Investigation into the gelation and crystallization of polyacrylonitrile

Lianjiang Tan [a], Huifang Chen [a], Ding Pan [a,*], Ning Pan [b]

[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, People's Republic of China
[b] Biological and Agricultural Engineering Department, University of California, Davis, CA 6561, USA

ARTICLE INFO

ABSTRACT

Polyacrylonitrile (PAN) is soluble in dimethyl sulfoxide (DMSO) and the resulting solution can gel by various mechanisms. The effects of temperature and water on the thermoreversible gelation of PAN have attracted much attention because of their importance in the fiber formation and film casting. Rheological tests were employed in this study to examine the gelation behavior and determine the gel point temperature of PAN–DMSO solution. Calorimetric studies of PAN–DMSO gels were conducted through Differential Scanning Calorimetry and no crystallization was discovered in these gels prepared at low temperature. X-ray diffraction of different PAN gels indicated that in the absence of water, gels resulted from PAN–DMSO solution by decreasing temperature were not crystallizable. In contrast, water-induced gelation led to crystallization of PAN gel. The water content in the formed gel is responsible for its crystallinity and average crystallite size.

1. Introduction

Physical gelation is the process of polymer chain crosslinking which reversibly transforms a polymer solution into a gel. The crosslinks of the network have a physical origin and therefore are sensitive to variations of temperature, PH, stress, etc. The term "physical gel" introduced by De Gennes [1] is often used to imply the thermoreversibility, the case with many such systems.

Polyacrylonitrile (PAN) exhibits thermoreversible gelation in various solutions [2]. The formation mechanisms of PAN gel have been extensively studied. Most commonly, reduced solvency, caused by either temperature reduction or addition of a poorer solvent into an otherwise well dissolved solution can give rise to the gelation of PAN solutions. However, it is still very difficult to fully understand the microscopic gelation behavior of PAN solution, i.e., what acts as the junction points or junction regions of PAN gel. As is well known, the main characteristics of PAN is the presence of a permanent dipole in the monomer unit caused by the bulky CN group with strong polarity. Labudzinska and Ziabicki concluded that the associated strong dipole–dipole forces between the macromolecules in PAN-DMF solution is responsible to formation of somewhat stable junction points and thus to gelation [3]. According to Ziabicki [2] and Beckmann [4], there were no differences between the X-ray diffraction patterns of PAN-DMF solutions and PAN-DMF gels. Other studies, however, reported that gelation was caused by a nucleation process of small crystallites and the junction points of PAN gel network were generated by crystallization [5,6]. Bashir used propylene carbonate (PC) as a solvent for PAN and found the X-ray patterns showed the presence of crystallites in PAN–PC gels [7,8]. These gels are particularly intriguing in that the junctions may be composed of crystallites in which PC is incorporated, i.e., the junctions are not the crystallites of pure PAN, but crystallites of a PAN–PC complex.

Dimethyl sulfoxide (DMSO) is a very popular solvent for PAN, especially in the spinning of PAN precursor fiber. The gelation behavior of PAN–DMSO solution and the possibility of the existence of small crystallites as crosslinking points in PAN–DMSO gel are important, because they affect significantly the process of fiber formation or film casting.

---

* Corresponding author.
  E-mail addresses: dingpan@dhu.edu.cn, tanlianjiang@126.com (D. Pan).
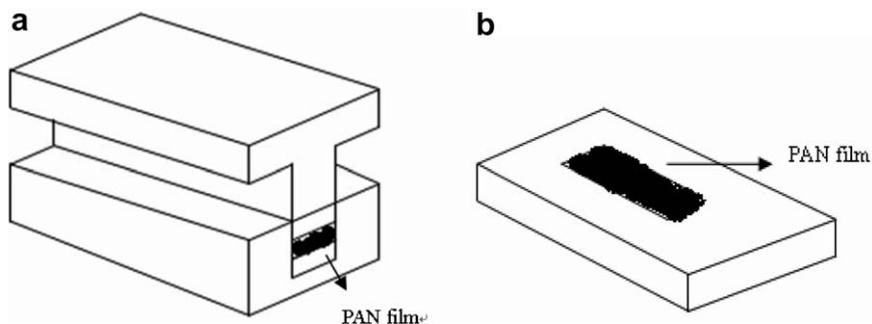
Fig. 1. (a) Schematic diagram of the mould used for making PAN films. (b) Schematic diagram showing the appearance of a PAN film.

The present paper focuses on the thermoreversible gelation of PAN–DMSO solution induced by decreased temperature or addition of nonsolvent (water) as well as the crystallization of PAN in different states (solution, or gels caused by different mechanisms). Concentrated PAN–DMSO solutions and PAN gels were subjected to rheological tests, Differential Scanning Calorimetry (DSC) and X-ray diffraction (XRD). Experimental results revealed the characteristics of gelation and crystallization of PAN.

