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Reversible Adsorption/Desorption of Target Molecules with Novel Temperature-Sensitive Heteropolymer Gels

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Abstract. SSS-VBTA gel was synthesized with sodium styrene sulfate (SSS) and vinylbenzyl trimethylammonium chloride (VBTA). The SSS-VBTA gel was found to show the thermo-reversible changes in its volume and properties, that is, shrunken and hydrophobic state at around room temperature while swollen and hydrophilic state at above room temperature. It was revealed that the SSS-VBTA gel concentrated trace amounts of Bisphenol-A present in very dilute aqueous solutions at around room temperature and released the concentrated Bisphenol-A above room temperature.

Keywords: adsorption, temperature-sensitive, gel, reversible

1. Introduction

Stimuli-sensitive polymer gels have attracted much attention because of their technological significance as well as scientific interest (Nakano et al., 2001; Zhan et al., 2001; Miyazaki et al., 2000; Seida et al., 1995). The thermo-sensitive polymer gels are one of the stimuli-sensitive polymer gels that respond to an infinitesimal change in external conditions such as solvent composition, pH, electric fields, light and so on (Nakano et al., 2002; Oya et al., 1999). They are well known to change not only their own volume but also their physical properties: hydrophilic-hydrophobic balance, in response to changes in the surrounding temperature. Some of researchers have attempted to utilize the thermo-sensitive polymer gels as an adsorbent for separation of hydrophobic organic compounds from aqueous solutions. When the thermo-sensitive polymer gels in the aqueous solutions are heated up, the gels in common use undergo a volume phase transition at a certain temperature which was called phase transition temperature, T_P. They become hydrophilic at lower temperatures than T_P and hydrophobic at higher temperature than T_P, which may cause that the gels adsorb hydrophobic organic compounds at high temperature and desorb them at low temperature. But, from the chemical engineering point of view, there are enormous differences in consumed energy when the gel is applied to the recovery system. Knowledge of how the physical properties can be controlled in engineering use of the thermo-sensitive polymer gels is needed. When the above thermo-sensitive polymer gels are applied to concentrate hydrophobic organic compounds present in very dilute solutions, a large amount of aqueous solutions containing trace amounts of compounds must be heated above the phase transition temperature of the gels. One of the major problems in this process is to consume vast energy on heating a large amount of aqueous solution. Thus, there is a need for the development of easily available thermo-sensitive polymer gels that can remove and recover hydrophobic organic compounds (target molecules) economically from the energy saving point of view.

The objective of the present investigation is to create a thermo-sensitive polymer gel that adsorbs to concentrate hydrophobic organic compounds at around room temperature and desorbs to recover the concentrated compounds utilizing the phase transition of

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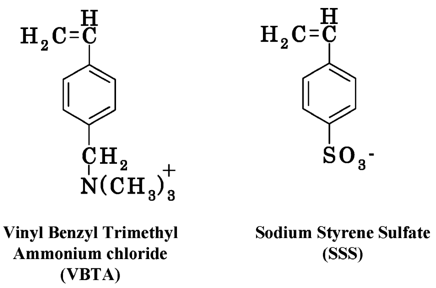

Figure 1. Chemical structures of main monomers constituting thermo-sensitive polymer gel.

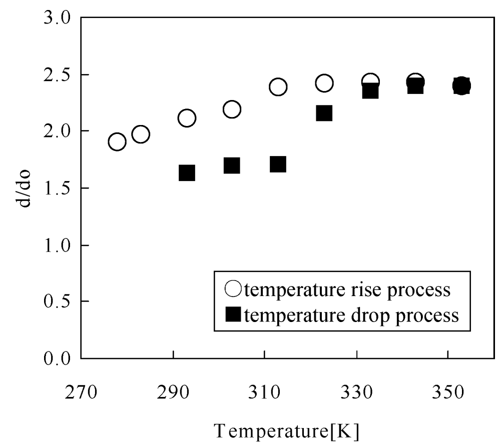

Figure 2. Temperature dependence of swelling of thermo-sensitive SSS-VBTA gel.

thermo-sensitive gels at somewhat higher than room temperature.

