Effect of Temperature on Dynamic Physical Behavior of Poly(vinyl chloride) Gel Structure with Ester Plasticizers

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Summary: Dynamic viscoelastic properties of poly(vinyl chloride) (PVC)/bis(2-ethylhexyl) phthalate (DOP) and PVC/di-n-butyl sebacate (DBS) gels with molecular weight distribution (M_w/M_n), of 2.16 and various polymer concentrations c, have been studied as a function of temperature. These PVC gels exhibited an elastic solid at room temperature T, and gradually became liquid (sol) with increasing temperature. The sol-gel transition took place at a critical gel temperature at which the scaling law of $G'(\omega) \sim G''(\omega) \propto \omega^n$ held, allowing an accurate determination of the critical gel temperature by means of the frequency ω independence of the loss tangent. In this study the scaling exponent n, was 0.75–0.77. This is in good agreement with the previous results observed at different temperatures and suggests the formation of a similar fractal structure of the PVC gels. The gel strength S_g, at the gel point increased with increasing PVC concentration. These results suggest a unique character and structure for the gel points of PVC-plasticizers.

Keywords: gel point; gel strength; plasticizer; poly(vinyl chloride); rheological observation; scaling exponent

1. Introduction

Poly(vinyl chloride) (PVC) has been manufactured commercially for over 60 years [1,2]. The physical properties of the PVC gels have been widely studied as a function of temperature (or time) [3], concentration [2], and types of plasticizers [3,4] for numerous interests. Since the mechanism of PVC gelation and the structure of the PVC gels have still not been fully elucidated, attention has been paid to the experimental analysis and the theoretical prediction of the molecular structure of the PVC gels [4]. A generally accepted model is the fringed-micelle structure model that describes a PVC gel where the network is composed of small crystallite domains, the junctions, and flexible chains connecting the junctions [5]. Physical gels, unlike chemical gels consisting of permanent chemical cross-links, are thermoreversible in nature with respect to the physical junctions. The physical junctions are formed by selfassociation, and reverse enhancement of temperature or dilution by a good solvent may make the junctions to dissociate [6,7]. Current studies on the physical gels provide one with just a partial image of the gelation behavior. It is of interest to have the entire rheological image of a physically gelling system as a function of concentration, temperature, plasticizer, and so on [3,4,8–10]. For this purpose, a series of poly(vinyl chloride) (PVC) solutions and gels with DOP and DBS plasticizers have been prepared over a wide range of concentrations hopefully allowing us to observe their rheological behavior before, near, and beyond the sol-gel transition as a function of concentration

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and temperature. The PVC commercial has been chosen for our studies, because the gelation mechanism and gel structure of this polymer has not been fully understood [11].

2. Experimental

2.1. Materials

The materials used in this study were poly(vinyl chloride) (PVC), bis(2-ethylhexyl) phthalate (DOP) and di-n-butyl sebacate (DBS) plasticizers. Commercial $(PVC)_E$, produced through emulsion polymerization by SABIC (K = 70), Saudi Basic Industries Corporation. Weight-average molecular weight of 128×10^3 determined from GPC. 2 wt % of a tin-type stabilizer were added to the samples at a PVC concentration higher than 7 wt %. The samples prepared in the present work are 45, 70, 80, 100, 200, 300 and 500 g/l for PVC/DOP and PVC/DBS gels (Table 1). The samples of PVC/plasticizer were physically mixed at room temperature and dissolved in tetrahydrofuran (THF, a good solvent for PVC). Samples tends to change it as a transparent liquid perfectly and little by little (Table 2). In this new method [22], Co-solvent of THF was mixed of super molecular of PVC into plasticizer completely. Using of this method allows samples physically to be mixed at room temperature to make a homogeneous solution and equilibrated with time instead of high temperature. Each sample was stable with time. On the other hand, the residual THF concentration (1-3 wt.ppm by Headspace Gas Chromatography) was found to be too low to affect the viscoelastic properties of PVC gels [7,21,22].

