Thermal and Rheological Properties of Poly(vinyl alcohol) Gel with Boric Acid as a Crosslinking Agent

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ABSTRACT: The gel of poly(vinyl alcohol) polymer with boric acid, added as a crosslinking agent, was made with a mixture of dimethyl sulfoxide and water. The thermal and dynamic modulus properties of poly(vinyl alcohol) gel were measured by a differential scanning calorimeter and a dynamic mechanical thermoanalyst. Results show that an increase of poly(vinyl alcohol) polymer or boric acid content to the gel makes an increasing of gel to sol transition temperature, endothermic enthalpy, and dynamic modulus. The maximum value of gel to sol transition temperature, endothermic enthalpy, and dynamic modulus happened at the volume ratio of 6 : 4 of dimethyl sulfoxide to water, which is independent on the poly(vinyl alcohol) and the boric acid content. According to the modified Eldridge–Ferry theory for thermoreversible gel, it is found that both the gel to sol transition temperature and the endothermic enthalpy versus poly(vinyl alcohol) content could be superimposed with respect to the boric acid content. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2219–2226, 1999

Key words: poly(vinyl alcohol); boric acid; chemical gel

INTRODUCTION

A polymer gel is a structure of a three-dimensional network chain that are crosslinked by chemical or physical junctions. Polymer gels with physical junctions can be classified into four types: crystallites, double helical, nodules, and polymer–solvent complexes.[1] The chemical gel can be formed by chemical crosslinking of polymer with metallic ions or crosslinking agent. Poly(vinyl alcohol) (PVA) polymer has been focused for many years because of its special chemical and physical properties, as well as its application, such as textile fiber, fiber binder, hollow fiber, and separation membrance.[2] The special properties of PVA come from the hydroxyl groups in the main chain that can react with many functional groups, such as formaldehyde, urea, and alkylene oxide. Nevertheless, hydrogen bonding also plays an important role in the physical properties of poly(vinyl alcohol) polymer.

Gel spinning technique is applied to polyethylene polymer for production of ultrahigh-strength fiber[3] and is also applied to poly(vinyl alcohol) polymer as well.[4] However, the poly(vinyl alcohol) polymer is necessary to remove the hydrogen bonding between hydroxyl groups during gel spinning.
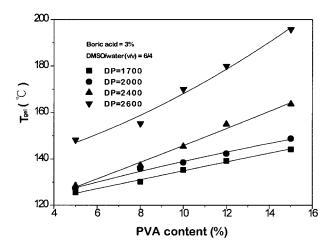
Poly(vinyl alcohol) can be formed physically or chemically into gel from its hydrogen bonding and/or its chemical reaction of hydroxyl groups. The hydrogen bonding plays an important role in its physical gelation. However, some inorganic ions, such as borate ions,[1,5] cupric ions,[6] titanic ions,[7] vanadate ions,[8] and congo ions[9] in poly(vinyl alcohol) solution can react with hydroxyl groups of poly(vinyl alcohol) under alkaline conditions to form a gel. The microstructures of these poly(vinyl alcohol) gels are not fully understood. Table I shows a qualitative comparison between the two types of poly(vinyl alcohol) gels.[10]

Table I Qualitative Comparison of the Hydrogel and the Alkaline Gel Prepared from Poly(vinyl alcohol) Aqueous Solution

Preparation	Hydrogel: Quenching of Poly(vinyl alcohol) Aqueous Solution	Alkaline Gel: Adding Borate Ion
Mechanical property	Nonrubberlike	Rubberlike
Optical property	Turbid	Clear
Gel–sol transition	Nonreversible	Reversible
Crosslinker	Microcrystallite	Borate-aided crosslinker

