

Molecular weight between entanglements for linear D-glucans

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Abstract Dynamic viscoelasticity measurements were carried out for concentrated solutions of linear D-glucans in BmimCl to examine the effect of the linkage between repeating units of glucose on the rheological properties. The values of molecular weight between entanglements (M_e) were determined for four D-glucans: curdlan, pullulan, cellulose, and amylose. From the concentration dependence of M_e , the value of M_e in the molten state ($M_{e,melt}$) for each D-glucan was estimated as a material constant. The order of $M_{e,melt}$ became cellulose < pullulan < curdlan < amylose, indicating that the linkage is actually influential in $M_{e,melt}$ for the linear D-glucans. The relationship between $M_{e,melt}$ and the molecular structure of the D-glucans were discussed assuming that the values of $M_{e,melt}$ for the D-glucans primarily reflect the chain stiffness such as the characteristic ratio C_∞ on the analogy of synthetic polymers. Although the trend was not so clear, it was shown that N_{unit} is a decreasing function of C_∞ .

Keywords D-glucan · Molecular weight between entanglements · Molecular structure · Linkage · Characteristic ratio

Introduction

The molecular weight between entanglements (M_e) is a material constant for polymers to characterize the rheological properties at long times [1, 2]. So far, M_e has been obtained for various kinds of melts of synthetic polymers [1], but the relationship between M_e and the molecular

structure of the polymers has not yet been fully understood [3–5]. Concerning polysaccharides, because M_e values available are quite limited [6–10], there is little information on the relationship with the molecular structure. We have reported [10] that M_e for galactomannans, which commonly have a side group of galactose, is not so sensitive to the galactose/mannose ratio, and therefore, the different introduction ratio of the bulky side group is not so appreciable for the polysaccharides. The average spacing of entanglement networks for linear polysaccharides, such as cellulose, agarose, and gellan, appeared to be almost independent of species of the repeating unit (linear polysaccharides here mean polysaccharides without a side group of monosaccharide or larger), but amylose had much larger M_e than the other polysaccharides probably due to a helical nature of amylose chain in a local scale [7]. Amylose and cellulose are categorized in linear D-glucans, and the linear D-glucans have a wide variety of molecular structures depending on the linkage between repeating units of D-glucose. Above-mentioned results suggests that the linkage type is influential in M_e and therefore in the rheological properties of the linear D-glucans. Systematic studies for D-glucans will give us more detailed information on the effect of the linkage type between repeating units on M_e . It should be also noted that such a variation based on the difference in linkage is characteristic of polysaccharides.

In this study, rheological properties were examined systematically for four kinds of linear D-glucans: pullulan, curdlan, cellulose, and amylose. Although rheological studies of the latter two polysaccharides were performed previously [7], we were able to obtain another grade of the polysaccharides and therefore tried to check the reproducibility for the polymers. The linkage of D-glucose units is β -(1,3) bond for curdlan; the sequence of α -(1,4), α -(1,4), and α -(1,6) bonds for pullulan [11]; β -(1,4) bond for cellulose; and α -(1,4) bond for amylose. Concentrated solutions of

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these glucans were prepared using an ionic liquid as a solvent and dynamic viscoelasticity was measured for the solutions. The values of M_e in the molten state (denoted by $M_{e,melt}$ in the following part) for the glucans were estimated from the concentration dependence of M_e in the solutions. To our knowledge $M_{e,melt}$ for curdlan and pullulan were firstly determined in this study, while $M_{e,melt}$ for cellulose and amylose were reevaluated using samples from a different manufacturer.

