

Reswelling Behavior of Polycation Hydrogels Carrying Charges on the Chain Backbone by Two-Step Surfactant Bindings

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ABSTRACT: Chemically crosslinked polycations carrying charges on the chain backbone, that is, x,y -ionene hydrogels ($x = 2$ or 6 , $y = 3$ or 6), were successfully synthesized, and their swelling and surfactant binding behaviors were studied. A two-step surfactant binding that produced swollen, complex hydrogels occurred for ionene hydrogels with a lower charge

density. The reswelling of the hydrogels was associated with an excessive amount of surfactant binding, which mainly occurred through a hydrophobic interaction with a one-to-one complex. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3791–3794, 2006

Key words: hydrogels; surfactants; swelling

INTRODUCTION

The interaction of surfactants with linear and cross-linked polyelectrolytes has been studied extensively.^{1–6} Ionic surfactants binding to oppositely charged macromolecules are generally highly cooperative because of strong electrostatic and hydrophobic interactions and, as a result, often form micellelike, organized structures even at concentrations nearly 1 order of magnitude lower than that in the absence of a polyelectrolyte. The thermodynamic and kinetic behaviors of surfactant binding to solubilized and crosslinked polyanions over a wide range of concentrations and ionic strengths have been studied. The binding is cooperative through side-by-side hydrophobic interactions of n -alkyl groups, and the surfactant is assumed to undergo one-to-one stoichiometric binding with respect to their complementary charges.⁷ We have found that an ionene polymer, which is a kind of polycation carrying charges on the chain backbone, undergoes two-step binding to give soluble complexes, and the formation of the soluble complexes is associated with an excessive amount of surfactant binding occurring mainly by a hydrophobic interaction with a one-to-one complex.^{8,9} In this study, polycation ionene hydrogels were synthesized, and the interaction be-

tween the ionene hydrogels and anionic surfactant sodium dodecyl sulfate (SDS) in water was examined.

EXPERIMENTAL

Materials

1,3-Dibromopropane and 1,4-dibromohexane were purchased from Shanghai Chemical Reagents Co. (Shanghai, China), and 1,6-dibromohexane was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) N,N,N',N' -Tetramethyl-1,6-diaminohexane was synthesized according to Leuckart's reaction,¹⁰ tetraethylenepentamine was purchased from Shanghai Baifang Chemical, Ltd. (Shanghai, China), and glycol diglycidyl ether was purchased from Wuxi Huili Compound Material, Ltd. (Jiangsu Province, China) N,N,N',N' -Tetramethylenediamine, N,N -dimethylformamide (DMF), and the rest were analytical-grade and were made in China; they were used as received without further purification.

Preparation of the ionene polymer

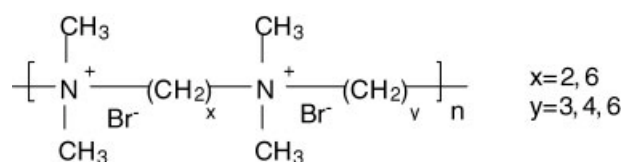
x,y -Ionene ($x = 2$ or 6 , $y = 3$, 4 , or 6) bromide polymers (Scheme 1) were synthesized through successive Menshutkin reactions of N,N,N',N' -tetramethyl-1, x -diaminoalkane and 1, y -dibromoalkane in DMF.¹¹

Preparation of the ionene hydrogel

N,N,N',N' -Tetramethyl-1, x -diaminoalkane and 1, y -dibromoalkane were dissolved in ethanol. The concentrations were 1.2 and 1.5 mol/L, respectively. Tetraethylenepentamine was used as an accelerant, and its

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x,y-ionene bromide polymer

Scheme 1

concentration was 0.4 mol/L. Glycol diglycidyl ether was used as a crosslinking reagent, and its concentration was 10–20% of the concentration of *N,N,N',N'*-tetramethyl-1,*x*-diaminoalkane and 1,*y*-dibromoalkane. The experiment was carried out at 60°C for 2 days. The obtained hydrogels were immersed in ethanol for 1 day and then were immersed in pure water for 1 week to wash away the unreacted substance. The equilibrated swelling ratio (SR) is defined as W_s/W_d , where W_s and W_d stand for the weights of the swollen and dry hydrogels, respectively. The degree of crosslinking (DCL) was defined as the molar ratio of the crosslinking reagent to the polymer.

