

Direct Detection of Isomeric Alcohols using Block Copolymer Photonic Gels

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Hydrogels coupled with optically active functional materials have been extensively investigated due to their broad potential applications in various fields of science and technology.^{1,2} Especially, the unique volume phase transition of hydrogels in response to various chemical and biological stimuli can be utilized in sensor applications when it is transduced to optical signal. For this reason, there have been lots of efforts of incorporating hydrogels in photonic crystals. Photonic crystals, artificial materials with a periodic refractive index, provide remarkable control of light and offer exciting prospects for optical devices.³⁻⁵ Hydrogel embedded photonic crystals respond to environmental changes with a visual color change and can be utilized as a colorimetric sensor, requiring no power source and no read-out system other than the human eye.⁶⁻⁹ For example, mesogels prepared from self-assembly of block copolymers have also been widely investigated for creating various photonic structures.¹⁰⁻¹⁶ Spontaneously assembled morphologies including lamellae, cylinders, gyroids and spheres were exploited to create 1D, 2D and 3D photonic crystals.¹⁷⁻¹⁹ Our group recently reported highly tunable photonic gels based on polystyrene-*b*-quaternized poly(2-vinyl pyridine) (PS-*b*-QP2VP).¹⁰⁻¹⁶ The swollen photonic gels found many applications including as an active component of reflective displays, memory and bio-sensors. Herein, we report block copolymer photonic gels as solvent sensor. We found that our photonic gel films are very sensitive to dielectric environment, and which is applicable for colorimetric alcohol sensors. Remarkably, our photonic gel sensors can detect isomeric alcohols with the naked eye.

The block copolymer photonic gel films were prepared as

previously described.^{10,12-14} Photonic gel films exhibited strong reflective colors upon immersing them in aqueous solutions, and the position of photonic stop band (PSB) was highly dependent on the dielectric environment. The changes of PSB were characterized by UV-VIS. As shown in Figure 1, the changes of PSB were investigated as a function of the dielectric constant of solution. In this set of experiments, the dielectric constant was modulated by mixing *t*-butyl alcohol ($\epsilon = 12.5$) and water ($\epsilon = 80.1$) with several different ratios. It is notable that there is a sharp transition in the range of $\epsilon = 10$ -30, which is attributed to the first-order volume transition of QP2VP gel layers in response to the change of dielectric environment.^{20,21} Such abrupt volume phase transition is quite useful for organic solvent sensor applications. Since the dielectric constants of many organic solvents are in the range of $\epsilon = 10$ -30, small changes of dielectric environment can induce significantly large photonic responses. Taking advantage of this, we have demonstrated that our photonic gel films can be utilized for detecting various alcohols. As shown in Figure 2, PSB varied with the species of solvent.

As the film was swollen with solvent, the position of PSB shifted to the shorter wavelength in the order of methanol ($\epsilon = 33.05$, $\lambda_{\text{peak}} = 764$ nm), ethanol ($\epsilon = 25.08$, $\lambda_{\text{peak}} = 724$ nm), *n*-propanol ($\epsilon = 20.01$, $\lambda_{\text{peak}} = 705$ nm) and *n*-butanol ($\epsilon = 17.64$, $\lambda_{\text{peak}} = 655$ nm). In this case, the sensitivity can be easily modulated by counter anions pairing with pyridinium groups. For example, the photonic gel films modified with

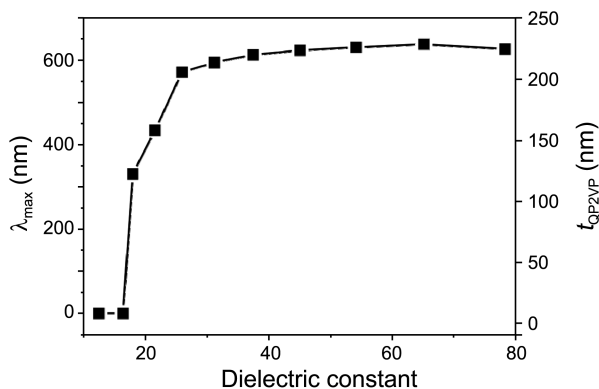


Figure 1. The change of PSB position of photonic gels with change of the dielectric constant of solution.

