

The Effect of Syndiotacticity on the Gelation of Aqueous Poly(vinyl Alcohol) Solutions with Congo Red

MASAYUKI KIUCHI, AKIMOTO UCHIKAWA, TETSUYA TANIGAMI, SHUJI MATSUZAWA,* KAZUO YAMAURA

Faculty of Textile Science and Technology, Shinshu University, Tokida 3-15-1, Ueda-city, Nagano-prefecture 386-8567, Japan

Received 1 June 2001; accepted 28 August 2001

ABSTRACT: The gelation of aqueous solutions containing syndiotacticity rich poly(vinyl alcohol) (*s*-PVA) and Congo red was studied. The gelation occurred even at 40°C, different from aqueous solutions containing atactic PVA (*a*-PVA) and Congo red. The melting point of gels, which were prepared from the solutions of *s*-PVA concentration of 2.5% and Congo red concentration of 0.1%, was around 90°C. The size of the junction points in *s*-PVA/Congo red hydrogels is larger than that of *a*-PVA/Congo red hydrogels at each fixed Congo red concentration. Syndiotactic sequence length plays an important role in gelation. The melting points and shear moduli of the gels prepared from dilute polymer solution at 0–40°C changed through a maximum at around 0.1–0.3% of Congo red concentration and also a maximum at around 1.5%, identical to results reported already for *a*-PVA/Congo red hydrogel prepared at 20°C. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 632–637, 2002

Key words: PVA; syndiotactic; Congo red; gelation; melting point

INTRODUCTION

The gelation of aqueous poly(vinyl alcohol) (PVA) solutions with Congo red was discovered by Herrmann and Haehnel in 1936 as a way to prepare hard PVA solids, and patented in several countries until 1943.¹ Investigations on the structure and properties of the gel were started in 1954 by Hirai, who attributed the elasticity of the gel to the entropic effect of PVA molecular segments,² and followed by Motoyama and Okamura, who discovered the specific effect of the Congo red with PVA and the polyelectrolytic property of the PVA–

Congo red complex.³ The rigidity and melting of the gel,⁴ the X-ray pattern of the dried gel,⁵ the relaxation of applied force of the gel,⁶ and the gelation process have been investigated since. Recently, the gelation ability was found not to increase monotonously with increasing Congo red concentration, but at a lower concentration, gel obtained was easier and crosslinks due to the complexation of the amino groups in the dye molecules were proposed to be influenced complicatedly by the Congo red concentration.

The PVA used so far was atactic (commercial) PVA (*a*-PVA), which has nearly equal amounts of isotactic and syndiotactic diads. In syndiotacticity-rich PVA (*s*-PVA) stable PVA–Congo red hydrogels were found to be formed. This article reports on the melting points and shear modulus of the gels, and electromicroscopic observation and X-ray analysis of the dried gels. The mechanism of the crosslinking is considered.

Correspondence to: K. Yamaura.

*Professor Emeritus.

Contract grant sponsor: Grant-in-Aid for COE Research by the Ministry of Education, Science, Sports and Culture of Japan; contract grant number: 10CE2003.

Journal of Applied Polymer Science, Vol. 85, 632–637 (2002)
© 2002 Wiley Periodicals, Inc.

EXPERIMENTAL

PVA Samples and Congo Red

The *s*-PVA samples were prepared through the ammonolysis of poly(vinyl trifluoroacetate) obtained through bulk polymerization at 60°C. The *s*-PVA with the *s*-diad % of ca. 57 and the degree of polymerization of 2660 (*s*-1), 2730 (*s*-2), and 2900 (*s*-3) were obtained. An α -PVA, with the degree of polymerization of 3000, was generously supplied by Shin-etsu Chemicals Co. Ltd. Congo red purchased from Wako Pure Chemicals Co. Ltd. was used without further purification.

Preparation of PVA–Congo Red Hydrogels

Fixed amounts of *s*-PVA were dissolved in water with a fixed amount of Congo red at 120°C in sealed glass ampoules. The ampoules were placed in a bath controlled to a temperature (0–40°C) to form a gel.