Formation of the ionene complexes

The complex formation was carried out at room temperature by the mixing of a relatively concentrated aqueous solution of the surfactant SDS (0.16 mol/L) and the *x,y*-ionene polymer (polycation concentration = 0.16 mol/L) in different ratios. The precipitates were collected by centrifugation (3000 rpm).

The ionene hydrogels (10 × 10 × 3 mm) were immersed in aqueous solutions of the surfactant SDS of various concentrations for 1 week to form the complexes at room temperature. The changes in the size of the hydrogels were studied by the measurement of the weight ratio of the hydrogels (W/W_0 , where W and W_0 are the weights of the swollen hydrogels in SDS solutions and distilled water, respectively).

The swelling kinetics of the ionene hydrogels in SDS solutions were studied. The hydrogels were immersed into SDS solutions quickly. The length of the hydrogels was measured with a vernier caliper at different times. The length ratio is defined as the ratio of the length after the ionene hydrogels were added to the SDS solution to their original size.

RESULTS AND DISCUSSION

Formation of the soluble complexes

When a relatively concentrated (0.16 mol/L) aqueous solution of SDS was added to a solution of *x,y*-ionene polymers (polycation concentration = 0.16 mol/L, $x = 2$ or 6 , $y = 4$ or 6) dropwise, a white, cottonlike precipitate appeared, and the amount of the precipitate increased with the amount of the surfactant

until the molar ratio of the surfactant to the polymer charge unit ($[\text{SDS}]/[\text{P}]$) was 1. However, when $[\text{SDS}]/[\text{P}]$ exceeded 1.0, the amount of the precipitate decreased dramatically, and all the precipitate disappeared at a certain mixing ratio, except for the 2,4-ionene polymer. The dissolved complexes were transparent and highly viscous.

Figure 1 shows the amount of the precipitate as a function of $[\text{SDS}]/[\text{P}]$. The yield of the complexes is defined as the percentage ratio of the weight of the precipitate in the experiments to the calculated amount in theory. In the beginning, the precipitate forms in proportion to the molar mixing ratio, and it reaches the theoretically evaluated value of $[\text{SDS}]/[\text{P}] = 1$, which indicates that a one-to-one stoichiometric complex has formed for each ionene polymer. The yields do not reach 100%, and this suggests that the neutral reaction of the charges, which is due to the electrostatic interaction, is not carried out fully. When an excessive amount of SDS is introduced into the one-to-one complexes, the amount of the precipitate of 2,4-ionene decreases inconspicuously and scarcely changes after $[\text{SDS}]/[\text{P}]$ is 1.5. This is because of the high charge density of 2,4-ionene. The short distance between two adjacent surfactants bound to the 2,4-ionene polymer leads to the strong side-by-side hydrophobic interaction, which forms lamellar-like packing.⁹ These lamellar-like complexes might prevent the additional binding of the extra amount of the surfactant and stay in water as insoluble one-to-one complexes.

In contrast to 2,4-ionene, the amount of the precipitate of 6,4-ionene decreases rapidly, and all the complexes completely dissolve at $[\text{SDS}]/[\text{P}] = 1.5$. The amount of the precipitate of 2,6-ionene decreases more slowly than that of 6,4-ionene, and the complexes completely dissolve at $[\text{SDS}]/[\text{P}] = 4.5$. This is due to the formation of nonstoichiometric com-

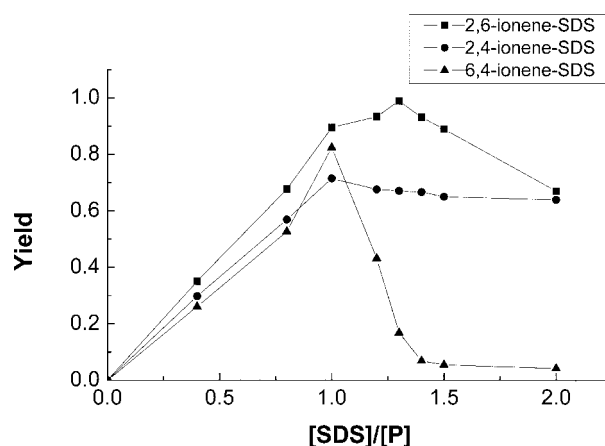


Figure 1 Relationship between the complex formation yield and the mixing ratio ($[\text{SDS}]/[\text{P}]$) for various ionene-SDS systems ($[\text{SDS}] = [\text{P}] = 0.16$ mol/L).

plexes with negative charges between the ionene polymer and excessive SDS by the hydrophobic interaction of SDS with the one-to-one complexes.

