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Stress-Optical Coefficients for D-Glucans in Ionic Liquid Solutions

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The relation between the stress (σ) and the birefringence (Δn) after a single-step shear deformation has been examined for three D-glucans cellulose, pullulan and curdlan in concentrated ionic liquid solutions. As expected from the stress-optical rule, σ for each solution can be fitted by Δn very well only with a stress-optical coefficient C_R . The value of C_R for cellulose is obtained to be positive and the absolute value is the largest among the D-glucans. Pullulan also has a positive C_R but the absolute value is much smaller. It has been confirmed that C_R for pullulan in ionic liquid is close to that for pullulan film. On the other hand, curdlan exhibits a negative C_R . The results indicate that the linkage between the repeating units of D-glucose is very influential in the sign and absolute value of C_R .

Key Words: D-glucan / Ionic liquid / Linkage / Birefringence / Stress-optical coefficient

1. INTRODUCTION

The relationship between the chain characteristics and the molecular structure has been an essential subject in polymer science; the same can be said of polysaccharides. In our earlier study, the molecular weight between entanglements (M_e) has been examined for D-glucans, which are polysaccharides consisting of repeating units of D-glucose with a variety of linkages in between¹⁾. It has been found that the linkage is much more influential in M_e compared to other factors such as the species of the repeating unit and the substitution by monosaccharide side groups. The results demonstrate that systematic studies for D-glucans would provide valuable information on the relationship between the chain characteristics and the molecular structure. It should be noted that the structural variation in terms of the linkage between monomer units is really specific of polysaccharides.

Once a polymer system is deformed macroscopically, a close correlation often holds between the birefringence (Δn) and the stress (σ), which is known as the stress-optical rule^{2, 3)}: $\Delta n = C_R \sigma$, where C_R is the stress-optical coefficient; more precisely, the rubber component attributed to the orientation of polymer segments. The stress-optical coefficient is one of important chain characteristics reflecting the molecular structure of the polymer. A number of stress-optical coefficients have been obtained for familiar polymers such as polystyrene and polycarbonate²⁻⁴⁾, but there are few

experimental results of the stress-optical coefficients available for polysaccharides. In fact, it is often difficult to find appropriate experimental conditions to determine C_R for polymer solutions. Although we have previously reported a set of the stress-optical coefficients for pullulan, a species of D-glucan, by means of uniaxial stretching of glassy amorphous films, it has been assumed that the orientation of polymer segments remains as deformed during the relaxation of the glass component after the uniaxial stretching⁵⁾. It might be necessary to confirm C_R under more appropriate conditions for determining C_R . It will be true that the relation between Δn and σ practically observed for polymer solutions is represented by $\Delta n = C_R \sigma$.

In this study, the stress-optical coefficients for D-glucans dissolved in ionic liquid solutions have been determined by using an oblique-light method reported in the literature⁶⁾. We have found that some ionic liquids are available as the solvents for preparing concentrated solutions of D-glucans with suitable viscosities¹⁾. Combining viscous samples of concentrated solutions with a homemade apparatus having the time-resolution from sub-second to second, the experiments have been designed for detecting C_R of D-glucans. Shear deformations have been applied to the sample solutions and the subsequent relaxation of Δn and σ have been examined. Not only is C_R for pullulan confirmed but also the effect of the linkage on C_R has been discussed.

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2. PRINCIPLES OF BIREFRINGENCE MEASUREMENT

The block diagram of the homemade apparatus for Δn based on the oblique-light method⁶⁾ as well as the top view of the sample box is shown in Fig. 1. The light beam is reflected at the mirror upward by the angle of elevation of 45° so that the liquid sample can be placed between horizontal quartz plates. The angle given to each optical element indicates the direction of the optical element in terms of the angle from the horizontal direction normal to the light path. The light intensity after passing through the optical elements and the sample is finally detected by the photodiode. By combining the two illustrations, it is realized that the light beam with the angle of incidence of 45° passes through the sample sandwiched between the quartz plates almost at the center of the rectangular window. The arrow drawn by the top view represents the direction of movement of the lower plate to apply a shear deformation to the sample.

