

Viscoelastic Properties for Physical Gelation of Polyacrylonitrile Solution induced by Freezing – Thawing Method

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Polyacrylonitrile (PAN) gel was prepared by the freezing and thawing method using the solvents of *N,N*-dimethylacetamide (DMA) and tetramethylene sulfone(sulfolane). The gelation time after a series of freezing and thawing was examined with varying PAN concentration of DMA solution and the freezing time. Dynamic viscoelasticity was measured in the course of gelation for DMA solution to observe the intermediate state called as the critical gel. Double endothermic peaks appeared in the heating DSC scans for gels prepared from sulfolane solutions.

Key words: polyacrylonitrile, dimethylacetamid, tetramethylene sulfone, gelation, freezing and thawing, viscoelasticity

1. INTRODUCTION

Polyacrylonitrile(PAN) and related copolymers have wide practical application.[1] In the industrial process PAN is well dissolved in good solvent, and then, goes through the injection moulding process with a nonsolvent to give spun manufactures. PAN solution forms gel in the coagulation bath during the spinning process. It is of interest to grasp the gelation of PAN solution extensively. Although, it is a well-known fact that PAN solution exhibit gelation for several solvents, there is hardly any research works for gels synthesized using freezing-thawing method. That is, a gel can be obtained when the PAN solution is left undisturbed, which is called as an ageing process in this experiment, after a series of freezing and thawing. Gelation by freezing and thawing takes place for limited solvents. Gels formed turn reversibly to sols by heating, therefore, it is a physical gel. The time of the ageing process required for gelation depends on the freezing temperature, freezing time, the cycles of freezing-thawing, ageing temperature, etc. The elasticity of the resultant gel is also influenced by these factors.

Although we have presented dynamic viscoelasticity data for the solution of PAN and *N,N*-dimethylacetamide in the previous paper, the experimental results were insufficient.[2] The main problem was in the freezing process of around -60°C which was unstable for the long time ~20h. Because of the unstable freezing process, the reproducibility was low, and reinvestigations have been desired. In addition, the effect of concentration on gelation in the freezing-thawing method is not explored. Conversely, it was successfully found in the previous paper that the long ageing time required for gelation is suitable to the viscoelastic measurement during sol-gel transition. The long gelation time effectively decouples the

frequency dependence and time dependence of the fluid properties, which enables us to obtain the complex moduli of G' and G'' with a conventional frequency sweep technique as the system structure evolves.

In this work, we attempted to improve experimental conditions. Also, the solution of slightly higher concentration was prepared to match rheological measurements.

2. EXPERIMENTAL

Polyacrylonitrile powdered sample, prepared by dispersion polymerisation, was supplied by Mitsubishi Rayon Co., Ltd. The viscosity average molecular weight was determined to be $\bar{M}=1.3 \times 10^5$ using the following equation.

$$[\eta] = 3.35 \times 10^{-4} \times \bar{M}^{0.72} \quad (1)$$

N,N-dimethylacetamide(DMA)and tetramethylene sulfone(sulfolane) were purchased from Nacal tesque, Inc. and Sigma-Aldrich, respectively.

Dynamic viscoelasticity data was acquired by dynamic rheometer of ARES 100FRT-FRTN1 (Rheometric Scientific) which is equipped with two force transducers allowing the torque measurement to range from 0.004 to 100gmcm. The geometry utilised is the parallel plates of 40mm. The shear storage modulus(G') and loss modulus(G'') were measured as a function of the angular frequency(ω) at a constant temperature of 25°C. For each frequency sweep test, a suitable shear amplitude, γ , was used to keep the linear viscoelasticity regime. The parallel plates were weighed before and after the measurement to estimate the evaporation of DMA. As a result, around 1–8% of DMA decreased during the measurement as long as 56h.

DSC heating scans were conducted with SEIKO DSC200, the module was slightly modified to enable the scanning of the large DSC cup. Aluminium sample cups of 70 μ L were used. The gel sample was cut to be contained

in the cup; the weight of the sample was ranged from 50 to 82mg. DMA and sulfolane have freezing points of -20 and 27.5°C respectively. In fact, very large endothermic peaks appear in -27 and 11°C for gel samples of DMA and sulfolane, respectively, in the heating scan. On the contrary, a small broad peak can be observed in response to the melting of gel.

