

Morphological Basis of Responsive Behavior in Modified Cellulose Gels

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Introduction

Certain hydrogels undergo volume transitions at a critical temperature related to the critical solution temperature of the parent polymer [1]. These materials have been explored as controlled drug release materials for many years. Hydroxypropyl cellulose (HPC) gel is a biodegradable, temperature-responsive gel with a transition temperature around 40°C. Since HPC has been approved by the U.S. Food and Drug Administration (FDA) as a food additive, it has not only aroused interest for the controlled release of drugs but has also been proposed for the controlled release of flavors in the food industry.

The physics of thermal volume transition are controlled by the hydrophobic interactions. As the temperature changes, the interaction between the polymer and water also changes. At a low temperature, the hydrophilic interactions dominate, so the gel is swollen. At a high temperature, hydrophobic interaction dominates, so the gel is shrunken. The volume transition of the temperature-responsive gels leads to a large permeability change [2]. That is the basis of controlled release applications. Our goal is to understand the physics of the thermal collapse transition of modified HPC gels and to determine the relationship between the collapse transition and the permeability change.

Methods and Materials

A cross-linkable version of HPC was synthesized by vinyl functionalization followed by exposure to uv radiation. A homogeneous gel is produced when the cross-linking reaction is carried out at room temperature. A heterogeneous gel is produced by using a modified thermally induced phase separation (TIPS) method, wherein the polymer is cross-linked above the critical solution temperature of the parent polymer [1].

The synthesized gel was cut into disks with a diameter of 10 mm and thickness of 1 mm. The disks were loaded into liquid cells with water for ultrasmall-angle x-ray scattering (USAXS) experiments. During experiments, the liquid cells were placed in a heater with a temperature controller. For each sample, the experiment was carried out at two temperatures: 25°C and 60°C. Before scattering data were collected, each sample was stabilized in water for 20 minutes to make sure the gel was in an equilibrium state.

Results and Discussion

The temperature-responsive behavior of the synthesized HPC gel is shown in Fig. 1. The gel shrinks at an enhanced temperature.

The volume transitions of both homogeneous and heterogeneous gels were studied (Fig. 2). The swelling degree is defined as w/w_0 , where w is the weight of the gel at a certain temperature and w_0 is the weight of the dried gel.

It can be seen that there is a transition temperature at around 40°C. The swelling degree of the homogeneous gel drops quickly from 20°C to about 5°C. For the heterogeneous HPC gel, the thermo-collapse transition is

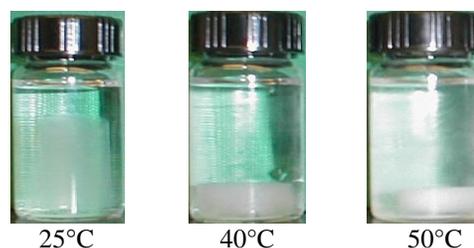


FIG. 1. Volume transition of homogeneous HPC gel.

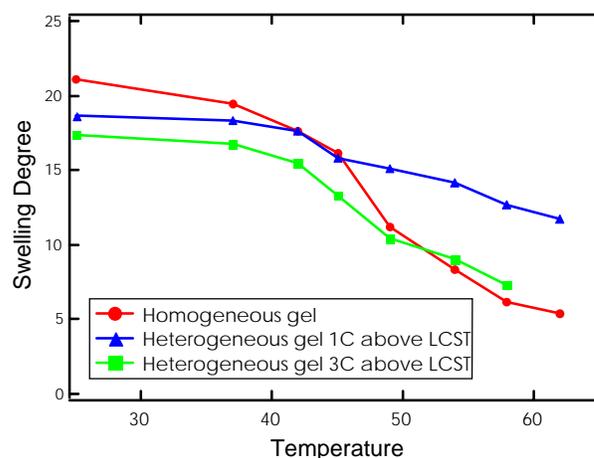


FIG. 2. Volume transitions of homogeneous and heterogeneous gels.

not as sharp as the homogeneous one. This result is important because it indicates that a fast-responding gel may not swell or shrink as much as a homogeneous gel.

The USAXS profiles of a homogeneous gel at two temperatures are displayed in Fig. 3. The profile of the homogeneous gel at room temperature shows a swollen gel with slope of -2 at a power-law region where $q = 0.02 \text{ \AA}^{-1}$. This slope is consistent with the statistical behavior of the suspended polymer chains. As the temperature increases, the scattering intensity increases, especially near $q \approx 0.01 \text{ \AA}^{-1}$, indicating enhanced contrast due to phase separation. The power-law slope in this region changes to -4 at 60°C . This change indicates that there must be some new interface formed that is smooth on a length scale of 10 \AA . At 60°C , the gel is in a collapsed state. It is believed that during the shrinking, the hydrophilic and hydrophobic segments on the polymer main chain will associate, leading to phase separation on the nanometer scale. Thus, phase separation on a scale of 100 \AA is observed at 60°C .

The USAXS profiles of a heterogeneous gel at two temperatures are displayed in Fig. 4. From Fig. 4, it can be seen that phase separation in the heterogeneous gel is also observed on a scale of 100 \AA at both low and high temperatures and that the domains are smooth (slope of -4) for both. The phase separation at room temperature can be explained by the fact that the gel was cross-linked in the high-temperature, collapsed state. The cross-linking reaction occurs above the lower critical solution temperature of HPC. In this case, the HPC solution is phase-separated. The cross-link densities in the two separated phases are different. After the cross-linking

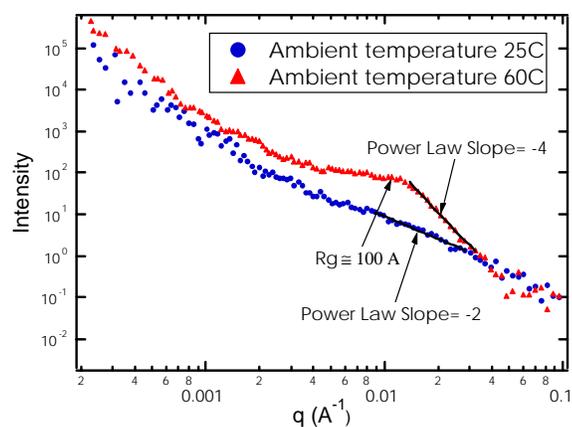


FIG. 3. USAXS profiles of a homogeneous gel at two ambient temperatures.

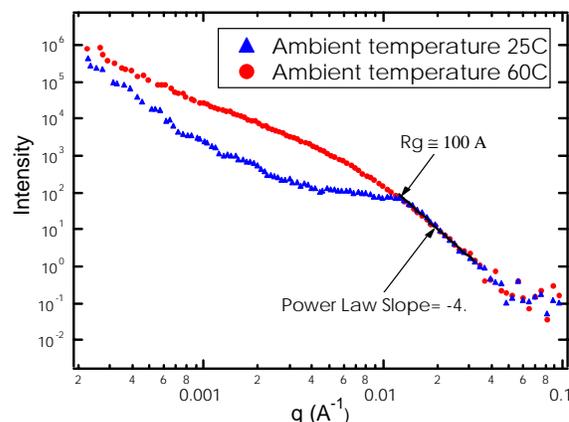


FIG. 4. USAXS profiles of a heterogeneous gel at two ambient temperatures.

reaction is complete and the gel is re-swollen, the difference in cross-link density is conserved, leading to fluctuations in cross-link density. When the cross-linked gel is again heated above the transition temperature, the 100-\AA domains appear on the scale of the original fluctuations in cross-link density.

Acknowledgments

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