-1} PAN (sample 5) solution in DMF at constant temperature of −5 °C

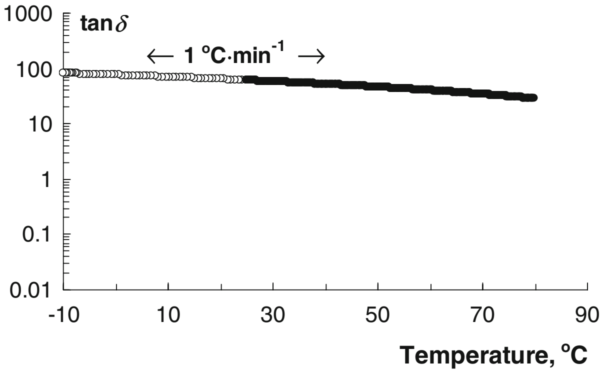

Fig. 4 Dependence of tan δ on temperature for a non-entangled PAN solution (1 g · dL^{-1}, sample 5)

considering the starting point of 25 °C for a PAN solution which was submitted to freezing or heating.

By taking into account a non-entangled solution (1 g · dL^{-1} PAN), for which $c \cdot [\eta] < (c \cdot [\eta])_{\mathrm{cr}}$, the loss tangent (Fig. 4) as well as the viscoelastic moduli decrease continuously with an increase in temperature, over a large domain of temperature (from −10 °C to 80 °C). The viscosity decreases with increasing temperature according to the Arrhenius law and the gelation does not occur. The activation energy varies from 5.05 kJ · mol^{-1} for a solution of 1 g · dL^{-1} PAN to 7.25 kJ · mol^{-1} for a solution of 4 g · dL^{-1} PAN [19].

Solutions of PAN in DMF with a polymer concentration higher than 4 g · dL^{-1}, for which $c \cdot [\eta] > (c \cdot [\eta])_{\mathrm{cr}}$, display a different behavior (Fig. 5). For a heating rate of 1 °C · min^{-1}, between 13 °C and 65 °C, the solution undergoes a liquid-like behavior and tan δ slowly decreases with increasing temperature. By further cooling/heating the polymer solution, a sharp decrease of the loss tangent (around three orders of magnitude) is observed. At these temperatures, a sol–gel transition occurs when the system evolutes from a liquid-like (high loss tangent values) state to a solid-like one (low tan δ values). The domain of temperature for liquid-like behavior is more extended

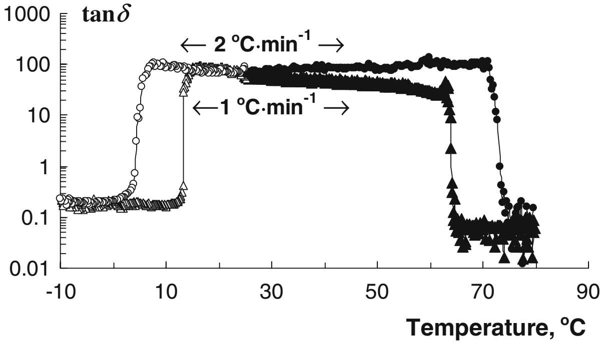

Fig. 5 Dependence of tan δ on temperature for an entangled PAN solution ($5\,g \cdot dL^{-1}$, sample 5)

if the heating/cooling rate is higher, as, for example, for $2\,°C \cdot min^{-1}$, the transition temperatures shifted to 4 °C and 74 °C, respectively. The polymer concentration has a smaller influence, i.e., for $14\,g \cdot dL^{-1}$ the transition temperatures were observed at 15 °C and 64.8 °C for $1\,°C \cdot min^{-1}$.

Above 50 °C, we observed some increases of the viscosity even for fresh PAN entangled solutions which were not submitted to freezing [10]. The activation energy increases to $17.2\,kJ \cdot mol^{-1}$ for $5\,g \cdot dL^{-1}$ and becomes higher for $10\,g \cdot dL^{-1}$ and $14\,g \cdot dL^{-1}$: $55.24\,kJ \cdot mol^{-1}$ and $63.6\,kJ \cdot mol^{-1}$, respectively [19].

From Fig. 5, it appears that for a constant rate of heating/cooling, a sample can exhibit two transition points: the first one is located in the region of low temperature and the second one is found at high temperatures. This can explain the anomalous increase of the viscoelastic parameters at high temperatures observed previously for entangled PAN solutions [10]. The gel obtained by cooling the PAN solution at temperatures lower than 15 °C is thermo-reversible and soluble in an excess of solvent; this is a physical gel. The gel obtained by heating the PAN solution at temperatures higher than 60 °C is not thermo-reversible; if it is submitted to a cooling test, the loss tangent conserves its low values. Also, it is insoluble in an excess of solvent, as the result of chemical crosslinking due to the interactions between –C≡N groups favored by the temperature increase.