The preparation of the solution of low concentration ($c < \text{c.a.} 3\%$) is straightforward, however, that of high concentration ($c > \text{c.a.} 10\%$) is a little complicated. At first, PAN powder was slurried with an appropriate amount of DMA by stirring at room temperature, which was then heated to 100°C using an oil bath 30min to turn to a homogeneous solution. Afterwards, the sample was kept in a water bath of 25°C 5min, and soaked into a cool methanol bath of -50°C for freezing. The freezing time (t_F) of the sample is the period of soaking in methanol. After a given t_F , the sample was moved to a water bath of 25°C , 5min to thaw. The measurement of ageing time (t_A) starts with the end of this 5min thawing. The length of time for the solution to reach from 25 to -50°C in freezing was 13min, and that to reach from -50 to 25°C in thawing was 3min.

In the viscoelastic measurement, the sample was transferred after the 5min thawing to the parallel plates cell of 25°C . The viscoelastic measurement was carried out as a function of t_A . The solution in freezing is opaque while it is transparent after it thaws.

3. RESULTS AND DISCUSSION

Sol-Gel Transition of PAN Solution

The time of ageing process required for gelation was measured by the inverse test tube method for 15 and 16% PAN solution of various freezing time. The test tube containing the sample solution was kept in the bath of 25°C after it thawed, and turned inversely to observe gelation in every 2 hours. The inner diameter of the test tube is 12mm. Figure 1 shows the relation of freezing time (t_F) and the ageing time required for gelation. t_F required for gelation differ approximately 10 times between 15% and 16% solutions. The longer freezing time presumably results in the larger error bar appeared in the plot of 15% solution. Large fluctuations are conceivable in the size and rigidity of junctions for such a long freezing. Alternatively, the experimental condition used in this study might still not be enough to give a stable cooling temperature. When the solution was frozen more than c.a. 200h, the solution already gelled at the time of thawing.

The ageing time of gelation decreased linearly with t_F for 16% solution. As for solutions higher than the concentration of 17%, they already gelled at the time of thawing with the freezing of only 30min. Further, the solutions higher than 22% gelled even without freezing.

DSC scans were carried out to acquire the

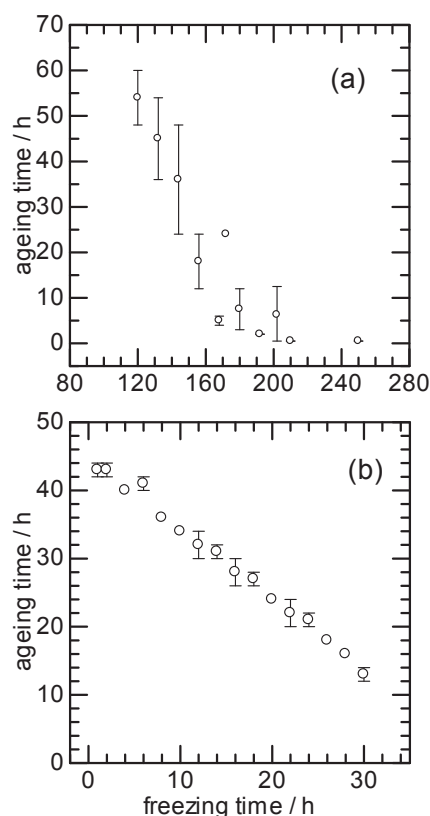


Figure 1. The relationship between freezing time and ageing time for gelation of (a) 15%, (b) 16%, PAN-DMA solution, determined by the inverse test tube method