Ultraviolet and Visible Light Absorption Spectra of a Gel

A gel was prepared from the aqueous PVA–Congo red solution in a test tube with an inner diameter of 12 mm. A test tube, with the gel cut to a length similar to the cell, was used as a cell for ultraviolet and visible light-absorption measurement, and the spectra were taken with use of a Shimadzu UV-160 spectrometer.

Melting Point of Gel

An ampule containing a gel was immersed upside down in a water bath, the temperature of which was controlled to the gelling temperature. The

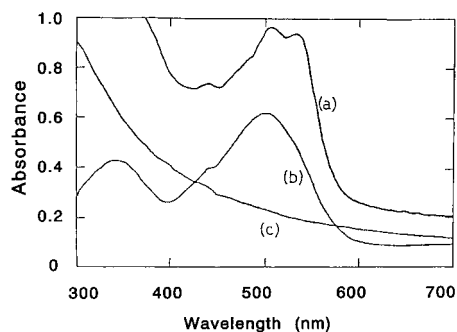


Figure 1 UV and Vs absorption spectra of *s*-PVA/Congo red hydrogel. (a): *s*-PVA(*s*-1)/Congo red hydrogel prepared at 0°C, (b): Congo red/water, (c): *s*-PVA/Water.

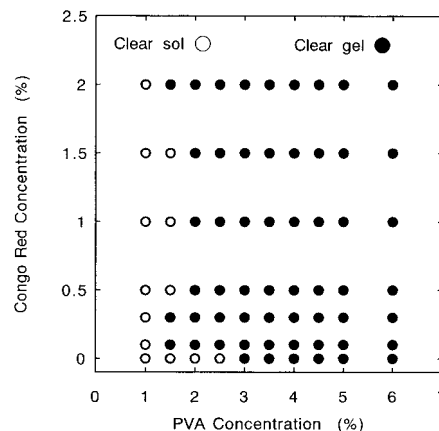


Figure 2 Sol-gel transition map of *s*-PVA(*s*-2)/Congo red/water at 40°C.

temperature of the bath was raised 2°C per minute. The temperature at which a gel flowed was assumed to be the melting point. In addition, ampoules with the gels prepared at 0°C were immersed in a bath controlled to 50°C, and the melting points were determined.

Shear Moduli of Gels

Shear modulus of a gel was determined using the concentric cylinder method developed by Schwed-off.¹⁰ The details of the method are described in the preceding article.¹¹

X-ray and Electron Microscopic Analysis of Gels

The X-ray patterns of frozen and dried gels were taken with a Shimadzu XD-610 at 30–40 kV with the camera length of 45 mm. The electron microscopic photographs of frozen and dried gels were taken with a JEOL JSM-220A electron microscope.

RESULTS AND DISCUSSION

Figure 1 shows the ultraviolet and visible light absorption spectra of *s*-PVA–Congo red hydrogel with aqueous Congo red and PVA solutions. The maximum in the spectra of Congo red in the hydrogel shifted to a longer wavelength and a new peak was found at 532 nm. Similar results had been found for α -PVA, although the separation between two peaks was not seen in the spectra.³ This fact suggests the formation of a complex between PVA and Congo red molecules.

Figure 2 shows the sol-gel transition map at

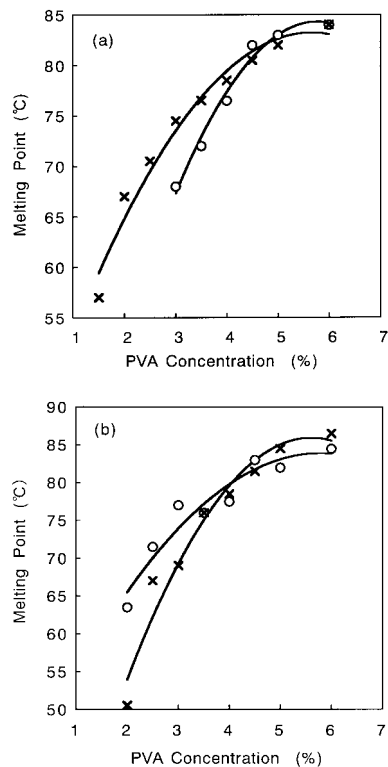


Figure 3 Relation between melting points and *s*-PVA(*s*-2) concentrations at different Congo red concentrations for the gels prepared at 40°C. (a) ○ Congo red 0%, × Congo red 0.1%, (b) ○ Congo red 0.5%, × Congo red 1.5%.

