

1 **Effects of side groups on entanglement network of cellulosic polysaccharides**

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Abstract

The transient entanglement network of cellulosic polysaccharides in concentrated solutions were characterized by the molecular weight between entanglements (M_e) using dynamic viscoelasticity measurements. From the concentration dependence of M_e , M_e for the cellulosic polysaccharides in the molten state ($M_{e,\text{melt}}$) was estimated as the material constants reflecting the chain characteristics. The values of $M_{e,\text{melt}}$ were compared among three cellulosic polysaccharides: cellulose, methylcellulose, and hydroxypropyl cellulose. Methylcellulose and hydroxypropyl cellulose were employed as cellulose derivatives having small and large side groups, respectively. It appeared that hydroxypropyl cellulose had significantly larger $M_{e,\text{melt}}$ compared with cellulose and methyl cellulose. However, the numbers of repeating glucose-ring units between entanglements were very close to each other among the three polysaccharides.

Keywords entanglement network· cellulosic polysaccharide· side group· concentrated solution· molecular weight between entanglements

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39 **Introduction**

40 Cellulose is the most familiar polysaccharide as the result of long years of use in human history.

41 In addition to cellulose in the natural form, many derivatives are known to be synthesized from

42 cellulose by modifying the hydroxyl groups. The main aim of introducing the substituents is to

43 change the physical properties of cellulose; for example, methylcellulose is water-soluble in

44 contrast to natural cellulose, because the methyl groups reduce the strength of hydrogen

45 bonding between cellulose chains. Currently, cellulosic polysaccharides, meaning cellulose as

46 well as its derivatives, are vital materials in several industries due to the various properties.

47 Cellulosic polysaccharides are also of interest in the field of chain characterization of

48 polymers. The chain dimensions of cellulosic polysaccharides in various dilute solutions have

49 been examined previously and the effects of side groups (substituents) on the unperturbed chain

50 parameters as well as on the hydrodynamic properties have been discussed based on the

51 accumulated data (Brown et al. 1963; Brown et al. 1964; Flory 1966; Kamide et al. 1978;

52 Kamide et al. 1987). Thus chain characterization of cellulosic polysaccharides using dilute

53 solutions has been successfully carried out. Studies on concentrated systems of cellulosic

54 polysaccharides are also making good progress (Chen et al. 2009; Gericke et al. 2009; Haward

55 et al. 2012; Kosan et al. 2008; Syang-Peng et al. 2009). A specific matter to concentrated

56 polymer systems such as polymer melts and concentrated solutions is the entanglement coupling

between polymer chains emerging from topological constraints of the interpenetrating polymer chains. It is recognized that entanglement coupling dominates the rheological behavior of concentrated polymer systems at long times (Doi et al. 1986; Ferry 1980). The entanglement coupling can be characterized by the molecular weight between entanglements (M_e), which corresponds to an average mesh size of the transient entanglement network. The value of M_e for a polymer melt ($M_{e,melt}$) especially is a material constant; namely, $M_{e,melt}$ is a type of chain characteristics obtained only by examining the rheological behavior of concentrated polymer systems. Until now, however, $M_{e,melt}$ for the better part of cellulosic polysaccharides have been unknown and effects of side groups on entanglement coupling for cellulosic polysaccharides has not even been considered.

In this paper, $M_{e,melt}$ for three cellulosic polysaccharides, cellulose (C), methylcellulose (MC), and hydroxypropyl cellulose (HPC), have been estimated from the rheological data for their concentrated solutions. It should be noted that MC has small substituents of methyl groups, while HPC has larger ones of hydroxypropyl groups, which is characterized by the molecular weight of a repeating unit (M_{unit}) below. Use of an ionic liquid as a solvent has made it possible to prepare solutions of these cellulosic polysaccharides at high concentrations where there is entanglement coupling. The values of $M_{e,melt}$ as well as the number of repeating glucose-ring units between entanglements (N_{unit}) have been compared among the three polysaccharides.