According to the literature⁶⁾, the relation between Δn and the light intensity I detected by the photodiode is theoretically represented by the following equation:

$$\Delta n = \frac{\lambda}{2\pi d \tan \theta} \left(\frac{I}{I_0} - \alpha^2 \right) \quad (1)$$

Fig. 1 Block diagram of the homemade apparatus for Δn based on the oblique-light method (upper) and the top view of the sample box (lower).

where I_0 , d , λ , and θ are the intensity of incident light, the gap between the quartz plates, the wavelength of light, and the angle of refraction in the sample, respectively. Assuming that the experimental error in the observed light intensity I' is represented by a factor r , namely $I' = rI$, eq 1 can be rewritten with I' at $\Delta n = 0$ (I'_0) instead of I_0 as

$$\Delta n = \frac{\alpha \lambda}{2\pi d \tan \theta} \left(\frac{I'}{I'_0} - 1 \right) \quad (2)$$

3. EXPERIMENTAL

3.1 Sample preparation

Three linear D-glucans cellulose (Sigma-Aldrich, USA), pullulan (TCI, Japan) and curdlan (Wako, Japan) were used without further purification and were dried under vacuum just before use. Two ionic liquids were used as received: 1-butyl-3-methylimidazolium acetate (BmimAc; Sigma-Aldrich, USA) was used for all the glucans, while 1-butyl-3-methylimidazolium chloride (BmimCl; Aldrich, USA) was used only for cellulose⁷⁾. Concentrated solutions of the glucans were prepared as follows. The powdery samples of the glucans were added into preheated ionic liquid in a dry glass vessel and the mixture was stirred on a hot plate at 80°C until transparent solutions were obtained. Then the solutions were kept under vacuum at 100°C until all bubbles were seemingly removed from the solutions. Apparent evaporation of the solvent did not occur during degassing due to the very low vapor pressure of the ionic liquids. The concentration of the D-glucans (c) was determined through preliminary tests to be the optimum condition in terms of the intensity of the signals and the force necessary for the shear deformation. That is, decrease in c weakened the signals to make the detection difficult, while excessive increase in c required greater force for deformation than the handmade sample box could apply. The cellulose solutions in BmimAc and BmimCl were prepared at $c = 1.0 \times 10^2 \text{ kgm}^{-3}$ (10 wt%) and c for the pullulan and curdlan solutions in BmimAc were $2.1 \times 10^2 \text{ kgm}^{-3}$ (20 wt%).

3.2 Measurements

Dynamic viscoelasticity and stress relaxation 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 angular frequency (ω) dependence of the storage modulus (G') and the loss modulus (G'') were measured in the range of ω from 0.1 to 100 s^{-1} . The

temperature (T) ranged from 20 to 80 °C. The amplitude of the oscillatory shear strain was set at 0.1 so that the linear viscoelasticity was realized. The stress relaxation after a single-step shear strain (γ) of 0.1 was monitored against time (t) over several hundred of seconds at 25 °C.

In this study, measurement of Δn by the apparatus illustrated in Fig. 1 was performed using a He-Ne laser as the light source, and the apparatus parameters were fixed at $\alpha = 5^\circ$ and $d = 1$ mm. To elucidate the relaxation of Δn , I' was measured after applying a single-step shear strain of $\gamma = 0.1$ over several hundred of seconds. The value of I'_0 was obtained as the baseline of I' when Δn can be considered zero at long times. The measurement was carried out at room temperature around 25 °C.

4. RESULTS AND DISCUSSION

4.1 Cellulose

Figure 2 shows the master curves of G' and G'' for the cellulose solution in BmimAc with the reference temperature (T_r) of 20 °C; a_T stands for the horizontal shift factor. The master curve indicate that the time-temperature superposition principle holds very well for the cellulose solution. Similar master curve for the cellulose solution in BmimCl has been obtained with a slight difference in the viscosity. There is a wide and clear rubbery plateau region in the curves, meaning that the entanglement coupling between cellulose chains exists in the solution⁸⁻¹⁰.

