

Unusual viscosity behavior of polyacrylonitrile in NaSCN aqueous solutions



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ABSTRACT

The rheological behaviors of polyacrylonitrile (PAN) and its copolymers in various NaSCN aqueous solutions are investigated. An unusual shear-viscosity behavior that is unique for PAN/NaSCN aqueous solutions is identified: both in the high and low NaSCN concentration (C_{NaSCN}) regimes, the PAN solution viscosities are higher, with the minimum occurring at $C_{\text{NaSCN}} = 48\text{--}50\text{ wt\%}$ for the 11wt% PAN solutions. Infrared spectroscopic and dynamic light scattering measurements are employed to elucidate the solution-structural changes that are responsible for this unusual viscosity behavior. Accordingly, a tentative dissolution mechanism in PAN solutions with high C_{NaSCN} and gelation mechanism with low C_{NaSCN} are proposed.

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1. Introduction

Polyacrylonitrile (PAN) homopolymer and copolymers are versatile polymers that have been widely used as a membrane material for water treatment and a substrate for nanofiltration and reverse osmosis [1]. They are also known as a popular high performance precursor for carbon fibers. These diverse applications make its solution properties to be an important research topic, particularly for fiber spinning. As a result, rheological properties of PAN solutions have received considerable attention [2]. Early studies are focused on the variables which influence the spinnability of the solution such as polymer concentration, molecular weight, temperature, and the solvent [3]. However, the requirement of fabricating higher performance PAN fibers has widened the scope of the research to the pre-gelled gel spinning which primarily involves physical gels [4].

Physical gels can be phenomenologically described as systems containing large quantities of fluid that display solid-like viscoelastic properties over a broad range of time-scales [5,6]. The detailed structure of physical gels is difficult to be clearly defined for the transient nature of physical network junctions which involve disparate forces like Columbic, dipole–dipole, van der Waals, hydrophobic or hydrogen bonding interactions, etc. [7] In many cases, combined with various dynamical processes, the

nature of the junctions is even more complicated. In homopolymer solutions, it combines with crystallization in crystalline materials such as polyethylene oxide (PEO) or with the conformation change of multiple helices in biopolymer solutions like gelatin [8]. For block copolymer solutions, the micro phase separation is the main reason for gelation, while sometimes specific and intricate interactions are introduced [9–11].

In addition to the parameters mentioned above, the solvent also plays an important role in determining the gelation mechanism. Taking PAN as an example, it exhibits physical gelation in various solvents, such as Dimethyl sulfoxide (DMSO), N, N-Dimethylformamide (DMF), propylene carbonate (PC), etc. However, the mechanism or the junction zones in PAN gels have different explanations even for a specific solvent. In earlier studies on PAN/DMF and PAN/Dimethylacetamide (DMAc) gels, it is not clear whether the junction zones crystallize, but the possibility of nuclei or small crystallites is believed to exist [12]. Moreover, there are no more than 2% of the PAN present as crystallites in the gels according to measured and theoretical values of the melting enthalpy [13–15]. On the other side, the mechanism of dipole–dipole forces between the nitrile groups was also suggested [13,16]. Later, the X-ray diffraction (XRD) studies of PAN/PC gels showed the presence of crystallites which are different from the normal crystallites of the corresponding homopolymer [17,18]. The author postulated them as the crystallites of the polymer–solvent complex. In recent works using DMSO and DMSO/water mixture as solvents, different opinions were proposed. In the work of Vettegren et al., the crosslinks were attributed to the dipole–dipole interactions between DMSO

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and PAN molecules in the absence of water, or hydrogen bonds between water and PAN molecules when water was introduced [19]. In the very recent work of Malkin et al., the copolymerization units of itaconic acid were postulated to incorporate in the three dimensional networks, i.e., DMSO crosslinking of nitrile and carboxylate groups in the absence of water, while a specific hydrogen bond of a DMSO–water crosslinking of the two carboxylate groups in the presence of water [10].

Another widely used solvent, aqueous solution of sodium thiocyanate (NaSCN), has been rarely studied [20,21]. It is one of the best solvents in the salt method for the manufacture of PAN fibers, and also known by biologists for its powerful protein denaturing ability. The structure geometry studies of the thiocyanate anion (SCN^-) were focused on its ambidentate nature with various metal ions by both S and N atoms. However, the hydration structure is hardly known because of the conventional XRD experiment used [22]. The difficulties are summarized by Kameda et al. as follows [22]. First, the correlations between the SCN^- anion and the water molecules are difficult to pick up due to the overwhelming water–water correlations in the aqueous solutions. Second, it is more difficult to determine the orientational configuration between an ion and its surrounding water molecules because of the extremely weak scattering factor of the hydrogen atoms [22]. Thus several intermolecular interactions were suggested, such as self-associations of NaSCN molecules [23], hydrates of NaSCN and water molecules [20]. Until recently, convincing evidence from neutron diffraction and isotopic substitution experiments verified the presence of the hydrogen bond interaction between the NaSCN and water molecules [21]. Two types of hydration around the nitrogen of the SCN^- anions with one arising from the hydrogen atoms of the water molecule bonding by means of sp^2 orbitals to the nitrogen atom of the SCN^- anion were suggested, while another was assigned to a hydration bond which was “presumably primarily Coulombic in nature” [21]. It should be pointed out that the measurement was carried out in a moderately dilute region with NaSCN concentration of 5M (~28.8 wt%). And the Raman spectroscopic measurements revealed two different types of vibration for hydrogen bond in water molecules with NaSCN concentration above or below 52wt%, respectively [20]. Thus the molecular structure for concentrated NaSCN solutions is still uncertain.

The studies on the dissolution mechanism of PAN in aqueous solution of NaSCN are even less [24–26]. Fischer et al. studied dissolution of PAN in NaSCN and KSCN low-temperature molten salts, in which a coordination of the acidic hydrogen in PAN main chains by SCN^- was assumed, accompanied by a coordination of the CN group by Na^+ , as shown in Scheme 1a [24]. However, the presence of water complicated the situation since no elucidated dissolved state for PAN in NaSCN aqueous solutions was proposed by analyzing ^{13}C NMR chemical shifts [27,28] or apparent Raman complexation peaks were observed [25,26]. Thus a dissolved structure was assumed by Edwards et al. with the rod-like SCN^- anions intercalating between the nitrile groups to prevent the intramolecular repulsions and intermolecular attractions, as shown in Scheme 1b [25,26]. To the best of our knowledge, none of these schemes has been reported to involve in gelation, even in a very recent study which reported that there was no gel for PAN in aqueous solution of 52wt% NaSCN [10].