Swelling behavior of the ionene hydrogel

Chemically crosslinked and water-swollen ionene hydrogels ($x = 2$ or 6 , $y = 3$ or 6), carrying charges on the chain backbone, were first successfully synthesized through the successive Menshutkin reactions of N,N,N',N' -tetramethyl-1, x -diaminoalkane and 1, y -dibromoalkane with glycol diglycidyl ether as the crosslinking reagent. The ionene hydrogels swelled in water and showed SR values of 47.9, 32.4, and 25.0 for 2,6-ionene, 6,3-ionene, and 6,6-ionene hydrogels, respectively. SR decreased with decreasing charge density because of the weakening of the electrostatic repulsion. Figure 2 shows the SR values of 6,3-ionene hydrogels with different crosslinking densities. As expected, the higher the crosslinking density becomes, the lower the SR value is.

Considering the different complex formation behaviors of ionene polymers with SDS solutions, we studied the swelling behaviors of ionene hydrogels in SDS solutions. Figure 3 shows the changes in the size of the hydrogels when 2,6-ionene, 6,3-ionene, and 6,6-ionene hydrogels are immersed in various SDS solutions. First, the three kinds of ionene hydrogels shrink as the SDS concentration increases because of the neutralization of the charges through electrostatic interactions. The higher the charge density becomes, the stronger the electrostatic interaction is, and the larger the hydrogel shrinkage is.

With an increase in SDS, the SR values of 2,6-ionene and 6,3-ionene hydrogels do not change even after the minimum is reached. This is the typical swelling behavior observed in many polyelectrolyte hydrogel-surfactant systems.^{7,12} Conversely, in the case of the 6,6-ionene hydrogel, SR decreases first and then gradually increases via a minimum with an increase in the SDS concentration; this agrees well

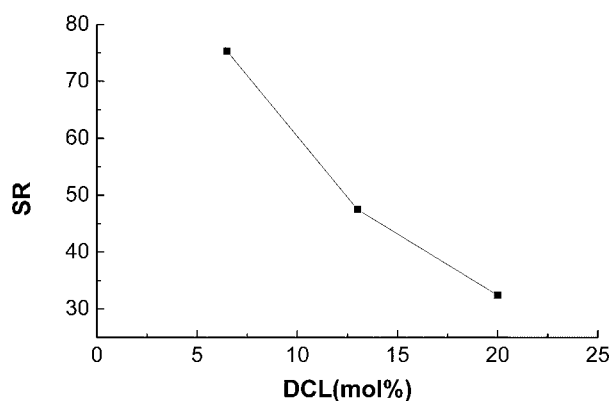


Figure 2 Relationship between SR and DCL for the 6,3-ionene hydrogel.

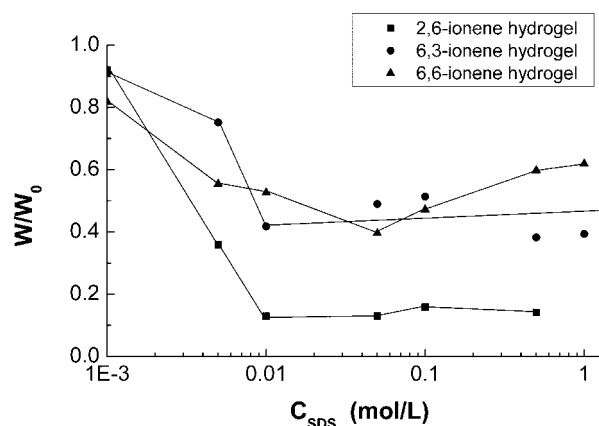


Figure 3 SDS concentration (C_{SDS}) dependence of SR of ionene hydrogels (DCL = 20%).

with SDS binding of ionene polymer solutions. The SDS concentration at the minimum SR values decreases much more than that of the 2,6-ionene and 6,3-ionene hydrogels.

