Tuning Structural Color Changes of Porous Thermosensitive Gels through Quantitative Adjustment of the Cross-Linker in Pre-gel Solutions

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2 AUTHORS:

Yukikazu Takeoka
Nagoya University

Masayoshi Watanabe
Yokohama National University

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Tuning Structural Color Changes of Porous Thermo-sensitive Gels Through Quantitative Adjustment of The Cross-linker in Pre-gel Solutions

Yukikazu Takeoka and Masayoshi Watanabe

Department of Chemistry and Biotechnology, Yokohama National University, 156 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan.

Tel & Fax: +81-45-339-3956 E-mail: *ytakeoka@ynu.ac.jp*

Chemical gels, which are covalently cross-linked polymer networks swollen with solvent, freely swell and shrink in response to environmental changes. Much of the current research on chemical gels has focused on the use of templates or matrices for additional functions. So-called "smart" gels for molecular recognition, catalysis, and separation can be easily fabricated by a templating technique, because the spatial position and the three-dimensional shape of the templates used can be memorized by the permanent cross-links formation.

Here we report the preparation of "Smart" porous gels with different optical behaviors by quantitative adjustment of the cross-linker in pre-gel solutions. A periodically ordered interconnecting porous structure could be created in the gels by using a closest-packing silica colloidal crystal as a template. The interconnecting porosity provides fast response to changes in temperature through the reversible swelling and shrinking of the gels, while the periodically ordered mesoscopic structure endows the porous gels with structural color, which can be tuned by simply changing the amount of the cross-linker in the pre-gel solutions.

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Yukikazu Takeoka*, and Masayoshi Watanabe
Department of Chemistry and Biotechnology, Yokohama,
Yokohama National University,
Yokohama, Kanagawa 240-8501 (Japan)
Fax: (+81) 45-339-3956
E-mail: ytakeoka@ynu.ac.jp

Abstract

"Smart" porous gels with different optical behaviors were synthesized by quantitative adjustment of the concentration of cross-linker and monomers in pre-gel solutions. A periodically ordered interconnecting porous structure could be created in the gels by using a closest-packing silica colloidal crystal as a template. The interconnecting porosity provides fast response to changes in temperature through the reversible swelling and shrinking of the gels, while the periodically ordered mesoscopic structure endows the porous gels with structural color, which can be tuned by simply changing the amount of the cross-linker and monomers in the pre-gel solutions.

Keywords porous gel; structural color; colloidal crystal

Introduction

A closest-packing colloidal crystal can be a template for preparing chemical gels exhibiting a desired structural color.[1] The pre-gel solution can easily be infiltrated into this space as a mini-vessel for making gels. After removing the crystal component in the gels obtained, the porous gel exhibits a bright structural color under white light illumination and undergoes fast and drastic changes in color in response to a variety of environments. The structural color is caused by the Bragg diffraction of visible light from the ordered voids regarded as crystallites.[1] The peak values of reflection spectra, λ_{max}, for the porous gel is obtained by:

$$\lambda_{max} = 1.633(d/m)(D/D_0)(n_a^2 - \sin^2\theta)^{1/2} \qquad (1)$$

where d is the diameter of a colloidal particle, m

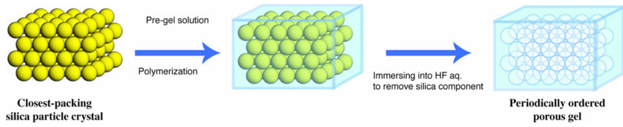

Fig. 1 Preparation of a closest-packing colloidal crystal.

is a constant, D/D_0 is the equilibrium swelling degree of the gel (D and D_0 are diameters of the gel in the equilibrium state at a certain condition and in the reference state, respectively.), n_a is the refractive index of the porous gel at a certain condition, and θ is the angle measured from the normal to the plane of the gel. According to this equation, we have only to experimentally know the environmental dependence of its swelling ratio (D/D_0), and the refractive index to pre-surmise the observed value of λ_{max} of the reflection spectrum for the gel, because d and θ can be arbitrarily chosen. The swelling ratio can be estimated by monitoring the diameter of a cylindrical gel prepared in a capillary with a diameter of 100μm using a temperature control system. The change in the refractive index of the porous gel with the varying conditions is then measured by a refract meter. Although the rate of change in n_a for the thermo-sensitive chemical gel composed of *N*-isopropylacrylamide (NIPA) is only 0.3% when the temperature is changed from 15°C to 60°C, the swelling ratio changes by about two times. Therefore, the swelling ratio is dominant over λ_{max} of the observed reflection spectrum for the porous NIPA gel, when d and θ are known.

Here, we report that the structural color from porous gels can be synthetically tuned. Specifically, we demonstrate how changing the concentration of the cross-linker (C_{xl}) and total monomer concentration (C_t) in pre-gel solutions affects the structural color of thermo-sensitive porous gels. Our work aims to establish how gels of desired optical performance can be obtained.

Result and Discussion:

The swelling ratio of gels in swollen state can be expressed as a function of the average length of a subchain between two connected cross-links, *N*. Here, *N* is defined as the number of monomeric links along the subchain. The more cross-linkers there are in a gel with a certain amount of monomers, the smaller the swelling ratio is in its swollen state. Bromberg et al. found that the length of subchains becomes shorter as the ratio of monomer concentration to cross-linker concentration for a pre-gel solution becomes smaller.[2] Consequently, the equilibrium swelling ratio of the swollen gel can be predicted by the initial amounts of the monomer and the cross-linker in the pre-gel solution.

Figure 1 shows the reflection spectra of porous gels having a different C_{xl} in water at 15.4 °C. The diffracted wavelength observed from each gel shifted to a lower wavelength with the decrease in its swelling ratio. Microscopic observation shows the difference in the structural color of each gel clearly. These results indeed verify our hypothesis.

Furthermore, each gel exhibited changes in its structural color depending on temperature. Thus, it is technically possible to prepare a gel membrane reflecting a specific color at a certain temperature by controlling the amount of the monomer and the cross-linker in the pre-gel solution.

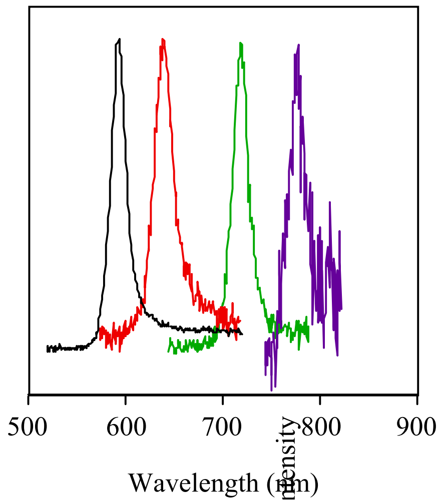

Fig. 2 Reflection spectra of porous gels having a different C_{xl} in water at 15.4 °C. C_t = 2M, C_{xl} = 20 mM, 33 mM, 67 mM, and 100 mM.

In summary, we have developed a family of periodically ordered porous hydrogels whose optical properties can be precisely tuned by the recipe for the gel synthesis and by thermally adjusting the size of the gel. These gels which exhibit a desired color can be tailor-made for arbitrary use. These gels have potential for use in sensors, optical devices, and displays.

References and Note

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