Solution Properties of a Novel Polysaccharide Derivative

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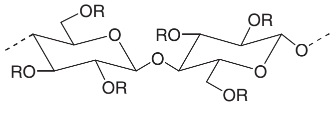
A novel self-assembly polysaccharide derivative; hydrophobically (stearyl alkyl group) and hydrophilically (sulfonic acid salt group) modified hydroxyethylcellulose (HHM-HEC), has the unique rheological properties in aqueous solutions.

Much recent attention has been paid to the water-soluble polymers from the view point of the environmental protection.[2–4] Especially, the water-soluble amphiphilic polymers have been extensively investigated not only by academic chemists but also by industrial scientists, and applied to various fields.[2–4] Many kinds of the block or random copolymers have been synthesized from various hydrophobic and hydrophilic monomers, and investigated intensively the self-assembly and aggregation of the amphiphilic polymers in aqueous solutions.[5–16] However, there are only a few reports on studies of the amphiphilic polysaccharide derivatives such as the nonionic hydrophobically modified polysaccharides.[17–21]

In this paper, we report on a novel self-assembling polymer (HHM-HEC), and it's unique rheological properties in aqueous solutions. The HHM-HEC was synthesized from hydroxyethylcellulose, stearyl glycidyl ether, and 3-chloro-2-hydroxypropanesulfonic acid in alkaline condition (Figure 1). We synthesized the HHM-HEC[1] that introduced hydrophobic substituent (0.0039), because it was insoluble in water when that exceeded 0.0080, and that introduced hydrophilic substituent(0.29), because it accelerated the water-insolubility when that replacement was few. Initially, we examined the relationship of viscosity or surface tension between the concentration of HHM-HEC in water. The viscosity and the surface tension of the aqueous solution of HHM-HEC at 25 °C were shown in Figures 2 and 3, respectively. In Figure 2, two break points were found at around 0.2 and 0.6 wt %. Such behavior in the viscosity is different from that of HEC or Carbopol® (the cross-linked polymer of polyacrylic acid), and should be attributed to the amphiphilic properties. Because HHM-HEC has both hydrophobic and hydrophilic moieties, so that it forms the aggregate, as well as a large number of conventional surfactants form micelle in water. The surface tension measurements were carried out to determine the critical



HHM-HEC

Figure 1. Hydrophobically (stearyl alkyl group) and hydrophilically (sulfonic acid salt group) modified hydroxylethylcellulose [R = H or $(CH_2CH_2O)_nH$ or $CH_2CH(OH)CH_2OC_{18}H_{37}$ or $CH_2CH(OH)CH_2SO_3Na$ or $(CH_2CH_2O)_nCH_2CH(OH)CH_2OC_{18}H_{37}$ or $(CH_2CH_2O)_nCH_2CH(OH)CH_2SO_3Na$].

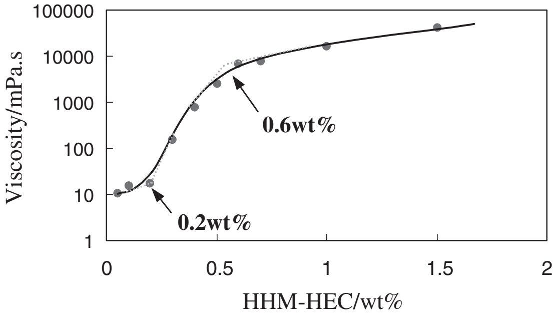


Figure 2. Viscosity of aqueous solution as a function of the HHM-HEC concentration at 25 °C.

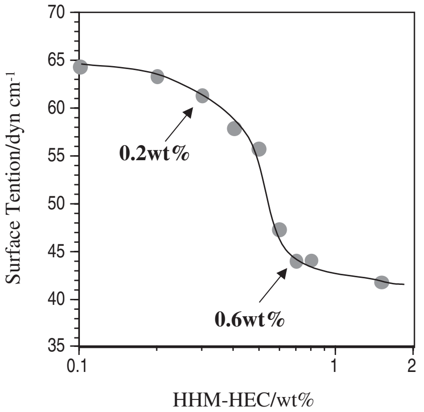


Figure 3. Surface tension of aqueous solution as a function of the HHM-HEC concentration at 25 °C (dyn = 10^{-5} N).