Mitsuhiro et al. had studied the possible chemical crosslinking reactive mechanism between the poly(vinyl alcohol) chain and the boric acid by [11]B nuclear magnetic resonance (NMR) spectroscopy[11] and proposed the models of the poly(vinyl alcohol)–borate ionic complex crosslinking mechanism,[11,12] that is, (1) the monodiol type, (2) the didiol type, and (3) the hydrogen or ionic bonding type. Besides, they also studied the sol–gel transition temperature of the physical gel of polyvinyl alcohol as a function of the poly(vinyl alcohol) content, the boric acid content, and the degree of polymerization. Mineo and Katsuyoshi[13] showed the thermal and rheological properties of the physical gel of poly(vinyl alcohol) in the mixtures of dimethyl sulfoxide and water and also demonstrated the stress relaxation and the thermal properties of partially saponificated poly-(vinyl alcohol)–dimethyl sulfoxide–water gel.[14] In this study, we focus on the chemically crosslinked gel of poly(vinyl alcohol) with boric acid as a crosslinking agent in the mixture of dimethyl sulfoxide and water and try to find the relationship of the gel to sol transition temperature and/or the enthalpy of poly(vinyl alcohol) gel to the poly(vinyl alcohol) content, the boric acid content, and the degree of polymerization. Moreover, we also investigate the effect of volumetric ratio of mixed solvent (dimethyl sulfoxide to water) on the gel to sol transition temperature and the enthalpy of poly(vinyl alcohol) gel. Finally, the relationship between the rheological property of poly(vinyl alcohol) gel with the poly(vinyl alcohol) content, boric acid content, and volumetric ratio of mixed solvent is discussed.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) polymer was supplied from Chang Chun Petrochemical Co. Ltd. Table II

Figure 1 The effect of gel to sol transition temperature on the poly(vinyl alcohol) content.

Figure 2 The effect of endothermic enthalpy on the poly(vinyl alcohol) content.

Table II The Characteristics of the Poly(vinyl alcohol) Polymer

Sample Code	Degree of Polymerization	Viscosity (cps)	Hydrolysis (mol %)
BF-26	2600	75–86	98.5–99.2
BF-24	2400	58–68	98.5–99.2
BF-20	2000	35–43	98.5–99.4
BF-17	1700	25–30	98.5–99.2

Table III   The Gel to Sol Transition Temperature of PVA Gel with Different PVA Contents and Solvent Ratios

Code	PVA Content (g/dL)					Mixed Ratio of DMSO to Water (V/V)						
	5	8	10	12	15	2/8	3/7	4/6	5/5	6/4	7/3	8/2
BF-17	126[a]	130	135	139	144	110[b]	115	120	123	144	126	125
BF-20	127	136	139	142	149	115	121	125	128	149	130	128
BF-24	129	137	146	155	164	128	130	134	138	160	140	137
BF-26	148	155	170	180	196	159	162	167	171	196	180	171

[a] The gel to sol transition temperature (°C) of PVA gel at boric acid is 3%; DMSO/water is 6/4, but with different PVA contents.
[b] The gel to sol transition temperature (°C) of PVA gel at boric acid is 3%; PVA content is 15%, but with different DMSO/water ratios.

shows the characteristics of polyvinyl alcohol polymer.

The poly(vinyl alcohol) gel was prepared from the poly(vinyl alcohol) polymer heated in the mixture solvent of dimethyl sulfoxide and water with boric acid as a crosslinking agent. After poly(vinyl alcohol) polymer being fully dissolved, it was then cooled to room temperature to form a gel.

Gel to Sol Transition Temperature Measurement

The measurement of gel to sol transition temperature (T_{gel}) of PVA gel was carried out by a sensitive Du Pont 910S differential scanning calorimeter and Thermal analyst 2000. About 5 mg of PVA gel was sealed into the aluminum pan. The temperature was raised at a heating rate 5°C per min under the nitrogen gas to observe the endothermic behavior of the gel to sol transition. From the heating curve, the temperature of endothermic peak was recorded as the gel to sol transition temperature of PVA gel.

Dynamic Young's Modulus Measurement

Dynamic Young's modulus (log E') was performed at 0.3–5 Hz by a Polymer Laboratory PL–

DMTA. The temperature was raised at a heating rate of 10°C per min. The loading weight 0.1N was used. The sample shape of poly(vinyl alcohol) gel for rheological measurement was rectangular (1×0.5 cm), and the thickness of sample was 3 mm.

RESULTS AND DISCUSSION
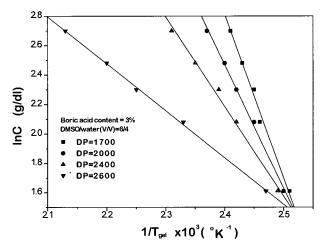
Thermal Properties of Poly(vinyl alcohol) Gel

Figures 1 and 2 and Tables III and IV show the relationship of gel to sol transition temperature (T_{gel}) and the endothermic enthalpy (ΔH_m) of PVA gel to the PVA content with four types of degree of polymerization (DP), respectively. It is found that both the gel to sol transition temperature and the endothermic enthalpy are increased with an increasing content of poly(vinyl alcohol). We suggest that the size of network junction of poly(vinyl alcohol) gel is decreased with the increase of the poly(vinyl alcohol) content; that is, the size of network junction in gel is short but numerous in higher polymer content.