The gelation time for the physical network strongly diminishes by decreasing the temperature, and it is also influenced by the polymer concentration and molar mass (decreases when c or M increases). According to the model of an ordered junction zone introduced by Beckman and Zenke [5], PAN having the chains high enough forms stable aggregates which are built-up by regular blocks and are formed as a consequence of a nucleation process in the solution. The critical concentration of gelation is determined by the number of regular blocks able to form ordered junction zones which are thermodynamically determined [20].

Bohidar [21] discussed the dynamics in the thermo-reversible gels considering the gel state as being a state of matter having both solid- and liquid-like properties. The macromolecular chains lose their identity and become part of a large three-dimensional and interconnected cluster pervading the entire volume. Such a fluid has both fluidity and elasticity. The elastic modulus characterizes the gel strength and porosity of the gel. Thus, the dynamical properties of these systems are very revealing.

The rise in molar mass or polymer concentration is accompanied by an increase in the number of crosslinking sites. As more and more such coupling points exist, the molar mass 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 [15], when the molar mass becomes infinite, the longest relaxation time is also infinite, so the sample no longer flows like a polymer solution. It has the properties of an equilibrium solid, and this corresponds to a gel state.

3.3 Gels Obtained by Freezing–Thawing Method

After freezing samples with different polymer concentrations, they were thawed and the viscoelasticity measurement was carried out with aging at 25 °C. The viscoelastic behavior of the solutions after freezing varies with an increase in the aging time, t_A. The slopes of both G' and G'' plot as a function of ω in the region of low frequencies decrease with an increase of t_A. The evolution of the loss tangent as a function of the aging time at different oscillation frequencies is given in Fig. 6.

For all frequencies, a crossover point is observed around 1,800 s when the gelation occurs, because the aging time is independent of frequency at the gelation point. By increasing the aging temperature, the crossover point shifts to higher aging time because the thermal motion does not destroy the crosslinked structures formed at low temperatures and the viscous-to-elastic ratio becomes higher.

Figure 7 shows the evolution of the elastic modulus as a function of the oscillation frequency for a PAN gel obtained from a 14 g · dL^{-1} solution in DMF at different freezing times, for a constant aging time of 30 min at an aging temperature of 25 °C.

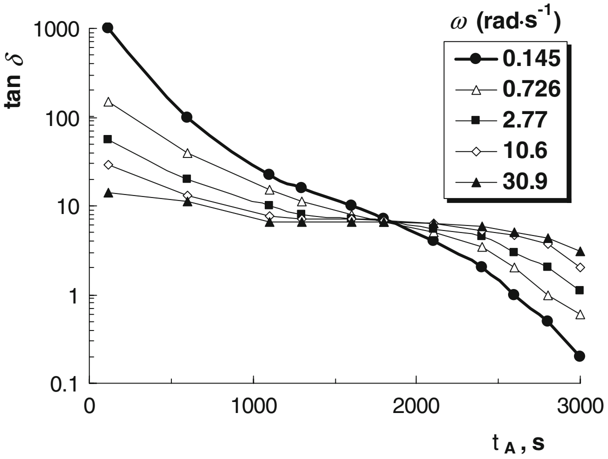

Fig. 6 Loss tangent plotted as a function of the aging time at different oscillation frequencies for PAN/DMF solution (14 g · dL^{-1}, sample 5), $t_F = 60$ min