2. Experimental

2.1. Materials

PAN copolymer (Acrylonitrile:Itaconic acid = 98:2) was polymerized in our laboratory with a viscosity-average molecular weight $\overline{M_\eta} = 7.8 \times 10^4$ g mol^{-1}. DMSO (analytically pure) was purchased from Shanghai Wulian Chemical Industry Co. Ltd., and deionized water was used in the study.

2.2. Preparation of PAN–DMSO solutions and gels

A certain amount of PAN copolymer was dispersed in a three-neck bottle, respectively in DMSO and in a mixture of DMSO and deionized water. The resulting slurry was left swollen at 50 °C for 2 h first, and at 60 °C for another 2 h, while stirred constantly by an electric paddle stirrer. Subsequently, it was stirred again at 70 °C for 6 h to produce a homogeneous viscous solution with 20 wt% PAN. Two such PAN solutions (without and with 4 wt% water) were deaerated in a vacuum drying oven at 70 °C and then kept at this temperature for 18 h before film making for experiments.

A mould (made of PMMA) with a U-shaped lower part and a T-shaped upper part (Fig. 1a) was employed to produce PAN films of 2 cm×1 cm×0.1 cm (Fig. 1b). The resultant films were then cooled in a freeze dryer at −10 °C for 48 h and two sheets of PAN gels were obtained.

The second type of gel sample was prepared by immersing the above-formed PAN film (made from the solution without water) in deionized water at room temperature (25 °C) for 5 min. When removed from the water, it weighed 0.227 g and was translucent (Fig. 2). As soon as the nascent gel was tested by X-ray diffraction, it was placed in a drying oven to facilitate the evaporation of

water in it. After drying for given time, the gel was taken out and weighed 0.093 g. When the gel was finally dried to the constant weight, it stabilized at 0.052 g.

2.3. Rheological measurements

The dynamic rheological measurements were conducted using an advanced Solution and Melt Rotation Rheometer ARES-RFS (TA, US) equipped with two parallel plates. The temperature control was done with a thermostatic bath within ±0.1 °C of the preset value. The parallel plate on which samples (PAN solutions) were placed was 25 mm in diameter and the sample thickness was 2 mm. A thin layer of paraffin oil was applied to protect the sample from dehydration or evaporation and thus minimize the testing errors. Strain scanning at different temperatures in both sol and gel states of the samples and over the oscillation frequencies from 0.1 to 10 Hz to detect the linear viscoelastic region of the samples. 1% was chosen as the set strain amplitude in the tests.

The traces of the storage modulus G' during the cooling and heating processes for the two PAN solutions were studied. The temperature scanning from 70 °C to 38 °C was carried out, immediately followed by a reversed scanning from 38 °C back to 70 °C. Both the cooling rate and the heating rate are 1 °C/min.

Fig. 2. The photograph of PAN nascent gel containing a large amount of water.

A frequency scanning from 100 rad/s to 0.5 rad/s at eight given temperatures (70 °C–42 °C, with interval of 4 °C) was also conducted to detect the gel point temperatures of the two PAN solutions. Then five temperatures corresponding to the sol state, sol–gel transition and gel state were chosen to perform frequency scanning from 100 rad/s to 0.1 rad/s for the solution without water. The storage modulus G', loss modulus G'' and the loss tangent $\tan\delta$ were obtained. Before the test at each temperature, the samples were kept at that temperature for 3 min to eliminate the effect of the thermal history.

2.4. Thermal analysis

Calorimetric studies were carefully conducted using Q-100 differential scanning calorimeter (TA, US) equipped with a thermal analysis data station. 9.6 mg of two PAN gels freshly made at low temperature was placed in a sealed aluminum pan, while an empty aluminum pan was used as a reference. After the gels were maintained at room temperature for 3 min, a heating process from room temperature to 80 °C was performed at the heating rate of 5 °C/min and the DSC traces were recorded. Baseline calibration was done before each test.

2.5. X-ray diffraction (XRD)

To investigate the crystallization as well as to calculate the crystallinity and crystal size of varied PAN samples, X-ray diffraction of either films or powdered specimens was conducted on a D/max-2500PC X-ray diffractometer (Rigaku, Japan) with nickel-filtered Cu Kα radiation. The radial scans on the samples were performed from $2\theta = 5$–$60°$. The data were collected at $0.02°$ intervals with counting for 0.12 s at each step.