Experimental

Materials

Four linear D-glucans, curdlan (Wako, Japan), pullulan (Wako, Japan), cellulose (Aldrich, USA), and amylose (Aldrich, USA) were used without further purification. The curdlan sample was ground with a pestle into fine grains prior to the solution preparation. The weight average molecular weight (M_w ; in grams per mole) of the pullulan sample was reported to be from 5×10^4 through 1×10^5 by the supplier, whereas M_w of the rest of samples were unavailable. An ionic liquid of 1-butyl-3-methylimidazolium chloride (BmimCl; Aldrich, USA) was used without further purification as a solvent. According to the manufacturer's data sheet, the melting point of BmimCl was reported to be 70 °C. The BmimCl solutions of the D-glucans were prepared as follows. The powdery samples of the glucans were added into preheated BmimCl in a dry glass vessel, and the mixture was quickly stirred with a stainless spatula on a hot plate at 80 °C. The mixtures were kept on a hot plate at 80 °C for 1 day for curdlan and cellulose and at 80 °C for 1 day and then at 100 °C for 1 day for pullulan. For amylose, the mixture was put in a vacuum oven at 120 °C and then kept for more than 12 h. The concentration of the D-glucans (c) ranged from 1.4×10^2 to 2.7×10^2 kg m⁻³ (about 13–25 wt%) for curdlan, from 4.2×10^2 to 5.2×10^2 kg m⁻³ (about 40–50 wt%) for pullulan, from 5.4×10^1 to 2.1×10^2 kg m⁻³ (about 5–20 wt%) for cellulose, and from 4.2×10^2 to 5.2×10^2 kg m⁻³ (about 40–50 wt%) for amylose. In the calculation of c , the density of BmimCl was assumed to be 1.08×10^3 kg m⁻³, as in the case of previous studies [7–10]. The densities for the D-glucans were commonly assumed to be 1.0×10^3 kg m⁻³, since the values for purely amorphous D-glucans are not available at present [7]. The sample preparation was carried out just before rheological measurements.

Measurements

Dynamic viscoelasticity measurements were carried out with a rheometer (ARES, now TA Instruments, USA) under nitrogen atmosphere. A cone-plate geometry with the

diameter of 25 mm and the cone angle of 0.1 rad was used. The temperature (T) ranged from 20 to 120 °C. Because the supercooled solutions were rather stable, we were able to execute the viscoelasticity measurements for the D-glucan solutions below the melting temperature of BmimCl (even at 20 °C) [6–10]. The angular frequency (ω) dependence curves of the storage modulus (G') and the loss modulus (G'') were measured in the range of ω from 0.01 to 100 s⁻¹. The amplitude of the oscillatory strain (γ) was set at 0.1 so that the linear viscoelasticity was realized; in some cases, however, a smaller γ of 0.01 was chosen to avoid slippage between the sample and the metal surface of the fixture. Finally, the master curves of G' and G'' were prepared by applying the time (or angular frequency)–temperature superposition principle to the G' and G'' curves at individual temperatures. The reference temperature (T_r) was set to be 80 °C, and the shift factor in the horizontal direction was designated by a_T .

Results and discussion

Figure 1 shows the master curves of G' and G'' for the curdlan solutions. To avoid overlapping, the curves are shifted upwards by a factor A as c increases. As can be seen from the figure, the applicability of the time–temperature superposition principle is fine for four solutions shown here. The shift factor a_T at a given temperature was almost independent of c although the data are not shown here, and the temperature dependence of a_T were well represented by an Arrhenius-type equation. On each G' curve, the so-called rubbery plateau is observed and the plateau becomes wider as c increases, although the plateau has a tilt due to a broad molecular weight distribution of curdlan used. The emergence of the plateau means that the entanglement coupling

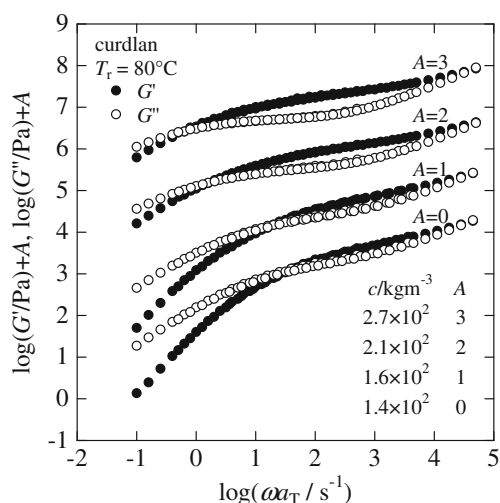


Fig. 1 Master curves of ω dependence of G' and G'' for curdlan solutions at $T_r=80$ °C. The curves are shifted upwards by A

exists at any concentration shown in the figure. For solutions at $c=1.4 \times 10^2$ and $1.6 \times 10^2 \text{ kg m}^{-3}$, the flow region can also be seen at low ωa_T . The master curves of G' and G'' for the pullulan solutions at $T_r=80^\circ\text{C}$ are shown in Fig. 2. Here, the vertical shift by A is made for the master curves, as is the case of Fig. 1. The rubbery plateau appears on each curve, although the plateau for pullulan is not as clear as for curdlan shown in Fig. 1. It should be noted for pullulan used here that the solutions at $c < 4.2 \times 10^2 \text{ kg m}^{-3}$ showed no rubbery plateau or, in other words, no entanglement coupling. In the figure, the flow zone is clearly observed at low ωa_T for each pullulan solution. Figure 3 shows the similar plots for the cellulose solutions. The rubbery plateau can be clearly observed in the middle ωa_T region. The master curves for the amylose solutions are shown in Fig. 4. The master curves for amylose resemble those for pullulan in shape, but the rubbery plateau as well as the flow zone appears for all solutions.

