

Viscoelastic Properties of Polyacrylonitrile Solution in *N,N*-Dimethylacetamide in the Sol-Gel Transition Region

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Dynamic viscoelastic properties were studied for polyacrylonitrile solution in dimethylacetamide in the process of sol-gel transition. Gel was prepared using freezing and thawing method; the solution was frozen at -50°C and then kept at 25°C so as to undergo gelation. The longer the freezing time was, the shorter the time to occur for gelation became. Loss tangent was ascertained to be independent of the frequency at the sol-gel transition point. The strength of the network, *S* and critical exponent *n* at the transition point were evaluated. The *S* value was ascertained to be invariable in spite of the variation of freezing time when the concentration of the solution was constant.

Key words: polyacrylonitrile, freezing and thawing, sol-gel transition, power law, viscoelasticity

1. INTRODUCTION

Polyacrylonitrile solutions in various solvents exhibit gelation. This phenomenon was a disadvantage for the traditional fiber solution in spinning process. However, in recent years, solvents have been sought for gel spinning of acrylonitrile[1]. From these background the gelation behaviors of polyacrylonitrile solution have been the subject of current study. Among them, the viscoelastic behavior of polyacrylonitrile gels has been investigated by only a few studies[2]. The viscoelastic properties of the nowadays so important gels of polyacrylonitrile and propylene carbonate has not yet been studied and hence this may be a fruitful area.

Concerning the viscoelastic properties in the process of sol-gel transition, several scaling laws are proposed and experimentally examined for various gelling systems[3]. The limiting behavior is of interest in studying the viscoelastic properties near sol-gel transition region. Winter et. al. have presented important researches to this area and gave an interpretation on the frequency dependence of dynamic viscoelasticity at the gel point[4-6]. They first experimentally found a power law of $G'(\omega)=G''(\omega)\sim\omega^{1/2}$ at the gel point and later it was generalized for gelling systems[7]. The material parameters were proposed as *S*, the strength of the network at the gel point, and relaxation exponent, *n*. There are some contradictions with several observations for viscoelastic materials; for example, a single material constant is the only adjustable parameter, while viscoelastic liquids or solids require a relaxation time spectrum. Nevertheless, they are the only parameters that characterize the linear viscoelastic properties. *S* is related with the complex modulus, $G^*(\omega)$ at the gel point with,

$$G^*(\omega)=S \cdot \Gamma(1-n) \cdot (i\omega)^n \quad (1)$$

where $\Gamma(n)$ is the usual gamma function[8]. The

exponent, *n*, may adopt values between 0 and 1.

Recently Aoki et. al. have presented a series of studies for the gelling system of Poly(vinyl chloride) in bis(2-ethylhexyl) phthalate and showed clear data which verified experimentally the validity of the power laws[9,10].

In order to ascertain the power law of complex modulus and angular frequency, we wanted to obtain the viscoelastic data during the process of gelation for polymer solution. There is an experimental difficulty that is essential for dynamic viscoelastic measurement of lower frequency, that is, to measure stress and strain of the gelling solution is difficult in the stationary state in the case that the change in the state is remarkable. Gelation of polyacrylonitrile solution is preferable to circumvent the above-mentioned situation since the solution forms a gel spending very long time by the freezing and thawing method[11]. The solution turned into solid-like one 30 hours after it was heated to 25°C in the preliminary test of our own, using U-tube method[12]. The time is 2000sec for measuring the viscoelasticity of low frequency around 0.01 rad/sec, which is short comparing with the spending time for gelation of the solution and it can be considered to be in its stationary state. The obtained viscoelastic data were interpreted according to the power law presented by eq.(1).

2. EXPERIMENTAL

2.1 Sample preparation

Polyacrylonitrile(PAN) was kindly supplied from Mitsubishi Rayon Co., Ltd., and used without further purification. The viscosity average molecular weight was reported to be 1.3×10^5 . Dimethylacetamide(DMA) was purchased from Nacalai. inc., and dehydrated. PAN solutions were prepared by heating the mixture of powdered PAN and DMA above 120°C. The weight percent concentration of the solution was 14%. After

the solution was prepared it was soaked to a bath of -50°C for various hours, then poured into a measurement cell. Freezing time, the length while a solution was frozen is noted as t_F hereafter. t_F varied from 2 to 35h.

2.2 Dynamic viscoelasticity measurements

The PAN/DMA solution was transferred into the dynamic rheometer of ARES 100-FRTN1, Rheometric Scientific (the torque range is 0.004 ~100gcm). The Couette Cell was used for the dynamic viscoelasticity measurement, which geometry is 32mm in inner diameter and 34mm in outer diameter. The experimental temperature was 25°C . Aging time, the time passed after the sample was heated to 25°C was noted as t_A . Prior to the measurement a suitable shear amplitude was determined by measuring the strain dependence of moduli to ensure the linearity of dynamic viscoelasticity.