In this study, the rheological behaviors of PAN and its copolymers in various NaSCN aqueous solutions within the dissolution region are investigated. The main studied concentration for the PAN polymers is 11wt%. Two NaSCN concentration regimes are identified according to the viscosity results. In the high NaSCN concentration regime ($52 \text{ wt}\% \leq C_{\text{NaSCN}} < 60 \text{ wt}\%$ (saturated at 20°C), there are high viscosities, and the solutions behave as fluid within the study period of about 2 years. Lowering the NaSCN

concentration down to 50–52 wt%, there exists a viscosity minimum. Further lowering the NaSCN concentration (for 11wt% PAN, $42 \text{ wt}\% \leq C_{\text{NaSCN}} < 50 \text{ wt}\%$), the viscosity of the solutions increases unexpectedly, and a gel-like behavior appears. Infrared spectroscopic (IR) and dynamic light scattering (DLS) measurements are employed to investigate the structural changes responsible for this unusual viscosity behavior. Accordingly, tentative dissolution and gelation mechanisms are proposed.

2. Experimental section

2.1. Materials

The properties of the PAN samples are listed in Table 1. NaSCN (analytically pure) was purchased from Sinopharm Chemical Reagent Co., Ltd. The polymers were dried at 70°C in vacuum oven for 12 h before use. The saturated NaSCN aqueous solution (60 wt% at 20°C) was prepared by directly mixed the NaSCN and deionized water. Its concentration was determined by titration of AgNO_3 standards with ferric ammonium alum as indicator. And then it was stored as mother liquid at a constant temperature ($>20^\circ\text{C}$). The other lower concentrations of NaSCN solutions were prepared by diluting the mother liquid.

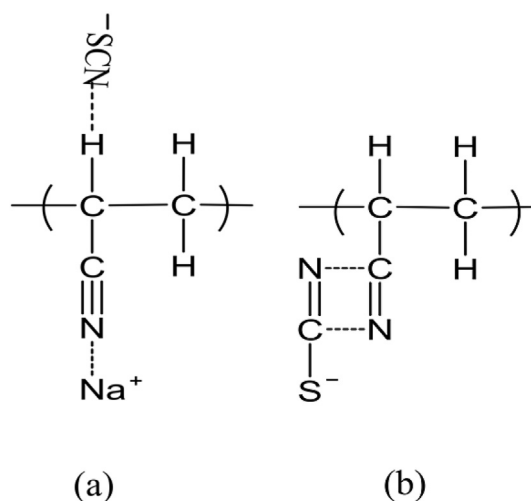
2.1.1. Preparation of PAN solutions

A certain amount of PAN copolymers were dispersed in various NaSCN aqueous solutions. All concentrations are given in weight percent. The slurry solutions were stirred and let stand in a sealed bottle for swelling at 35°C for 0.5 h, and dissolved in 85°C for 1 h to produce a homogeneous viscous solution. This method can largely prevent water evaporation and restrain bubbles during the dissolution.

2.2. Characterization of PAN solutions

2.2.1. Rheology

The rheological measurements were performed on a Hakke Mars III rheometer with Peltier temperature control. Oscillation measurements were carried out with parallel plate geometry (diameter 35 mm, gap 1 mm). Uniform steady shear was obtained by a cone and plate geometry (cone diameter 20 mm, angle between cone surface and plate 2°). Solutions were directly



Scheme 1. The two models for PAN dissolved in NaSCN solution as described by Fischer et al. (a) and Edwards et al. (b).

Table 1
The properties of the PAN samples.

Sample	AN: MA: IA ^a (wt%)	Molecular weight ($\times 10^{-4}$ g mol ⁻¹)	Source
PAN-1	96.6: 2.6: 0.8	8.8	Shanghai Petrochemical Co.
PAN-2	95.2: 3.2: 1.6	8.7	Shanghai Petrochemical Co.
PAN-3	100: 0: 0	15	Sigma–Aldrich
PAN-4	100: 0: 0	2.6	Polymer source

^a AN, MA, and IA stand for acrylonitrile, acrylate, and itaconic acid, respectively.

introduced on the plate which was at the preset desired temperature within ± 0.1 °C. After the preparation, a thin layer of a nonvolatile and incompatible liquid, silicon oil, was put around the sample surface in order to prevent water absorption. The solutions were kept for 3 min before test and a new solution was used for each test to avoid the memory effect.

The following regimes of shearing were used: (i) oscillation strain sweep for determination the linearity region of the samples under study at constant frequency, f , equal to 1 Hz with varying amplitude of deformation, γ ; (ii) oscillation frequency sweep in the linearity region of viscoelastic with $\gamma = 1\%$ and frequency in the range from $f = 0.01$ –70 Hz; (iii) flow curve measurements covering the shear rate range from 0.1 to 100 s⁻¹, or shear stress ranging from 0.1 to 3000 Pa; (iv) evolution of apparent viscosity, η , with time at constant shear stress.

2.2.2. FTIR

The FTIR spectroscopy of PAN solutions were carried out on the FTIR spectrometer Nicolet 6700 (Thermo Scientific) by placing the samples between two Calciumfluoride covers.

2.2.3. Dynamic light scattering (DLS)

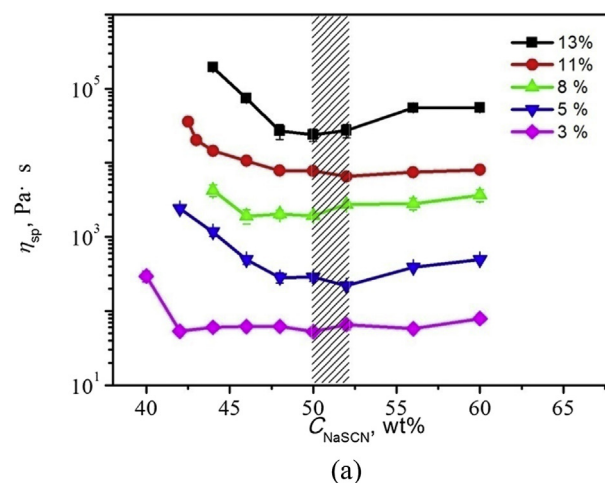
Dynamic Light scattering measurements were carried out on PAN aqueous solutions with PAN concentration of 2 mg/ml (~0.2 wt %), and NaSCN 45 wt%, 52 wt% and 59 wt%, respectively. All the solutions were filtered through a 0.45 μ m membrane. A commercial light scattering spectrometer (ALV/CGS-3, $\lambda = 632.8$ nm) equipped with an ALV-7002 multi- τ digital time correlator was used. The scattering angle was 90°.