The relaxation of Δn and σ for the cellulose solution is shown in Fig. 3; Δn is plotted using the right axis for ease of identification. It is seen that both Δn and σ decrease with time in a similar manner. Then according to the relation $\Delta n = C_R \sigma$, σ is fitted by $C_R^{-1} \Delta n$ as plotted in the figure. The curve of $C_R^{-1} \Delta n$ coincides with that of σ very well except for the clear

Fig. 2 Master curves of G' and G'' for cellulose solution in BmimAc. The reference temperature is 20 °C.

Fig. 3 Relaxation of Δn and σ for cellulose solution in BmimAc. Cross mark represents the fitting curve of $C_R^{-1} \Delta n$.

separation observed at about $t < 0.2$ s. The disagreement at the beginning of relaxation is attributed to the shear deformation applied to the sample. In fact each apparatus used in this study takes a finite time to apply the shear deformation; especially, the homemade sample box for Δn takes 0.13 s for the shear strain of $\gamma = 0.1$. Therefore data points of $t < 0.3$ s are disregarded to reduce the influence of the shear motion on the estimation of C_R . The value of C_R for cellulose in BmimAc is estimated to be $2.6 \times 10^{-8} \text{ Pa}^{-1}$.

The stress relaxation of the cellulose solution in BmimCl and the fitting with the measured Δn and a constant C_R are shown in Fig. 4. The σ curve agrees very well with $C_R^{-1} \Delta n$ curve at $t > 0.3$ s. The obtained value $C_R = 2.7 \times 10^{-8} \text{ Pa}^{-1}$ is about the same as that for the BmimAc solution given above. It seems that C_R for cellulose does not depend on the species of ionic liquid. Here we acknowledge that C_R for cellulose in BmimCl has been reported to be $1.0 \times 10^{-8} \text{ Pa}^{-1}$ under oscillatory shear flow¹¹, which might be significantly smaller than our value. The small C_R for cellulose reported in the literature could be due to the absence of entanglement. However, performing the measurement for more diluted solutions is technically difficult due to the signal reduction, as mentioned above. Actually, the lower limit of c for the cellulose sample using our apparatus was 5 wt%, but the rubbery plateau was still observed for that solution. It has been confirmed that C_R for the 5 wt% solution is $2.4 \times 10^{-8} \text{ Pa}^{-1}$, suggesting negligible c -dependence of C_R for the cellulose solution around this c -range¹². Figure 5 shows the similarity in the relaxation behavior between the BmimAc and BmimCl solutions. The σ and $C_R^{-1} \Delta n$ curves for the BmimAc solution, which are identical to those in Fig. 3, are drawn by the solid lines. The small triangles represent the σ and $C_R^{-1} \Delta n$ curves for the BmimCl solution, but they are horizontally shifted toward small t to check the validity of superposition. As demonstrated in the

Fig. 4 Relaxation curve of σ and the fitting curve of $C_R^{-1}\Delta n$ for cellulose solution in BmimCl.

Fig. 6 Master curves of G' and G'' for pullulan solution in BmimAc. The reference temperature is 20 °C.

Fig. 5 Superposition of relaxation curves for cellulose solutions in BmimAc and BmimCl. Data points for BmimCl (triangle) were horizontally shifted toward small t .

Fig. 7 Relaxation curve of σ and the fitting curve of $C_R^{-1}\Delta n$ for pullulan solution in BmimAc.

figure, the curves for BmimAc and BmimCl solutions coincide with each other only by the horizontal shift in the double-logarithmic plot. This indicates that the relaxation behavior of cellulose is the same in both ionic liquids at a given concentration in spite of the difference in the solvent viscosity.

4.2 Pullulan

Figure 6 shows the master curves of G' and G'' for the pullulan solution in BmimAc at $T_r = 20$ °C. In the master curve, the rubbery plateau as well as the terminal flow behavior $G'' \propto \omega$ is observed. Despite the fact that the pullulan solution has twice as high c as the cellulose solution, the rubbery plateau appears narrower compared to the cellulose solution shown in Fig. 2. Although the molecular weights of these glucans are unknown, this might be partly due to the high M_e of pullulan compared to cellulose¹⁾. It is also seen that the relaxation of G' and G'' is much faster than the cellulose solution.