40°C. Similar maps were obtained at 0, 10, 20, and 30°C. At any gelling temperature 1.5% PVA solutions with Congo red concentrations of 0.1, 0.3, and 2.0%, respectively, gelled, whereas those with Congo red concentrations of 0.5, 1.0, and 1.5% (except at 30°C) did not gel. This suggests that there might be a Congo red concentration region that makes the solution difficult to gel. Similar results are found for aqueous α -PVA/Congo red solutions at 20°C, although above 20°C this was not the case, as the solutions did not gel.

Figure 3(a) and (b) shows plots of the melting point against *s*-PVA concentration for different Congo red concentrations. Figure 4(a) shows the plots of the melting point against Congo red concentration for the gels prepared at 40°C with fixed *s*-PVA concentrations. Figure 4(b) shows similar plots for the gels prepared at different temperatures with *s*-PVA concentration of 2%. At lower *s*-PVA concentrations the melting behaviors of the gels were not in accordance with Congo red concentration with a minimum at the Congo red concentration of around 1.5%, whereas at higher

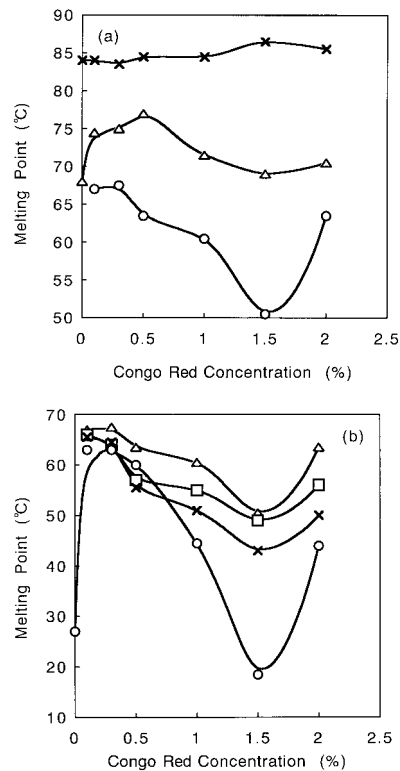


Figure 4 Relation between melting point and Congo red concentration for the gels prepared at different temperatures. (a) 40°C, *s*-PVA (*s*-2) conc.: ×; 6%, △; 3%, ○; 2%. (b) *s*-PVA conc. 2%, △; 40°C, □; 30°C, ×; 20°C, ○; 0°C.

PVA concentrations they are almost identical to those of pure *s*-PVA hydrogels.

Figure 5 shows plots of shear modulus against Congo red concentration for the gels with *s*-PVA concentration of 2% at 30°C. Similar plots were obtained for gels prepared at 0°C. A similar curve

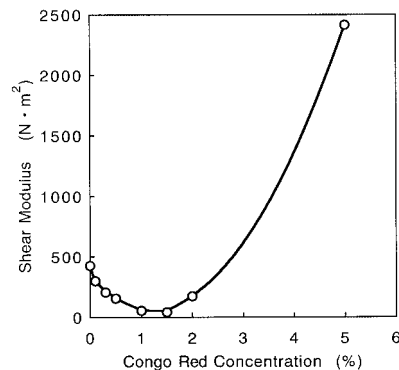


Figure 5 Relation between shear modulus and Congo red concentration for the gels prepared at 30°C, *s*-PVA (*s*-3) concentration 2%.