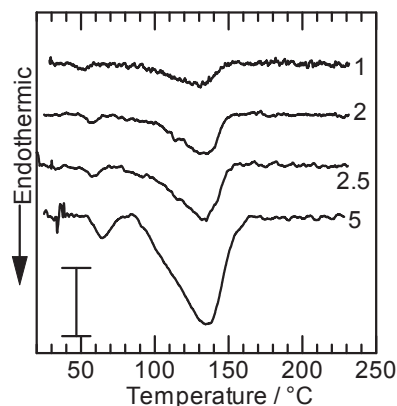


Figure 2. DSC curves of various heating rates for 30% PAN-sulfolane gels. Numbers denote the heating rates in $^{\circ}\text{C}/\text{min}$. The vertical bar inside the figure shows the heatflow of $400\mu\text{W}$.

data of network formation. Neither the heating nor the cooling scan showed peaks in DSC data for gels of DMA in the concentration of 20–25%. However, obvious peaks appeared in the heating scans for gels of sulfolane. The gelation behaviour for sulfolane solutions depends on the concentration like DMA solutions; that is, low concentration solution gels as it experiences the freezing and thawing while the solution of high

concentration, $c \geq c.a.15\%$, gels without the freezing and thawing.

Figure 2 shows the results of heating DSC scans of various rates for 30% gels of sulfolane. A broad peak appeared in the temperature range from 80 to 170°C, which corresponded with the heat of melting of $\Delta H=4.1\text{J/g}$, almost independent of the heating rate. The peak temperature shifts little as the decrease in scan rate, which is in consistent with other gel samples seen in literature.[3,4]

Sub-DSC peaks can be found around 60°C. The pioneering works have already been reported concerning DSC data of PAN gels; where double peaks are seen for gels of propylene carbonate. [5,6] The DSC peaks were assigned with crystallisation and melting in the report of Bashir. However, an obvious crystalline formation was not reported in the recent research works using SAXS for gels of mixed solvents of DMSO and water.[7] We cannot give the plain comparison between these data because of the difference in solvents of gel samples.

The result of no DSC peak found for gel of DMA might be interpretable taking account of the boiling point of solvents; they are 165°C and 285°C for DMA and sulfolane, respectively. If the temperature of gel melting is higher than 165 °C, it would account for the result of no DSC peak in the gel of DMA.

Dynamic Viscoelasticity of Sol-Gel Transition

Viscoelastic measurement was carried out for the solution of 16% right after the thawing to observe how the freezing process affects DMA solution (see Figure 3). The samples were frozen for 0–4h, $t_F=0$ means no freezing, and brought back to water bath of 25°C; right after they thawed, the samples were transferred to the parallel plates.

G' was double logarithmically plotted against ω in Figure 3. The acquired data almost follow liquidlike behaviour of $G'(\omega) \sim \omega^2$ as $\omega \rightarrow 0$, which is often called as the terminal flow. The frequency range where it appears shifts to lower side as the increase in t_F , showing the effect of freezing, and thus the evolution of sol-gel transition. Few examples can be found in the literatures for the relation between the evolution of gelation and the frequency shift of terminal flow.[8-11] However, these few papers give us interesting information concerning the viscoelastic properties and the growth of network formation, in particular, the increase in the extent of bifurcation.

It can be said that the frequency shift appeared in Figure 3 shows the increase in the extent of bifurcation which comes from the junction formation by PAN chain. The longer t_F is, the more accelerates the junction formation. The number of junctions increases rapidly during thawing; as a result, it enhances the extent of bifurcation. The extent of bifurcation can be estimated by the steady state compliance (J_{pol})

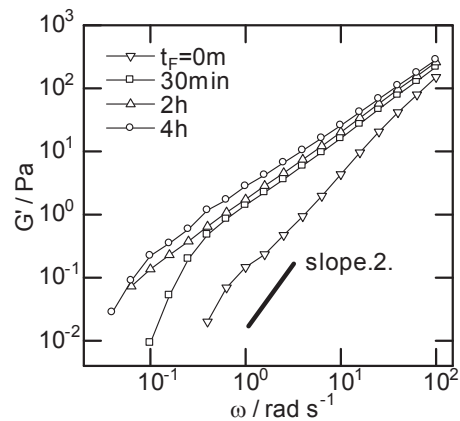


Figure 3. Storage modulus(G') of 16%PAN–DMA solution right after the thawing process. The freezing times of samples are shown inside the figure.