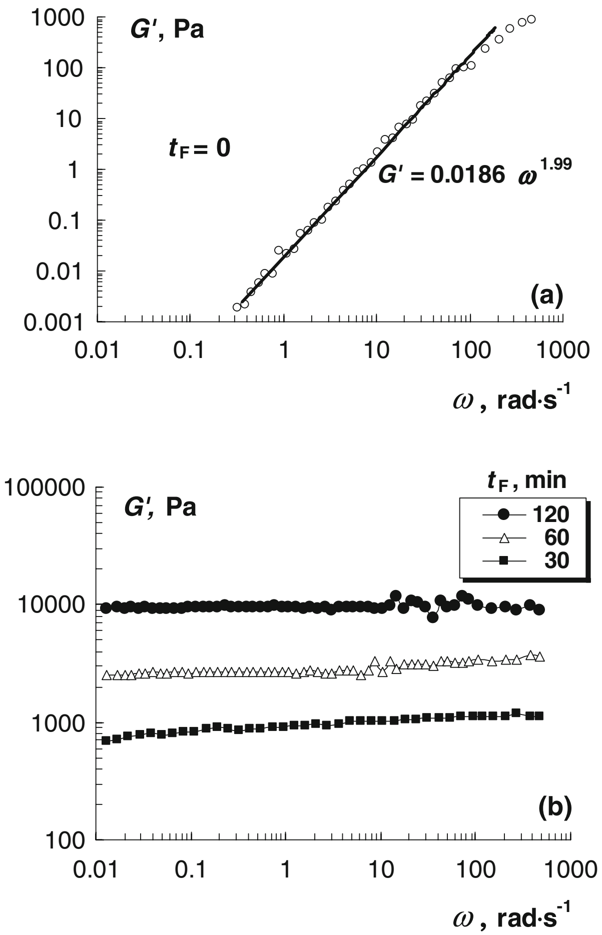

Fig. 7 Elastic modulus as a function of oscillation frequency for a solution of 14 g · dL^{-1} PAN (sample 5) in DMF at 25 °C for an aging time $t_A = 30$ min and (**a**) $t_F = 0$ and (**b**) different freezing times

In the absence of freezing, G' scales as ω^2 (Fig. 7a). For $t_F = 30$ min, G' slowly increases with increasing ω until the plateau is attained (Fig. 7b); for higher freezing times (60 min and 120 min, respectively), G' shows a constant value for all ranges of frequencies, which increases with increasing t_F. For $t_F = 150$ min, the G' value does not change significantly as compared with its value obtained for $t_F = 120$ min, but the experimental data are more scattered (10^4 Pa ± 2 %).

Generally, the gelation is characterized by a growth of viscosity [22]. Figure 8 presents the dependence of the shear and complex viscosities as a function of shear rate ($\dot{\gamma}$) and oscillation frequency, respectively, for the PAN gel obtained from the 14 g · dL^{-1} solution in DMF for $t_F = 120$ min and different aging temperatures as compared with the same solution without freezing ($t_A = 30$ min). The validity of the Cox–Merz rule is demonstrated.

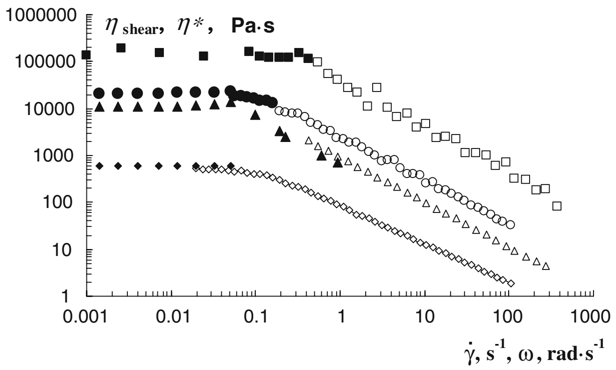

Fig. 8 Shear and complex viscosity as a function of $\dot{\gamma}$ and ω, respectively, for a solution of 14 g · dL^{-1} PAN (sample 5) in DMF at 25 °C for $t_A = 30$ min and $t_F = 0$ min (rhomb) or $t_F = 120$ min at different aging temperatures—25 °C (*triangle*), 40 °C (*circle*), and 75 °C (*square*). Full symbol: shear viscosity; open symbol: complex viscosity

At 25 °C, the frozen sample presents a higher viscosity than the sample which was not frozen, the difference of the Newtonian viscosity is more than one decade in magnitude. This can be due to the formation of crosslinks at low temperature which are not fractured by thermal motion or low shear rates. By increasing the aging temperature, the flow curves are shifted upwards: a higher aging temperature determines an increase of the viscosity. Also, the power law describing the non-Newtonian flow for the sample without freezing is $\eta^* \propto \omega^{-0.81}$, typical for the polymers in the entangled state [23], whereas the scaling exponent increases for the frozen samples from 0.93 to 1 corresponding to aging temperatures of 25 °C and 70 °C, respectively.

We suppose that one of the segments of the linear chain in the solution can form crosslinks 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 molar mass increases, determining a viscosity increase. An increase of the aging temperature determines an increase of the viscosity when a superposition between physical and chemical gelation can occurs.