According to the modified Eldridge–Ferry theory of gel melting,[11,12] the poly(vinyl alcohol) con-

Table IV   The Endothermic Enthalpy of PVA Gel with Different PVA Contents and Solvent Ratios

Code	PVA Content (g/dL)					Mixed Ratio of DMSO to Water (V/V)						
	5	8	10	12	15	2/8	3/7	4/6	5/5	6/4	7/3	8/2
BF-17	62[a]	64	66	69	73	57[b]	60	65	70	73	69	64
BF-20	68	70	74	75	79	62	65	71	76	79	75	70
BF-24	73	74	77	80	84	69	72	76	82	84	80	76
BF-26	78	80	82	85	88	72	75	80	85	88	84	79

[a] The experimental value of endothermic enthalpy $(\Delta H_m)_e$ (J/g) of PVA gel at boric acid is 3%; DMSO/water is 6/4, but with different PVA contents.
[b] The experimental value of endothermic enthalpy $(\Delta H_m)_e$ (J/g) of PVA gel at boric acid is 3%; PVA content is 15%, but with different DMSO/water ratios.

Figure 3 Dependence of the logarithm of the poly(vinyl alcohol) content on the reciprocal of the gel to sol transition temperature.

tent (C) in gel is related to the boric acid content (B) and the degree of polymerization of polyvinyl alcohol polymer (P) and is given by

$$\ln(CBP) = \text{constant} + \Delta H_m/RT_{gel} + \ln\{([H^+] + Ka)/Ka\} \quad (1)$$

where Ka is the ionic constant of boric acid and R and [H$^+$] are the gas constant and proton concentration, respectively. Since [H$^+$] is much smaller than Ka, the item of $\ln\{([H^+] + Ka)/Ka\}$ can be neglected. Equation (1) is rewritten as

$$\ln(CBP) = \text{constant} + \Delta H_m/RT_{gel} \quad (2)$$

As both the degree of polymerization (P) and the boric acid content (B) are kept constant, eq. (2) is rewritten as

$$\ln(C) = \text{constant} + \Delta H_m/RT_{gel} \quad (3)$$

Based on eq. (3), the relationship between the logarithm of poly(vinyl alcohol) content ($\ln C$) with reciprocal of the gel to sol transition temperature ($1/T_{gel}$) can be plotted and shown in Figure 3. As seen in the figure, the experimental data are roughly falling onto a straight line, as expected from the theory and the theoretical enthalpy ($(\Delta H_m)_t$) of the gel can be evaluated from the slope of the curve. The theoretical value is compared to the experimental value [$(\Delta H_m)_e$], which is obtained from the differential scanning calorimetry (DSC) measurement, is listed in Table V. The theoretical value seems to be larger than the experimental one.

Moreover, in case of the poly(vinyl alcohol) content (C) and the degree of polymerization (P) are kept constant, eq. (2) can be rewritten as

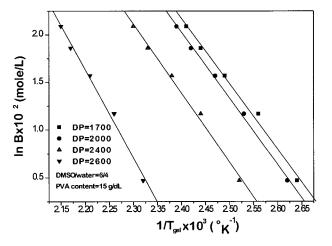$$\ln(B) = \text{constant} + \Delta H_m/RT_{gel} \quad (4)$$

Figure 4 illustrates the logarithm of boric acid content ($\ln B$) with the reciprocal of the gel to sol transition temperature of poly(vinyl alcohol) gel. The theoretical endothermic enthalpy of the gel can be calculated from the slope of the curve and is listed in Table VI. It demonstrates that the theoretical value is larger than that the experimental one. Besides that, it is also found that both the temperature of endothermic peak (T_{gel}) and the experimental endothermic enthalpy ($\Delta H_m)_e$ are increased with an increase in the boric acid content. It is believed that as the boric acid used a crosslinking agent in the poly(vinyl alcohol) polymer, it can form a didiol complex with the PVA by hydrogen bonding.[5] An increase

