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Viscoelastic Properties of Polyacrylonitrile Gels: Dependence of Sol-Gel Transition on Concentration and Aging Time

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Summary: Dynamic viscoelasticity was observed for polyacrylonitrile solution in dimethylacetamide in the process of sol-gel transition. The gel was prepared by the freezing and thawing method, i.e., the solution was frozen at -50°C and then kept at 25°C so as to undergo gelation. The longer the freezing time, the shorter was the gelation time. Also the higher the concentration, the shorter the gelation time. The strength of the network, S and critical exponent *n* at the transition point were evaluated. The S value increased with increasing concentration and was constant in value in spite of the variation of freezing time when the concentration of the solution was constant.

Keywords: freezing and thawing; gelation; polyacrylonitrile; power law; properties; viscoelastic

Introduction

It is well-known that many polymers, synthetic and natural, form physical, thermoreversible aggregates in dilute solutions, whereas in moderately concentrated solutions gels can be formed.[1] The physical gelation processes are called sol-gel transitions. Among the several physical properties, viscoelasticities change dramatically during the gelation process of a polymer solution: the system is liquid-like before cross-linking starts and remains a liquid until the viscosity becomes infinite. The purpose of our study is to give quantitative accuracy to the physical gelation process. That is, to understand the relation between the formation of the network and the viscoelastic behavior as a function of the parameter that governs the gelation process. For example, polymer concentration, temperature, gelation time, molecular weight, and so on. As a first step for this purpose, we studied the viscoelastic behaviour of polyacrylonitrile (PAN) - N, N-dimethylacetamide (DMA) gel. The gel was prepared by the freezing and thawing method.

Concerning the viscoelastic properties in the process of sol-gel transition, several scaling laws are proposed and experimentally examined for various gelling systems. The limiting behaviour is of interest in studying viscoelasticity near the sol-gel transition region. Amongst many research results, the power law dependence of the dynamic viscoelastisity, proposed by Winter, attracts our attention, i.e. $G'(\omega) \propto G''(\omega) \propto \omega^{n}$.[2-4] In this study the validity of the power law was examined for the sol-gel transition of PAN solution.

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Experimental

Sample Preparation

Polyacrylonitrile(PAN) was kindly supplied by 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. After the solution was prepared it was cooled in a bath at -50°C for several hours, then poured into a measurement cell at 25°C. Freezing time, tF, the time taken for a solution to freeze, varied from 2 to 35h.

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 ~100gmcm). A couette cell and a parallel plate cell were used for the measurements. The geometry is 32mm in inner diameter and 34mm in outer diameter for the couette cell, and 50mm in diameter for the parallel plate cell. The experimental temperature was 25°C. Aging time, tA, i.e., the time passed after the sample was heated to 25°C, was noted. Prior to the measurement a suitable shear amplitude was determined by measuring the strain dependence of moduli to ensure the linearity of dynamic viscoelasticity.

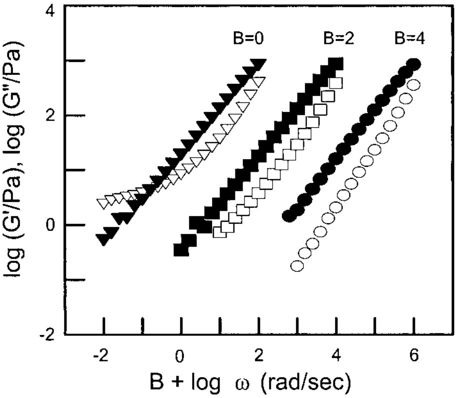

Fig. 1. G'(open symbols) and G"(filled symbols) for 14% PAN/DMA solution (tF=2h) plotted as a function of angular frequency ω at various tA indicated below. The data are shifted along horizontal axes by shift factors B to avoid overlapping.

tA / min	1560	1830	2190
B	4	2	0

Results and Discussion

Effect of Freezing Time

The solution of the concentration of 14% was prepared and the storage moduli, G', and loss moduli, G", were measured before freezing. The results were found to follow those expected for a liquid-like system, i.e.

$$G'(\omega) \propto \omega^2, \qquad G''(\omega) \propto \omega \qquad (\omega \to 0) \qquad (1)$$

The plots of slope 2 for G'(ω) and that of slope 1 for G"(ω) were observed on a log-log scale. After freezing the sample was thawed and the viscoelasticity measurement was carried out with aging at 25°C. The viscoelastic behaviour of the solution after freezing varied with an increase in tA; for example, the solution of tF=2h was liquid-like as shown by eq.(1) at tA=30min, while the deviation from this relation becomes more pronounced in the course of time. The slopes of both the G' *vs* ω plot and the G" *vs* ω plot in the lower frequency region decreased with the increase in tA. Figure 1 shows G' and G" plotted against frequency on a log-log scale for the solution of tF=2h. As can be seen from Figure 1, the slopes of G' and G" take a common value at a certain tA. The slope of the G' *vs* ω plot in the lower frequency region decreased further and eventually reached 0 at tA=3330min; showing the frequency independent modulus. This means that the sample behaves like a solid. Therefore, the liquid – solid transition took place during aging at 25°C and the power law behaviour of $G', G'' \propto \omega^n$ could be observed. The G' value in the higher frequency region remained almost constant during aging, showing the relaxation strength didn't vary in the liquid – solid transition. A similar viscoelastic behaviour was observed for 14% PAN/DMA solutions of different freezing time.