The main characteristic of PAN macromolecules is the presence of a permanent dipole in every monomer unit caused by a strongly polar C≡N group. Due to the attractive dipole–dipole forces between neighboring segments of the PAN chains, the gelation of PAN/DMF solutions occurs. The structural features of PAN–DMF gels were investigated by DSC, swelling, light scattering, and X-ray diffraction experiments [5,16]. They did not find any differences between a homogeneous solution and a gel, and concluded that strong intermolecular interactions between the macromolecules in solution realized at low temperatures give rise to the formation of more or less stable junction points, and as a result, a gelation occurs. This infirmed the hypothesis of Bisschops [11] which have considered that gelation is caused by a nucleation process of small crystallites. In addition, it was found that PAN does not crystallize from DMF [4].

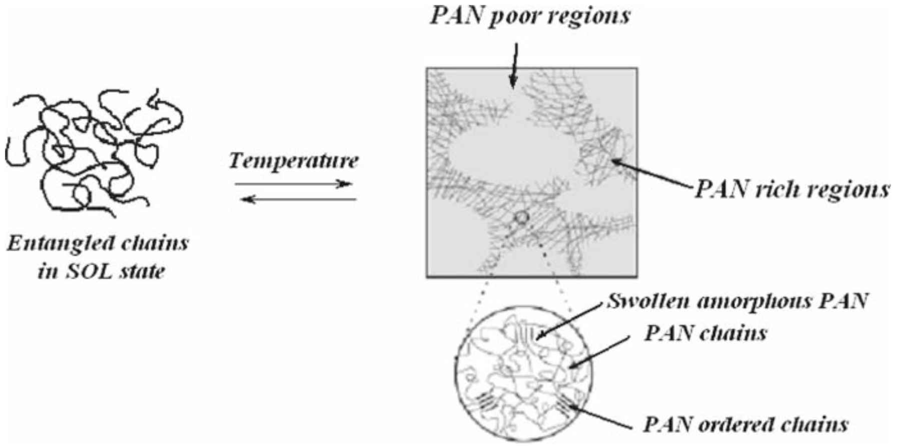

Fig. 9 Schematic representation of the sol and gel states obtained for PAN in solution through the change of temperature

The classic theory of gelation [24] considers that a gel is formed if the chains pass in the mean more than two junction points. The number of potential blocks in PAN chains is large enough to form the number of aggregates needed for gelation.

Figure 9 gives a schematic representation of the sol state and bicontinuous structure of a PAN gel obtained by freezing–thawing homogeneous solutions. The microgel fraction that forms in the unfrozen liquid microphase (during freezing, the solution is at subzero temperatures) acts as a building block to form the network structure in PAN-rich regions which alternates with PAN-poor regions. The two phases coexist due to the vitrification of PAN chains on cooling, forming a thermoreversible gel, as was evidenced by oscillatory measurements.

According to Beckmann and Zenke [5], the ordered junction zone, despite its small extension, becomes thermodynamically stable because the strongly attractive dipole–dipole interactions between the interacting sequences is strong enough to prevent decomposition and to maintain the gel states at any aging temperature. This confirms our hypothesis which considers the gelation as being attributed to the formation of temporary junction points due to the polymer–polymer interactions favored at low temperatures.

4 Conclusion

The gelation of polymer solutions is a complex process which depends on experimental conditions as well as on the sample characteristics. Dynamic viscoelastic measurements demonstrated that it is possible to obtain polyacrylonitrile gel from solution using temperature variation alone.

For entangled polyacrylonitryle solutions, a reversible gelation was observed in the region of low temperatures (below 15 °C) due to the formation of a crosslinked structure with a small region of order; in an excess of solvent this gel dissolves completely.

The polymer–solvent interactions are thermally responsive. The transition takes place for entangled polymer solutions when strong polymer–polymer interactions are exhibited at low temperatures. These interactions are not destroyed by thermal motion or by small shear rates. The onset of gelation is not solely due to the collapse of the polymer in the solution, but also to the formation of intermolecular associations with small ordered regions involving the neighboring segments belonging to one or more polymer chains. In the same experimental conditions, the gelation was not observed for non-entangled polyacrylonitrile solutions.

Physical gels can be also obtained by freezing and thawing polyacrylonitrile entangled solutions. In order to obtain good elastic properties, freezing time and aging time should be taken into account.

At high temperatures (above 60 °C), another sol–gel transition occurs. The obtained gel is not reversible because it is the result of chemical crosslinking.

The gelation of polyacrylonitrile solutions depends on the thermal history of the solution, its composition, and experimental conditions. As a consequence, the gelation point is not a constant for polyacrylonitrile solutions, being identified at well established conditions.

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