3. Results and discussion

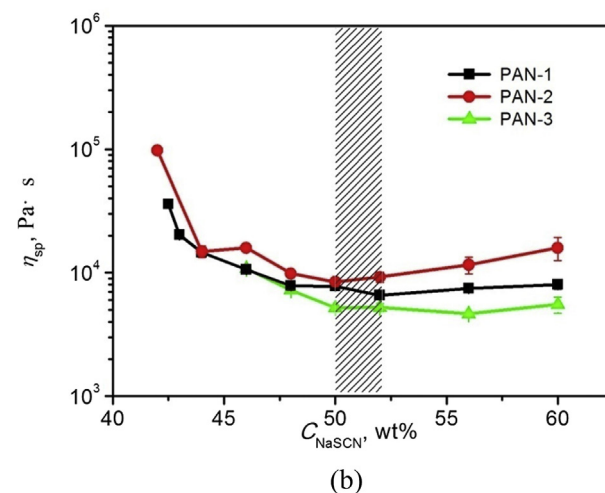
3.1. Anomalous shear-viscosity dependence for PAN in various concentrations of NaSCN aqueous solutions

Fig. 1 shows the steady-state shear viscosity (η)–shear rate ($\dot{\gamma}$) dependence of 11 wt% PAN-1 in aqueous solutions with NaSCN concentrations from 42 wt% to 60 wt%. All the solutions exhibit a Newtonian plateau and a shear thinning regime at NaSCN concentrations from 43 wt% to 60 wt%, except for 42 wt% which shows only a shear thinning regime within the shear rate from 0.1 to 100 s⁻¹. The appearance of shear thinning moves to a lower shear rate with the decrease of NaSCN concentration. It suggests a longer relaxation time of PAN-1 in aqueous solutions with a low NaSCN concentration. Note the striking shear viscosity difference between 42% and 43% NaSCN concentrations. We believe this phenomenon is related to the phase separation of the ternary system. According to our experiments, at 25 °C the location of 11 wt% PAN/42 wt% NaSCN(aq) is very close to the cloud point, at which large fluctuations come into play.

The zero-shear viscosity (η_0) – C_{NaSCN} dependence is interesting as shown in the inset of Fig. 1 (η_0 for PAN-1 in 42 wt% NaSCN solution is obtained at $\dot{\gamma} = 0.1$ s⁻¹). η_0 decreases only to NaSCN concentration of ~48 wt%, and then it increases nonlinearly with the reduction of NaSCN content, i.e., the shape of η_0 curve is like an



(a)



(b)

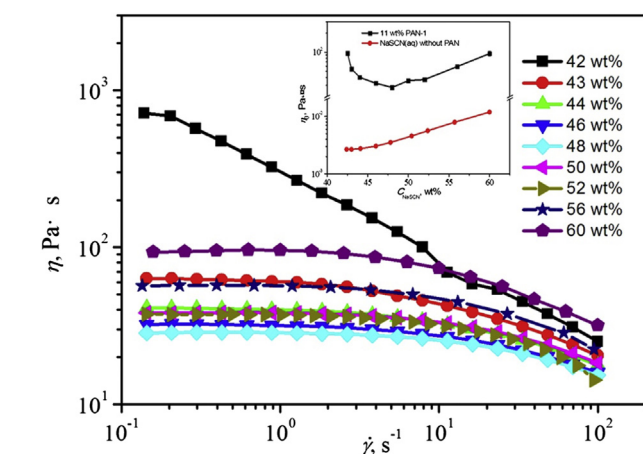


Fig. 1. Steady state shear-viscosity vs. shear rate for 11 wt% PAN-1 in aqueous solutions with NaSCN concentration ranging from 42 wt% to 60 wt%. In the inset, NaSCN concentration dependences of the zero-shear viscosity for 11 wt% PAN-1/NaSCN(aq) solutions and NaSCN aqueous solution without PAN are shown.

Fig. 2. Specific viscosity of PAN polymers in NaSCN aqueous solutions for: a) the concentration of PAN-1 ranges from 3 wt% to 13 wt%; b) PAN-1, PAN-2 and PAN-3 with the same concentration of 11 wt%.

“U” with the minimum at $C_{\text{NaSCN}} = 48\text{--}50\text{ wt\%}$. This is very different from the aqueous solution of NaSCN without PAN, which shows a monotonous dependence on C_{NaSCN} , as shown in the inset of Fig. 1. The anomalous of viscosity behavior has been reported in protein aqueous solutions by the addition of certain structurally related organic solvents, such as tetramethylurea (TMU), DMSO, DMF, and hexamethylphosphortriamide [29]. The remarkably high viscosity for protein in the solvent mixture was attributed to a conformational transition of the polypeptide backbone from α -helical to β -sheet structures and short-lived interchain contacts at a critical concentration of protein and organic solvent [29]. However, the similar effect as in PAN/NaSCN (aq) system, i.e. the viscosity- C_{NaSCN} curve shapes like an “U”, has not been observed yet either in biopolymer or synthetic polymer solutions, to the best of our knowledge.

To explore the anomalous viscosity behavior for PAN in aqueous solutions of NaSCN, the specific viscosity (η_{sp}), expressed as $\eta_{\text{sp}} = (\eta_0 - \eta_s)/\eta_s$ (where η_0 and η_s are the zero-shear viscosities of the solution and the viscosity of the solvent, respectively), is chosen to exclude the solvent influence, as shown in Fig. 2. All the $\eta_{\text{sp}}-C_{\text{NaSCN}}$ curves are similar to the η_0-C_{NaSCN} curve of 11 wt% PAN-1 solutions no matter what the concentrations (Fig. 2a) or the components (Fig. 2b) of the polymers are, except for the minimum located at $C_{\text{NaSCN}} \approx 50\text{--}52\text{ wt\%}$, as shown in Fig. 2a and b, respectively. We therefore divide them into two regimes. In the first one, corresponding to higher NaSCN concentrations, $50\text{ wt\%} \leq C_{\text{NaSCN}} < 60\text{ wt\%}$, the viscosity gradually reduces about 4 times with the decrease of C_{NaSCN} , and it is reasonably attributed to the partial collapse of the PAN polymer chains caused by the decrease of the PAN solubility in poorer solvent. We note that the solutions in this regime are always in flow state within the study period of about 2 years. There is a minimum specific viscosity in the solution with NaSCN concentration of 50–52 wt%, which suggests the chain collapse happens at a maximum degree. In the second regime with lower NaSCN concentrations, $42\text{ wt\%} \leq C_{\text{NaSCN}} < 50\text{ wt\%}$, the viscosity of the PAN solution gradually increases with the decrease of C_{NaSCN} and the solutions can gel and then phase separate as stated below. This viscosity increment induced by the deterioration of solvent is rarely reported and the reason is explored here.

