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A SYNTHETIC HYDROGEL WITH THERMOREVERSIBLE GELATION. II. EFFECT OF ADDED SALTS

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ABSTRACT

The sol–gel transition temperature of a thermoreversible hydrogel composed of poly (*N*-isopropylacrylamide)-*b*-poly(ethylene glycol) was determined from dynamic viscoelastic measurement. The sol–gel transition temperature was affected by the amount and sort of added salts. With increasing salt concentration, salts with a salting-out nature decreased the sol–gel transition temperature whereas salts with a salting-in nature increased the sol–gel transition temperature. The effect of various anions on the sol–gel transition temperature was interpreted by their influence on the hydrophobic effect.

INTRODUCTION

To study the effects of added salts on aqueous solutions of polymers involves biological significance. This is because it has been known that salts affect the structure and function of biopolymers as typically seen in protein denaturation. The order of tendency of various salts to perturb the denaturation temperatures of proteins is known as the Hofmeister series or the lyotropic series [1]. Salts do not interact with polymers directly but affect the soluble state of polymers through the interaction with solvent water. With respect to synthetic polymers, the effects of salts on the lower critical solution temperatures (LCSTs) of aqueous solutions of poly(ethylene glycol) (PEG) [2], poly(vinyl methyl ether) (PVME) [3], or poly (*N*-isopropylacrylamide) (PNIPAAm) [4] were investigated, and the salt effects in these studies were consistent with the lyotropic series. PVME and PNIPAAm especially attract interest for their biological aspects because they exhibit an LCST at 34 and 32°C in pure water, respectively, which is close to the body temperature of homeothermic animals.

Recently, we found that an aqueous solution of a block copolymer composed of PNIPAAm and PEG shows a thermoreversible sol-gel transition at about 35°C [5]. This system is interesting as a model of biological systems which provide a three-dimensional structure. We report here on the effect of salts on the sol-gel transitions temperature.

EXPERIMENTAL

The preparation and characterization of PNIPAAm-*b*-PEG were described elsewhere [5]. The molecular weights of the PNIPPAAm block and of the PEG block in the block copolymer were estimated as about 3×10^4 and 1×10^4, respectively. The PEG content in the block copolymer was calculated as 38 wt% from elemental analysis. All the inorganic salts (KCl, KBr, KI, KSCN) were Special Grade reagents from Wako Pure Chemical Co. and were used without further purification. PNIPAAm-*b*-PEG was dissolved in distilled water at a concentration of 10 wt%. Salts were added at concentrations of 0.1, 0.5, or 1.0 M.

Dynamic viscoelastic measurement of aqueous solutions of PNIPAAm-*b*-PEG with or without salts was performed by a controlled stress rheometer (Carri-Med, CSL-500) using a flat stainless plate with a 4-cm diameter as the measuring system. The dynamic moduli G' (storage modulus) and G'' (loss modulus) of the samples were analyzed at constant temperatures from 5°C up to 45°C at an oscillating frequency of 1 Hz.

RESULTS AND DISCUSSION

An aqueous solution of PNIPAAm-*b*-PEG is a viscous fluid at below the critical temperature, and it solidifies to a hydrogel above the critical temperature. This change was observed as a reversible function of temperature. Below the critical temperature, G'' was larger than G', which means that viscosity is dominant in the sample. On the other hand, G' was larger than G'' above the critical temperature, which demonstrates that elasticity is dominant in the sample. Therefore, we determined it to be the sol-gel transition temperature of the sample; that is, the crossover temperature of G' and G'' observed at an operation frequency of 1 Hz [5].

Typical results of the dynamic viscoelasticity change of aqueous solutions of PNIPAAm-*b*-PEG as a function of temperature are shown in Fig. 1. With no salts, the crossover of G' and G'' was observed at about 35°C, i.e., this is the sol-gel

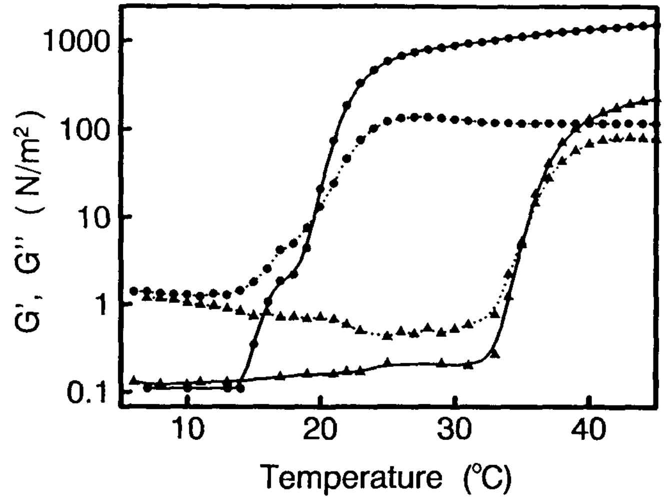

FIG. 1. Temperature dependence of the dynamic moduli of an aqueous solution of PNIPAAm-*b*-PEG at a concentration of 10 wt% with (circles) or without (triangles) KCl at a concentration of 1.0 M. Storage modulus (G', solid lines) and loss modulus (G'', dotted lines) were measured at an oscillatory frequency of 1 Hz. The lines are drawn only as guides.

transition temperature of a control system. When KCl was added to the sample, the sol-gel transition temperature decreased with the concentration of KCl, as shown in Fig. 1.