The crystallinity was estimated by Eq. (1):

$$W\% = \frac{\sum I_c}{\sum I_a + \sum I_c} \tag{1}$$

where W is the crystallinity; I_c the diffracted intensity of the crystalline region and I_a the diffracted intensity of the amorphous region. The average crystallite size was estimated by the Scherrer equation:

$$L_c = \frac{K\lambda}{\beta cos\theta} \tag{2}$$

where L_c is the average crystal size; β is the full width at half maximum intensity at $2\theta = 17°$; K is the Scherrer constant, here 0.89; and $\lambda = 1.54$ Å is the wavelength of the X-ray used.

3. Results and discussion

3.1. Rheological behavior of PAN–DMSO solution

Thermal-induced gelation is the most common gelation mechanism for PAN solutions. For instance, within a few hours at 0 °C, PAN–DMSO solution will lose its flowability and turn into elastic gel. This PAN gel is thermoreversible, which can be seen from the rheological measurement of the storage modulus G'. The gelation temperature T_{gel} is defined as the temperature at which the polymer solution begins to gel. Among various methods for detecting T_{gel}, rheological tests are convenient and effective [9,10]. It was suggested that the method based on the temperature dependence of the loss tangent $\tan\delta$ at different oscillation frequencies was feasible for determining T_{gel}, i.e., T_{gel} is the temperature at which $\tan\delta$ becomes frequency independent, i.e., all curves at different oscillation frequencies converge at this point [11,12].

Water is a strong cohesive solvent due to the strong intermolecular forces caused by hydrogen bonds. It promotes the aggregation of PAN solution [13] as through forming hydrogen bonds with the solvent molecules, which weakens the interactions between PAN molecular chains and the solvent. The aggregation then produces or causes physical crosslinking initiation points for the system to gel.

Through cooling and heating the two PAN–DMSO solutions, with and without water, the thermoreversibility of PAN gel was observed. In Fig. 3, the storage modulus G' grows with decreased temperature and the sol–gel transition starts below a certain temperature, represented by a rapid growth of G'. When the solutions are heated from a low temperature (gel–sol transition), G' decreases following a trace similar to that when the solutions are cooled. Nevertheless, the storage modulus in this case is slightly
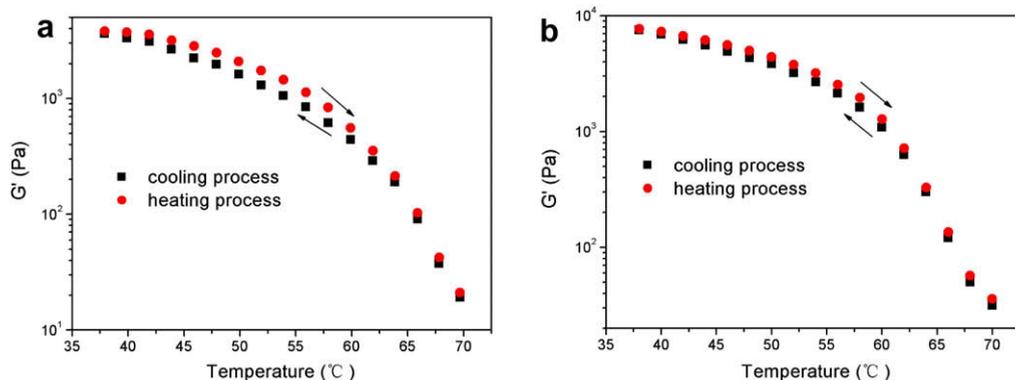
Fig. 3. G' versus temperature in both cooling and heating process for 20 wt% PAN-DMSO solutions: (a) without water and (b) with 4 wt% water.
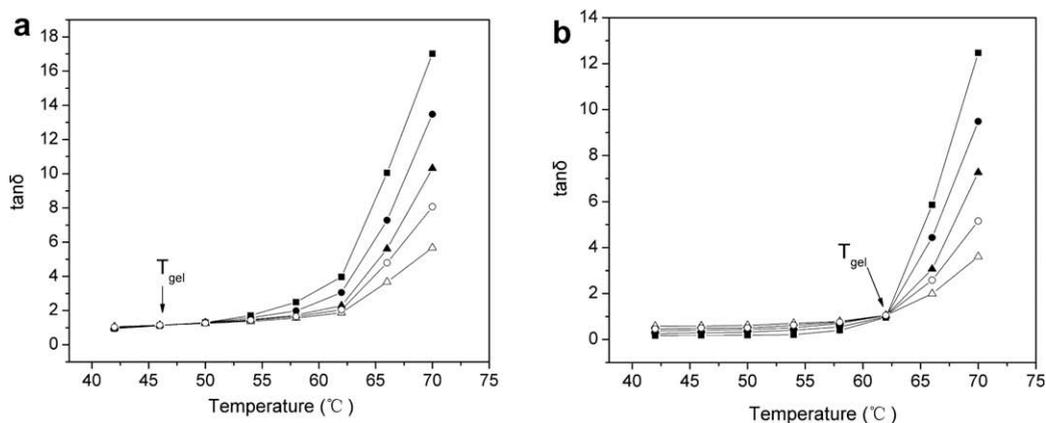
Fig. 4. tan δ versus temperature obtained from the frequency scanning tests for PAN-DMSO solutions: (a) without water and (b) with 4 wt% water at selected oscillation frequencies of ■—0.63 rad/s, ●—2.5 rad/s, ▲—6.3 rad/s, ○—25 rad/s, △—63 rad/s.