Then the samples were transferred into flat laboratory glass dishes.The evaporation of THF from each solution proceeded at room temperature (25 °C), and it took longer than 3 weeks. After the THF evaporated completely, transparent and viscoelastic samples were obtained. Since a sufficiently long time was taken for the evaporation of THF and the equilibrium for gelation prior to rheological measurements, each sample was considered to be stable with time. The gelling systems were prepared at room temperature from THF solutions of PVC and plasticizer. The rheological reproducibility was confirmed for some selected samples [11,19,22].

Table 2.
Amounts of using materials

PVC/plasticizer (g/l)	45	70	80	100	200	300	500
THF (wt %)	68.5	74.5	76	79	82	86	91

2.2. Measurements

The dynamic rheometer (UDS200) was employed to measure the storage shear modulus G′ and loss modulus G″ as a function of angular frequency ω at a certain temperature. Parallel plates (25 mm diameter) were used, depending on the viscoelastic properties of each sample. Then the PVC/DOP or PVC/DBS gels were transferred from the flat laboratory dish into the rheometer. All frequency sweep measurements were carried out by using a variable temperature step from 40 °C to the complete flow temperature or 180 °C. The moduli measured on heating are used in this paper and the gels were equilibrated at room temperature (~25 °C) during the sample preparation process. The PVC/DOP and PVC/DBS gels, mounted in the rheometer at room temperature, were slowly heated from 40 °C up to respective flow temperatures (above the gelation points). During this heating procedure,

Table 1.
Characteristics of using plasticizers

Plasticizer	Formula	Density (g/cm³)	Molar mass (g/mol)	Viscosity dynamic Pa · s (20 °C)
DOP	$C_{24}H_{38}O_4$	0.98	390.57	0.076–0.080
DBS	$C_{18}H_{34}O_4$	0.94	314.47	0.051–0.056

the temperature T was kept constant at several selected points where the moduli were measured. Prior to the measurements, the gels were annealed at the selected T at least for 20 min [7,21,22].

3. Results and Discussion

3.1. Dynamic Viscoelastic Properties through the Sol-Gel Transition

The PVC gel is a three-dimensional network formed from flexible chains through either chemical cross-linking or physical phase transformation. The polymeric liquid dramatically changes in to a solid-like state at a critical time, temperature and polymer concentration. The critical change from the liquid state to the solid state is known as the sol-gel transition. The sol-gel transition takes place in a thermodynamically non-equilibrium state like the glass transition where polymer chains are physically frozen from the melt. Even though studies of gels are not new and various theoretical models have been proposed to explain the formation and properties of gels [12–16]. Gels are especially complex systems and each gel has its own complexities. The complexities of gels have long been studies for chemically [17–18] or physically gels [2–8,10,19–22].

The shear storage moduli G' and loss moduli G'' are illustrated in Figure 1 as a function of angular frequency ω for the PVC gel series. The PVC/DOP and PVC/DBS gels temperature ranges from 60 to 180 °C for 300 g/l as indicated. The dynamic mechanical behavior of the PVC solutions follows the liquidlike terminal behavior at very high temperature:

$$G'(\omega) \propto \omega^2 \quad G''(\omega) \propto \omega \ (\text{at } \omega \to 0) \qquad (1)$$

The deviation from the above relations becomes more pronounced for the higher concentrations of PVC. The behavior, $G'(\omega) = \text{constant}$ at $\omega \to 0$, is consistent with the results reported by Nijenhuis and Winter [3], indicating the formation of a gel plateau. The slope of the $G'(\omega)$ vs ω curve (at $\omega \to 0$) on the log-log scale undergoes a change from 2 to 0, while that of the $G''(\omega)$ vs ω curve (at $\omega \to 0$) varies from 1 to 0. Therefore, it is reasonable to consider that the liquid-solid transition should take place at some value of the slope between 0 and 2 for the $G'(\omega)$ curves or at a slope between 0 and 1 for the $G''(\omega)$ curves. Furthermore, it is obvious at the gel point that both slopes take a common value between 0 and 1. The range of polymer concentration c where the sol-gel transition is observed was dependent on the PVC gel systems.