3.2. Rheological properties of PAN/NaSCN aqueous solutions

3.2.1. Dynamic viscoelasticity of PAN/NaSCN aqueous solutions

The shear frequency effect on gelation of the PAN-1/NaSCN aqueous solutions is studied using dynamic viscoelastic measurements. Frequency dependencies of the storage modulus (G') and loss modulus (G'') for 11 wt% PAN-1 in aqueous solutions with NaSCN ranging from 42 wt% to 60 wt% are presented in Fig. 3. The deformation strain is 1%, which is in the linear viscoelasticity regime, and the frequency sweep ranges from 0.01 to 70 Hz. In a Maxwell fluid, the terminal relaxation of a polymer solution follows a scaling law of $G' \sim \omega^2$ and $G'' \sim \omega$, where ω is the frequency. It happens for PAN polymers in aqueous solutions with NaSCN concentration higher than 50 wt%. However, gel-like plateau of G' appears for PAN polymers in aqueous solution with NaSCN concentration lower than 48 wt% at low frequencies. Moreover, when lowering the NaSCN concentration down to 42 wt%, the storage modulus G' of the PAN solution is slightly larger than G'' and the two moduli are slightly dependent on frequencies, which suggests a weak gel or structured liquid behavior [7]. This behavior is out of the expectation of the authors [10] who only studied for PAN aqueous solutions with NaSCN concentration larger than 50 wt%.

As we know, storage modulus originates from the elastic network structures and its terminal relaxation plateau can be related to the plateau modulus of the gel. An expression is proposed as

$G' = G_N^0 = \rho RT/M_e$, in which ρ is the density of the gel, R the gas constant, T the absolute temperature, M_e the molecular weight of the network strand [30]. According to the above equation, cross-linking density is calculated to be about 1.8% per chain for 11 wt% PAN in 42 wt% NaSCN solution, assuming $\rho = 1.2\text{ g/cm}^3$. While for 11wt% PAN in 43 wt% NaSCN solution, it is 10 times less. In other words, the quantity of water has a great effect on the gelation of PAN/NaSCN aqueous solution systems.

3.2.2. Critical stress and aging

Gel-like fluid sometimes has a character of yield stress, which is defined as the stress at which the fluid just starts/stops moving [31]. However, in our system, there is no yield stress as indicated by the viscosity-shear stress curve, as shown in Fig. 4. The reflection of the critical flow strength which divides the linear and nonlinear viscoelastic regimes is going to lower shear stress for 11 wt% PAN in the aqueous solution with the concentration of NaSCN lowering down to ~42 wt%. Moreover, the solution is aging with time. The time evolution of the viscosity with different applied stresses is shown in Fig. 5 for 11 wt% PAN/42 wt% NaSCN (aq). For stresses smaller than a critical stress (<200 Pa here), the steady-state

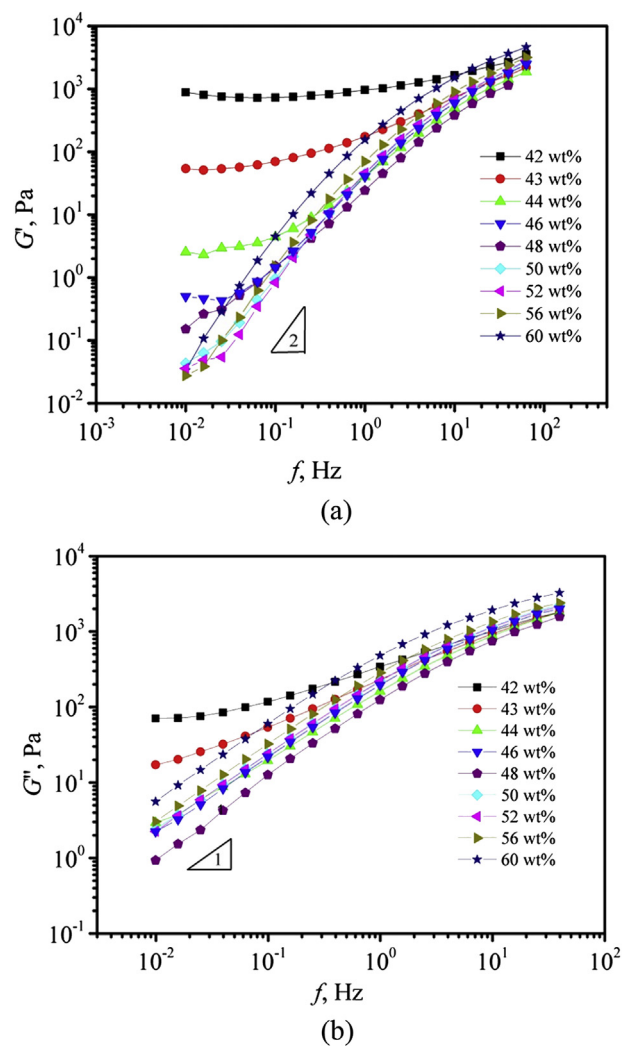


Fig. 3. Frequency dependencies of the storage modulus (a) and loss modulus (b) of 11wt% PAN-1 in aqueous solutions with NaSCN ranging from 42 wt% to 60 wt%. The deformation strain is 1%. The numbers shown in the figure are weight concentrations of NaSCN in aqueous solution.

viscosity is going to infinite, which corresponds physically to the buildup of the colloidal gel. On the other hand, for a stress slightly above the critical stress, the viscosity decreases with time towards a low steady-state value ($\sim 45 \text{ Pa} \cdot \text{s}$ here). The detailed physical description can be referred to the work of Møller et al. [32].

3.2.3. Cox–Merz rule

The classical Cox–Merz rule has been established in many polymeric liquids [33] and it was expressed for PAN/NaSCN system as shown in Fig. 6. The equivalence of the shear rate dependence of the apparent viscosity, $\eta(\dot{\gamma})$, and the frequency dependence of the absolute dynamic viscosity, $|\eta^*(\omega)|$, takes place for PAN polymer in aqueous solutions with NaSCN concentration higher than 50 wt%. However, the situation for PAN in aqueous solutions with lower NaSCN concentration, for example 11 wt% PAN in 42 wt% NaSCN(aq), is different. Actually, there is no equivalence neither at low shear rates nor at high shear rates for the curves of $\eta(\dot{\gamma})$ and $|\eta^*(\omega)|$ for each PAN aqueous solution with NaSCN concentration ranging from 42 to 44 wt%. The failure of the Cox–Merz rule can be visualized as structural change, yield stress, liquid-to-solid transition, and structural ripening, etc. It is reasonable to attribute it in this system to the liquid-to-solid transition.