larger than that of the cooling process, likely due to the energy difference between the phase change processes, and the addition of water seeming to diminish the difference.

The results of the frequency scanning tests for the two 20 wt% PAN–DMSO solutions are shown in Fig. 4. We can see that the five curves of tan δ at different frequencies cross over at a point, which is considered to be the critical gel point T_{gel}. It is noticeable that the gel point T_{gel} increases, and the loss tangent tan δ decreases when the solution contains water. Water favors the aggregation of PAN molecules in solution so as to promote the thermal-induced gelation of PAN solution. Alternatively, the addition of water worsened the solvency of DMSO and thus facilitated the crosslink of PAN molecular chains for gelation. tan δ is a measure of the viscous/elastic ratio for the solution. At a given temperature, the PAN solution with water exhibits a more gel-like (elastic) behavior and the tan δ is therefore depressed. We also find that the tan δ values are around 1.15 in both cases. According to Eq. (3) [14–16], the n value which characterizes the nature, especially the crosslinking density of gel structure [17–19] is 0.544. Generally, a lower value of n implies the formation of a more elastic gel [20]. Low relaxation exponents n (between 0.1 and 0.25) are characteristic for crystallizing polymers [21]. From the n value of our system, we can expect PAN/DMSO gels with little crystallinity and moderate density of crosslinks.

$$\tan \delta = G''(\omega)/G'(\omega) = tan(n \cdot \pi/2) \qquad (3)$$

Moreover, the gel point T_{gel} of the solution containing 4 wt% water is at 62.6 °C, much higher than that of the solution without water, 46.2 °C. That is, while reducing temperature alone can result in gelation of PAN–DMSO solution, the existence of water however significantly accelerates the thermal-induced gelation. On the other hand, water doesn't change the crosslinking density of PAN/DMSO gel, as the n value implies.

Fig. 5 shows the changes of dynamic moduli with the oscillation frequency at five selected temperatures, for the 20 wt% PAN–DMSO solution without water. In all the five plots, both G′ and G″ fall with decreased frequency.

Of course all materials can behave as either liquid or solid, depending upon the timescale [22]. At high frequencies, the solution behaves more like an elastic solid. By contrast, it gradually becomes viscous fluid when the frequency decreases, as indicated by the reduction in both G′ and G″. In plots (a) and (b) corresponding to temperatures above gel point T_{gel}, the solution is in sol state and the viscous modulus G″ is larger than the elastic modulus G′ over the whole frequency range. G′ and G″ show steeper slopes at lower frequencies. When the temperature reaches 45 °C which is in the vicinity of the gel point, both G′ and G″ become very close regardless of the frequency. The gelation of the solution proceeds when the temperature is further reduced. G′ shows a plateau over low-frequency in Fig. 5e, which seems to signify a lack of viscoelastic relaxation.

The changes of loss tangent tan δ with oscillation frequency for the same solution are depicted in Fig. 6. The value of tan δ increases with temperature, which is even more obvious in the low temperature region. At 45 °C near the gel point T_{gel}, tan δ is almost constant despite the frequency. At the temperatures below 45 °C, the solution becomes more elastic than viscous (tan δ < 1) and a lower temperature is more favorable for gelation because of a greater degree of supercooling. Another phenomenon is that tan δ decreases with increased frequency before the gelation occurs whereas increases as the solution gels. When the solution is in sol state, there is not enough time for the rearrangement of PAN molecules at high frequencies, which makes the solution solid-like. When the solution transforms to a somewhat stable gel, the number of crosslink points reduces as the frequency increases, due to the stronger shearing and more active micro-Brownian motion of PAN molecular chains.

