

Hierarchic Structure of Poly(vinyl alcohol) Gels

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We studied the structure and its formation process of poly(vinyl alcohol) gels formed in a mixture of deuterated dimethyl sulfoxide (DMSO- d_6) and heavy water at 25 °C, using various kinds of scattering techniques such as wide-, medium-, small- and ultra small-angle neutron scattering and light scattering to cover a wide Q -range of 10^{-4} to $10 \text{ \AA}^{-1}$, corresponding to a real space of 0.63 to 63000 Å. On the basis of the results, we will discuss the hierarchic structure of PVA gels, which is basically determined by competition between the rate of liquid-liquid phase separation and the rate of crystallization or formation of cross-linking points.

Keywords : Spinodal Decomposition / Phase Separation / Light Scattering (LS) / Ultra Small-Angle Neutron Scattering (U-SANS) / Small-Angle Neutron Scattering (SANS) / Wide-Angle Neutron Scattering (WANS)

Extensive studies on polymer gels have been performed from various points of view because a wide variety of polymer gels can provide various interesting features. One of the most interesting gel-forming polymers is poly(vinyl alcohol) (PVA), which can form gels on cooling in various solvents including water.

In the previous studies, we determined the sol-gel diagram and observed the turbidity of the PVA gels in a mixture of DMSO and water (60/40 v/v) as a function of temperature and PVA concentration [1, 2]. These macroscopic observations implied that the liquid-liquid phase separation plays an important role in the formation of the structure of the gels, suggesting that the studies of mesoscopic structure in μm scale as well as microscopic structure in nm scale are very important to understand the properties of the gels.

In this paper, we report the results of structural

studies of a PVA gel formed in a mixture of DMSO and water (60/40 v/v) at 23°C using wide-angle neutron scattering (WANS), small-angle neutron scattering (SANS), ultra small-angle neutron scattering (U-SANS) and light scattering techniques covering a very wide Q range from 10^{-4} to $10 \text{ \AA}^{-1}$ where $Q=4\pi\sin\Theta/\lambda$, 2Θ and λ being scattering angle and wavelength of neutrons.

Wide-Angle Neutron Scattering measurements [3]. PVA is one of typical crystalline polymers, and hence the cross-linking points or junction points in the gels are believed to be crystallites though it has never been directly confirmed. First of all, we conducted WANS measurements on the PVA gel in the Q range of 0.8 to $10 \text{ \AA}^{-1}$. In this experiment, we employed a deuterated PVA to reduce the incoherent scattering background. In the scattering curve shown in Figure 1, a strong peak is

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Scope of research

The structure and molecular motion of polymer substances are studied using mainly scattering methods such as neutron, X-ray and light with the intention of solving fundamentally important problems in polymer science. The main projects are: the mechanism of structural development in crystalline polymers from the glassy or molten state to spherulites; the dynamics in disordered polymer materials including low-energy excitation or excess heat capacity at low temperatures, glass transition and local segmental motions; formation process and structure of polymer gels; the structure and molecular motion of polyelectrolyte solutions; the structure of polymer liquid crystals.



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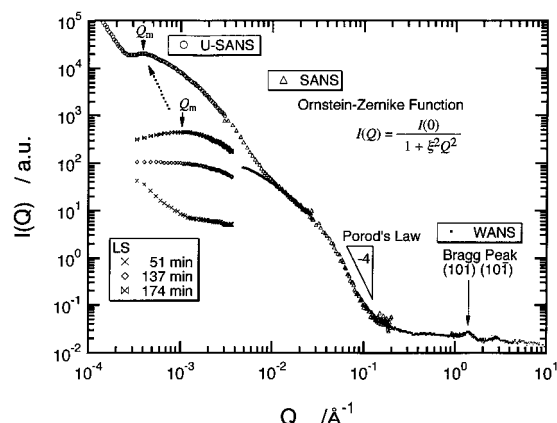


Figure 1. Scattering intensity $I(Q)$ of the PVA gel in DMSO- d_6 /D $_2$ O (60/40 v/v) with $C_p = 5$ g/dL, which was constructed by combining $I(Q)$'s measured by various scattering methods.

observed at $Q = 1.39 \text{ \AA}^{-1}$ which corresponds to the Bragg diffractions from (101) and (10 $\bar{1}$) planes of PVA crystals, confirming that there exist crystallites in the PVA gel. It was also shown that the Bragg peak disappears at about 75°C when the temperature increases. This temperature agrees with the melting temperature of the PVA gel, suggesting that the cross-linking points of the gel are crystallites.