Experimental

Materials

The cellulosic polysaccharides, C (Aldrich, USA), MC (Aldrich, USA), and HPC (Wako, Japan), were used without further purification. According to the manufacturers, the degree of substitution per repeating unit were 1.7 and 3.8 for MC and HPC, respectively; therefore, M_{unit} for C, MC, and HPC were estimated to be 162, 186, and 383, respectively. The viscosities for 2 % aqueous solutions of MC and HPC at 20 °C were reported by the manufacturers to be 4000 cP and 1000-4000 cP, respectively, whereas that for C was unavailable. An ionic liquid 1-butyl-3-methylimidazolium acetate (BmimAc; BASF, Germany) was used as received. As far as we tested, BmimAc was the only common solvent to prepare concentrated solutions of the three polysaccharides. Each polysaccharide sample was added into liquid BmimAc in a dry glass vessel, and then the mixture was stirred on a hot plate at about 80 °C for more than 6 h until complete dissolution. The concentration of the polysaccharides (c) ranged from 1.1×10^2 to $2.1 \times 10^2 \text{ kgm}^{-3}$ (ca. 10 to 20 wt %) for C, from 4.2×10^1 to $7.5 \times 10^1 \text{ kgm}^{-3}$ (ca. 4 to 7 wt %) for MC, from 5.2×10^1 to $2.6 \times 10^2 \text{ kgm}^{-3}$ (ca. 5 to 25 wt %) for HPC; the lowest c was slightly above the critical concentration for entanglement coupling, while the highest c was determined by the solubility. In the calculation of c , the densities of melts of the polysaccharides were

commonly assumed to be $1.0 \times 10^3 \text{ kgm}^{-3}$ and that of BmimAc was quoted to be $1.055 \times 10^3 \text{ kgm}^{-3}$ (Horinaka et al. 2013).

Rheological measurements

The angular frequency (ω) dependence of the storage modulus (G') and the loss modulus (G'') for the polysaccharide solutions was measured with an ARES rheometer (now TA Instruments, USA) under a nitrogen atmosphere. The geometry for the measured sample was a cone-plate with a diameter of 25 mm and a cone angle of 0.1 rad. The value of ω ranged from 0.1 to 100 s^{-1} and the amplitude of the oscillatory strain (γ) was fixed at 0.1 so that the measurement could be performed in the linear viscoelasticity region. The above measurement was carried out at several temperatures (T) from 0 to $80 \text{ }^\circ\text{C}$.

Results and Discussion

Figure 1 shows the ω dependence of G' and G'' for the C solutions; the curves are shifted upwards by A to avoid overlapping for different c . Each of the curves is the so-called master curve at the reference temperature (T_r) of $80 \text{ }^\circ\text{C}$ obtained by means of a horizontal shift by a factor of a_T for each T according to the frequency-temperature superposition principle. It appears that the time-temperature superposition principle holds well for the C solutions. At low

ωa_T , flow of the system can be seen for each c , although the terminal relation of $G'' \propto \omega$ is observed only for the solution of $c = 1.1 \times 10^2 \text{ kgm}^{-3}$. In the middle ωa_T region, there is a plateau region in each G' curve where $G' > G''$, which becomes wider as c increases; this is the so-called rubbery plateau, indicating the existence of entanglements coupling in the C solutions. The reason that the plateau of G' is slightly tilted is probably the polydispersity of the sample employed, although actual data on the polydispersity are not available. In Figures 2, $\log a_T$ is plotted against $1/T$. All data points can be fitted by a single line regardless of c , as drawn in the figure, indicating that the T -dependence curve of a_T can be represented by an Arrhenius-type equation. This trend implies that the solutions are homogeneous.

Figure 3 shows the master curves of the ω dependence of G' and G'' at $T_r = 80 \text{ }^\circ\text{C}$ for the MC solutions obtained in the similar way to Figure 1. Although the rubbery plateau region in each G' curve is not obvious compared with that in Figure 1 partly due to the low c , the rubbery plateau as well as the flow region is seen for each c in the G' and G'' curves, which is typical of polymer solutions with entanglement coupling. The T -dependence curve of a_T for the MC solutions is shown in Figure 4. The values of a_T at a given T are almost identical regardless of c , and all data points in the figure appear to fall on a single line.