3.2. Thermal behavior of PAN–DMSO gel

As PAN–DMSO gel is thermoreversible, endotherm or exotherm of certain degree is thus expected when the DSC measurement is performed. In general, pure PAN powder does not exhibit a melting endotherm when heated. Instead, an intense exotherm is observed at about 320 °C
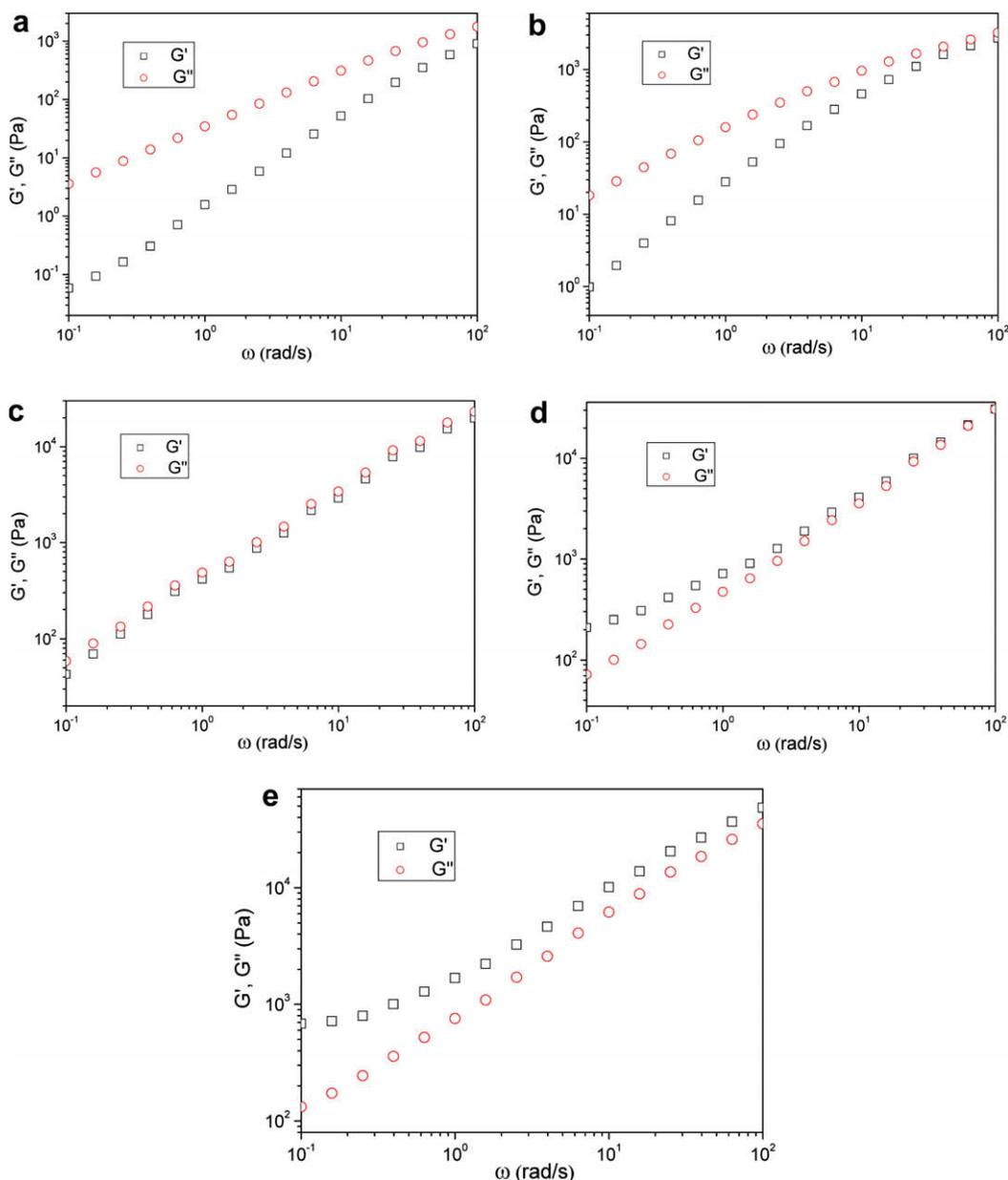
Fig. 5. *G′*, *G″* versus oscillation frequency for the 20 wt% PAN–DMSO solution without water at (a) 65 °C, (b) 55 °C, (c) 45 °C, (d) 30 °C, and (e) 15 °C.

[23]. For PAN–DMSO solution, no obvious exotherms were detected in a cooling process from 70 °C down to room temperature. However, a heating process from room temperature up to 80 °C resulted in an endothermic peak for the two 20 wt% PAN–DMSO gels formed at low temperature.