Table V   The Theoretical and the Experimental Endothermic Enthalpy of PVA Gel with Different PVA Contents

| | PVA Content (g/dL) | | | | | | | | | |
| | 5 | | 8 | | 10 | | 12 | | 15 | |
Code	Theo[a]	Exper[b]	Theo	Exper	Theo	Exper	Theo	Exper	Theo	Exper
BF-17	66	62	69	64	73	66	76	69	80	73
BF-20	72	68	77	70	79	74	83	75	86	81
BF-24	76	73	81	74	84	77	88	80	92	84
BF-26	81	78	88	80	90	82	92	88	95	88

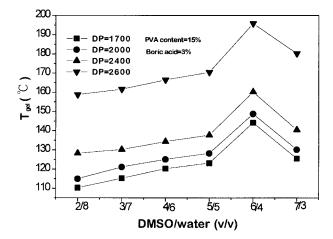[a] Theoretical value of endothermic enthalpy in PVA gel $(\Delta H_m)_t$ (J/g).
[b] Experimental value of endothermic enthalpy in PVA gel $(\Delta H_m)_e$ (J/g).

Figure 4 Dependence of the logarithm of the boric acid content on the reciprocal of gel to sol transition temperature.

Figure 5 The effect of the gel to sol transition temperature on the volumetric ratio of mixed solvent.

of the boric acid content can result in a higher degree of crosslinking since the average distance between the nearest crosslinked points becomes shorter. The molecular chain of gel behaves less mobile. Thus, a higher temperature of endothermic transition and the endothermic enthalpy of PVA gel are the result.

As seen in Figures 5 and 6 and Tables III and IV, it is found that both the gel to sol transition temperature and the endothermic enthalpy of PVA gel transition are dependent on the mixed solvent volumetric ratio. It exhibits a maximum value of the endothermic peak temperature at the volumetric ratio of 6 : 4 in the mixed solvent (dimethyl sulfoxide to water), irrespective of the content of polyvinyl alcohol (Fig. 5). Figure 6 also shows the relationship of the endothermic enthalpy of poly(vinyl alcohol) gels to the mixed

solvent volumetric ratio. The maximum value is occurred similar to the result of the gel to sol transition temperature with a maximum value at 6 : 4 of the mixed solvent volumetric ratio. It can be explained that although the poly(vinyl alcohol) polymer can be dissolved in dimethyl sulfoxide or water, but it is difficult to form a strong gel. Since water is a poor solvent for poly(vinyl alcohol), it retards the molecular chain of polymer to swell.[14]
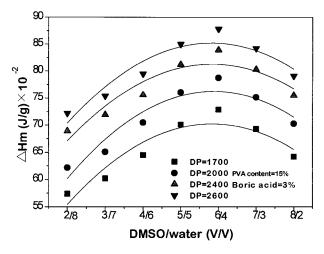
Generally speaking, the state of poly(vinyl alcohol) gel is dependent on a balance of the crystallinity and the solubility.[13,14] As the volumetric ratio of dimethyl sulfoxide to water increased from 2 : 8 to 6 : 4, both the gel to sol transition temperature and the endothermic enthalpy are increased (Figs. 5 and 6), it is attributed to the decrease of the free water (unreacted water) in the mixed solvent. As the free water content is more, the ability to form a poly(vinyl alcohol) gel

Table VI   The Theoretical and the Experimental Endothermic Enthalpy of PVA Gel with Different Boric Acid Contents

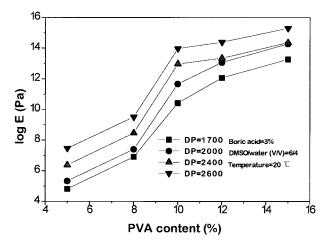|	Boric Acid Content (%)									
	1		2		3		4		5	
Code	Theo[a]	Exper[b]	Theo	Exper	Theo	Exper	Theo	Exper	Theo	Exper
BF-17	70	65	76	70	81	73	82	76	86	78
BF-20	81	74	87	79	90	81	90	85	96	87
BF-24	83	76	90	81	93	84	95	87	104	89
BF-26	86	80	93	85	98	88	99	91	109	93

[a] Theoretical value of endothermic enthalpy in PVA gel $(\Delta H_m)_t$ (J/g).
[b] Experimental value of endothermic enthalpy in PVA gel $(\Delta H_m)_e$ (J/g).

Figure 6 The effect of endothermic enthalpy on the volumetric ratio of the mixed solvent.