The master curves of the ω dependence of G' and G'' at $T_r = 80 \text{ }^\circ\text{C}$ for the HPC solutions are given in Figure 5. The rubbery plateau region becomes wider as c increases, so that the flow

region goes out of sight for the solution of $c = 2.1 \times 10^2 \text{ kgm}^{-3}$. The Arrhenius-type plot of a_T for the HPC solutions is shown in Figure 6. As is the case of C and MC, the data points fall on a single line; namely, a_T for these solutions show almost the same T -dependence being independent of c . This result supports that the HPC solutions are homogeneous within the c range examined.

As demonstrated above, the rubbery plateau appears for all the solutions examined. From the analogy with the rubber elasticity, M_e (in gmol^{-1}) for a polymer in solution at the concentration of c can be given by

$$M_e = \frac{10^3 cRT}{G_N^0} \quad (1)$$

Here, G_N^0 is the plateau modulus, which corresponds to the height of the plateau, and R is the gas constant (Doi et al. 1986; Ferry 1980). It should be noted that G_N^0 is independent of the molecular weight of the polymer itself as long as the molecular weight is sufficiently greater than $2M_e$ and the plateau appears (Ferry 1980; Onogi 1970). As seen in the above figures, the actual plateaus obtained in this study were tilted to some extent, and therefore we defined G_N^0 as the G' value at ωa_T where the loss tangent ($\tan \delta = G''/G'$) attained the minimum in the rubbery plateau region (Horinaka et al. 2011; Horinaka et al. 2013). For example, G_N^0 for the HPC solution at $c = 2.1 \times 10^2 \text{ kgm}^{-3}$ is determined to be $1.9 \times 10^4 \text{ Pa}$ in Figure 5, which gives M_e of 3.2×10^4 from eq. 1 with $T = T_r$. The values of M_e for the C, MC, and HPC solutions

obtained in this manner are double-logarithmically plotted against c in Figure 7. For each polysaccharide, a straight line with a slope of -1 is drawn with the best fit method, because it has been reported that a relation of $M_e \propto c^{-1}$ holds for many concentrated solutions of polymers (Doi et al. 1986; Masuda et al. 1972). It is seen that data points in the figure are fitted well by the line, indicating that the $M_e \propto c^{-1}$ relation also holds for the C, MC, and HPC solutions examined in this study. Hence, $M_{e,melt}$ for the cellulosic polysaccharides can be estimated to be M_e at $c = 1.0 \times 10^3 \text{ kgm}^{-3}$ of the fitted line in Figure 7 as we assume the density of the polysaccharides to be $1.0 \times 10^3 \text{ kgm}^{-3}$. The obtained values of $M_{e,melt}$ are 2.9×10^3 , 2.5×10^3 , and 6.2×10^3 for C, MC, and HPC, respectively. Here, it is noted that $M_{e,melt}$ for C estimated in the current study is consistent within the experimental error with that for C obtained in our previous study where another ionic liquid 1-butyl-3-methylimidazolium chloride has been used as the solvent (Horinaka et al. 2011; Horinaka et al. 2012). The value of $M_{e,melt}$ for MC obtained in this study is slightly smaller than that for C. Considering the experimental error, this difference might be negligible. On the other hand, $M_{e,melt}$ for HPC is significantly larger. These results suggest that the effects of side groups on $M_{e,melt}$ are apparent but not monotonous against M_{unit} . It has been reported earlier that there is an irregular tendency for the effect of M_{unit} on a chain stiffness parameter of cellulosic polysaccharides in dilute solutions, although direct comparison with our result is impossible (Brown et al. 1964). It should be noted that