Figure 2(a) shows how a PVC gel changes from the gel state to the sol state by passing through the sol-gel transition

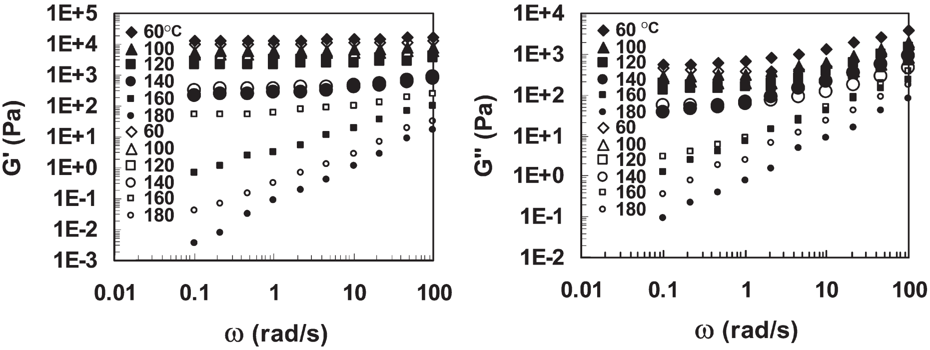

Figure 1.

Plots of storage modulus G' and G'' against angular frequency ω for the PVC gels ($c = 300$ g/l) at various temperatures as indicated. The filled symbols indicate c of the PVC/DOP gel and the open symbols are for the c of the PVC/DBS gel obtained in this study.

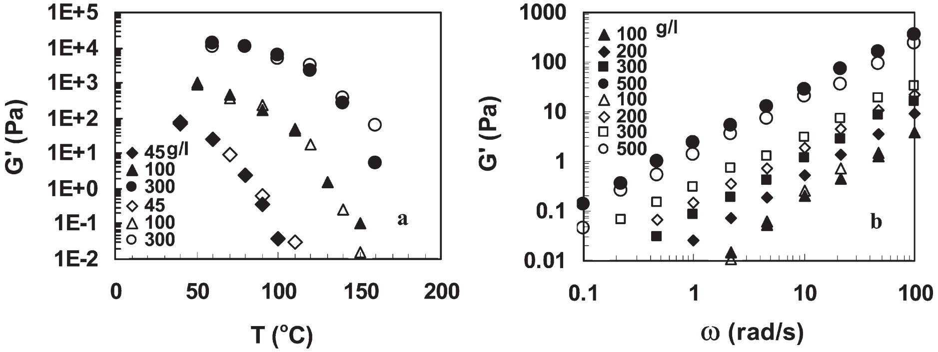

Figure 2.
(a) Storage modulus G′ of PVC gels as a function of temperature at an angular frequency ω of 1 rad/s. The polymer concentration c ranges from 45 to 300 g/l. (b) Plots of storage modulus G′ against angular frequency ω for the PVC gels ($T = 180\,^{\circ}C$) at various concentrations ($c < c_g$) as indicated. The filled symbols indicate T and c of the PVC/DOP gel and the open symbols are for the PVC/DBS gel obtained in this study. c_g is the sol-gel transition concentration.

temperature in a heating process. Dynamic viscoelastic properties of PVC/DOP or PVC/DBS gels passing through the sol-gel transition temperature is illustrated here in Figure 2(a) to shows how a PVC gels change from the gel state to the sol state by passing through the sol-gel transition temperature in a heating process and in Figure 2(b) to shows how a PVC gels change from the high concentration to the low concentration with kind of plasticizer in constant temperature. In Figure 2(a), the storage modulus G′ is presented as a function of temperature for the PVC/DOP or PVC/DBS gels with polymer concentrations of 45, 100 and 300 g/l at the frequency of 1 rad/s. All the samples shown in this figure were in the gel state at room temperature. The measuring temperature was varied from 40 to 160 °C. For each concentration of PVC, there appears a gel plateau of G′ at low temperatures and G′ decreases with increasing temperature. As a result, the sol-gel transition took place at a temperature for each concentration. On the other hand, the dependence of the gel modulus on polymer concentration can be simultaneously observed in the following way. The gel plateau at low temperatures, which represents the gel elasticity G_e, increases with concentration by complying with the scaling law of $G_e \propto \varepsilon^z$, where z is the scaling exponent. The sol-gel transition shifts to high temperatures with increasing PVC/DOP or PVC/DBS gels. In Figure 2(b), G′ decreases significantly with decreasing concentration. In this figure, the terminal region at 180 °C, and low frequencies ($G' \propto \omega^2$) indicate the sol state.