From the analogy with the rubber elasticity, M_e at a polymer 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, and R is the gas constant [1, 2, 12]. As stated previously, the G' curves obtained in this study were tilted, and therefore, we defined G_N^0 as the G' value at ωa_T where the loss tangent ($\tan \delta = G''/G'$) vs. ωa_T curve attained the minimum in the rubbery region [6–10]. For example, G_N^0 for the curdlan solution at $c=2.7 \times 10^2 \text{ kg m}^{-3}$ is determined to be $1.9 \times 10^4 \text{ Pa}$, which gives M_e of 4.1×10^4 from Eq. 1 with $T=T_r$. The values of M_e for the other solutions in Figs. 1, 2, 3, and 4 can be obtained in a similar manner. Now that we have the information of M_w for pullulan (M_w ranging from 5×10^4 to 1×10^5), we can check

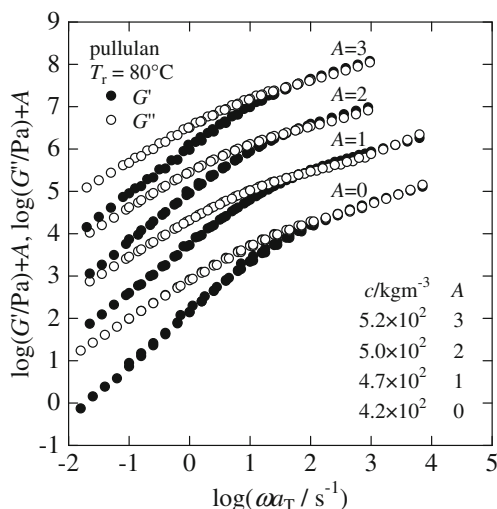


Fig. 2 Master curves of ω dependence of G' and G'' for pullulan solutions at $T_r=80^\circ\text{C}$. The curves are shifted upwards by A

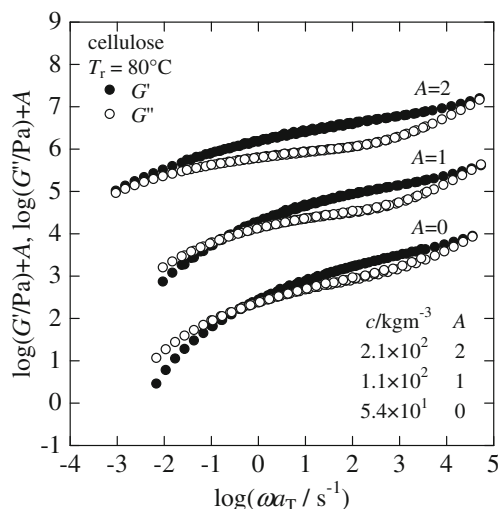


Fig. 3 Master curves of ω dependence of G' and G'' for cellulose solutions at $T_r=80^\circ\text{C}$. The curves are shifted upwards by A

the reliability of obtained M_e for pullulan by comparing the value with M_w . Generally M_e is c -dependent, and the largest M_e is realized at the critical concentration for entanglements below which the entanglements vanish. For the largest value of M_e , we can expect $M_w=2M_e$ [1]. For pullulan, the solution at $c=4.2 \times 10^2 \text{ kg m}^{-3}$ showed the rubbery plateau (which gives M_e of 2.6×10^4), but at lower c , we did not have the plateau. This suggests that c of $4.2 \times 10^2 \text{ kg m}^{-3}$ is close to the critical concentration. If we take c of $4.2 \times 10^2 \text{ kg m}^{-3}$ as the critical one, then we have 5.2×10^4 for M_w from $M_w=2M_e$. This value is close to the lower bound of the supplier's data of $5 \times 10^4 - 1 \times 10^5$. The rubbery plateau was not so clear for pullulan (Fig. 2), but the above discussion strongly supports the entanglements really exist at c higher than the critical concentration.