Figure 7 displays the stress relaxation for the pullulan solution; the left axis has to be extended down, as expected from the fast relaxation of G' and G'' . The relaxation of Δn is fitted to σ as $C_R^{-1}\Delta n$ in the figure. The $C_R^{-1}\Delta n$ curve agrees with the σ curve and the obtained value is $C_R = 1.7 \times 10^{-9} \text{ Pa}^{-1}$. It should be noted that C_R for pullulan is much smaller than that for cellulose, which is very likely to explain the slightly-scattered data points of $C_R^{-1}\Delta n$ for pullulan due to the weakness of signals. This result indicates that the linkage between repeating units of glucose is influential in C_R for D-glucans, as it is in M_e . Assuming that the anisotropy of polarizability of the repeating units is the same between pullulan and cellulose, a smaller C_R for pullulan suggests that the Kuhn segment length of pullulan is smaller than that of cellulose. According to the literature¹³⁾, the Kuhn segment length of pullulan is estimated to be significantly smaller than that of cellulose. The influence of linkage on C_R might be interpreted as the difference in the Kuhn segment length between pullulan and cellulose. It is also noticed that C_R for D-glucans in

BmimAc is close to $C_R = 1.9 \times 10^{-9} \text{ Pa}^{-1}$ for pullulan film determined in our previous study⁵⁾. This would verify our former assumption on the relaxation of R- and G-components in glassy pullulan films, and suggests that dissolution in an ionic liquid does not change C_R from the value for the bulk system.

4.3 Curdlan

The master curves of G' and G'' for the curdlan solution in BmimAc is shown in Fig. 8. A clear rubbery plateau is mainly observed in the master curves in comparison with pullulan at the same T_r and c drawn in Fig. 6. Figure 9 shows the relaxation curves of σ and $C_R^{-1}\Delta n$ for the curdlan solution; the curves coincide with each other. As expected from the dynamic viscoelasticity, the relaxation is much slower than the pullulan solution, so that the fitting is possible even at $t > 100$ s. Now, it should be emphasized that the obtained C_R for curdlan is negative; namely, $C_R = -1.8 \times 10^{-9} \text{ Pa}^{-1}$. That is, it is quite possible for D-glucans that even the sign of C_R changes depending on the linkage between the glucose units. It is known that polystyrene exhibits a negative value of $C_R = -5.0 \times 10^{-9} \text{ Pa}^{-1}$, because the polarizability along the main chain axis is lower than that along the direction normal to it due to the phenyl ring as the side group²⁾. Curdlan might have similar polarizability due to the β -1,3 linkage. Here we assume that a glucose unit is optically anisotropic and the C1-C4 direction has a larger polarizability than other directions normal to it. Concerning cellulose, the C1-C4 direction tends to be parallel with the main chain axis owing to the β -1,4 linkage, which explains the large positive C_R for cellulose. Curdlan has the β -1,3 linkage and therefore the C1-C4 direction would be off-parallel to the direction of the main chain axis. Although it is impossible to mention the critical condition that the sign of C_R turns opposite, at least the small

Fig. 8 Master curves of G' and G'' for curdlan solution in BmimAc. The reference temperature is 20 °C.

Fig. 9 Relaxation curve of σ and the fitting curve of $C_R^{-1}\Delta n$ for curdlan solution in BmimAc.

absolute value of C_R for curdlan compared to cellulose is attributable to the off-parallel condition owing to the β -1,3 linkage.

5. CONCLUSION

The relaxation behavior of σ and Δn after a single-step shear deformation has been measured for three D-glucans cellulose, pullulan and curdlan in BmimAc. The dynamic viscoelasticity has indicated that each solutions has the entanglement coupling. It has been shown that σ for each solution can be fitted by Δn very well only with a single parameter C_R . The value for cellulose $C_R = 2.6 \times 10^{-8} \text{ Pa}^{-1}$ is the largest among the D-glucans and agrees with that for cellulose in BmimCl. Pullulan has a much smaller positive value of $C_R = 1.7 \times 10^{-9} \text{ Pa}^{-1}$. It has been confirmed that C_R for pullulan in BmimAc is close to that for pullulan film. The value of C_R for curdlan has been estimated to be negative: $C_R = -1.8 \times 10^{-9} \text{ Pa}^{-1}$. It has been found that the signs and absolute values of C_R for D-glucans are much affected by the linkage between the repeating units of glucose.

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