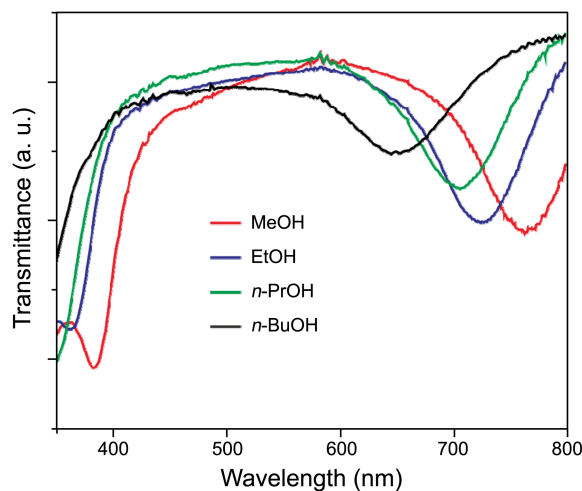


Figure 2. The PSB changes of PS-*b*-QP2VP block copolymer photonic gel films swollen with various alcohols.

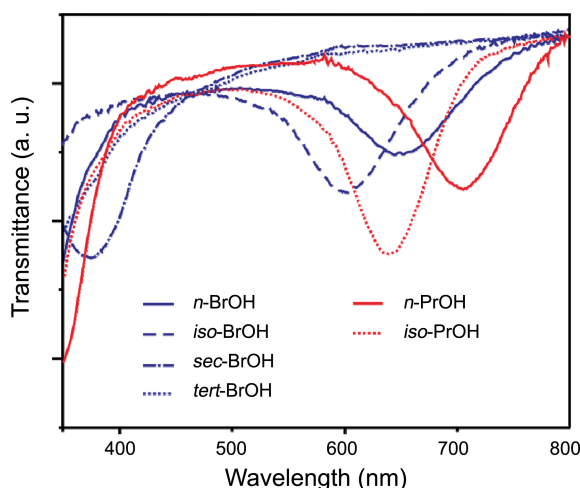


Figure 3. The PSB changes of PS-*b*-QP2VP block copolymer photonic gel films swollen with isomeric alcohols; *n*-propanol and *iso*-propanol, *n*-butanol, *iso*-butanol, *sec*-butanol and *tert*-butanol.

acetate showed much larger sensitivity and broader detection range of solvent than those modified with chloride or bromide. For this reason, the photonic gel films modified with acetate were mainly used in our experiments.

Photonic gel films can detect isomeric alcohols without complicate instrumentation. The optical signal of photonic gel films swollen with *n*-propanol was significantly different from that of the film swollen with *iso*-propanol (Figure 3). The position of PSB for the films swollen with *n*-propanol ($\lambda_{\text{peak}} = 705$ nm) was 70 nm higher than that of the film swollen with *iso*-propanol ($\lambda_{\text{peak}} = 635$ nm). Considering their almost same dielectric constants ($\epsilon_{n\text{-PrOH}} = 20.01$, $\epsilon_{i\text{-PrOH}} = 19.25$), such large difference in optical response is quite remarkable. We attributed the unusually large optical change in isomeric alcohol solutions to the mutual effects of sharp volume phase transition of photonic gel in the range of $\epsilon = 10\text{--}30$ and the conformation dependent hydrogen bonding of alcohol. It is known that the more branched an alcohol is, or the more centrally located the hydroxyl group, the smaller its extended hydrogen-bond network, which induces deswelling of QP2VP gel layers.²² This trend is also apparent for the detection of isomers of butanol. The position of PSB for four different isomers of butanol shifted to the shorter wavelength regime in the order of *n*-butanol ($\epsilon_{n\text{-BuOH}} = 17.64$, $\lambda_{\text{peak}} = 651$ nm), *iso*-butanol ($\epsilon_{i\text{-BuOH}} = 17.94$, $\lambda_{\text{peak}} = 601$ nm), *sec*-butanol ($\epsilon_{\text{sec-BuOH}} = 16.56$, $\lambda_{\text{peak}} = 372$ nm) and *tert*-butanol ($\epsilon_{\text{tert-BuOH}} = 12.5$, $\lambda_{\text{peak}} = 0$ nm) (Figure 3). While the dielectric constant of *iso*-butanol is slightly higher than that of *n*-butanol, its PSB was lower than that of *n*-butanol, and which implies that the hydrogen effect is significant in QP2VP gel layers.

In conclusion, we have demonstrated block copolymer photonic gel films as colorimetric alcohol sensors. Our results

showed that PS-*b*-QP2VP photonic gel films exhibited extremely sensitive responses to the dielectric environment change, and which is useful for solvent sensors. Remarkably, photonic gel films are sensitive enough to distinguish various conformational isomers. We demonstrated this for propanol (*n*-propanol and *iso*-propanol) and butanol (*n*-butanol, *iso*-butanol, *sec*-butanol and *tert*-butanol).

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