The thermogram in Fig. 7 shows two DSC curves of the PAN–DMSO gels, each with an endotherm peak. The enthalpy of the endothermic transition can be estimated from the area under the peak. For the PAN–DMSO gel without water, the peak temperature is 55.18 °C and the dissolution (or melting) enthalpy H_{gel} = 0.264 J/g, i.e., H_{PAN} = 1.32 J/g. For the PAN–DMSO

gel with 4 wt% water, they are 57.2 °C and 0.332 J/g (H_{PAN} = 1.651 J/g), respectively. Beevers [24] calculated the heat of fusion per structural unit of a completely crystalline PAN, which is 4.5–4.8 kJ/mol, i.e., 84.9–90.57 J/g. On the assumption that the monomer unit of PAN describes the structure unit of an ideal PAN crystal, and the junctions are crystallites or crystal nuclei, the degree of crystallinity estimated of the PAN–DMSO gel is only less than 2%. It is thus highly possible that the gelation of PAN–DMSO solution is not caused by crystallization, whether there is water in it or not. This can also be verified by the absence of exothermic peak when the solution is cooled.
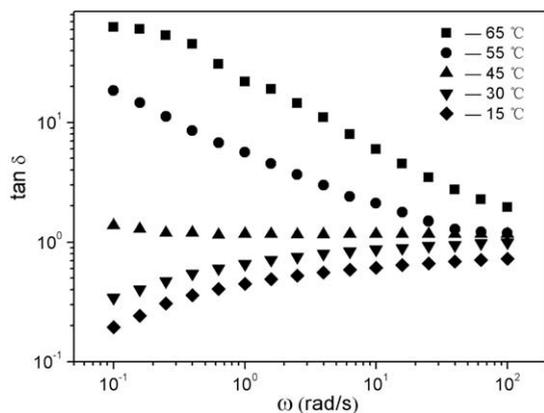
Fig. 6. tan δ versus oscillation frequency for the 20 wt% PAN-DMSO solution without water at the five temperatures.

Fig. 8. X-ray diffractogram of PAN-DMSO gel prepared by cooling PAN-DMSO solution at 25 °C sufficiently.

Fig. 7. DSC thermograms for PAN gels obtained by quenching the 20 wt% PAN-DMSO solutions without water and with 4 wt% water at −10 °C for 48 h.

Liquid–liquid phase separation is one of the gelation mechanisms [8]. In this case, the macroseparation may be hindered by kinetic impediments and only local microseparation is allowed to occur. If the separating phases are connected (e.g. by dipole–dipole force between nitrile groups), a gel is then formed. Water can lead to liquid–liquid phase separation and thus promote the gelation of PAN–DMSO solution. The dissolution enthalpy of the PAN–DMSO gel with 4 wt% water is larger than that of the gel without water, likely due to its relatively higher polydispersity [25]. The dissolution temperature range of the two gels is comparable to their own gel point T_{gel} determined in rheological tests, confirming the thermoreversibility of PAN–DMSO gel. However, though there is significant difference between the gel points of the two solutions, the two gels have similar structure and intermolecular forces, which is concluded from the slight change in the peak temperature.

3.3. X-ray diffraction of PAN gels

The study of the crystal morphology of PAN, in both powder and gel forms, has been the subject of many inves-

tigations [7,26]. Solutions of PAN in some solvents, e.g. dimethyl formamide (DMF), dimethyl acetamide (DMAc) and DMSO can give rise to gel formation. Gelation from these PAN solutions is nonetheless slow and is affected by the presence of water.

Wide-angle X-ray diffractograms were employed to analyze the crystallization of the PAN gels in this study. A 20 wt% PAN–DMSO solution without water was kept at 25 °C (lower than its gel point T_{gel}) for sufficient time until it could not flow when the bottle containing it was turned upside down. Then a piece of this sample was subjected to XRD and the diffractogram is shown in Fig. 8. It is found that only an amorphous peak at about $2\theta = 20°$ exists in the full range of 2θ. Another gel sample prepared from the 20 wt% PAN–DMSO solution with 4 wt% water was also analyzed and the same result was obtained (not shown). The X-ray diffractogram of the PAN–DMSO gel (without water) prepared at even lower temperature is shown in Fig. 9. We can see that this result also shows little evidence of crystallinity. It reveals that initial water content in PAN–DMSO solution exerts no effect on the crystallization of PAN–DMSO gel made from it, though water affects the
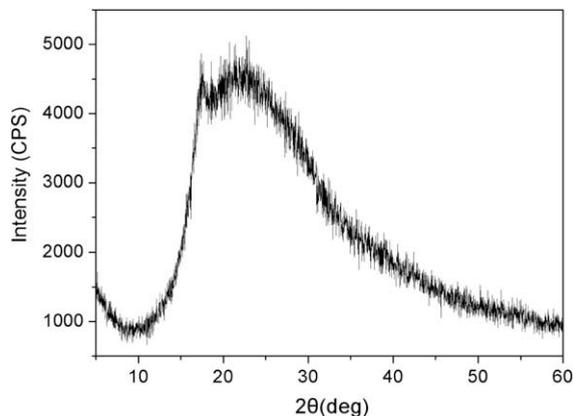
Fig. 9. X-ray diffractogram of PAN-DMSO gel obtained by quenching the 20 wt% PAN-DMSO solution at −10 °C for 48 h.
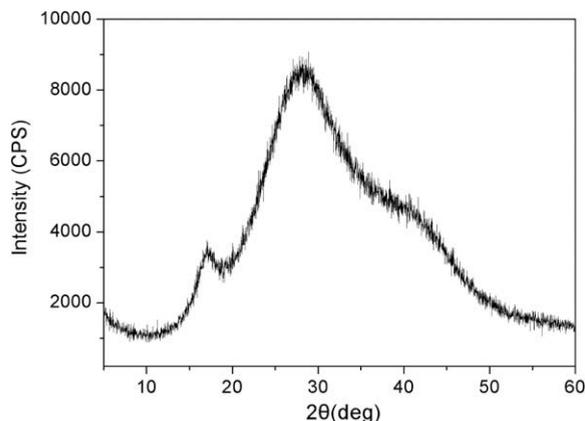
Fig. 10. X-ray diffractogram of PAN nascent gel obtained by coagulating in distilled water.