Therefore it is possible consider the sol-gel transition at a certain temperature. Selected number of huge PVC data were used to study the transition temperature of sol-gel with plasticisers.

3.2. Determination of the Gel Point

To study a gelling system, it is important to know how to determine its gel point. Traditionally, many researchers use the crossover of $G'(\omega)$ and $G''(\omega)$ as an indicator of the gel point. This method is simple, but not valid in general. A valuable contribution to this area is attributed to the studies of chemical and physical gelations in Winter's laboratory [3,17–21]. They first experimentally found a scaling law of $G'(\omega) = G''(\omega)\ \alpha\omega^{1/2}$ at the gel point and later generalized it to be for all gelling systems [7,8].

$$G'(\omega) \sim G''(\omega) \sim \omega^n \quad 0 < n < 1 \tag{2}$$

or

$$G''(\omega)/G'(\omega) = \tan\delta = \tan(n\pi/2) \tag{3}$$

n, is the scaling exponent for the scaling law in equation 2. The frequency independence of the loss tangent in the vicinity of the gel point has been widely examined for chemical and physical gels [6,7–14,16–20] and also been employed to determine the gel point (Figure 3). The definition of the gel point by this power law is excellent because a gelation variable loses its dependency on frequency and converges at the gel point. The experimental results have shown that this method is reliable and valid for determination of the gel point such as the critical gelation time and the critical gelation temperature [6–10,14–18].

Experimentally, n is found not to be constant, but it has a value between 0 and 1 [9,15]. On the other hand, in the theoretical field, Martin et al. predict that n is between 2/3 and 1 [16]. Therefore, it seems that there is no universal value of n, probably because n is related to the specific nature of each gelling system.

Dynamic behavior of PVC/DOP and PVC/DBS systems at T ≥ 50 °C in Figure 3 shows the loss tangent (tan δ) of these systems (c = 100 g/l). Gels with DOP and DBS in this figure were well developed at gel point, $T_{gel} = 131.2$ °C for PVC/DOP gel and $T_{gel} = 142.6$ °C for PVC/DBS gel and to exhibit ω-independent tan δ for each concentration.

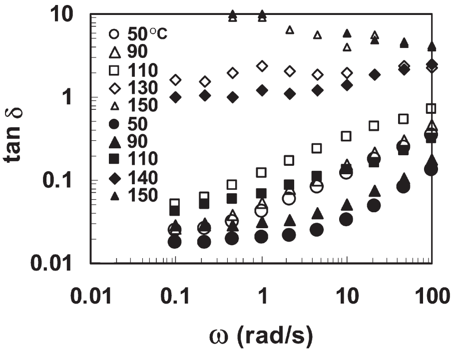

Figure 3.

Plots of loss tangent (tan δ) against angular frequency ω for the PVC gels (c = 100 g/l) at various temperatures as indicated. The open symbols indicate T of the PVC/DOP gel and the filled symbols are for the T of the PVC/DBS gel obtained in this study.

Traditionally, many people use the crossover temperature of G′ and G″ at a constant frequency as a measure of the gel point. Since the crossover is frequency-dependent, however, we do not use this way to determine the sol-gel transition temperature. As confirmed by a number of experiments [17–21] the method, called the frequency independence of loss tangent, is able to give an accurate determination of the gel point.