3.2.4. Temperature response

This section describes the influence of temperature on the gelation process for PAN in NaSCN aqueous solution at different temperatures from 0 to 25 °C by using oscillatory rheology. The widely used power law of Winter and Chambon [34], i.e., $G'(\omega) \sim G''(\omega) \sim \omega^n$, $0 < n < 1$, for gelling systems, was usually adopted in chemical or physical gelation systems. However, it is time consuming especially for the corrosive solvent of NaSCN solution used here. Thus we used the crossover of G' and G'' instead to define the gel time. It is frequency dependent, but does not affect the conclusion we made here by using the same frequency [35].

The relationship of G' (G'') with time evolution was tested at $\gamma = 1\%$, $f = 1 \text{ Hz}$, and the crossover (at which $G' = G''$) is defined as gel time t_{gel} at a specific temperature. The gel time t_{gel} vs. the inverse of temperature $1/T$ dependence is shown in Fig. 7 for PAN-1/43 wt% NaSCN(aq), PAN-2/43 wt% NaSCN(aq), and PAN-1/DMSO systems with PAN concentration of 11 wt%. In all the three systems, t_{gel} decreases with temperature decreasing. For the solutions with the same solvent but slightly different PAN copolymers (PAN-1 and PAN-2 in 43 wt% NaSCN aqueous solutions, respectively), t_{gel} is much closer. However, it is clear that the different solvents used

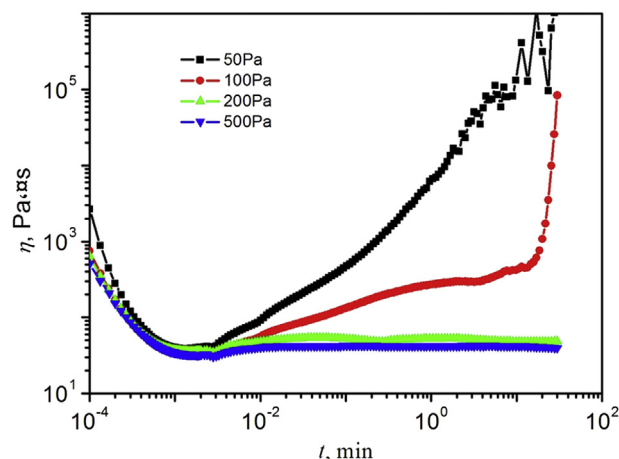


Fig. 5. Shear viscosity-time dependence at a specific shear stress for 11 wt% PAN-1/42 wt% NaSCN solution.

significantly affect the gelation rate. According to a recent work of Malkin et al. [10] in PAN/DMSO solutions with PAN concentration lower than 17 wt%, three-dimensional network structures can develop by DMSO bridging between the nitrile and carboxylate groups. It can be concluded that the overdose small DMSO molecules provide a larger chance for the development of the network structures to overcome the steric effect. It seems that PAN in 43 wt% NaSCN aqueous solution has not such advantage. The mechanisms for the gelation of PAN in the two solvents may be different. And the AN segments are responsible for the gelation in NaSCN aqueous solutions.

3.3. Characterization of PAN/NaSCN(aq) aqueous solutions

3.3.1. FTIR

To investigate the gelation mechanism for PAN/NaSCN aqueous solutions, FTIR spectroscopic measurements were used. The polymer solutions were tested as soon as it was dissolved. The PAN-1 polymer concentrations were fixed at 11 wt%, the NaSCN concentration ranges from 43 wt% to 60 wt%. All the IR spectra are similar to each other. There are no complex peaks in the measured region, which coincides with the conclusion of Edward et al. [25,26] who

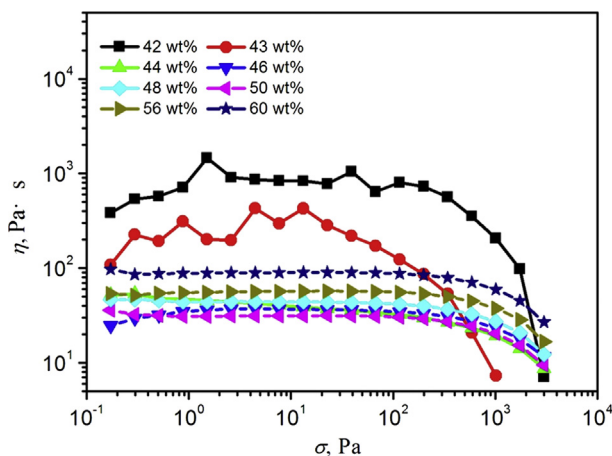


Fig. 4. Viscosity-shear stress dependence for 11 wt% PAN-1 in aqueous solutions with NaSCN concentration ranging from 42 wt% to 60 wt%.

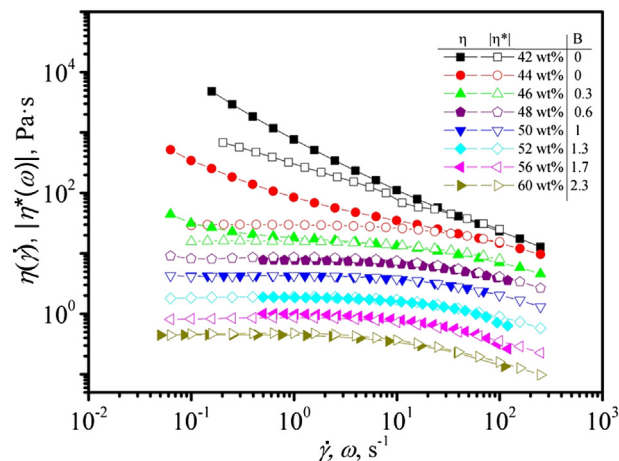


Fig. 6. Cox–Merz rule for PAN-1 in aqueous solutions with NaSCN concentration ranging from 42 wt% to 60 wt%. The data are shifted along the vertical axis by the given B values to avoid overlapping.

