A Preparation Method of Thermoreversible Poly(vinyl chloride) Gels

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Introduction

Poly(vinyl chloride) (PVC) forms physical gels in various solvents, and the structures and physical properties of these gels have been extensively investigated.[1,2] Recently, we have conducted a series of rheological studies for PVC in bis(2-ethylhexyl) phthalate (DOP).[3−8] We determined the gel point by means of the frequency independence of the loss tangent by Winter and Chambon.[9,10] The following scaling laws have been found to hold well before, at, and beyond the sol−gel transition concentration.

$$\eta_0 \propto \epsilon^{-\gamma} \quad \text{for } c < c_g \tag{1}$$

$$G'(\omega) \sim G''(\omega) \propto \omega^n \quad \text{for } c = c_g \tag{2}$$

$$G_e \propto \epsilon^z \quad \text{for } c > c_g \tag{3}$$

where ϵ ($= |c - c_g|/c_g$) is defined as the relative distance to the gel point c_g, η_0 is the zero shear viscosity, G' and G'' are the dynamic moduli as a function of angular frequency ω, and G_e is the quasi-equilibrium modulus. We have found that $n = 0.75$,[3] $\gamma = 1.5$,[4] and $z = 2.6$[5] for PVC/DOP systems. The scaling exponents in eqs 1−3 were independent of molecular weight[3−5] and molecular weight distribution of PVC[7] and the measuring temperature,[8] suggesting the similarity of the fractal structure of the PVC gels.

In these studies, we prepared PVC gels as follows. First, PVC and DOP were dissolved into tetrahydrofuran (THF). Then, evaporation of THF from each solution proceeded very slowly at room temperature. After about 2 weeks, the weight of each sample became constant. After about 1 month from the evaporation, we measured the viscoelastic properties of the gels. We supposed that the gels are in equilibrium since a sufficiently long time was taken for evaporation of THF. However, it is an important problem to be confirmed whether the gels are in equilibrium.

On the other hand, a few reviewers pointed out that our preparation method for PVC gels/sols, starting from THF solutions, is rather strange and wondered whether THF is actually removed totally. Therefore, in this study we first measured the residual THF concentration in the gels by using headspace gas chromatography (HSGC). HSGC represents a technique for trace analysis of chemicals. The reason for this is that, by the proper selection of the equilibrium temperature, one can build up a relatively high concentration of a given solute in the headspace, even if it is present at a low concentration in the sample proper.

Walter[11] studied time evolution of Young's modulus for PVC/DOP containing from 5 to 70% PVC from time after the rapid cooling from higher temperature to room temperature. He reported that equilibrium was reached within a few months for the PVC gels of very low concentrations, but at high PVC concentrations an apparent state of equilibrium was not observed even after 2 years. Te Nijenhuis et al.[12−14] studied the aging process of PVC/DOP gels from the sol state (150 °C) to the desired aging temperature (−20 to 110 °C). They also found that the time required to reach equilibrium at a constant temperature is surprisingly long.

In this paper, we first measured the residual THF concentration of as-prepared PVC gels using HSGC and then measured the dynamic viscoelastic properties of the aged PVC/DOP gels for very long times after quenching the solutions from 120 to 25 °C. We compared the viscoelastic properties of the aged gels with those of the as-prepared gels and discuss whether the as-prepared gels are in equilibrium. The viscoelastic properties must be recovered after cooling to room temperature from the temperature above the critical gel temperaruture T_{gel}, if as-prepared samples are in equilibrium.

Experimental Section

Materials and Sample Preparation. A PVC sample, coded as PVC4 in the previous studies,[3−8] was used. This sample was synthesized by suspension polymerization and has a weight-average molecular weight of 39.4×10^3 (determined from light scattering), a polydispersity index (M_w/M_n) of 1.89 (determined from GPC), and a triad tacticity of syndio:hetero:iso = 0.33:0.49:0.18 (determined from NMR). The PVC concentration was 70 (PVC4-07), 101 (PVC4-10), and 154 g/L (PVC4-15). The critical gel temperatures T_{gel} of these samples are as follows: T_{gel}(PVC4-07) = 54 °C, T_{gel}(PVC4-10) = 82 °C, and T_{gel}(PVC4-15) = 105 °C.[8]

As in the previous work, the samples were prepared by the following method: Prescribed amounts of PVC4 and DOP were first dissolved in excess THF (a good solvent of PVC) at room temperature to make a homogeneous solution (about 70 wt % of THF). Then, at this temperature, THF was allowed to evaporate from the solution placed in a shallow glass dish. Within 2 weeks, the weight of the system became constant, and the evaporation of THF was completed. Well-developed PVC/DOP gel systems (as-prepared samples) were recovered on completion of this procedure. The viscoelastic properties of these as-prepared gels did not change with time.