In this work, we also examine this method for determining the sol-gel transition temperatures of the PVC gels. Since tan δ loses its dependence on frequency and converges at the gel point, the gel point is determined from a multifrequency plot of tan δ vs gelation time, cross-linking degree, concentration, or temperature, depending on which variable governs the gelation process. We have used the method to determine the sol-gel transition concentration c_g for the PVC/DOP and PVC/DBS gels [1,5]. In this work, since the gelation variable was temperature, we plotted tan δ against temperature in order to decide the critical temperatures by the method. An example for this kind of plot is presented in Figure 4 for the PVC/DOP and PVC/DBS of 45 and 500 g/l. In this figure, each kind of symbol represents the tan δ measured at a certain angular frequency ω. The angular frequency ranged from 0.465 to 100 rad/s. One can observe the convergent point of all tan δ vs temperature curves, which is then defined as the sol-gel transition temperature T_{gel}.

At $T_{gel} = 86.7$ °C for PVC/DOP gel and $T_{gel} = 99.8$ °C for PVC/DBS gel at 45 g/l and $T_{gel} = 170.6$ °C for PVC/DOP gel and $T_{gel} = 173.2$ °C for PVC/DBS gel at 500 g/l All curves pass through a common point. For the gels of various c, Figure 4 shows c dependence of T_{gel} determined in this way. This ω-independence for the gels of various c and plasticizer, Figure 5 shows c dependence of T_{gel} determined in this way. These T_{gel} data agree with the previous data [7,11,19,20].

The results for concentration of gels are shown in Table 3, from equation 3. The loss

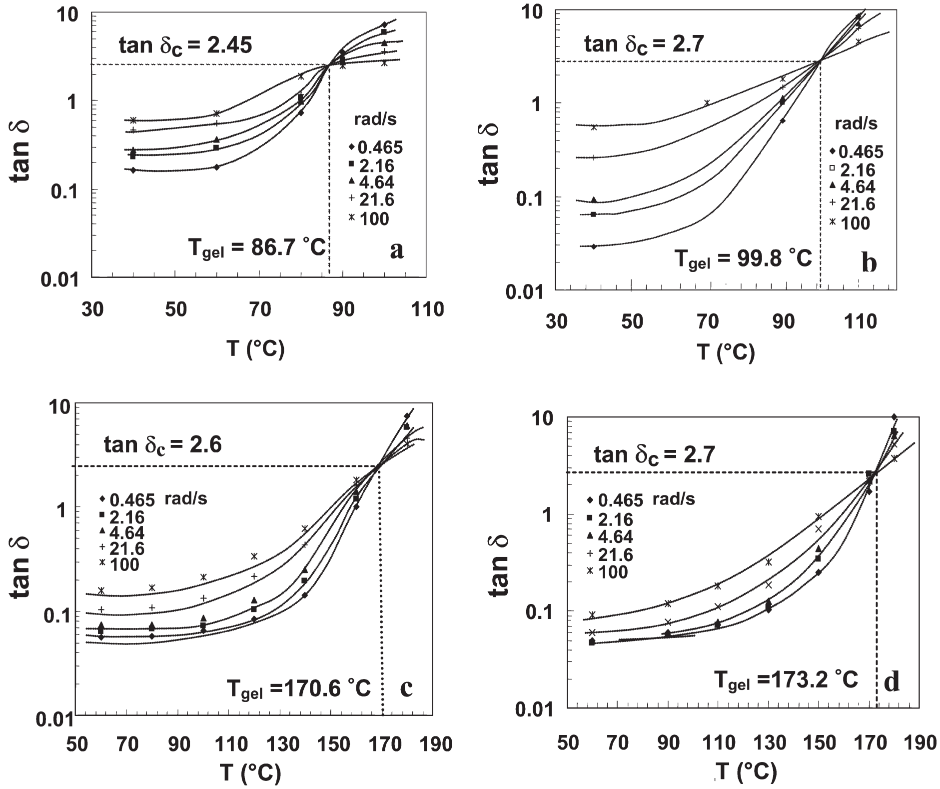

Figure 4.
Plots of loss tangents tan δ against temperature T for the PVC/DOP (a) and PVC/DBS (b) gels (c = 45 g/l) and the PVC/DOP (c) and PVC/DBS (d) gels (c = 500 g/l) at various angular frequencies, ω = 0.465, 2.16, 4.64, 21.6, 100 rad s^{-1}. T_{gel} is the sol-gel transition temperature.

tangent is constant, tan δ = (2.57 ± 0.125) for PVC/DOP and PVC/DBS gels. These results indicate that the scaling exponent n is independent of the sol-gel transition temperature. We were able to accurately determine their sol-gel transition temperatures in this way within reasonable experimental error.