3. RESULTS AND DISCUSSION

The storage moduli, G' , and loss moduli, G'' , were measured for unfrozen solution as a function of angular frequency, which results were found to follow such a liquidlike one as;

$$G'(\omega) \propto \omega^2, \quad G''(\omega) \propto \omega \quad (\omega \rightarrow 0). \quad (2)$$

The viscoelastic behavior of frozen solution varied with the proceeding of t_A ; for example, the solution of $t_F=8\text{h}$ was liquidlike at $t_A=30\text{min}$ as shown by eq.(2), while the deviation from this relations becomes more pro-

nounced with the course of time. The frequency dependence of G' and G'' of the solutions of $t_F=8\text{h}$ and 20h are shown in Figs.1 and 2 on the log-log scale at various t_A values. The data in Figs. 1 and 2 were shifted along horizontal axes by shift factors B to avoid overlapping. The slopes of both G' vs. ω and G'' vs. ω plots in lower frequency region decreased with the increase in t_A . We could see from Figs.1 and 2 that the slopes of G' and G'' would take a common value at a given t_A value. The slope of the G' vs. ω plot in lower frequency region decreased further and reached to 0, showing the appearance of frequency independent modulus which is related with the behavior of solid sample. Therefore, the liquid - solid transition took place during the course of time and the power law behavior of $G'(\omega)$, $G''(\omega) \sim \omega^n$ could be observed. G' value in higher frequency region remained almost constant with the increase in t_A , showing the relaxation strength didn't vary in the process. The similar viscoelastic behavior was observed for PAN/DMA solutions of different freezing time.

The following equation has been shown as the expression of power law, which indicates that loss tangent is independent of frequency when gelation occurs[13].

$$G'(\omega) = G''(\omega) / \tan\delta = S \cdot \omega^n \cdot \Gamma(1-n) \cdot \cos\delta. \quad (3)$$

The phase angle δ between stress and strain is indepen-

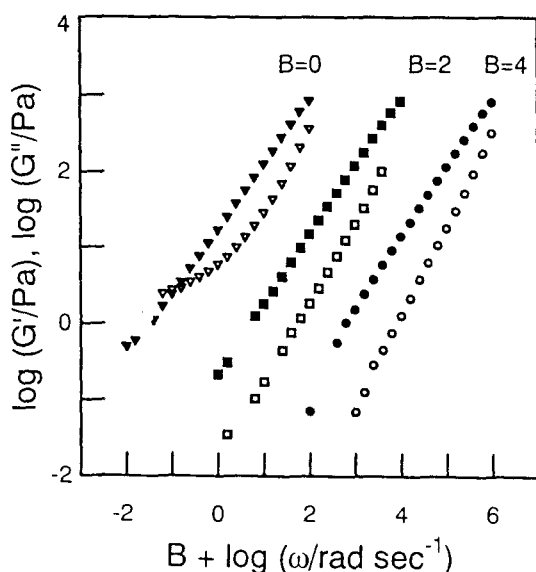


Fig. 1. G' (open symbols) and G'' (filled symbols) for 14% PAN/DMA solution($t_F=8\text{h}$) plotted as a function of angular frequency ω at various t_A described below. The data are shifted along horizontal axes by shift factors B to avoid overlapping.

t_A / min	1560	1830	2190
symbols	○	□	▽

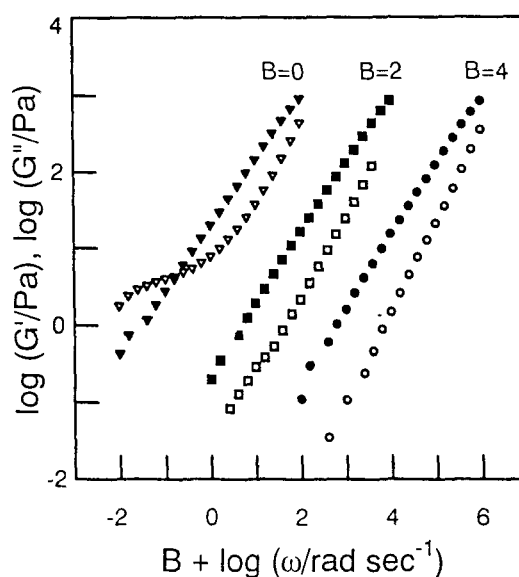


Fig. 2. G' (open symbols) and G'' (filled symbols) for 14% PAN/DMA solution($t_F=20\text{h}$) plotted as a function of angular frequency ω at various t_A described below. The data are shifted along horizontal axes by shift factors B to avoid overlapping.

