

学 位 論 文 要 旨

Structure and Dynamics of Chemically Modified Cellulose Ethers in Aqueous Solution

水溶液中での化学修飾セルロースの構造とダイナミクス

環境資源共生科学専攻 森林資源物質科学大講座
新井 健悟

The water soluble cellulose ether samples, WSCEs, are widely used for various applications because of their unique excellent properties. However, the reason why WSCEs demonstrate temperature dependent water solubility, and the conformation of WSCEs in aqueous solution have not been fully understood. The goals of this thesis are to understand the temperature dependent dynamics of the aqueous WSCEs systems from two different perspectives, water and solute molecules, and to clarify the structure of WSCEs dissolved in water.

In Chapter 2, the hydration numbers for WSCEs, such as methyl cellulose, MC, hydroxypropylmethyl cellulose, HpMC, hydroxyethylmethyl cellulose, HeMC, hydroxyethyl cellulose, HeC, and hydroxypropyl cellulose, HpC, in aqueous solution were determined by using extremely high-frequency dielectric spectroscopy techniques. The critical hydration number for mainly methylated cellulose ethers (MC, HpMC and HeMC) necessary to be dissolved in water was evaluated to be ca. 5 because the hydration numbers observed just below their lower critical soluble temperatures (LCST) were close to 5 irrespective of their molecular weights. In the case of HeC, the dehydration behavior with increasing temperature was obviously gentler than that of the mainly methylated cellulose ethers. The hydration numbers for the examined HeC samples were substantially larger than the critical hydration number, ca. 5, even at a high temperature of 70 °C. Therefore, the HeC samples keep their high water solubility even in a high temperature range. On the other hand, although the hydration number of HpC obtained just below its LCST

value of $T = 45$ °C was much larger than the critical hydration number of ca. 5, the aqueous HpC system demonstrated a cloud point at 46 °C because of the intermolecular interaction between its substitution groups. It was concluded that larger hydration numbers of cellulose ethers than their critical hydration numbers are necessary to keep their solubility in water over a wide temperature range. When the hydrophobicity of the substitution groups is slightly high, the required hydration number to be dissolved in water becomes substantially large.

In Chapter 3, the gelation mechanism for aqueous solutions of MC and HpMC was investigated by using dynamic viscoelastic measurements. A small part of MC and HpMC polymer chains formed a weak network structure possessing a long relaxation time. The weak network structure gradually grew to a strong network structure due to dehydration behavior with increasing T . Additional increase of temperature led to spreading the strong network throughout the solution, and MC and HpMC demonstrated gelation behavior. Aqueous solutions of MC and HpMC did not show the critical gel behavior, which is usually observed in many gel forming systems. The conformation of HpMC in aqueous system was investigated by using viscoelastic measurements. The obtained dependence of the average relaxation time, τ_w , and the average modulus (the reciprocal value of steady state compliance), J_e^{-1} , on concentration, c , the number density of polymer chains, ν , and weight-average molecular weight, M_w , for HpMC was quite similar to the theoretically predicted relationships for entangled rigid rod-like particles. Therefore, HpMC molecules behave as rod-like particles possessing high rigidity in aqueous solution.

In Chapter 4, the dynamic viscoelastic properties for aqueous solutions of HpC and HeC were investigated. Although a weak network structure appeared and grew in aqueous HpC system with increasing temperature as in the aqueous MC and HpMC systems, the HpC system showed the critical gel behavior. Then, the gelation mechanism of aqueous HpC solution is essentially different from that of aqueous solutions of MC and HpMC. The reason for this discrepancy would be that the hydrophobicity of substitution groups for HpC is slightly higher than that for MC and HpMC. On the other hand, although the aqueous HeC system demonstrated a shoulder in storage modulus, G' , with increasing temperature, the system never showed gelation behavior even at a high temperature of $T = 70$ °C. This is because the dehydration behavior of HeC with increasing T is very much gentler than that of other WSCEs. The obtained c , ν and M_w dependence of τ_w and J_e^{-1} for aqueous HeC solutions suggested that the HeC molecules in aqueous system cannot keep their rigidity and the flexibility becomes pronounced with increasing molecular weight. The comparison of viscoelastic behavior between aqueous solutions of HeC and HpMC indicated that the substitution by hydroxyethyl groups significantly affects not only the hydration behavior of cellulose ethers, but also their conformation in aqueous solution.