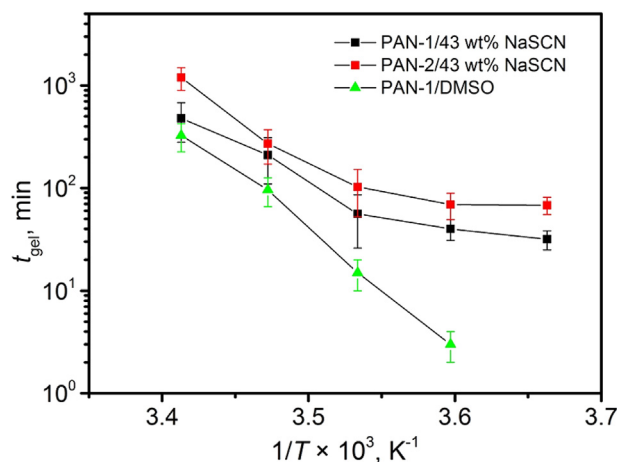


Fig. 7. Gelation time vs. the inverse of temperature for PAN-1/43 wt% NaSCN(aq), PAN-2/43 wt% NaSCN(aq) and PAN-1/DMSO systems with all PAN concentrations fixed at 11 wt%.

studied the vibration of nitrile group in several inorganic salt solutions including NaSCN. However, there are differences of the nitrile stretching vibration peak position in this study as the structure changes in the PAN-1/NaSCN(aq) solutions, as enlarged in Fig. 8. It appears at 2254 cm^{-1} when PAN-1 dissolved in 60 wt% NaSCN solution and a slight bathochromic shift (about $1\text{--}2\text{ cm}^{-1}$) in 50 wt% NaSCN solution. There is no more shift of the CN peak for PAN dissolved in aqueous solution with a lower NaSCN concentration (43 wt%) until the polymer solution was cured to form a gel. When it turned to be a white gel, $\nu(\text{CN})$ appears at 2243 cm^{-1} which is the vibration frequency for PAN in solid state [25,26]. A strong and rather specific interaction was used to explicate the vibrational spectra of 2243 cm^{-1} as an antiparallel alignment of the $\text{C}\equiv\text{N}$ groups of interacting pairs of AN segments [36]. The similar results happened for $-\text{CH}_2$ bending vibrations and $-\text{CH}$ deformation vibrations except for a bluechromic shift of $1\text{--}3\text{ cm}^{-1}$ (data not shown here) for PAN aqueous solutions with 60 wt% NaSCN to a white gel for PAN cured in 43 wt% NaSCN aqueous solution. There is no distinguishable difference of $-\text{CN}$ stretching vibrations at 2054 cm^{-1} for NaSCN (data not shown here) because of the broad peak due to the solvation effect. Because of rare works on PAN/

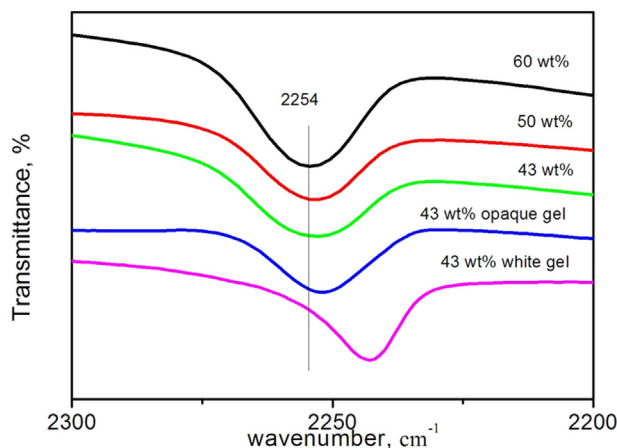


Fig. 8. FTIR spectra of 11 wt% PAN-1 in aqueous solutions with NaSCN concentrations of 43 wt%, 52 wt% and 60 wt%, respectively, and the opaque and white gels or 11 wt% PAN-1 in 43 wt% NaSCN aqueous solution.

NaSCN aqueous solutions, the peak changes as shown here have not been reported in literature.

In the gel curing process, the obvious bathochromic shift of $-\text{CN}$ group and bluechromic shift of $-\text{CH}_2$ and $-\text{CH}$ groups suggest that it is a gel accompanied with phase separation. The slight $-\text{CN}$ spectra changes for PAN dissolved in aqueous solution with NaSCN concentrations from 60 wt% to 50 wt% can be attributed to a conformation change which corresponding with the viscosity decrement of the solutions as stated above.

3.3.2. Dynamic light scattering

To further explore the underlying mechanism for the anomalous viscosity behavior, DLS measurements were carried out on 2 mg/ml ($\sim 0.15\text{--}0.17\text{ wt}\%$) PAN-4 in aqueous solutions with NaSCN concentrations of 45 wt%, 52 wt% and 59 wt%, respectively. The molecular coil size distributions by volume for the respective solutions are shown in Fig. 9. For all the dilute solutions, the coil sizes are between 1 and 10 nm. The smallest coil size (1.6 nm) happens for the PAN-4 polymers in aqueous solution with 52 wt% NaSCN. It shares about 40% by volume with a broader size distribution. The coil sizes for the other two PAN-4 solutions are about two times larger with 3.3 nm sharing 47% by volume for 45 wt% NaSCN, and 3.4 nm sharing 66% by volume for 59 wt% NaSCN, respectively. These results are coinciding with the viscosity behavior which has viscosity minimum for PAN polymers in aqueous solution with $\sim 52\text{ wt}\%$ NaSCN.

3.4. Discussion

We have seen that PAN in aqueous solution with various NaSCN contents exhibited an anomalous behavior in steady-state shear viscosities. With the decrement of NaSCN concentration, the viscosity of PAN/NaSCN(aq) solution decreases first and then increases, with a minimum observed at $C_{\text{NaSCN}} \approx 48\text{--}50\text{ wt}\%$ (with fixed PAN concentrations). The shape of the viscosity- C_{NaSCN} curve is like an “U”. This phenomenon is independent of the type (homo or copolymer) or concentration of the PAN polymer. The anomalous viscosity affected by solvent concentration was reported for protein in DMSO/ H_2O solvent mixture, and the mechanism was attributed to the deterioration of the solvent for the solvent mixture showing reflections of viscosity and refraction index at a certain DMSO content [29]. Another viscosity increment caused by deterioration of solvent has been reported in the PAN/DMSO system [37].

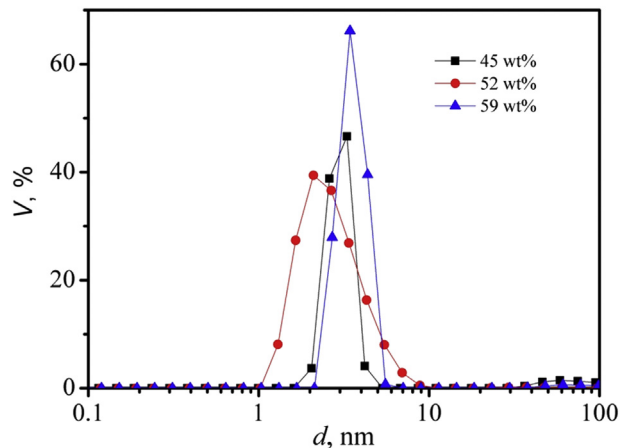


Fig. 9. Coil size distributions by volume for 2 mg/ml ($\sim 0.15\text{--}0.17\text{ wt}\%$) PAN-4 in aqueous solutions with NaSCN concentrations of 45 wt%, 52 wt% and 59 wt%, respectively.