of the melting point vs. Congo red concentration had also been obtained. For α -PVA alone the aqueous solution with polymer concentration of 5% gelled and those with concentrations below 2% did not gel. The reason why the melting point or shear modulus have a minimum at a Congo red concentration for dilute PVA concentrations was in accordance with the explanation of Shibayama et al.⁸ as follows: at lower Congo red concentration two amino groups in a Congo red anion form a hydrogen bond with hydroxyl groups in different PVA molecules leading to crosslinking. With increasing Congo red concentration each PVA molecule bonded to an amino group in Congo red anion becomes repulsive to render crosslinking. At high Congo red concentration the repulsion of Congo red anions is reduced due to positive sodium cations leading to crosslinking. The easier gelation for an s -PVA/Congo red/water system than α -PVA/Congo red/water system was considered as follows. Solid α -PVA has a certain amount of intramolecular hydrogen bonds and intermo-

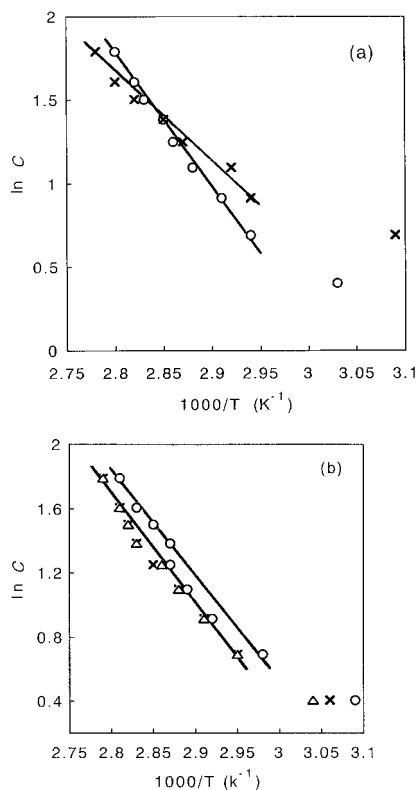


Figure 6 Plots of logarithm of concentration against reciprocal absolute temperature. (a) Congo red conc.: ○; 0.1%, ×; 1.5%, gelling temperature 40°C. (b) gelling temperature: ○; 0°C, ×; 20°C, △; 30°C, Congo red conc.: 0.1%.

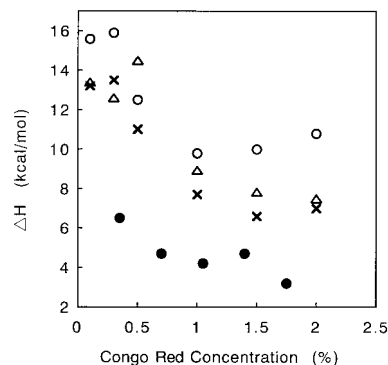


Figure 7 Dependence of ΔH on Congo red concentration. Gelling temperature: ○; 40°C, △; 30°C, ×; 0°C. ●; α -PVA/Congo red hydrogel.⁸

lecular hydrogen bonds.¹² With increasing syndiotacticity intramolecular hydrogen bonds decrease and intermolecular hydrogen bonds increase. Therefore, hydroxyl groups in s -PVA molecules are considered to be easy to bond with Congo red anions in water. The enthalpies of fusion ΔH were estimated by the Eldridge-Ferry relation $\ln C = \text{Const} - \Delta H/RT$ (C : the concentration, R : the gas constant, T : the absolute temperature). Straight lines were obtained except for the melting points at the lowest concentration of s -PVA when $\ln C$ was plotted against $1/T$ [see Fig. 6(a) and (b)]. Figure 7 shows the plots of ΔH against Congo red concentration. In this figure the ΔH value for α -PVA reported by Shibayama et al. are also shown. The ΔH of s -PVA/Congo red hydrogel was higher than that of α -PVA/Congo red hydrogel at a fixed Congo red concentration. The ΔH changes through maximum to a minimum with increasing Congo red concentration in both kinds of hydrogels. The maximum and minimum correspond to easy and uneasy gelation systems, respectively. The ΔH for the gel prepared at 40°C was higher than that at 0°C. These facts suggest that s -PVA/Congo red hydrogels have larger junction points than α -PVA/Congo red hydrogel at a fixed Congo red concentration. This corresponds to easy gelation of the s -PVA/Congo red/water system. The size of the junction points increases with increasing gelling temperature.