Measurements. Headspace gas chromatography (HSGC, Shimadzu) was utilized for the analysis of residual THF in the samples to check whether THF was actually removed. Here, a 30 m × 0.53 mm i.d. capillary column with a 5 μm thick film was used.

Linear viscoelastic measurements were carried out with a strain-controlled rheometer (ARES-2KFRTN1, Rheometric). Parallel-plate fixtures were utilized. The plate diameter (25 or 50 mm) was chosen according to the magnitude of the sample moduli.

The measurements of time development within 6 h were conducted as follows. The gel was brought into the parallel plate of the rheometer, and then a temperature of 120 °C (above T_{gel}) was maintained for 1 h. After the destruction of the gel structure on heating and starting from the PVC/DOP solution at high temperature, the sample was cooled quickly to room temperature. After 30 min at room temperature we started the measurements for 6 h. For short aging times (0.5 and 1 h) the frequency range was very limited, because changes in the moduli during the measurement were large.

On the other hand, long aging time measurements over 1 day were conducted as follows. After the gel samples placed in a shallow glass dish were put into an oven at 120 °C for 1 h, they were quenched and maintained at room temperature

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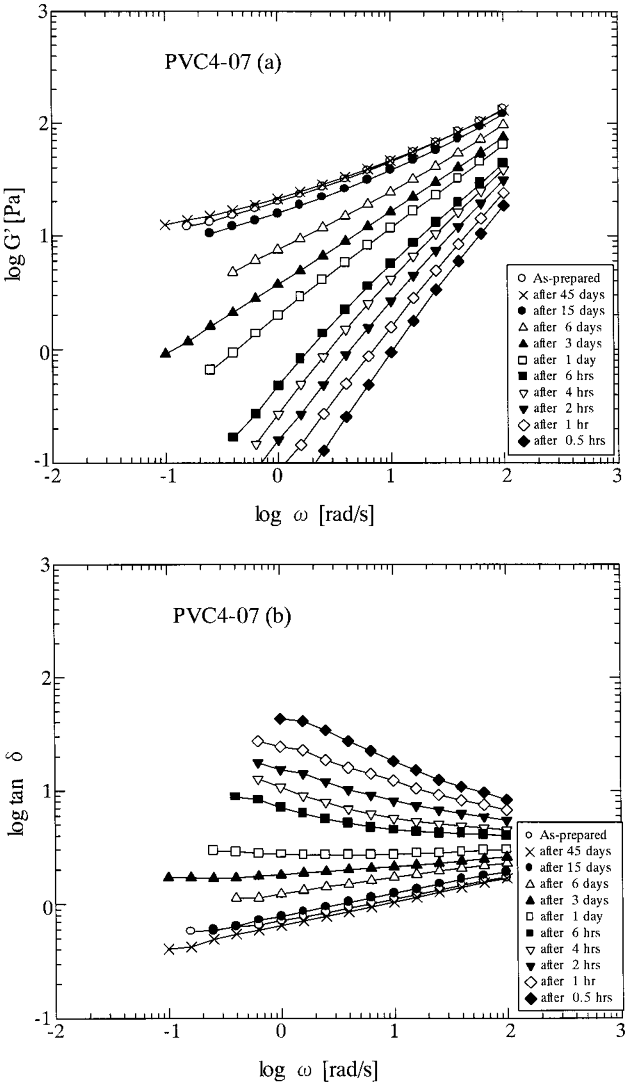

Figure 1. Storage modulus *G'* (a) and loss tangent tan *δ* (b) of PVC4-07 plotted against angular frequency *ω* for various aging times at 25 °C after quenching from 120 °C.

Table 1. THF Concentration in As-Prepared Samples by Headspace Gas Chromatograpy

sample	THF/wt·ppm
PVC4-07	3
PVC4-10	1
PVC4-15	1

for desired times. Then we measured the viscoelastic properties of the aged gels. For long aged samples the time of measurement is comparatively short, as changes in the moduli that occur during the measurement are small.

Results and Discussion

Table 1 shows residual THF concentration in the as-prepared samples measured by HSGC. The concentrations for the PVC4-10 and -15 were about 1 ppm, and that for PVC4-07 was 3 ppm. These values indicate that residual THF is too low to affect the physical properties of PVC gels. Commercial DOP, in general, contains impurities above several hundred ppm. Therefore, we can conclude that residual THF has been actually eliminated.