However, there is no similar behavior for NaSCN aqueous solutions to show reflections of viscosity and refraction index at a certain NaSCN content as that for DMSO/H₂O [38]. And the “U”-shape of the viscosity- C_{NaSCN} curve for PAN/NaSCN(aq) solutions is rarely found in other synthetic or biopolymer solutions.

According to the unusual viscosity- C_{NaSCN} curve, the two regimes have been divided. And the rheology, FTIR and DLS measurements revealed three conformations of PAN chains. Despite the industrial importance for fiber solution spinning in manufacture, the available literature on PAN/NaSCN solutions is far from comprehensive [20,28], not to mention the gelation mechanism. There are obstacles such as complicated solvation structure for PAN in NaSCN aqueous solution [28], and even the molecular structure of NaSCN concentration solution itself is not clear. In addition, the direct technique to reveal the microstructures of PAN polymers in solution by SEM and/or TEM is not suitable for this solution system for phase separation occurs at low temperature or in evaporation process. In view of this, a phenomenological explanation is proposed as below. We should emphasize here that the phenomena are determined by an integrated dynamic process, which related to the NaSCN/H₂O mixture structure and the AN segment.

In the first regime corresponding to higher NaSCN contents of 52–60 wt% in PAN/NaSCN aqueous solution, except for the high viscosities reported in the PAN/NaSCN(aq) solutions with PAN content larger than 3wt%, we also notice that the intrinsic viscosity for the dilute PAN solution with saturated NaSCN (60wt%) is 2.16 dL/g (determined by Ubbelohde viscometer at 25 °C, for PAN/DMSO solution, it is about 2.06 dL/g). According to the well-known Fox–Flory equation $[\eta] = \Phi(R_{\text{dilute}}^3/M)$, in which $\Phi = 2.5 \times 10^{23} \text{ mol}^{-1}$, R_{dilute} is the end-to-end distance of an ideal linear polymer chain in dilute solution. R_{dilute} for PAN coils in saturated NaSCN solution is larger than that in DMSO which is known to be a good organic solvent for PAN. Moreover, DLS confirmed the existence of larger coils for PAN polymers in aqueous solutions with 59 wt% NaSCN. Thus a swelling conformation for PAN polymers in aqueous solutions with high NaSCN contents is proposed, as shown in Scheme 2a. The hydrated NaSCN molecules (NaSCN·xH₂O) essential for PAN dissolution scatter around the PAN molecules to destroy the intramolecular interactions between the cyano groups (which cause collapse of PAN chains). The most possible binding structure can be referred to the model of Edwards et al. [25,26] as mentioned above.

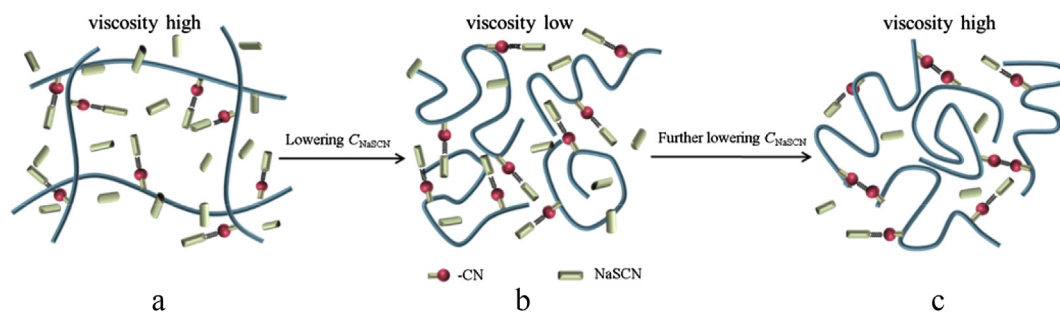
Lowering the NaSCN contents to 50–52 wt%, the hydrated structure of NaSCN·xH₂O molecules are destroyed to cause the PAN solubility decrease in the solvent mixture. Contraction of the PAN molecules happens until reaching the minimum, as shown in Scheme 2b. In this process, there are enough hydrated NaSCN molecules around the PAN polymer to inhibit most of the self-association of cyano groups. However, the chances for dynamic matching between a few cyano groups are possible. The quantity is

so small that they cannot obviously induce the reduction of the linear region in the steady-state shear measurement and the appearance of the gel-like plateau in the dynamic frequency measurements, as shown in Figs. 1 and 3, respectively. However, by using FTIR, a bathochromic shift of 1–2 cm⁻¹ for cyano group can be identified.

In the second regime, corresponding to lower NaSCN contents of 42–50wt%, there are gel structures in studied 11 wt% PAN/NaSCN(aq) solutions. The formation of the cross-linkers has been disputed. First, it is known that PAN can gel in several solvents such as DMSO, DMF, DMAc, and PC. The chemical state of the junction regions are specific for the used solvents, such as microcrystalline for PAN in DMAc [12], crystallites of polymer–solvent complex for PAN in PC [17,18], and dipole–dipole pairs between PAN and DMSO or hydrogen bonds between PAN and water when water was absent or present [19]. Recently, the conclusion by Malkin et al. [10] intrigues us about whether the comonomers also take a part in the three-dimensional networks in PAN/NaSCN(aq) solutions. The existence of MA and IA segments can promote the dissolution of the PAN polymers; conversely disrupt the gelation, as shown in Fig. 7. This result coincides with that of Paul who used vinyl acetate as the comonomers [12]. The addition of the comonomers not only can defect the stereoregularity of cyanide monomer units, but also change the interaction with the solvent. All these results suggest that the cross-linkers should be attributed to the AN segments. The FTIR results prove these conclusions by the existence of the asymmetric vibrations peaks of RCOO^{-1} at 1583 cm⁻¹ from flow to gel state for PAN-1 in NaSCN-D₂O solvent mixture (D₂O was used to avoid the peak overlapping of H₂O), as shown in Fig. 10.