The plots of the light transmittance of 800 nm of the gel against Congo red concentration are shown in Figure 8. The curves are similar to that of the melting point, shear modulus, and ΔH dependencies on Congo red concentration, i.e., the transmittance has a minimum at the Congo red concentration of 1.0%. This suggests that the gel

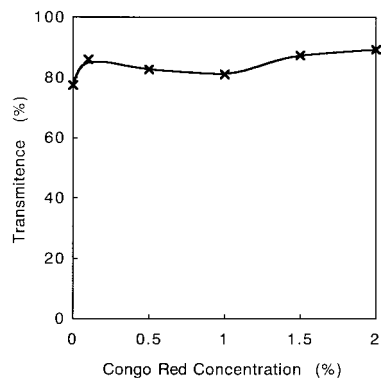


Figure 8 Dependence of transmittance of light of 800 nm on Congo red concentration. *S*-PVA (*s*-2) 2%, Gelation temperature; 0°C.

prepared at one Congo red concentration has a more heterogeneous structure than the gel prepared at other Congo red concentrations.

At higher *s*-PVA concentrations the melting point of *s*-PVA/Congo red hydrogel and that of *s*-PVA hydrogel are nearly equal at a fixed polymer concentration. The structure of both kinds of gels are, however, not equal, because the *s*-PVA hydrogels prepared at 0°C melted when immersed in a bath controlled to 80°C, whereas *s*-PVA/Congo red hydrogels did not do so. Figure 9 shows the plots of the melting point against Congo red concentration for the experiment. In *s*-PVA hydrogels with concentrations above 4.0%, when the gels prepared at 0°C were heated gradually from 0°C they melted at temperatures above 50°C due to the growth of the junction points.¹⁵

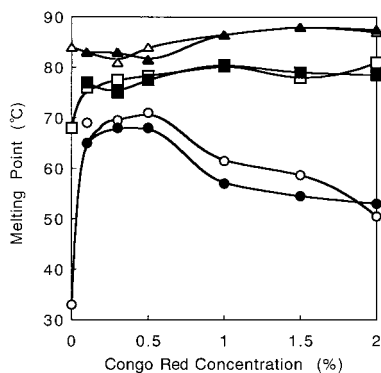


Figure 9 Comparison of melting points of the 0°C gels measured starting from 0 and 50°C, respectively. ○ from 0°C, ● from 50°C. PVA conc.; 6% □ from 0°C, ■ from 50°C. PVA conc.; 4% △ from 0°C, ▲ from 50°C. PVA conc.; 2.5%.

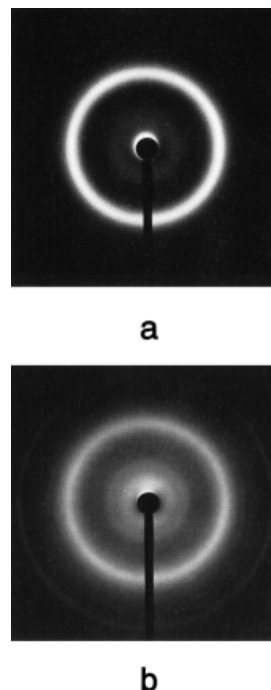
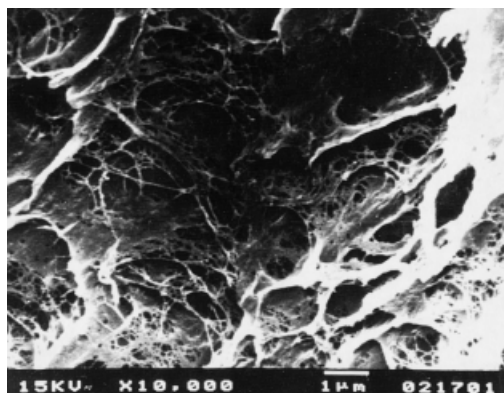


Figure 10 X-ray patterns of frozen and dried *s*-PVA (*s*-1)/Congo red hydrogels (*s*-PVA 2%). Congo red conc.: (a) 0.1%, (b) 1.5%.