t_A / min	480	840	1020
symbols	○	□	▽

dent of frequency but proportional to the relaxation exponent.

$$\delta = n\pi/2.$$

Since the phase angle varies from 0 to $\pi/2$ as n takes a value between 0 and 1, n measures the rheological distance from a complete elastic solid to a complete viscous solid. Earlier pioneering studies presented a plot of $\tan\delta$ vs. the parameter which governs the gelation process for different frequencies so as to show $\tan\delta$ was independent of frequency[9,10,13,14]. Values of $\tan\delta$ were plotted against aging time in Fig.3 and 4 for PAN/DMA solutions with $t_F=2$ and 8h, respectively. All curves in each figure pass through a common point at a certain aging time, which determines the gel point t_{A_g} . The appearance of the common point is consistent with eq.(3). The occurrence of the frequency independent $\tan\delta$ during sol-gel transition was observed for other solutions with different t_F . The relaxation exponent was determined from $\tan\delta$ and summarized in Table I together with t_{A_g} . In spite of different t_F , values of n were found to be almost constant and consistent with gelation theory that predicts the exponent to be between 0 and 1. Although we don't understand the whole meaning of the exponent as of the present, the explanation about it among the gels of different chemical species is expected by further researches of our own. A number of studies have been reported to determine the exponents for both chemical gels and physical gels. It was also experimentally found that increasing the cross-linking density led to a reduction of n in the case of chemical gels especially in end-linked polymers[13,14].

We attempted to evaluate S value. S has a complicated dimension of Pa s^n , which was said to be

Table I Gelation time, t_{A_g} , gel strength, S and critical exponent, n for 14% PAN/DMA solutions treated with various freezing time.

t_F/h	t_{A_g}/min	$S/\text{Pa s}^n$	n
2	2252	2.8	0.86
8	2045	2.4	0.87
14	1162	3.2	0.87
20	896	2.5	0.87
35	650	2.2	0.89

composed of a material characteristic modulus and a time. An explanation was given on the meaning of S with the expression, $S = G(t) \times t^n$, $G(t)$ is the shear relaxation modulus. When $n=0$, S equals the elastic modulus, that describes the rigidity of the system, while S represents the viscosity for $n=1$ [9]. Eq.(3) suggests the existence of a crossover between G' and $G'' / \tan(\pi n/2)$ at the gel point. Therefore, the value of G' at the gel point should be obtained by plotting G' and $G'' / \tan(\pi n/2)$ as a function of aging time for different frequencies, and then S would be easily calculated. An example of this kind of plot is shown in Fig.5 for PAN/DMA solution with $t_F=2h$. Each crossover point appeared at the same t_{A_g} , which agreed with t_{A_g} determined from the $\tan\delta$ vs. aging time plot, as indicated by dashed line in Fig.5. Values of S for different frequencies were evaluated using eq.(3) and confirmed, within the experimental errors, not to depend on crossover point used. We choose to adopt an averaged value from the six points as S to avoid any unreliability following the earlier studies[9]. S values were obtained for solutions with other t_F and summarized in

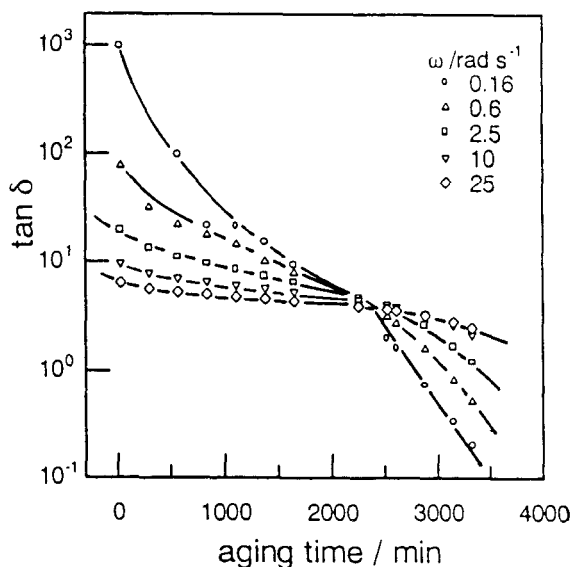


Fig. 3. Loss tangent plotted as a function of aging time at various frequencies, ω for 14% PAN/DMA solution frozen for 2hours.