The following equation has been proposed as the expression of the power law.

$$G'(\omega) = G''(\omega) / \tan\delta = S\,\omega^n\,\Gamma(1-n)\cos\delta \qquad (2)$$

The phase angle δ between stress and strain becomes independent of frequency at the gelation point and has a relation with the relaxation exponent, *n* i.e.,

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

Table 1. Gelation time, tA_g , gel strength, S and critical exponent, *n* for 14% PAN/DMA solutions treated with various freezing times.

tF/h	tA_g/min	S/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

Since the phase angle varies from 0 to $\pi/2$ as n takes values between 0 and 1, n measures the rheological distance from a complete elastic solid to a complete viscous liquid. Earlier pioneering studies showed that $\tan\delta$ will be independent of frequency when gelation occurs.[5,6] Because of these studies, we plotted $\tan\delta$ against aging time in Figure 2 for PAN/DMA solution with tF=2h. All curves in the figure pass through a common point at a certain tA, which determines the gelation point, tA_g. The position of the common point is consistent with eq.(2). The frequency independent $\tan\delta$ was also observed for other 14% solutions of different tF during sol-gel transition. The relaxation exponent was determined from the value of $\tan\delta$ at the gelation point and is listed in Table 1 together with tA_g. The value of S is also shown in Table 1; the manner to determine it is described later. In spite of different tF, values of n were almost constant. Although we don't understand the whole meaning of the exponent here, a detailed explanation among gels of different chemical species is expected to be given by our further research. The experimental results reported that the increase in cross-link density led to the reduction of n in chemical gels, especially in end-linked polymers.[7,8]

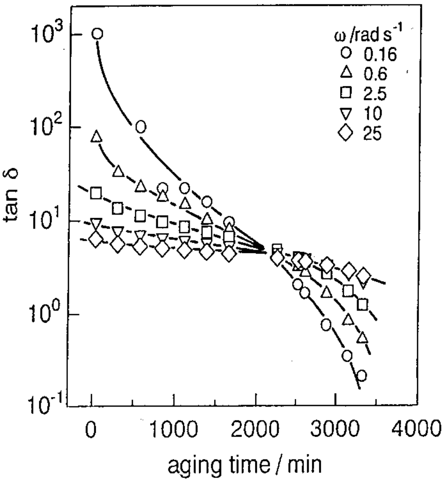

Fig. 2. Loss tangent plotted as a function of aging time at various frequencies, ω for 14% PAN/DMA solution frozen for 2hours.

We attempted to evaluate S using eq.(2). S has a complicated dimension of Pa s^n, which is written in the literature to consist of a material characteristic modulus and a time. Eq.(2) suggests the existence of a crossover between G' and G"/$\tan(n\pi/2)$ at the gelation point. Therefore, the value of G' at the gel point can be obtained by plotting G' and G"/ $\tan(n\pi/2)$ as a function of tA for different frequencies, therefore S can be easily calculated. An example of this kind of plot is shown in Figure 3 for PAN/DMA solution with tF=2h. Each crossover point appeared at the same tA, which agreed with the tA_g determined from the plot of tanδ *vs.* tA, as indicated by the dashed line in Figure 3. Values of S for different frequencies were evaluated using eq.(3) and confirmed not to depend on the crossover point used. We chose to adopt an averaged value from the six points of S to avoid any unreliability following the earlier studies.[5,6] S values were obtained for solutions with other tF and summarized in Table 1. They remained almost constant with the variation of tF. S is said to be related to the total mass of polymer in the solution taking into account the relationship between S and the number of junction zones in the unit volume at the gelation point.[7] Since the concentration of the solution is constant in the experiments, S remained invariable in spite of the variation of tF. The value of tA_g decreased with the increase in tF. The results obtained suggest that the freezing time doesn't influence the number of junction zones formed at the gelation point, whereas, it does influence the rate of formation of the junction zone.

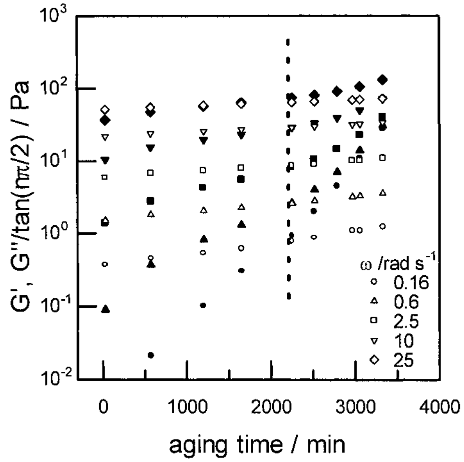

Fig. 3. G' (filled symbols) and G"/tan(nπ/2) (open symbols) plotted as a function of aging time at various frequencies, ω for 14% PAN/DMA solution frozen for 2hours.

Effect of Concentration

We have examined the viscoelastic behaviour for solutions of other concentrations. The concentrations were 11, 12, 12.5 and 14 wt%. tF was 2.5h for all the solutions measured. The solution of 11% didn't show gelation, thus, there must be minimum concentration for the gelation of PAN/DMA solution.

Table 2. Gelation time, tA_g, gel strength, S and critical exponent, *n* for PAN/DMA solutions treated with fixed freezing time of 2.5hours.

Conc. / wt %	tA_g/min	S/Pa s^n	n
11*	–	–	–
12	2430	0.46	0.89
12.5	2006	0.70	0.89
14	1300	2.65	0.86

The solution showed the liquid behaviour expressed by eq.(1) against the viscoelastic measurement before freezing. The solution also showed power law behaviour described in the previous section, after the freezing and thawing treatment, except for the solution of 11%. Gelation time, tA_g, gel strength, S and critical exponent, *n* determined for these solutions are listed in Table 2. Gel strength increased with concentration. This is consistent with the gelation theory where S is related with the total mass of polymer in the solution. On the other hand, *n* value didn't vary with a change in concentration. It can be said that the critical exponent is independent of the total mass of polymer in the solution.

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