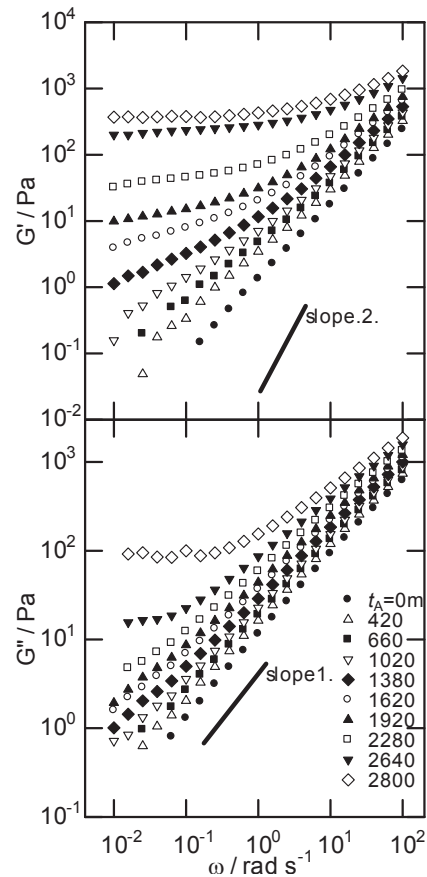


Figure 4 Storage modulus G' and loss modulus G'' of DMA solution of $t_F=3\text{h}$ as a function of angular frequency ω for various ageing times (t_A) as indicated.

written in eq.(2).[11] η_s is the viscosity of DMA.

$$J_{pol} = \left(\frac{G' / \omega^2}{((G'' / \omega) - \eta_s)^2} \right)_{\omega \rightarrow 0} \quad (2)$$

Values of $J_{pol} = 0.020\text{--}0.30\text{Pa}^{-1}$ could be obtained. They increased with t_F , showing that the bifurcation was enhanced as the freezing time was extended.

G' and G'' data were acquired in the course of the ageing process for DMA solutions of various t_F . The viscoelastic behaviour varied with the increase in t_A . The data were shown in Figure 4 as the double logarithmic plot for the solution of $t_F=3h$, which is liquidlike at $t_A=0h$ as shown by the following relations.

$$G'(\omega) \sim \omega^2, G''(\omega) \sim \omega \text{ as } \omega \rightarrow 0 \quad (3)$$

The deviation from this relations becomes significant as the gelation progresses. The slopes of both G' vs ω and G'' vs ω plots in lower frequency region decreased with the increase in t_A . They would take a common value at a given t_A . The slope of G' vs ω plot in lower frequency region decreased further and reached to 0, which is often called as plateau modulus and related with the solidlike behaviour. Also plateau value can be observed for G'' of $t_A=2800\text{min}$. Therefore, the liquid – solid transition took place during the course of time and the power law behaviour of $G'(\omega)$, $G''(\omega) \sim \omega^n$ could be observed. The fact of $G'(\omega)$, $G''(\omega) \sim \omega^n$ is also confirmed by constructing the plot of $\tan\delta$ vs ω for DMA solution of $t_F=3h$, which ensures the frequency independence of the loss tangent at $t_A=660\text{m}$. (see Figure 5.) The similar viscoelastic behaviour was observed for DMA solutions of different freezing time.

The data of $G'(\omega)$, $G''(\omega) \sim \omega^n$ reflect the transient structure which is called as the critical gel (the polymer at the gel point).[12] It is of interest that $\tan\delta$ at the critical gel is larger than one; in other words, G'' is larger than G' at gel point. It attracts great attention from a rheological point of view whether or not the gel flows by its own weight at this instance, which is one of the future works. t_A of gelation determined by the inverse test tube method described above might mean the gel sample which has already passed through the critical gel.

The relaxation index, n was determined to be 0.85, almost independent of t_F . n relates the geometry of network and its strength at the gel point.[12] Many research works already reported n value for different gels.[12-15] The value of $n=0.85$ obtained in this work is relatively large in comparison with other polymer. That is, the intermediate state of PAN–DMA gel is more liquidlike one.