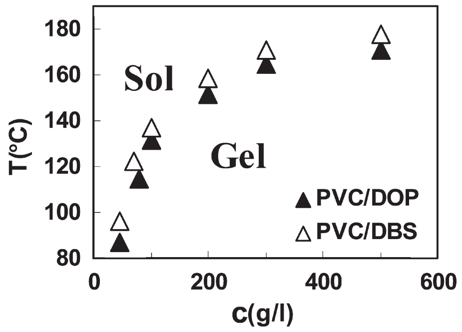

Figure 5.
Variation of the sol-gel transition temperature with PVC concentration c. The filled symbols indicate T of the PVC/DOP gel and the open symbols are for the T of the PVC/DBS gel obtained in this study.

Table 3.
Sol-Gel transition temperature T_{gel} as a function of PVC concentration c for PVC/DOP and PVC/DBS gel systems, determined by the method shown in figures of 3 and 4

Gel	c_{gel} (g/l)	T_{gel} (°C)	tan δ_c
PVC/DOP	45	86.7 ± 0.7	2.45
	80	115 ± 1.25	2.5
	100	131.2 ± 0.65	2.55
	200	151.2 ± 0.45	2.6
	300	164.7 ± 1.54	2.57
	500	170.6 ± 1.1	2.6
PVC/DBS	45	99.8 ± 1.2	2.7
	70	122 ± 0.4	2.65
	100	142.6 ± 0.98	2.5
	200	155 ± 0.75	2.7
	300	170.5 ± 1.3	2.7
	500	173.2 ± 0.95	2.7

3.3. Exponent n and Gel Strength S_g

The power laws describe the critical behavior of a gelling system before and beyond the sol-gel transition respectively, and no power laws are able to predict the whole range covering before and beyond the gel point. The well-used scaling law for the rheological behavior of a gelling system in the vicinity of the gel point is the relation in equation 4 or equation 5. For example, the linear shear relaxation modulus G(t) is predicted to obey a power law relaxation [9–16] and a similar expression can also be applied for dynamic moduli G′ [17,18] at the gel point.

$$G(t) = S_g t^{-n} \tag{4}$$

and

$$G'(\omega) = S_g \omega^n \Gamma(1-n)\cos(n\pi/2) \tag{5}$$

and

$$n = (2/\pi)\delta_c \tag{6}$$

$\Gamma(1-n)$ is the gamma function. The value of n was found to be constant from equation 6 ($n = 0.75 - 0.77$ is named the critical relaxation exponent), independent of the PVC gel systems [16–18]. Values of S_g and n determined in Table 4 and S_g were plotted against the gelation concentration c_g in Figure 6. Here S_g is the gel strength and has an unusual unit of Pa s^n.

The physical meaning of S_g may be somewhat abstract due to its unusual dimensions. One may simply understand that gel strength S_g is the relaxation modulus at the gel point [8,9]. The expression of S_g in $S_g = G(t)\ t^n$ may help one to understand the physical meaning of S_g for gel systems from equation 5. $n = 0$ gives $S_g = G_0$, that describes the rigidity of the system, while S_g represents the viscosity for $n = 1$ [8–12].