gelation of PAN–DMSO solution. In addition, temperature alone cannot lead to crystallization, i.e., purely thermal-induced gel has almost no crystallinity.

To investigate the water effect on the crystallization of PAN gel, firstly a nascent gel mentioned in Section 2 was also subjected to X-ray diffraction. In Fig. 10, there is only one relatively obvious crystalline peak at $2\theta = 17.1°$. The crystallinity of this gel is 4.06%, calculated by Eq. (1) after peak fitting. The nascent gel is a water-induced gel in which a large amount of water is trapped (77.1 wt% water). Although crystallization exists, the crystallinity is low, due likely to the presence of water which hinders the molecular chains from packing closely together in a regular array.

Based on the fact that equatorial reflections were found only in diffraction patterns of oriented fibers and single crystals [27–29], most studies have concluded that PAN has only two-dimensional order with no periodicity along the chain axis. PAN is therefore called paracrystalline or laterally ordered polymer. Most commonly, PAN crystals show two diffraction peaks at around 17° and 29°. Some used an orthorhombic lattice to describe the crystal structure of PAN [30,31]. But it turns out to be valid only in the presence of solvent. For dry PAN, the hexagonal lattice is a normal one. Bashir reported that the two diffraction peaks

were indexed as (010) and (300), respectively, on the basis of hexagonal packing of PAN molecules [7,32].

The X-ray diffractograms of water-induced PAN gels are shown in Fig. 11. The gel with a certain amount of water in it shows two peaks centered at $2\theta = 16.88°$ and 25.76°, respectively. The crystallinity is 42.06% and the average crystallite size is 2.99 nm. Whereas the gel with almost no water shows two peaks centered at $2\theta = 16.74°$ and 25.28°, respectively, with the crystallinity 54.81% and the average crystallite size 3.35 nm. It can be seen from these data that the dried PAN gels possess much higher crystallinity than the nascent PAN gel. Both the crystallinity and the average crystallite size grow with decreased water content in the gel. The possible cause is that with the evaporation of water, PAN molecules gradually aggregate and pack regularly to form crystallites. Reduced water in the gel also makes the growth of crystallites easier. Furthermore, the second diffraction peaks of the two PAN gels deviate a lot from 29°, denoting the distortion and irregularity of the crystal structure. Although the gel in our work is dry PAN, the hexagonal lattice model does not fit to its crystallites, which may be caused by factors during the preparation of the gel.