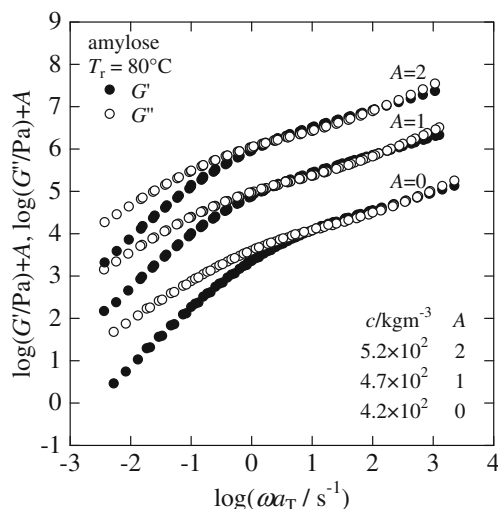


Fig. 4 Master curves of ω dependence of G' and G'' for amylose solutions at $T_r=80^\circ\text{C}$. The curves are shifted upwards by A

In Fig. 5, the values of $\log M_e$ for the linear D-glucans are plotted against $\log c$. This figure also contains the results for the cellulose and amylose obtained in the previous study [7]. As no marked difference (or splitting) appears to exist between the previous and current data for the polymers, we can conclude for the two series of polymers that M_e data are reproducible. A straight line with a slope of -1 is drawn to fit the plots for each D-glucan since we have the knowledge that M_e is inversely proportional to c for many polymer systems [2, 13, 14]. It is seen that data points for each D-glucan are well fitted by the straight line, indicating that the c^{-1} dependence of M_e really holds for the D-glucans in this study. Assuming the density of all D-glucans to be $1.0 \times 10^3 \text{ kg m}^{-3}$, $M_{e,\text{melt}}$ for the D-glucans can be determined as the value of M_e at $c = 1.0 \times 10^3 \text{ kg m}^{-3}$ in Fig. 5. The obtained values of $M_{e,\text{melt}}$ are 1.2×10^4 , 1.1×10^4 , 3.5×10^3 , and 2.4×10^4 for curdlan, pullulan, cellulose, and amylose, respectively. In the previous study, we had $M_{e,\text{melt}}$ of 3.2×10^3 for cellulose and that of 2.5×10^4 for amylose [7], which are very close to the current results. It is also possible to use another measure describing the entanglement spacing in melt, namely, the number of monosaccharide units between entanglements in the molten state (N_{unit}). We define N_{unit} by $N_{\text{unit}} = M_{e,\text{melt}}/M_{\text{unit}}$, with M_{unit} being the molecular weight of the repeating unit. For the linear D-glucans used in this study, M_{unit} is identical for the four polymers (i.e., $M_{\text{unit}} = 162$), so that N_{unit} becomes 71, 68, 22, and 148 for curdlan, pullulan, cellulose, and amylose, respectively. These are summarized in Table 1 together with $M_{e,\text{melt}}$. We do not know exactly why $M_{e,\text{melt}}$ (or equivalently N_{unit}) differs from a D-glucan to another, but this fact strongly suggests that some molecular parameters such as chain stiffness affect the entanglement spacing characterized by $M_{e,\text{melt}}$. In the

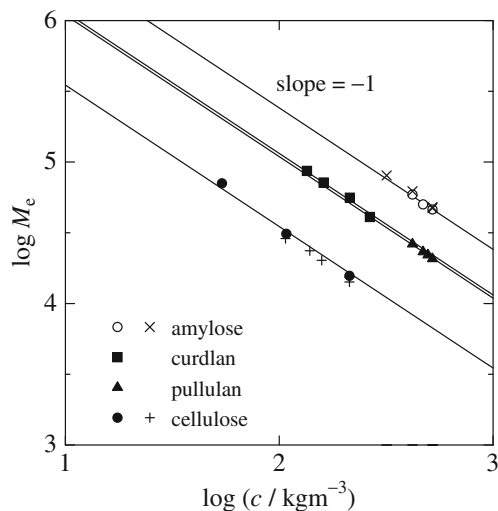


Fig. 5 Double-logarithmic plot of M_e against c for D-glucans in solution. Each line is the best fit one with a slope of -1 . $M_{e,\text{melt}}$ for D-glucans is determined as M_e at $c = 10^3 \text{ kg m}^{-3}$. Data for cellulose (plus symbol) and amylose (ex symbol) in the previous study⁷ are added