Figure 2 shows the shift of the sol-gel transition temperature caused by various potassium salts (Cl^-, Br^-, I^-, SCN^-). KCl and KBr decreased the transition temperature, but the effectiveness of KBr was smaller than that of KCl. On the other hand, when KSCN was added to an aqueous solution of PNIPAAm-*b*-PEG the sol-gel transition temperature of the system increased with the concentration of KSCN. KI exerted little influence on the transition temperature.

We previously proposed that the mechanism of hydrogel formation of PNIPAAm-*b*-PEG is based on intermolecular hydrophobic interaction between the PNIPAAm blocks [5]. The hydrophobic interaction is a kind of force that associates hydrophobic substrates in water due to the entropy gain from reducing an "iceberg," which is an entropically unfavorable water structure (hydrogen-bonded ice-like structure) formed adjacent to the hydrophobic substrates [6].

In this study we examined the effect of salts of various anions on a sol-gel transition because it is well known from previous reports [1-4] that a salt's effect on aqueous solutions of nonionic polymers depends strongly on anion species rather than on cation species. As shown in Fig. 2, the sol-gel transition temperature depended on the added anion species, and the increasing order of the tendency of anions in increasing the sol-gel transition temperature is $Cl^- < Br^- < I^- < SCN^-$. This is consistent with the order of increasing ionic radius.

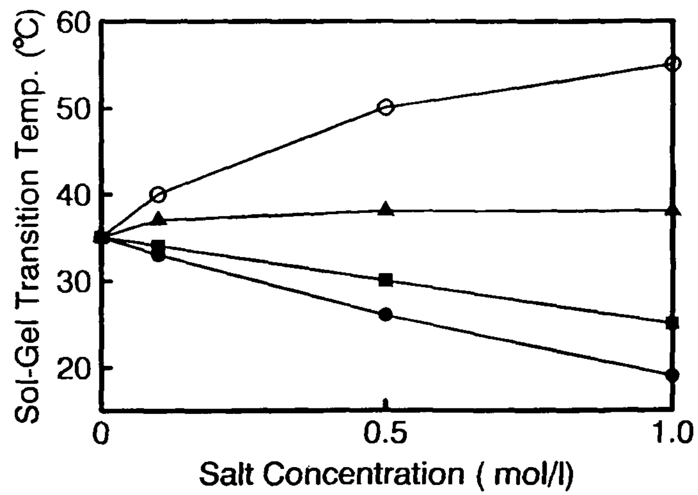

FIG. 2. Effect of various salts on the sol–gel transition temperature of aqueous solutions of PNIPAAm-*b*-PEG: (●) KCl, (■) KBr, (▲) KI, (○) KSCN.

The influence of the ionic radius radius of the added anions on hydrophobic interaction has been discussed in the literature [1–3, 6] as follows. Anions with a small ionic radius have a strong electrostatic field around them, and they strongly interact with water dipoles. As a result, the water dipoles are highly oriented and an ordered water structure is formed (the positive hydration decreasing entropy, $\delta S < 0$). Such anions are called water-structure makers, and they enhance the hydrophobic interaction by their salting-out effect. On the other hand, anions with a large ionic radius show a weak interaction between the anion and water dipoles. The weak interaction can break the water–water hydrogen bond but it is too weak to make an oriented water structure (the negative hydration increasing entropy, $\delta S > 0$). Such anions are called water-structure breakers or are sometimes called chaotropic ions. The SCN^- anion is a typical chaotropic ion which strongly induces protein denaturation. The water-structure breakers show a salting-in effect and stabilize the hydrophobic substrates in water by destroying the iceberg. That is, hydrophobic interaction is weakened with the increasing ionic radius of the added anions.

The above discussion looks at the reason why the shift of the sol–gel transition temperature of an aqueous solution of PNIPAAm-*b*-PEG depends on the added anion species. Conversely, it can be evidence for hydrophobic interaction being the driving force of thermoreversible hydrogel formation of the PNIPAAm-*b*-PEG in an aqueous system that the influence of added anions on water-structure predominates at the sol–gel transition temperature.

In biopolymers such as proteins, the hydrophobic interaction plays an important role in building up the three-dimensional structure. The order of the effectiveness of the anions in causing transitions of helix-coil in collagen gel or a native-denatured structure in ribonuclease [1] is consistent with the order of anions in shifting the sol–gel transition temperature obtained here. Such a correlation shows that the sol–gel transition described in this paper can be an interesting model of protein denaturation.

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