4. Conclusion

The gelation behaviors of 20 wt% PAN–DMSO solutions without and with 4 wt% water were investigated through rheological measurements. The traces of the storage modulus G' in cooling and heating processes indicate the gelation of PAN–DMSO solution thermoreversible. The solution containing water gels at much higher temperature (gel point) than the one without water. The viscoelastic properties of the PAN solution at selected temperatures during a frequency scanning were also involved to further study the characteristics of gelation. DSC thermograms of the two PAN–DMSO gels indicated that temperature alone is not enough to cause crystallization in the gel, and gelation may be resulted from liquid–liquid phase separation. The result of X-ray diffraction agreed well with that of the rheological measurements and the thermal analysis in the respect of the impossibility of crystallization in purely thermal-induced PAN gel. Besides, water-induced PAN gel
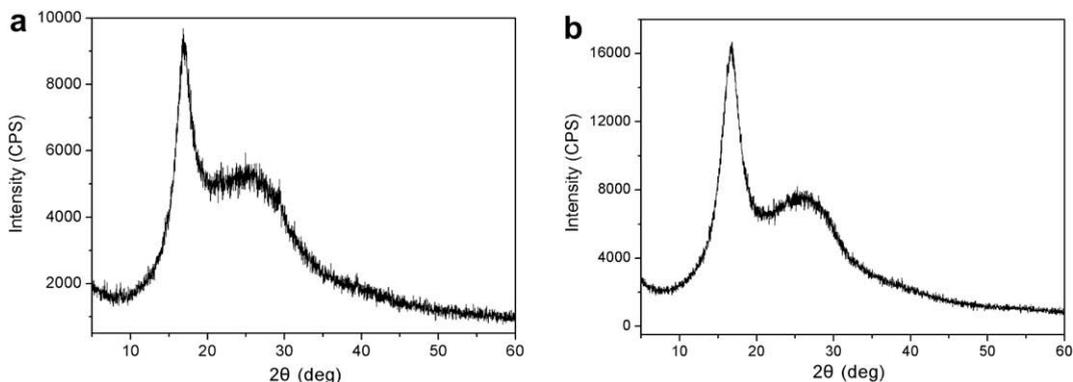
Fig. 11. X-ray diffractograms of PAN gels: (a) containing 44 wt% water and (b) dried to constant weight.

indeed induces crystallization, and the crystallinity and average crystallite size increase with decreased water content in the gel. The crystal structure of dried PAN gel in our work is distorted and cannot be described by hexagonal lattice.

Acknowledgement

References

[1] De Gennes PG. Scaling concepts in polymer physics. NY: Cornell University Press; 1985.
[2] Klaas te Nijenhuis. Adv Polym Sci 1997;130:96–105.
[3] Labudzinska A, Ziabicki A. Kolloid Z 1971;21:243.
[4] Beckmann J, Zenke D. Colloid Polym Sci 1993;271:436–45.
[5] Flodin P. Macromol Chem Macromol Symp 1988;22:253.
[6] Bisschops J. J Polym Sci 1955;12:583.
[7] Bashir Z. Polymer 1992;33(30):4304–13.
[8] Bashir Z. J Polym Sci Polym Phys 1992;30:1299–304.
[9] Sugimoto M, Hida H, Taniguchi T, Koyama K, Aoki Y. Rheol Acta 2007;46:957–64.
[10] Yamaguchi M. J Polym Sci Polym Phys 2001;39:228–35.
[11] Winter HH, Morganelli P, Chambon F. Macromolecules 1988;21:532.
[12] Madbouly SA, Otaigbe JU. Macromolecules 2005;38:10178–84.
[13] Piculell L, Thuresson K, Lindman B. Polym Adv Technol 2001;12: 44–69.
[14] Winter HH, Chambon F. J Rheol 1986;30(2):367–82.
[15] Lue A, Zhang L. J Phys Chem B 2008;112:4488–95.
[16] Cho J, Heuzey M-C. Colloid Polym Sci 2008;286:427–34.
[17] Gao S, Nishinary K. Biomacromolecules 2004;5:175–85.
[18] Nordby MH, Kjoniksen A-L, Nystrom B, Roots J. Biomacromolecules 2003;4:337–43.
[19] Kjoniksen A-L, Hiorth M, Roots J, Nystrom B. J Phys Chem B 2003;107: 6324–8.
[20] Gao S, Nishinari K. Biomacromolecules 2004;5:175–85.
[21] Winter HH, Mours M. Adv Polym Sci 1997;134:165–234.
[22] Kavanagh GM, Ross-Murphy SB. Prog Polym Sci 1998;23:533–62.
[23] Grassie N, McGuchan R. Eur Polym J 1971;7:1091.
[24] Beevers RB. Macromol Rev 1968;3:1968.
[25] Ohta Y, Murase H, Sugiyama H, Yasuda H. Polym Eng Sci 2000;40(11): 2414–22.
[26] Allen RA, Ward IM, Bashir Z. Polymer 1994;35(10):2063–71.
[27] Bohn CR, Schaefgen JR, Statton WOJ. Polym Sci 1961;55:531.
[28] Klement JJ, Geil PHJ. Polym Sci 1968;6:138.
[29] Jin-Shy Tsai, Chung-Hua Lin. J Appl Polym Sci 1991;42:3039.
[30] Yamazaki H, Kajita S, Kamide K. Polym J 1987;19:995.
[31] Colvin BG, Storr P. Eur Polym J 1974;10:337.
[32] Bashir Z, Atureliya SK, Church SP. J Mater Sci 1993;28:2730.