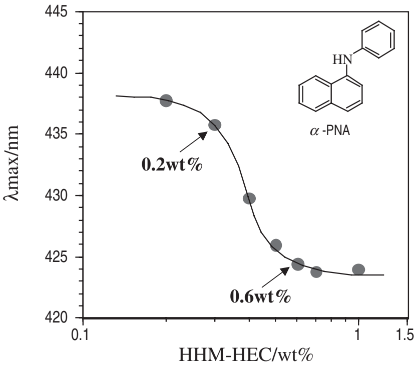


Figure 4. Emission maximum of α-PNA (λmax) as a function of the HHM-HEC concentration at 25 °C (α-PNA = 1.0×10^{-6} mol dm^{-3}).

micellization concentration (CMC). In Figure 3, a clear break point at around 0.6 wt % was observed of the aqueous solution of HHM-HEC and was belived to be the CMC. While at a concentration of 0.2 wt % another characteristic can be observed. It should be noted that the viscosity of solution is greatly increasing, beginning at this concentration (see Figure 2). Therefore, it is likely that the intermolecular crosslinking (growth of gel network) based on the hydrophobic interaction of stearylalkyl moieties occurs immediately from 0.2 wt % concentrations. To test this hypothesis, we have conducted an experiment using, α-phenylnaphthylamine (α-PNA) as the fluorescence probe, because it is well known as a neutral, hydrophobic probe, and its maximum wavelength of a fluorescence spectrum shifts to short wavelength with decreasing the polarity of environment around the probe.[22] Figure 4 shows the variation of the maximum wavelength with the HHM-HEC concentrations. Going from 0.2 to 0.6 wt % of HHM-HEC concentrations, the fluorescence maximum wavelength of α-PNA shifted to a lower wavelength. In a region of more than 0.6 wt % concentrations, it showed an almost fixed wavelength. It can be seen that the aggregation of hydrophobic stearylalkyl moieties in HHM-HEC occurs from 0.2 wt % concentration, and the formation of aggregates is completed at 0.6 wt % concentration (aggregation number of stearylalkyl groups were determined). Above 0.6 wt % there is an increase in the number of aggregates but it is likely that the aggregation number of stearylalkyl groups remains the same.

Thus the thickening mechanism of HHM-HEC consists of three steps. First step: HHM-HEC exists as monomer solution below the CAC (critical aggregation concentration). Second step: Intermolecular aggregation of its alkyl groups starts at CAC. Therefore the alkyl domains that play the role of crosspoints in intermolecular network are formed. After that, as its concentration is increased, the alkyl domains also increase in size (the number of aggregated alkyl chains increase). Third step: Growing of alkyl domains stops at CMC (the number of aggregated alkyl chains stop increasing). While increasing the concentration of HHM-HEC, the number of domains increases but the number of alkyl chains per domain remains the same.

As described above, HHM-HEC, an anionic associated thickener, can dramatically increase the viscosity of an aqueous solution above CAC. Ordinarily, it has been seen that ionic associated compounds depress their CAC with increasing the ionic strength of that solution. The case of HHM-HEC isn't an exception, either. To utilize these properties, we found it can induce specific behavior on rheology in an aqueous solution. Figure 5 shows the relationship of NaCl concentration and solution viscosity (HHM-HEC concentration is 0.5 wt %, constantly). It's clear that the viscosity of aqueous HHM-HEC solution increases while increasing the concentration of NaCl. It can be seen that the networking of HHM-HEC proceeds with increasing the ionic strength of that solution. General thickeners reduce the viscosity of their solution while increasing the ionic strength in that solution. And also, even the polysaccharides that show excellent viscosity in ionic aqueous solutions do not cause the viscosity to decrease. This finding is very interesting because there is no previous report of a thickener in low concentrations that shows this unique behavior.

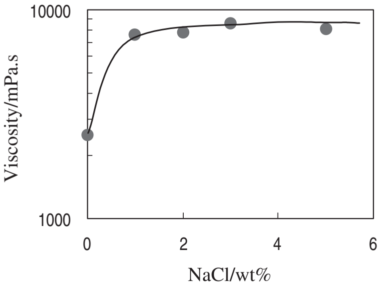


Figure 5. Viscosity of HHM-HEC solution as a function of the NaCl concentration at 25 °C. (HHM-HEC = 0.5 wt %)

In summary, we synthesized a novel self-assembling polymer; (HHM-HEC), and reported on it's unique rheological properties. The thickening mechanism in aqueous solution consists of three steps. And we found that the viscosity of aqueous solution increases while increasing the ionic strength of that solution. From now, we will proceed with the analytical approaches to realize the mechanism of viscosity that increased in ionic conditions.

References and Notes

1 Data for HHM-HEC: The average degree of replacement by the hydrophobic substituent (stearyl alkyl group) is 0.0039 per constituent monosaccharide residue as determined by Zeisel's method[23] and that by the hydrophilic substituent (sulfonic acid salt group) is 0.29 per constituent monosaccharide residue as determined by colloidal titration. Weight-average molecular weight is 1900000 (7300 glucose unit) as determined by light scattering method. This novel polysaccharide derivative was synthesized by the method of Japanese patent [JP3329668].

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