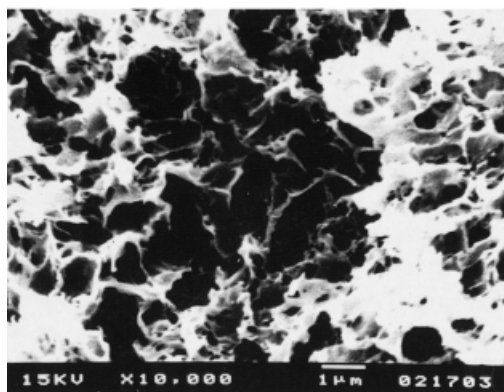
Figure 10(a) and (b) shows X-ray patterns of the frozen and dried gels prepared from gels with maximum and minimum melting points in Figure 4. No *s*-PVA crystals were observed, although in Figure 10(b) the diffraction due to Congo red crystals was found. Figure 11(a) and (b) shows electron microscopic photographs of the samples used for taking X-ray patterns. The sample prepared from the gel with the maximum melting point had a fine network, whereas the gel with the minimum melting point had a coarse network.

CONCLUSIONS

Aqueous solutions of *s*-PVA containing Congo red gel, even at 40°C, were different from aqueous solution of *a*-PVA containing Congo red. Syndiotactic sequence length might play an important role in gelation. The size of the junction points in *s*-PVA/Congo red hydrogels was larger than that of a *a*-PVA/Congo red hydrogel at each fixed Congo red concentration. The melting points and shear moduli of the gels, prepared from the dilute polymer solution at 0–40°C, changed through a maximum at around 0.1–0.3% of Congo red concentration and also a minimum at around 1.5% of



a



b

Figure 11 Electromicroscopic photographs of samples used for X-ray patterns. *S*-PVA 2%. Congo red conc.: (a) 0.1%, (b) 1.5%.

Congo red concentration, which were identical with the results reported already for α -PVA/Congo red hydrogel prepared at 20°C.

The authors are grateful to Associate Prof. K. Hamada, Shinshu University, for helpful discussions, and to Dr.

M. Islam and Mr. M. S. Shaheen, Shinshu University, for assistance in the article preparation. A part of this work was supported by Grant-in-Aid for COE Research (10CE2003) by the Ministry of Education, Science, Sports and Culture of Japan.

REFERENCES

- Herrmann, W. O.; Hachnel, W. Fr. Pat. 807, 042 (1936); Br. Pat. 476, 314 (1937); U.S. Pat. 2, 125, 374 (1938); Ger. Pat. 686, 123 (1940); Ger. Pat. 743, 091 (1943) to Chemische Forschungsgesellschaft m.b.H.
- Hirai, N. Nippon Kagaku Zasshi 1954, 25, 693, 695, 697.
- Motoyama, T.; Obamura, S. Kobunshi Kagaku 1954, 11, 23.
- Dittmar, C.; Priest, W. J. J Polym Sci 1955, 18, 275.
- Orada, A.; Sakurada, I. Kobunshi Kagaku 1958, 15, 671.
- Arakawa, K. Bull Chem Soc Jpn 1959, 32, 1248, 1568.
- Beltman, H.; Lyklema, J. Faraday Discuss Chem Soc 1974, 57, 92.
- Shibayama, M.; Ikkai, F.; Moriwaki, R.; Nomura, S. Macromolecules 1994, 27, 1738.
- Shibayama, M.; Ikkai, F.; Nomura, S. Macromolecules 1994, 27, 6383.
- Schuedoff, Th. J Phys (Paris) 1989, 8, 341.
- Matsuzawa, S.; Yamaura, K.; Maeda, R.; Ogasawara, K. Makromol Chem 1979, 180, 229.
- Hu, S.; Horii, F.; Odani, H. Bull Inst Chem Res Kyoto Univ 1991, 69, 165.
- Horii, F.; Hu, S.; Ito, T.; Odani, H.; Kitamaru, R.; Matsuzawa, S.; Yamaura, K. Polymer 1992, 33, 2299.
- Eldridge, J. E.; Ferry, J. D. J Phys Chem 1954, 58, 992.
- Matsuzawa, S.; Yamaura, K.; Maeda, R.; Ogasawara, K. Makromol Chem 1979, 180, 229.