Figure 7 The effect of the modulus of gel on the poly(vinyl alcohol) content.

is poor. On the contrary, at the volumetric ratio ranged from 6 : 4 to 8 : 2, both the gel to sol transition temperature and the endothermic enthalpy are decreased. It is the result of the increase of free dimethyl sulfoxide. As the free dimethyl sulfoxide content increased, the solubility of poly(vinyl alcohol) gel is enhanced. Thus, at the point of volumetric ratio of 6 : 4 (dimethyl sulfoxide to water), both the gel to sol transition temperature and the endothermic enthalpy reach a maximum value, and the free water and the free dimethyl sulfoxide content has a minimum value. Dimethyl sulfoxide is a polar solvent with a large dielectric constant. Its affinity with water is high. The interaction between dimethyl sulfoxide and water is very strong. The mixture of water and dimethyl sulfoxide shows a special characteristics.[13] Schichman and Amey[15] and Bowen et al.[16] had reported that the structure of hydrated compound of water and dimethyl sulfoxide is $(CH_3)_2SO \cdot 2H_2O$ by viscometric and ultrasound velocity methods. But Rasmussen and MacKenzie[17] had also sug-

gested that it is $(CH_3)_2SO \cdot 3H_2O$ by neutron diffraction method.
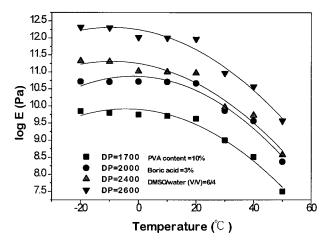
Rheological Properties of Poly(vinyl alcohol) Gel

Figure 7 and Table VII shows that the relationship of the modulus of poly(vinyl alcohol) gel to the poly(vinyl alcohol) content with four types of degree of polymerization. The modulus of poly(vinyl alcohol) gel is proportionally increased with an increasing of poly(vinyl alcohol) content. It is known that the elastic modulus of many gels, such as gelatin, agar–agar, and carrageenan, are approximately proportional to the fourth power of the polymer content at lower concentration, but proportional to a second power beyond a certain polymer content.[18] The elasticity of poly(vinyl alcohol) gel is resulted from the microBrowian motion of long chain molecules between the crosslinking junctions. These crosslinking junctions are formed not by primary chemical bonds (covalent bonds), but rather by secondary bonds, such as hydrogen bonds formed with boric acid as

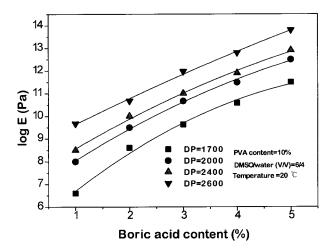**Table VII   The Modulus of PVA Gel at Different PVA and Boric Acid Contents**

Code	PVA Content (g/dL)					Boric Acid Content (%)				
	5	8	10	12	15	1	2	3	4	5
BF-17	4.81[a]	6.91	10.42	12.07	13.27	6.60	8.60	9.63	10.58	11.5
BF-20	5.33	7.41	11.67	13.07	14.27	8.01	9.50	10.67	11.50	12.51
BF-24	6.37	8.47	12.97	13.35	14.25	8.50	10.01	11.02	11.90	12.91
BF-24	7.47	9.51	13.97	14.39	15.29	9.67	10.67	11.97	12.80	13.81

[a] The modulus (Pa) of poly(vinyl alcohol) gel at different PVA and boric acid contents.

Figure 8 The effect of the modulus of poly(vinyl alcohol) gel on the temperature.

Figure 9 The effect of the modulus of poly(vinyl alcohol) gel on the boric acid content.