aggregation behavior of the cellulosic polysaccharides does not account for the difference in $M_{e,melt}$. It has been reported that side groups of cellulosic polysaccharides affects the solubility in conventional solvents and extremely high substitution is necessary to obtain the molecularly dissolved solutions (Burchard 2003). For the ionic liquid solutions of cellulosic polysaccharides, it is recognized that dissolution on the molecular level is achieved by forming hydrogen bonds between the anions of the solvent and the hydroxyl protons of the solute, and therefore even cellulose can be molecularly dissolved in ionic liquids, as demonstrated by a light scattering study (Chen et al. 2011; Swatloski, Spear, Holbrey, Rogers 2002). Our results in Figures 1, 3, and 5 also indicate that there are no aggregates of the polysaccharides in all the solutions examined in this study; if the aggregates exist in the solution, another plateau (or at least shoulder), the so-called second plateau, should appear in the flow region before reaching the terminal behavior. Maeda et al. have explained the dynamic viscoelasticity data for an ionic liquid solution of cellulose over a wide range of frequency from the flow to the glassy zone successfully without taking the aggregated state of cellulose into consideration (Maeda, Inoue, Sato 2013). Now, we consider N_{unit} instead of $M_{e,melt}$. Since cellulosic polysaccharides have a common backbone structure of repeating glucose-ring units, the contour length between entanglement coupling points can be compared using N_{unit} . In other words, N_{unit} represents the mesh size of the entanglement network in terms of length. The values of N_{unit} calculated from

$M_{e,melt}$ and M_{unit} are 18, 13, and 16 for C, MC, and HPC, respectively. The values of N_{unit} come closer to each other compared with $M_{e,melt}$.

Conclusions

The effects of side groups on entanglement network of cellulosic polysaccharide were examined in terms of the rheological properties $M_{e,melt}$ and N_{unit} . Dynamic viscoelasticity measurements for the concentrated solutions of C, MC, and HPC in BmimAc provided $M_{e,melt}$ of 2.9×10^3 , 2.5×10^3 , and 6.2×10^3 , respectively, indicating that there was an dependence of $M_{e,melt}$ on M_{unit} , although the dependence appeared rather complicated. On the other hand, the effects of side groups were very small regarding N_{unit} .

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240 Figure Captions

241 **Fig. 1** Master curves of ω dependence of G' and G'' for the C solutions at $T_r = 80$ °C. The
242 curves are shifted upwards by A .

243 **Fig. 2** Shift factor for the C solutions plotted against the reciprocal of T . All data points fall on
244 a single line.

245 **Fig. 3** Master curves of ω dependence of G' and G'' for the MC solutions at $T_r = 80$ °C. The
246 curves are shifted upwards by A .

247 **Fig. 4** Shift factor for the MC solutions plotted against the reciprocal of T . All data points fall
248 on a single line.

249 **Fig. 5** Master curves of ω dependence of G' and G'' for the HPC solutions at $T_r = 80$ °C. The
250 curves are shifted upwards by A .

251 **Fig. 6** Shift factor for the HPC solutions plotted against the reciprocal of T . All data points fall
252 on a single line.

253 **Fig. 7** Double-logarithmic plot of M_e vs. c for the cellulosic polysaccharides in solution. Each
254 line is the best fit one with a slope of -1 . $M_{e,melt}$ is defined as M_e at $c = 10^3 \text{ kgm}^{-3}$.