Table 1 Chain characteristics for linear D-glucans

glucan	$M_{e,\text{melt}}$	N_{unit}	C_∞	References for C_∞
curdlan	1.2×10^4	71	9.58 ^a –10.5	[17–19]
pullulan	1.1×10^4	68	2.4–4.3	[11, 16, 20]
cellulose	3.5×10^3	22	20.8–25.0 ^b	[21, 26]
amylose	2.4×10^4	148	4.5–12 ^c	[23–26]

^a In DMSO solution

^b In aqueous solution

^c Referred in [26]

previous study [7], we found a considerable difference in $M_{e,\text{melt}}$ between cellulose and amylose, and the difference was attributed to a helical nature of amylose chain in a local scale although amylose chain has a random coil conformation as cellulose chain has in a global scale. For pullulan and curdlan, it has been reported that the local conformation of a curdlan chain is close to the 6/1 helix like an amylose chain [15], while pullulan has no helical nature [16].

Several attempts have been made to connect $M_{e,\text{melt}}$ with the characteristic ratio C_∞ , a well-known molecular parameter of real (flexible) polymer chain. For example, Graessley and Edwards have considered that G_N^0 is a function of the contour chain length per unit volume as well as of the Kuhn step length ($=C_\infty l_0$; l_0 being the average length of the main chain bonds) [3], which gives $M_{e,\text{melt}} \propto C_\infty^{-1}$ if parameters other than $M_{e,\text{melt}}$ and C_∞ are eliminated. Wu [4] has obtained another expression of $M_{e,\text{melt}} \propto C_\infty^2$ by using a pseudo-topological model. Fetters et al. [5] have proposed $M_{e,\text{melt}} \propto C_\infty^{-3}$ if we focus on just $M_{e,\text{melt}}$ and C_∞ . Although the relation between $M_{e,\text{melt}}$ and C_∞ is still a matter of controversy even for synthetic polymers, the relationship between $M_{e,\text{melt}}$ and C_∞ is now considered for the linear D-glucans. Of course, we encounter another problem in this

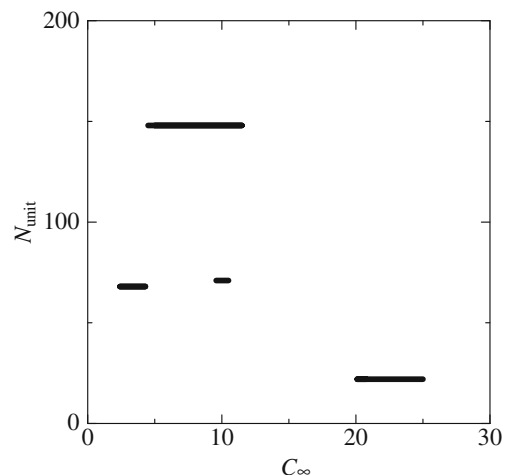


Fig. 6 N_{unit} vs. C_∞ plots for four D-glucans. The range of C_∞ plots for each D-glucan is indicated by a horizontal bar

case that we do not have C_∞ from a single data source, but the fact that C_∞ has been reported implies for these glucans in solution that the favorable chain conformation is a random coil. Even at high c where entanglements are generated, the random-coil conformation appears to be favorable for glucans. In Table 1, C_∞ for the D-glucans is also listed with the source. Quoted values are all experimental data in the literature, although the measurement conditions are not necessarily the same [11, 16–26]. The data of C_∞ obtained by model calculations were not employed because they have large scattering from researcher to researcher. Figure 6 shows the N_{unit} vs. C_∞ plots for the linear D-glucans, where each bar stands for a pair of N_{unit} and C_∞ range. We cannot find out a clear trend from the figure, but it may appear that N_{unit} is a decreasing function of C_∞ . In this case, the Wu relation should be excluded for the linear D-glucans.

Conclusions

The values of $M_{e,\text{melt}}$ as well as N_{unit} for linear D-glucans were determined from the dynamic viscoelasticity measurement for their concentrated solution in BmimCl. It was found that $M_{e,\text{melt}}$ as well as N_{unit} for linear D-glucans depends much on the linkage between glucose repeating units. The order of $M_{e,\text{melt}}$ was determined to be cellulose < pullulan < curdlan < amylose. The relationship between $M_{e,\text{melt}}$ and the molecular structure of the D-glucans was considered assuming that $M_{e,\text{melt}}$ can be connected with the chain stiffness C_∞ , as attempted for synthetic polymers. A subtle trend that N_{unit} , namely, $M_{e,\text{melt}}$, is a decreasing function of C_∞ was obtained.

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