a crosslinking agent. The elasticity supported by secondary bonds will be destroyed with the breaking of these bonds at a higher temperature.[18] The decrease of modulus of poly(vinyl alcohol) gel with an increasing temperature is due to the segmental movement of poly(vinyl alcohol) gel. As seen in Figure 8 and Table VIII, it demonstrates that the moduli of poly(vinyl alcohol) gel show no significant difference in the temperature range of $-20 \sim 20°C$; but it drops quickly as the temperature is higher than 20°C. The reason for the decrease of $\log E'$ is believed to be the breakage of the hydrogen bonds of the poly(vinyl alcohol) gel above 20°C. In poly(vinyl alcohol) gel, the breakage of hydrogen bonds with heat, which can be reformed during cooling (a thermoreversible hydrogen bond), is the behavior of our system. On the contrary, the crystallites, which are responsible for the elasticity in the poly(vinyl alcohol) hydrogel, cannot be easily reconstructed at room temperature while they are broken. Therefore, the temperature dependence of modulus for poly(vinyl
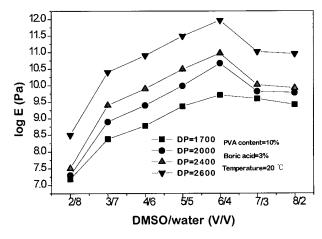
alcohol) gel with boric acid as a crosslinking agent is similar to that of agar–agar.[18]

A simple gel model[13] has been proposed here to explain the phenomena of temperature dependence of elasticity of thermoreversible poly(vinyl alcohol) gel. The gel molecule can be considered as consisting of Langevin chains, whose both ends are loosely fixed in crystalline junction regions in such a way that the segments near each end are bound densely in one of the junction region. According to the model, the segments are assumed to be released from the junction zone at a higher temperature just as thread is released from a wheel. When all the segments in one of the ends are liberated from the junction zones, the chain is called a free chain as in the theory of rubber elasticity and would cease to contribute to the elasticity. Figures 9 and 10 show the relationship of the modulus of poly(vinyl alcohol) gel with different boric acid contents and the volumetric ratios of the mixed solvent, respectively. As seen in Figure 9 and Table VII, it demonstrates that the

Table VIII   The Modulus of PVA Gel at Different Temperature

Code	Temperature (°C)							
	-20	-10	0	10	20	30	40	50
BF-17	9.85[a]	9.80	9.75	9.71	9.63	9.01	8.51	7.5
BF-20	10.72	10.71	10.72	10.71	10.67	9.87	9.57	8.37
BF-24	11.32	11.30	11.02	11.01	10.97	9.97	9.73	8.57
BF-26	12.32	12.30	12.02	12.01	11.97	10.97	10.57	9.57

[a] The modulus (Pa) of poly(vinyl alcohol) gel at different temperatures.

Figure 10   The effect of the modulus of poly(vinyl alcohol) gel on the volumetric ratio of the mixed solvent.

Table IX   The Modulus of PVA Gel at Different Solvent Ratios

	Mix Ratio of DMSO to Water (V/V)						
Code	2/8	3/7	4/6	5/5	6/4	7/3	8/2
BF-17	7.18[a]	8.38	8.78	9.37	9.71	9.60	9.42
BF-20	7.30	8.19	9.40	9.99	10.67	9.82	9.78
BF-24	7.80	9.41	9.90	10.49	10.97	10.02	9.92
BF-26	8.51	10.40	10.91	11.49	11.97	11.02	10.95

[a] The modulus (Pa) of poly(vinyl alcohol) gel at different solvent ratios.

modulus of poly(vinyl alcohol) gel is increased with an increasing of boric acid content. This suggests that the modulus of thermoreversible gel is proportional to the number of crosslinkings in the junction zone if the conformations of flexible chains are the same.[13] The number of crosslinkings in junction zone will be increased with an increasing of the boric acid content, so the modulus of poly(vinyl alcohol) gel is increased. Also, as seen in Figure 10 and Table IX, the modulus of poly(vinyl alcohol) gel exhibits a maximum value at the volumetric ratio of 6 : 4 (dimethyl sulfoxide to water). It is consistency with the behavior found in the gel to sol transition temperature and the endothermic enthalpy, as found in Figures 5 and 6, respectively.

CONCLUSIONS

With boric acid as a crosslinking agent, the thermal and rheological properties of polyvinyl alcohol gel have been studied in the article. It is found that the gel to sol transition temperature, the endothermic enthalpy, and the dynamic modulus are increased with an increase in the poly(vinyl alcohol) or the boric acid content. The modified Eldridge–Ferry theory is successful to describe the relationship between the logarithm of poly(vinyl alcohol) content and/or the boric acid content to the reciprocal of the gel to sol transition temperature. Moreover, it is also manifested that the maximum value of gel to sol transition tempera-

ture, endothermic enthalpy, and dynamic modulus happens at the volumetric ratio of 6 : 4 in the mixed solvent of dimethyl sulfoxide to water, irrespective of the content of poly(vinyl alcohol).

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