2. Experimental

We synthesized a novel gel which was called SSS-VBTA. It is made of negatively charged monomer, sodium styrene sulfate (SSS), and positively charged monomer, vinylbenzyl trimethylammonium chloride (VBTA). The chemical structures are shown in Fig. 1. They were mixed with composition of 700 mM SSS and 700 mM VBTA in sodium chloride aqueous solution (3.0 M, 10 ml). N,N'-methylene-bis-acrylamide (8.6 mM) was added as a cross-linker. The monomers were polymerized by radical polymerization in the micropipettes of 1 μL at 353 K for 24 h. After gelation, the cylindrical gels were taken out of the micropipettes and washed thoroughly with distilled water to remove residual monomers and sodium chloride. Equilibrium diameter, d, of the cylindrical gels was measured as a function of temperature in pure water under a microscope equipped with CCD/VIDEO camera (Hamamatsu photonic K.K., C2400) and an image processing soft ware (Poladigital, Micro Analyzer).

The SSS-VBTA gel obtained was put into the solution containing Bisphenol-A. The concentrations of Bisphenol-A in the aqueous solution were determined by measuring the UV adsorption (275 nm) of the solution in equilibrium using UV-VIS spectrometer (U-2000, Hitachi). The amount of organic compound adsorbed onto the SSS-VBTA gel was calculated from the mass balance.

3. Results and Discussion

The temperature dependence of the swelling is shown for SSS-VBTA gel with composition of 700 mM SSS and 700 mM VBTA in Fig. 2. The degree of swelling was defined as d/d_0, where d and d_0 are the diameters of cylindrical gels in equilibrium with pure water and at synthesis, respectively. When the temperature of pure water was raised from 293 to 353 K, the SSS-VBTA gel underwent a volume phase transition at around 313 K and swelled above the phase transition temperature. On the other hand, the SSS-VBTA gel shrank when the temperature was lowered below 313 K. This temperature dependence, swelling upon heating, is similar to the phase transition in hydrogen bondable gels and opposite to the phase behavior of hydrophobic gels such as N-isopropylacrylamide (NIPA) gel commonly used as a thermo-sensitive polymer gel. The temperature dependence of the swelling observed on the SSS-VBTA gel in pure water indicates that the SSS-VBTA gel becomes hydrophilic at temperatures above the phase transition temperature of 313 K and hydrophobic below the temperature. Such phenomena can be elucidated as follows. The SSS and VBTA units in the network polymer chain are held together simply by electrostatic attraction of the opposite charges at temperatures below 313 K so that the SSS-VBTA gel behaves like hydrophobic gels. On heating beyond 313 K, the thermal motion of the SSS and VBTA units overcomes the attraction of their opposite charges and they are separated to negative and positive charges each other, resulting in the ionic SSS-VBTA gel behaving like hydrophilic gels.

Figure 3 shows the adsorption isotherm over the temperature range of 293 to 353 K. The vertical axis exhibits the equilibrated adsorption amount of Bisphenol-A per gel volume at synthesis. The amount

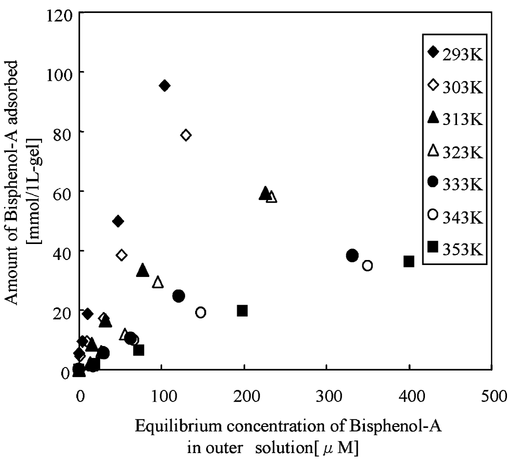

Figure 3. Adsorption isotherm of Bisphenol-A for SSS-VBTA gel.

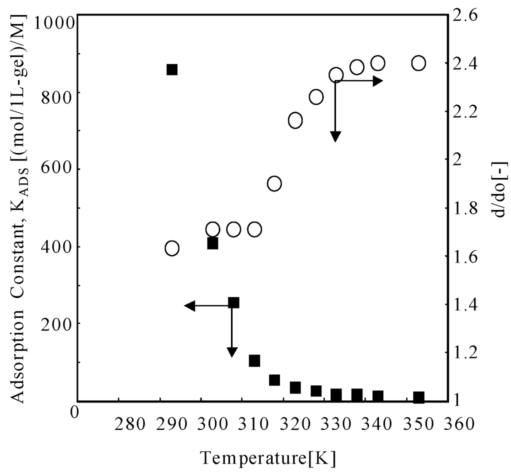

Figure 4. Adsorption constant of Bisphenol-A as a function of temperature in aqueous solution.

of Bisphenol-A adsorbed onto the SSS-VBTA gel decreased with a rise in temperature of the outside solution. This implies that the SSS-VBTA gel is able to change its property from hydrophobic to hydrophilic state while the temperature is raising from 293 to 353 K. From the results in Fig. 3, the adsorbed amount of Bisphenol-A can be described by the following equation in the low concentration region:

$$q = K'_{\mathrm{ADS}} C_{T,L} \tag{1}$$

where K'_{ADS} is the apparent adsorption constant, q is the amount of Bisphenol-A adsorbed per polymer gel volume at synthesis, and $C_{T,L}$ is the equilibrated concentration of Bisphenol-A in the outside solution.