These different experimental results clearly show the importance of the hydrophobic nature of the chain backbone: if the charge density of ionene is high, like that for 2,6-ionene and 6,3-ionene hydrogels, only a one-to-one complex is formed; if it is low, like that for 6,6-ionene hydrogels, two-step surfactant binding that produces swollen, complex hydrogels occurs. For 2,6-ionene and 6,3-ionene hydrogels, the short distance between two adjacent surfactants that are bound leads to strong side-by-side hydrophobic interactions that form lamellar-like packing, which might prevent the additional binding of the extra amount of SDS and hold one-to-one complexes. For the 6,6-ionene hydrogel, the long distance between two adjacent binding sites will make it difficult to form adjacent organization among the bound surfactants; instead, they will align in parallel with the main-chain backbone through their hydrophobic interaction. This allows subsequent binding of additional surfactants to produce complex reswell-

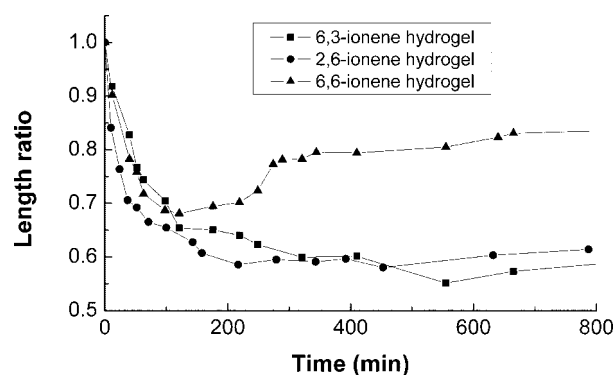


Figure 4 Swelling kinetics of ionene hydrogels in SDS solutions (DCL = 20%, [SDS] = 1.0 mol/L).

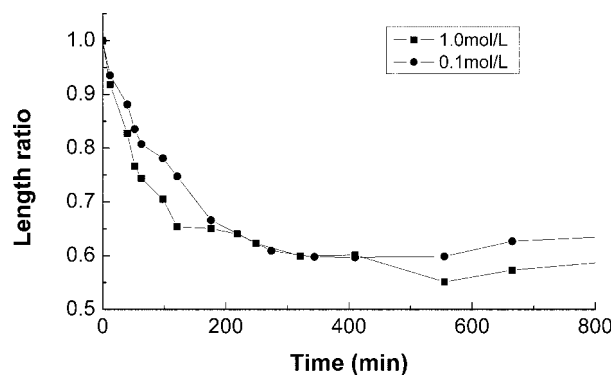


Figure 5 Changes in the size of the 6,3-ionene hydrogel in different SDS solutions (DCL = 20%).

ling due to the charges of the surfactant. This confirms the important contribution of the hydrophobic interaction to the complexation.

Kinetic behavior of the surfactant binding to the ionene hydrogel

The swelling kinetics of ionene hydrogels in SDS solutions were studied. Figure 4 shows the changes in the size of ionene hydrogels with time. In the first 2 h, the three kinds of ionene hydrogels shrink rapidly, and their sizes change linearly. Their length becomes 60–70% of the original length. The contraction in size of the ionene hydrogel is caused by the strong electrostatic and hydrophobic interactions; they can adsorb surfactants with opposite charges. The 2,6-ionene hydrogel shrinks most rapidly because of its high charge density.

After 2 h, the swelling behaviors of the three kinds of ionene hydrogel show differences: the sizes of the

2,6-ionene and 6,3-ionene hydrogels continue to decrease slowly and then saturate, whereas the size of the 6,6-ionene hydrogel becomes minimal and then increases with time. The reswelling of the ionene hydrogels is due to the excessive SDS binding of stoichiometric complexes by hydrophobic interactions; as a result, nonstoichiometric complexes with negative charges are formed.

The influence of the SDS concentration on changes in the size of the hydrogels was also studied, and the results are shown in Figure 5. The highly concentrated SDS solution leads to hydrogels shrinking more rapidly because of the stronger electrostatic interactions with the ionene hydrogels.

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