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Entanglement Network of Agarose in Various Solvents

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Running Head: Entanglement of Agarose in Various Solvents

INTRODUCTION

The molecular structure of polysaccharides has led to the belief that these polymers are stiff. The characteristic ratio (C_∞) for polysaccharides is rather high, although reported C_∞ values are limited to typical polysaccharides such as cellulose[1] and gellan.[2] If we can prepare concentrated solutions of polysaccharides, we can determine the molecular weights between entanglements in the molten state ($M_{e,melt}$) for these polysaccharides,[3-5] which reflects the chain properties, i.e., the flexibility of the chain. Since the first report that cellulose has good solubility in ionic liquids,[6] many studies have been conducted to determine the solution properties of polysaccharides at high concentrations. We prepared concentrated solutions of several kinds of polysaccharides in an ionic liquid 1-butyl-3-methylimidazolium chloride (BmimCl) and carried out rheological measurements for the solutions to determine $M_{e,melt}$ for the polysaccharides.[7-9] The experiments yielded rather small values of $M_{e,melt}$ for the polysaccharides; for example,[8] $M_{e,melt}$ was 2.3×10^3 for agarose, which is composed of (1,3)-β-D-galactopyranose and (1,4)-3,6-anhydro-α-L-galactopyranose.[10] This value appears to be much smaller than expected for a stiff polymer and is actually comparable to the $M_{e,melt}$ for the simplest flexible polymer polyethylene ($M_{e,melt} = 1.3 \times 10^3$),[3] although no reported value of C_∞ for agarose is available. Why the $M_{e,melt}$ for polysaccharides is so small is not clear at present. The $M_{e,melt}$ for amylose was also determined and was much larger than that for cellulose.[7] To

explain the $M_{e,melt}$ values, it is necessary to examine whether the use of an ionic liquid as a solvent affects the estimation of $M_{e,melt}$. It has been proposed that ionic liquids form three-dimensional structures even in the liquid state due to cation-anion hydrogen bonding and cation-cation ring stacking.[11-13] The three-dimensional structure may contribute to the modulus of the solutions; if the elasticity due to the network of solvent molecules contributes to the plateau modulus (G_N^0), then $M_{e,melt}$ is reduced. The aim of this study is to clarify whether or not the network formed by the ionic liquid molecules contributes to G_N^0. Concentrated solutions of agarose were prepared by using formamide (FA), *N*-methylformamide (MFA), and BmimCl as solvents. Angular frequency (ω) dependence curves of the storage and loss moduli (*G'* and *G''*, respectively) were compared among these solutions.

EXPERIMENTAL PROCEDURE

Agarose (Research Organics, USA) was used without further purification. FA (Wako, Japan) and MFA (Aldrich, USA) were used as received. The ionic liquid BmimCl (Aldrich, USA) was the same as that described in the previous studies.[7,8] Agarose solutions were prepared as follows. Agarose was added to each solvent (for BmimCl, the solvent was preheated to convert it into the liquid state) in a dry glass vessel, and the mixture was quickly stirred with a stainless spatula on a hot plate at approximately 80 °C. Then, the vessel was sealed and left on

the hot plate for complete melting. The concentration of agarose (c) was 1.0×10^2 kgm^{-3} or

2.0×10^2 kgm^{-3}, i.e., ca. 10 or 20 wt %. In the calculation of c, 1.0×10^3 kgm^{-3} was assumed for

the density of agarose, and 1.14×10^3 kgm^{-3}, 1.00×10^3 kgm^{-3}, and 1.08×10^3 kgm^{-3} were used for

the densities of FA,[14] MFA,[14] and BmimCl,[7,8] respectively. To minimize the effect of moisture

absorption, a fresh bottle of solvent was used every time agarose samples were prepared, and

the rheological measurements were made just after finishing the sample preparation.