Moreover, the excessive water molecules can further destroy the hydrated structure of NaSCN·xH₂O to increase the chances for the self-association of the cyano groups. A three-dimensional network can be developed if the cross-linking density reaching a percolation threshold and a frequency independent plateau in storage modulus shows up in dynamic shear measurements. Correspondingly, in IR spectra as shown in Fig. 8, the stretching vibrations for cyano groups are gradually bathochromic to 2243 cm⁻¹, which is the vibration frequency for CN group in solid state. DLS results also show that there are larger coils for PAN/45 wt% NaSCN dilute solutions. The aggregation of PAN molecules and the self-association of CN groups result in viscosity increase for PAN/NaSCN(aq) solutions.

Besides, Hofmeister effect can also explain the unusual dissolution behavior of PAN in NaSCN aqueous solution. In the typical order of Hofmeister's anion series, $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{S}_2\text{O}_3^{2-} > \text{H}_2\text{PO}_4^- > \text{F}^- > \text{Cl}^- > \text{Br}^- \geq \text{NO}_3^- > \text{I}^- > \text{ClO}_4^- > \text{SCN}^-$, the species on the left of Cl⁻ are referred to as water structure maker, while those on the right of Cl⁻ are called water structure breaker [39]. SCN⁻ anions have strong capacity to break the hydrogen bonds among water molecules. Therefore, a mechanism of the dissolution process may be proposed for PAN polymers in NaSCN(aq) as



Scheme 2. Proposed conformational changes for PAN in aqueous solutions with NaSCN contents of: a) 59 wt%, b) 50 or 52 wt%, c) 45 wt%. ●: cyano group; ■: NaSCN.

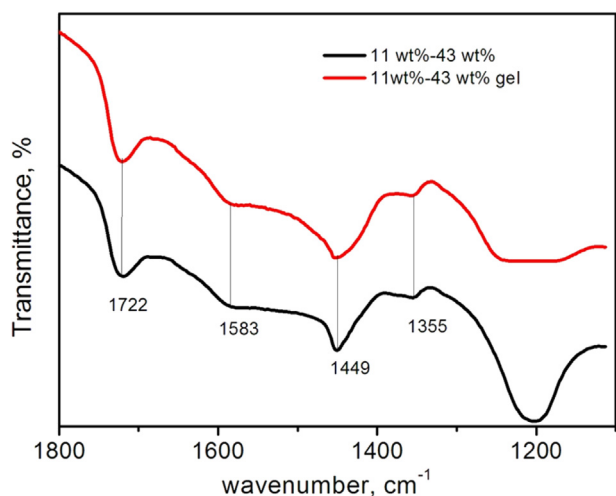


Fig. 10. IR spectra of 11 wt% PAN-1 in D₂O with NaSCN concentration of 43 wt% for fluidic and gel-like solutions. Classification of peaks: 1355 cm⁻¹, C–H deformation vibrations (δ_{C-H}) in CH; 1451 cm⁻¹, δ_{C-H} in CH₂; 1583 cm⁻¹, asymmetric vibrations of the R-COO⁻ group; 1722 cm⁻¹, C=O stretching absorption.

follows: while the hydrogen bonds between water molecules are broken by SCN⁻ anions, new hydrogen bonds could be formed between water molecules and the cyan groups on PAN main chains, leading to the dissolution of PAN polymers. With the increasing of NaSCN content (>50 wt%), there are more hydrogen bonds of water being broken, and the dissolution of PAN polymers is better. The better dissolved PAN polymers are swelled, and the viscosity of the solution is higher. However, when reducing the NaSCN concentration down to ~50 wt% and lower, the ability for NaSCN to break the hydrogen bonds of water is hindered, thus the solubility for PAN polymers is lowered. The unassociated PAN chains are responsible for the high viscosity and the appearance of the gel-like behavior. There is no related reports in literature as stated above, therefore, more experiments need to be done to analyze down to molecular level how NaSCN aqueous solutions dissolve the PAN polymers, such as neutron diffraction and isotopic substitution experiments which beyond the scope of the present study.

4. Conclusions

The rheological study for PAN polymers in aqueous solutions with various NaSCN contents has revealed an anomalous shear-viscosity behavior that is unique for PAN/NaSCN aqueous solutions. The curve of viscosity–NaSCN concentration shapes like an “U” with the minimum happening at $C_{NaSCN} = 48$ –50 wt%. Two NaSCN concentration regimes are identified according the viscosity results.

In the first regime, corresponding to higher NaSCN contents, 50 wt% $\leq C_{NaSCN} < 60$ wt%, the solutions behave as fluid within the study period of about 2 years. When NaSCN content between 52 wt% and 60 wt%, IR spectroscopic measurements indicate that there is no complex peaks or obvious changes for the groups of –CN, –SCN, and –CH. However, DLS reveal the existence of larger coils (two times larger than those for PAN polymers in aqueous solutions with 52% NaSCN) for PAN dilute aqueous solutions with 59 wt% NaSCN. According to the results stated above, a swelling conformation for PAN polymers in aqueous solutions with high NaSCN contents is proposed, as shown in Scheme 2a. The hydrated NaSCN molecules (NaSCN·xH₂O), essential for PAN dissolution, scatter around PAN molecules to destroy the intramolecular interactions between the cyano groups (which cause collapse of the PAN chains).

Lowering the NaSCN concentration to 50–52 wt%, there are viscosity minima for the solutions. IR spectroscopic measurements show a slight bathochromic shift off 2254 cm⁻¹, about 1–2 cm⁻¹, for the nitrile stretching vibration. It is believed to be caused by the collapse of PAN polymers (as shown in Scheme 2b) when the solvent is deteriorated. DLS has affirmed the results by showing up the minimum radius for PAN polymers in aqueous solutions with 52 wt% NaSCN.

In the second regime, corresponding to the lower NaSCN contents of 42–50 wt% in PAN/NaSCN aqueous solutions, the viscosities show up an anomalous increment with the NaSCN contents decreasing. Large coils in PAN dilute aqueous solution with 45 wt% NaSCN as determined by DLS measurement are responsible for the high viscosities of the solutions in this regime. Dynamic frequency and Cox–Merz rule measurements have verified the existing of gel-like structure. The most possible chemical structure responsible for the three-dimensional networks is proposed to be the self-association of the cyano groups, as shown in Scheme 2c.

NaSCN aqueous solution is equivalent to other common solvents for PAN dissolution and spinning, such as DMSO, DMF, N-methyl-2-pyrrolidone (NMP), etc. However, it has attracted less attention than other solvents. The present work takes further step toward a thorough understanding of the rheological behavior of PAN/NaSCN aqueous solutions, which should be helpful to improve the structure and performance of PAN precursor fibers fabricated through wet-spinning.

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