Table 4.
Critical concentration c_g for the sol-gel transition, scaling exponent n and gel strength

Gel	c_{gel} (g/l)	S_g (Pa s^n)	n
PVC/DOP	45	0.26	0.753
	80	0.65	0.758
	100	0.98	0.75
	200	2.4	0.766
	300	4.6	0.764
	500	8.7	0.766
PVC/DBS	45	0.14	0.771
	70	0.28	0.77
	100	0.47	0.769
	200	1.5	0.758
	300	2.94	0.771
	500	6.93	0.768

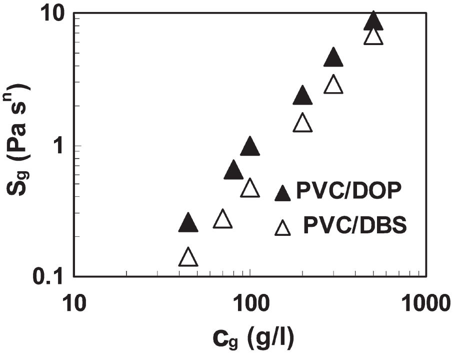

Figure 6.
Relation between S_g and c_g.

4. Conclusions

The series of poly(vinyl chloride)/DOP and PVC/DBS gelling samples were prepared from THF solutions. A stable state in each sample was achieved after a sufficiently long time of evaporation for equilibrium. We conducted dynamic viscoelastic studies on these stable samples as a function of polymer concentration and temperature. Decreasing temperature gradually from the liquid state to the solid state allowed us to observe rheologically the sol-gel transition. The gel point T_{gel} was accurately determined by the frequency-independence of loss tangent in the vicinity of the sol-gel transition relying on polymer concentration. The scaling exponent $n = (0.75 - 0.77)$ obtained was constant, independent of the plasticizer. The gel strength S_g was a linear function of the gelation concentration c_g and it was dependent on the plasticizer. The sol state was observed in the terminal region of $G' \propto \omega^2$ at low frequencies. There appears a gel plateau of G′ at low temperature for each concentration of PVC and G′ decreases with increasing temperature at low concentration. The storage modulus of gel samples of PVC/DOP and PVC/DBS were evaluated at difference concentrations, temperatures and frequencies. Gel samples of PVC/DBS had low sensitivity to temperature.

[1] Kaufman M., The History of PVC, Maclaren & Sons, London, (1969).

[2] Schmieder K., Wolf K., Kolloid-Z, 127, 65 (1952).

[3] Nijenhuis K., Winter H., Macromolecules, 22, 411 (1989).

[4] Mutin P.H., Guenet J.M., Macromolecules, 22, 843 (1989).

[5] Keller A., Faraday Discuss., 101, 1 (1995).

[6] Ferry J.D. Viscoelastic Properties of Polymers, John Wiley & Sons, New York (1980).

[7] Kakiuchi M., Aoki Y., Watanabe H., Osaki K., Macromolecules, 34, 2987 (2001).

[8] Garcia A., Munoz M.E., Pena J.J., Santamaria A., Macromolecules, 23, 5251 (1990).

[9] Najeh M., Munch J.P., Guenet J.M., Macromolecules, 25, 7018 (1992).

[10] Mijangos C., Lopez D., Munoz M.E., Santamaria A., Macromolecules, 26, 5693 (1993).

[11] Li L., Aoki Y., Macromolecules, 30, 7835 (1997).

[12] Flory P. J., Principles of Polymer Chemistry, Cornell University Press: Ithaca, New York (1953).

[13] Stockmayer W. H., J. Chem. Phys., 12, 125 (1944).

[14] de Gennes P. G., Scaling Concepts in Polymer Physics; Cornell University Press: Ithaca, NY, and London, (1979).

[15] Stauffer D., Introduction of Percolation Theory; Taylor and Francis: London, (1985).

[16] Martin J. E., Adolf D., Wilcoxon J. P., Phys. Rev. Lett., 61, 2620 (1988).

[17] Winter H., Chambon F., J. Rheol., 30, 367 (1986).

[18] Scanlan J.C., Winter H., Macromolecules, 24, 47 (1991).

[19] Aoki Y., Li L., Kakiuchi M., Macromolecules, 31, 8117 (1998).

[20] Watanabe H., Osaki K., Kakiuchi M., Aoki Y., Macromolecules, 34, 666 (2001).

[21] Nijenhuis K., Thermoreversible Gels and Network (1997).

[22] Aoki Y., Macromolecules, 34, 3500 (2001).