We have to look back the result that n was independent of t_F . It is shown from Figure 3 that, the junctions at the time of the end of thawing increases as the increase in t_F . However, t_F doesn't influences the strength of the network at the gel point. Although the increase in t_F gains the speed of junction formation, and hence the speed of network formation, its viscoelastic properties will not be influenced by t_F . It is not clear what happens molecularly while the solution is frozen, for the motion of PAN molecule must be lost while freezing.

As a speculation, the thawing process plants the seeds which causes the junction formation in the ageing process. The junction formation is

so slow for the short t_F that the increases in both G' and G'' are discernible. It is necessary to clarify experimentally these speculations.

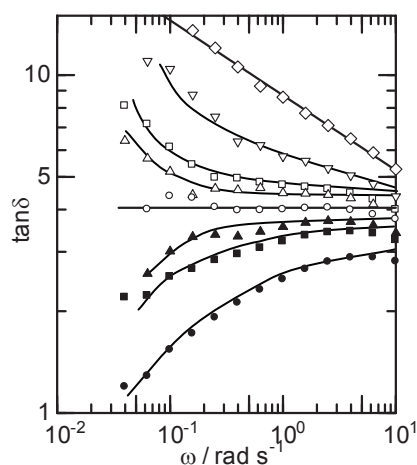


Figure 5. The loss tangent ($\tan\delta$) versus frequency at different ageing time (t_A) for DMA solution of $t_F=3h$. Different symbols depict t_A in min.: 0(\diamond), 180(∇), 420(\square), 540(\triangle), 660(\circ), 720(\blacktriangle), 1020(\blacksquare), 1380(\bullet). The estimated t_A of gelation is 660m(\circ).

REFERENCES

- [1] Acrylic Fiber Technology and Applications; ed. by J. C. Masson, Marcel Dekker, NY1995.
- [2] M. Yasuhara, Y. Tanaka, S. Saeki, Trans. Mat. Res. Soc. Jpn., 26(2), 593-596(2001)
- [3] Frederick P. Schwarz, Thermochimica Acta, 177, 285-303(1991)
- [4] E. Miyoshi, T. Takaya, K. Nishinari, Food Hydrocolloids, 8(6), 529-542(1994)
- [5] Z. Bashir, J. Mat. Sci. Lett. 12, 598 (1993)
- [6] Moon Bae Ko, Ick Hwan Kwon, Won Ho Jo, Tae Won Son, J. Polym. Sci., Part B: Polym. Phys., 32(5), 945-951 (1994)
- [7] S. Nakano, N. Tomita, G. Matsuba, Sen'i Gakkaishi, 69(7), P210-P215(2013)
- [8] E. Nicol, T. Nicolai, D. Durand, Macromolecules, 34, 5205-5214(2001)
- [9] J. H. Lee, L. J. Fetters, L. A. Archer, Macromolecules, 38, 10763(2005)
- [10] D. R. Daniels, T. C. B. McLeish, B. J. Crosby, R. N. Young, C. M. Fernyhough, Macromolecules, 34, 7025(2001)
- [11] H. Watanabe, K. Osaki, M. Kakiuchi, Y. Aoki, Macromolecules, 34, 666-670(2001)
- [12] H. H. Winter, Progr. Colloid Polym. Science, 75, 104-110(1987)
- [13] Geraldo Hidalgo, Llinas; S. H. Dong, Daniel T. Mallin, Marvin D. Rausch; Y. G. Lin, H. H. Winter, James C. W. Chien, Macromolecules, 25(4), 1242-1253(1992)
- [14] Y. Tanaka(2012) Viscoelastic Properties for Sol-Gel Transition, Rheology, J. D. Vicente(Ed.), InTech, Available from: <http://www.intechopen.com/books/rheology/viscoelastic-behaviour-for-gelation>
- [15] L. Li, Y. Aoki, Macromolecules, 30, 7835-7841(1997)

(Received March 27, 2014; Accepted May 15, 2014)