The time dependencies of the storage modulus *G'* and loss tangent tan *δ* of the PVC4-07 system after quenching from 120 °C to room temperature (25 °C) are shown in Figure 1. The aging of the sample can be observed from the rise of the *G'* and the reduction of the tan *δ* with time, as already reported by te Nijenhuis and Winter.[14] The sample shows a transformation from the sol to the gel state. At short aging times from 0.5 to 6 h, the system behaves like a liquid, and therefore the *G'* depends strongly on angular frequency *ω*, whereas as the aging proceeds, the frequency dependence of the *G'* becomes very weak. To determine the critical gel time t_{gel} of the PVC4-07 at 25 °C, log tan *δ* is plotted against log *ω* for various aging times in Figure 1b. According to Winter and Chambon,[9,10,14] t_{gel} is the time when the tan *δ* is independent of *ω*. The t_{gel} of the PVC4-07 can be estimated to be about 1 day. The *G'* curve after 1 day of aging time is a linear one with a slope of 0.75, which is in agreement with *n* obtained previously.[3,6,7] This is an indication of the t_{gel} at 25 °C for the PVC4-07 sample. The *G'* and tan *δ* after about 15 days of aging time come close to those of the as-prepared gel. Those after 45 days almost coincide with the values of the as-prepared gel within experimental error.

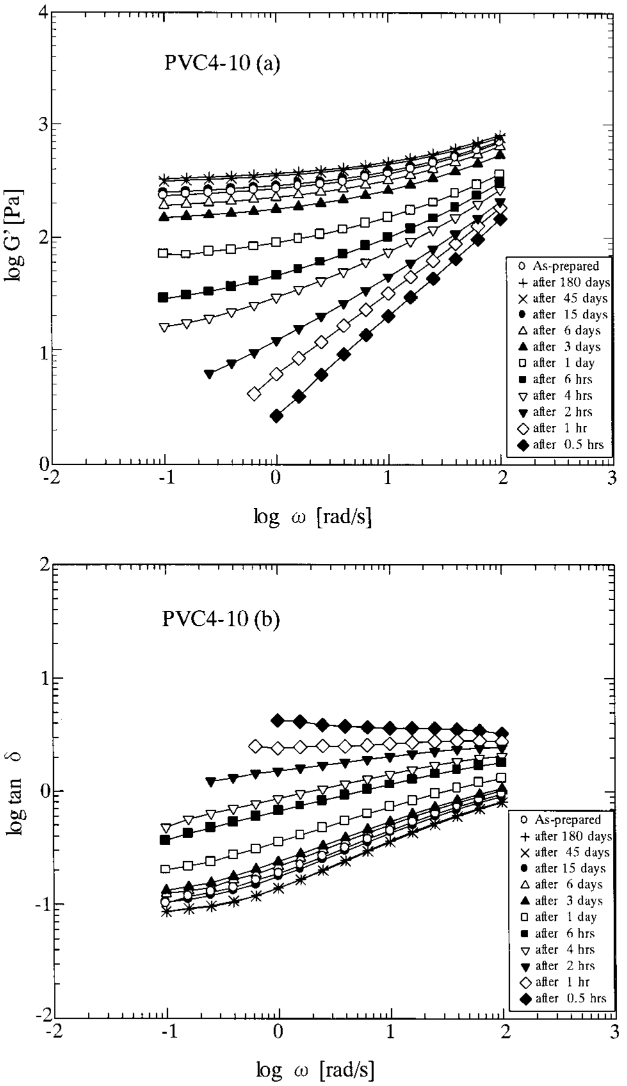

Figure 2. Storage modulus *G'* (a) and loss tangent tan *δ* (b) of PVC4-10 plotted against angular frequency *ω* for various aging times at 25 °C.

Analogous plots are given in Figures 2 and 3 for the *G'* and tan *δ* of the PVC4-10 and PVC4-15 systems, respectively. The t_{gel} can be observed between 0.5 and 1 h for the PVC4-10. The change of the *G'* with time becomes quicker than for the PVC4-07. After 3 days,