To evaluate the adsorption amount of Bisphenol-A as a function of temperature, the apparent adsorption constant K'_{ADS} was calculated from the initial slope of isotherm in Fig. 3. For such a thermo-sensitive polymer gel, the amount of adsorption per gel volume in equilibrium should be evaluated using the adsorption constant K_{ADS} that the volume changes of the gel are considered, because the equilibrated volume of gel is able to change in response to surrounding temperature so that the concentration of monomers in the gel alters. K'_{ADS} can be converted to K_{ADS} using $V_{G,0}/V_G$ as follows:

$$\begin{aligned} K_{\mathrm{ADS}} &= K'_{\mathrm{ADS}}(V_{G,0}/V_G) \\ C_{M,G} &= C_{M,G,0}(V_{G,0}/V_G) \end{aligned} \tag{2}$$

where V_G is the equilibrated volume of gel, and $V_{G,0}$ is the volume of gel at synthesis. $C_{M,G}$ and $C_{M,G,0}$ are the concentrations of benzene ring per gel volume in equilibrium and at synthesis, respectively.

The value of K_{ADS} was extremely high at around room temperature and decreased rapidly with a rise in temperature, as shown in Fig. 4. The value became smaller above 313 K which corresponded to the phase transition temperature. K_{ADS} of SSS-VBTA gel for Bisphenol-A at room temperature was found to be about 100 times that of the gel at 353 K.

The thermo-sensitive characteristics of SSS-VBTA gel for adsorption/desorption of Bisphenol-A were examined by means of a stepwise temperature change, as shown in Fig. 5. The adsorption amount of

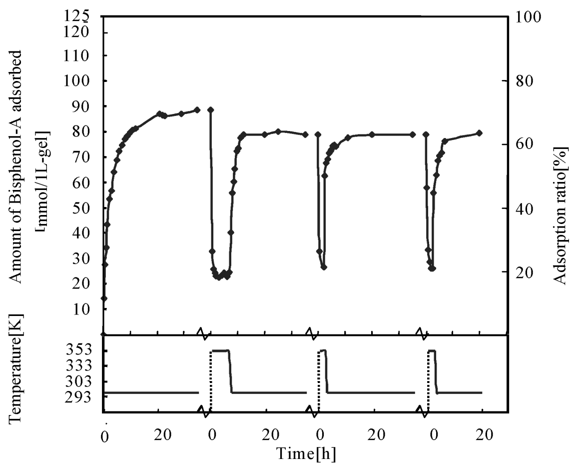

Figure 5. Reversible adsorption and desorption of Bisphenol-A for temperature swing operation.

Bisphenol-A increased gradually with the elapse of time and went up to 80% adsorption ratio after 24 h at 298 K. When the temperature was changed stepwise from 298 to 353 K, desorption occurred quickly and the adsorption ratio fell down to 20% after 2 h. When the adsorption and desorption were repeated several times, the following adsorption proceeded more rapidly compared with the first one. In addition, the adsorption and desorption took place reversibly in response to such a temperature swing operation.

4. Conclusion

We have developed the thermo-sensitive polymer gel consisting of negatively charged monomer, sodium styrene sulfate (SSS), and positively charged monomer, vinylbenzyl trimethylammonium chloride (VBTA). The SSS-VBTA gel becomes hydrophobic at around room temperature and hydrophilic above the phase transition temperature of 313 K. We proposed a separation process to concentrate Bisphenol-A present in very dilute solutions at room temperature and recover the concentrated Bisphenol-A above the phase transition temperature. The SSS-VBTA gel was found to be very useful for the concentration of trace amounts of Bisphenol-A through the changes of hydrophobic-hydrophilic balance. For example, the adsorption constant of the SSS-VBTA gel for Bisphenol-A at room temperature was found to be about 100 times that of the gel at 353 K. This work will provide useful information in designing the separation process using such a thermo-sensitive polymer gel.

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