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Figure 1

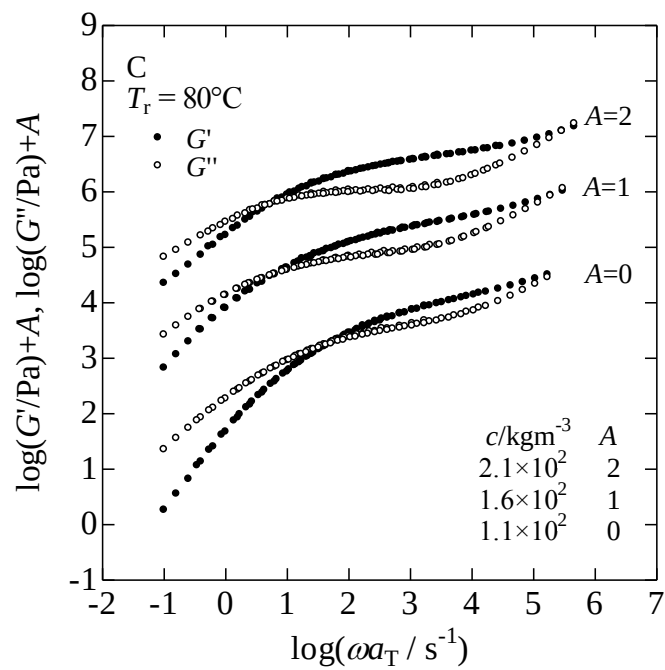


Figure 2

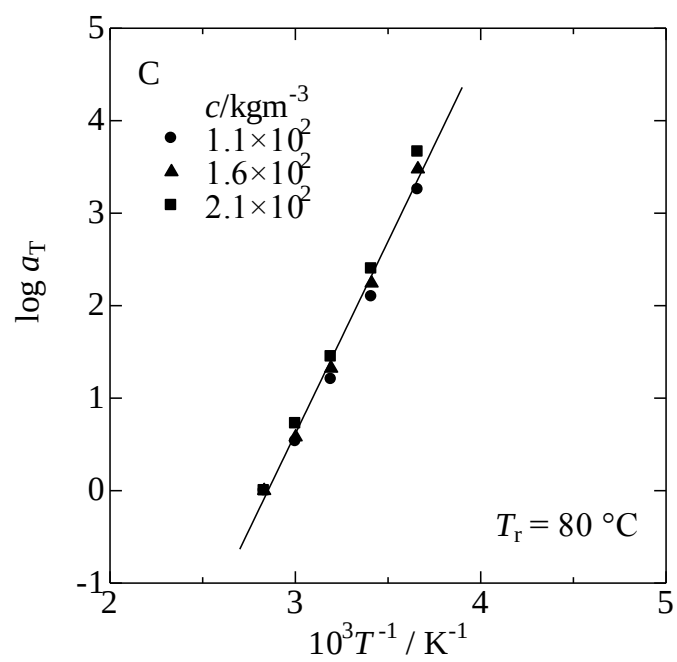


Figure 3