Small-Angle Neutron Scattering measurements [3, 4]. SANS measurements were made on the PVA gel in the Q range from 0.003 to 0.2 $\text{\AA}^{-1}$. In the Q range above about 0.05 $\text{\AA}^{-1}$, the scattering intensity $I(Q)$ decreases with increasing Q according to the -4th power law (the Porod's law),

$$I(Q) \sim Q^{-4} \quad (1)$$

indicating that the surfaces of the crystallites are very smooth. On the other hand, the scattering intensity $I(Q)$ in the Q range below 0.045 $\text{\AA}^{-1}$ can be described by the Ornstein-Zernike (OZ) formula

$$I(Q) = \frac{I(0)}{(1 + \xi^2 Q^2)} \quad (2)$$

where ξ is a correlation length and $I(0)$ is the scattering intensity at $Q=0$. The values of ξ in the gel is about 180 $\text{\AA}$, which corresponds to the distance between the nearest neighboring crystallites. The scattering intensity $I(Q)$ of the opaque PVA gel deviates from the OZ formula and shows an upturn below about 0.008 $\text{\AA}^{-1}$ while the transparent gel, which was obtained by quenching the homogeneous solution at 100 °C to -40 °C, obeys the OZ formula in the low Q range down to 0.003 $\text{\AA}^{-1}$. This indicates that the opaque gels have a larger heterogeneity than the network structure. It is easily expected that this heterogeneity arises from the structure due to phase separation.

Light scattering measurements [4]. In order to get direct evidences for the phase separation, time-resolved light scattering (LS) measurements were carried out on the PVA gel after quenching to 25°C from 100 °C. The

scattering intensity $I(Q)$ shows a maximum at about $Q = 1.1 \times 10^{-3} \text{ \AA}^{-1}$, which does not change during the measurements. On the other hand, the peak intensity I_m at Q_m increases according to an exponential law in the early stage. These facts suggest that the phase separation or spinodal decomposition certainly occurs in the PVA solution. The characteristic length scale in the early stage of the phase separation is calculated to be 0.57 μm through the relation $2\pi/Q_m$.

U-SANS measurements. In the late stage of the phase separation, the PVA gel is so opaque that it is impossible to perform LS measurements on them. We therefore conducted U-SANS measurements to see the structure of the opaque PVA gel. As shown in Figure 1, the observed scattering intensity $I(Q)$ shows a broad maximum at $Q = 0.35 \times 10^{-3} \text{ \AA}^{-1}$, giving a characteristic length of 1.8 μm . This value is 3.2 times larger than that evaluated in the early stage, suggesting that the structural growth further proceeds even in the late stage against the elasticity of the gel network.

As was shown in this report, the PVA gel has a hierarchic structure in a very wide spatial scale from several $\text{\AA}$ to several μm and this structure is certainly related to the interesting properties of the PVA gel. Finally a schematic sketch of the hierarchic structure of the PVA gel is given in Figure 2.

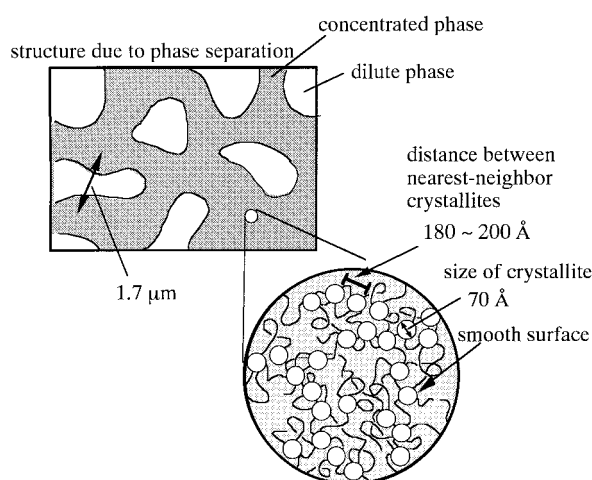


Figure 2. Schematic sketch of a PVA gel in DMSO- d_6 /D $_2$ O (60/40 v/v) with $C_p = 5$ g/dL elucidated in this work.

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