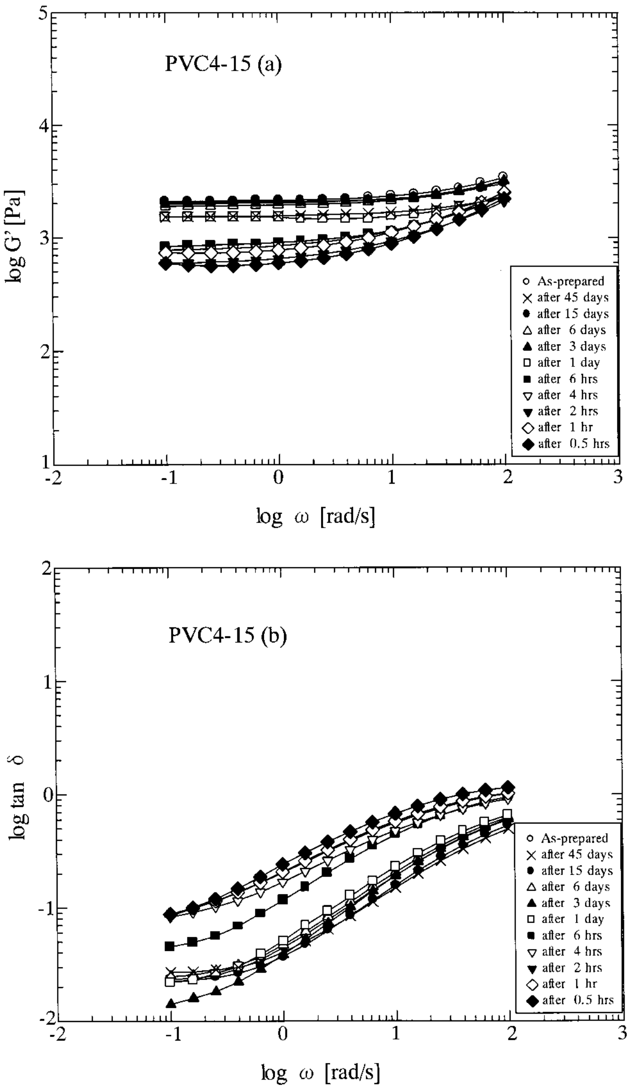

Figure 3. Storage modulus G' (a) and loss tangent tan δ (b) of PVC4-15 plotted against angular frequency ω for various aging times at 25 °C.

the ω dependence of G' becomes very weak at low frequency. The evolutions of the G' and tan δ with time become very weak, too. The G' and tan δ after 180 days are equal to the values after 45 days for the PVC4-10. These values should be equilibrium values for the PVC4-10, although slightly larger than those of the as-prepared gel. For the PVC4-15, a gel is formed immediately after cooling a sol from 120 °C to room temperature. After 3 days, the G' and tan δ for the aged sample coincide with those of the as-prepared sample.

Figure 4 shows the storage moduli G' at $\omega = 1$ rad/s for the PVC4-07, PVC4-10, and PVC4-15 plotted against log t at 25 °C. The duration of the aging process strongly depends on PVC concentration. With the PVC4-15 (relatively high concentration) sample an equilibrium value of the G' and tan δ was reached within 3 days on aging at 25 °C, whereas the PVC4-07 (lower concentration) sample reached an equilibrium value at about 1 month. It was found that the aging process is faster at higher PVC concentration.

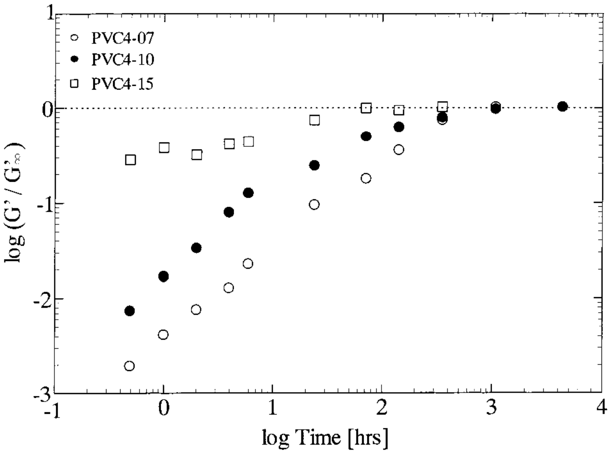

Figure 4. Normalized storage modulus (G'/G'_∞) at $\omega = 1$ rad/s of the three PVC/DOP systems plotted against aging time at 25 °C.

Walter[11] showed that an equilibrium value of the Young's modulus was reached after aging time of 1 month at room temperature for a 10% solution of PVC/DOP system using a PVC of $M_n = 6.6 \times 10^4$. Te Nijenhuis et al.[12–14] also studied the aging process of PVC/DOP gels using a PVC sample of $M_w = 24 \times 10^4$. The concentration of PVC was 100 g/L (about 10 wt % of PVC). They could not find equilibrium values of the storage modulus. Both studies indicated that the time required to reach equilibrium is surprising long. In this study we found that the time required to reach equilibrium is shorter for lower molecular weight PVC. We suppose that the aging speed depends strongly on the molecular weight and concentration of PVC and the aging temperature. It is of interest to study the reason why the aging speed is different. This is considered as important future work.

Concluding Remarks

We prepared PVC/DOP gels by evaporation of THF from PVC/DOP/THF solutions. Residual THF concentration in the gels was measured with HSGC. The residual THF concentration was found to be too low to affect the viscoelastic properties of PVC gels. The viscoelastic properties were examined for both the as-prepared gels and the aged samples from their sol state (120 °C) to 25 °C. Equilibrium values of the G' and tan δ for the aged samples were in good agreement with the corresponding values of the as-prepared samples. These facts strongly support that the as-prepared samples from THF solutions are in equilibrium. This preparation method is fit for PVC gels, because the PVC does not suffer thermal history at higher temperature.

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