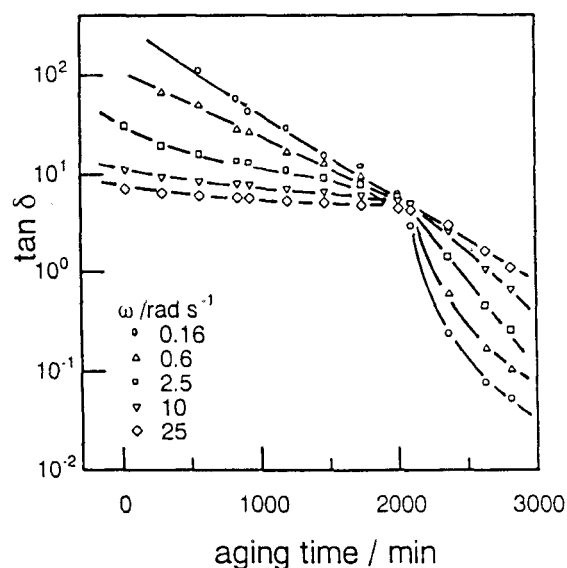


Fig. 4. Loss tangent plotted as a function of aging time at various frequencies, ω for 14% PAN/DMA solution frozen for 8hours.

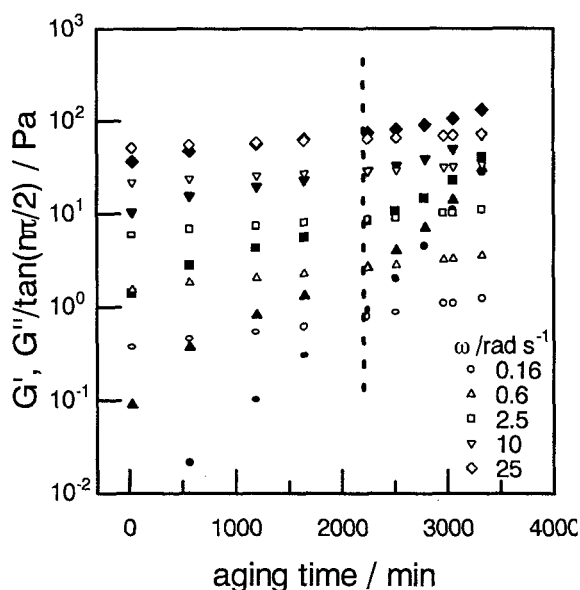


Fig. 5. G' (filled symbols) and $G''/\tan(n\pi/2)$ (open symbols) plotted as a function of aging time at various frequencies, ω for 14% PAN/DMA solution frozen for 2 hours.

Table I. They remained almost constant with the variation of tF . It was reported that S might be related with the total mass of polymer in the solution, taking account of the relation between S and the number of junction zone in unit volume at the gel point[9]. Since the concentration of the solution didn't vary in this experiment S remained invariable in spite of the variation of tF . The value of tA_g decreased with the increase in tF . The obtained results suggest that the freezing time doesn't influence the number of junction zones formed at the gel point, whereas it influences the rate of formation of the junction zone.

4. ACKNOWLEDGEMENT

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5. REFERENCES

- [1] "Acrylic fiber technology and applications", Ed. by James C. Masson, Chap.4, M. Dekker, New York, M. Dekker, 69-103(1995)
- [2] K. te Nijenhuis, *Adv. Polym. Sci.*, **130**, 100(1997)
- [3] Y. Tanaka and Y. Osada, *J. Thermosetting Plastics Jpn.*, (in Japanese), **15**(4), 195-208(1994)
- [4] F. Chambon and H. H. Winter, *Polymer Bulletin*, **13**, 499-503(1985)
- [5] H. H. Winter and F. Chambon, *J. Rheology*, **30**(2), 367-382(1986)
- [6] F. Chambon and H. H. Winter, *J. Rheology*, **31**(8), 683-697(1987)
- [7] CHR. Friedrich and L. Heymann, *J. Rheology*, **32**(3), 235-241(1988)
- [8] T. A. Vilgis and H. H. Winter, *Colloid & Polymer Sci.*, **266**, 494-500(1988)
- [9] L. Li and Y. Aoki, *Macromolecules*, **30**, 7835-7841(1997)

[10] Y. Aoki and M. Kakiuti, *Macromolecules*, **31**, 8117-8123(1998)

[11] J. Bisschops, *J. Polym. Sci.*, **17**, 89-98(1955)

[12] Y. Tanaka, "Gel Handbook" Ed. by Y. Osada, K. Kajiwara (in Japanese), NTS, Tokyo, 31-38(1997)

[13] J. C. Scanlan and H. H. Winter, *Macromolecules*, **24**, 47-54(1991)

[14] A. Koike, N. Nemoto, Y. Watanabe and K. Osaki, *Polymer J.*, **28**(11), 942-950(1996)

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