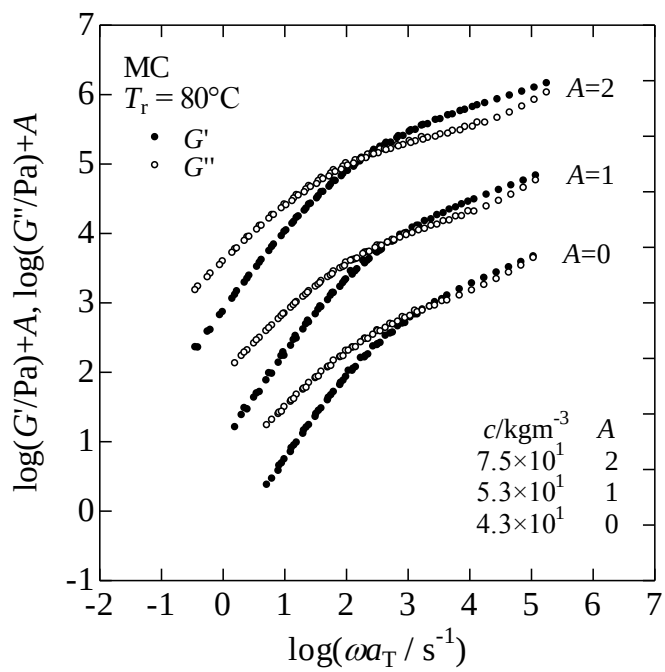


Figure 4

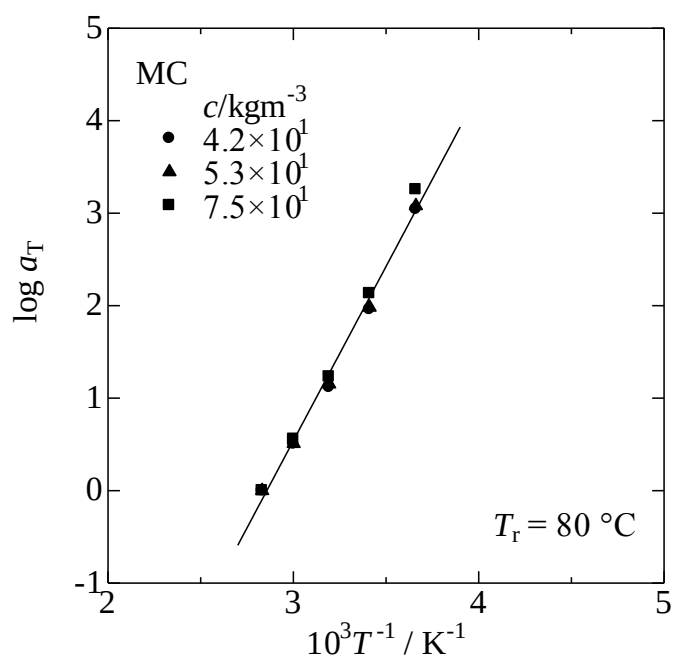


Figure 5

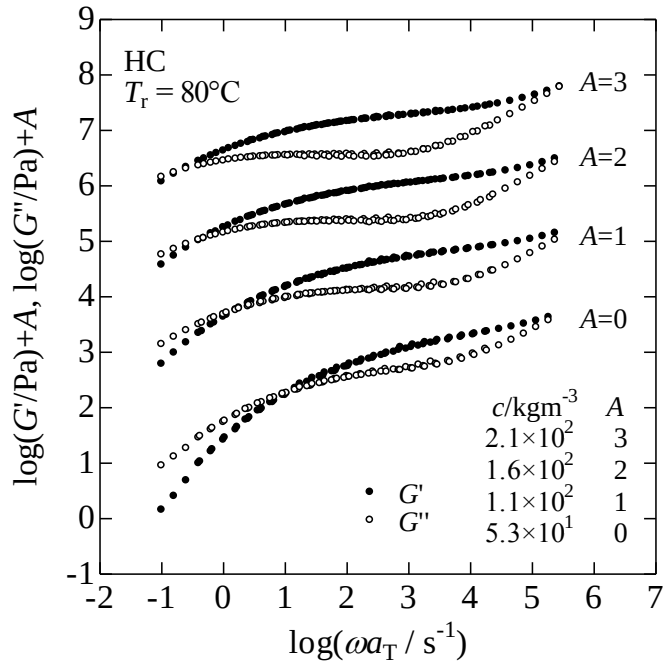


Figure 6

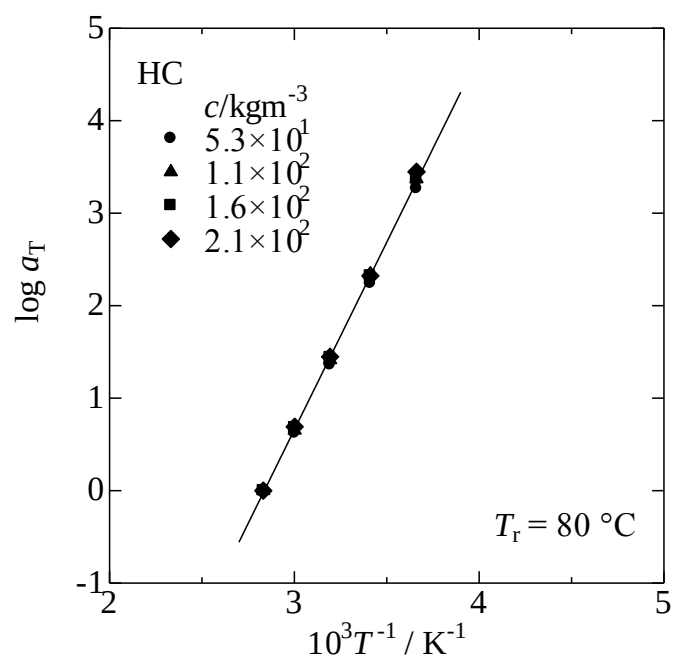


Figure 7