Rheological measurements (dynamic viscoelasticity measurements in this study) were

carried out with an ARES rheometer (now TA Instruments, USA) using the dynamic operation

testing mode under a nitrogen atmosphere. A cone-plate geometry with a diameter of 25 mm

and a cone angle of 0.1 rad. was used. The ω-dependence of G' and G'' for the solutions was

measured with a strain amplitude (γ) of 0.1. Because the melting temperatures (T_m) of FA[14] and

MFA[14] are reported to be 2.6 °C and -5.4 °C, respectively, the temperature (T) ranged from 5 to

40 °C for the FA solution and from 0 to 30 °C for the MFA solution. The T-range for the

BmimCl solution was 20 to 120 °C. For BmimCl, T_m is ca 70 °C, but the supercooled state of

the BmimCl solutions was rather stable. Thus, viscoelasticity measurements were successfully

taken even at 20 °C. The master curves in each solvent were prepared using only a horizontal

shift with the shift factor a_T.

RESULTS AND DISCUSSION

In Figure 1(a) the master curves of the ω dependence of the dynamic viscoelastic

functions (G' and G'') for the BmimCl and FA solutions of agarose at $c = 100$ kgm^{-3}. The

time-temperature superposition principle held very well for the G' and G'' curves for these

solutions and for the other solutions examined in this study, as will be discussed below. The

reference temperature (T_r) in the figure was set to 80 ^{o}C for both solutions. For the FA solution,

the dynamic viscoelasticity measurements were taken in the T-range of 5 to 20 ^{o}C. The master

curves were prepared initially at 20 ^{o}C, and then the master curves were shifted so that $T_r = 80$

^{o}C using the extrapolated values of a_T. In the master curves for BmimCl solution (BmimCl

curves), the rubbery plateau and the terminal (flow) zones are clearly observed; the rubbery

plateau is designated as the region of G' at log ωa_T of 2.2 to 4.7. Here, the plateau modulus G_N^0

can be defined as the G' value at ωa_T where the loss tangent (tan$\delta = G''/G'$) curve attains a

minimum[7-9,15] and is related to the molecular weight between entanglements (M_e) by

$$G_N^0 = \frac{cRT}{M_e} \tag{1}$$

where R is the gas constant. It should be noted that M_e in the above equation should be in

kgmol^{-1}. For the BmimCl solution at $c = 100$ kgm^{-3}, we have a G_N^0 of 1.2×10^4 Pa for the

BmimCl solution, which gives an M_e of 2.4×10^4. This value is consistent with the M_e values

obtained in a previous study.[8] In the master curves for the FA solution (FA curves), the flow

zone is clearly observed. Concerning the rubbery plateau, however, only an onset of the plateau, i.e., the intersection of the G' and G'' curves, emerges at the high ωa_T limit, and the height of the intersection is identical to that on the BmimCl curves. Figure 1(b) shows the same data as Figure 1(a), but here the FA curves are horizontally shifted to have the best overlap with the BmimCl curves. The extent to which the curves were shifted is expressed by the parameter A, and $\log A = -1.14$ for the FA curves; for the BmimCl curves, $\log A$ is taken to be 0. As can be seen from the figure, the horizontal shift was applied successfully. Our results suggest that the FA solution at $c = 100$ kgm^{-3} has the same number of entanglements as the BmimCl solution, although the high melting temperature of FA prevents measurements at low temperatures, and thus we were not able to obtain direct evidence of the dynamic viscoelasticity. The number (or more precisely, the number density) of entanglements appears to be independent of the solvent species as long as the solutions are homogeneous, as is well established for the synthetic polymers. Focusing on the properties of the ionic liquid BmimCl, it is well known that BmimCl forms a three-dimensional structure, although the structure is not very strong. The lack of enhancement of G_N^0 in BmimCl compared with that in FA indicates that the lifetime of the BmimCl structure is sufficiently short, and therefore, the formation of the structure does not contribute to the modulus in the rubbery and terminal zones. In other words, M_e in the BmimCl solution depends purely on the chain-chain entanglements.

The parameter A defined previously is related to the ratio of the zero-shear viscosity

(η_0) for the FA solution to that for the BmimCl solution, because A is a type of horizontal shift

factor and therefore has the same meaning as a_T. Although we do not have detailed data on η_0,

pure BmimCl and pure FA are expected to have very different η_0 values. However, at $c = 100$

kgm^{-3}, the difference becomes rather small, only approximately one order of magnitude, because

$\log A = -1.14$.

The plots of a_T versus T^{-1} for the BmimCl and FA solutions of agarose at $c = 100$

kgm^{-3} are shown in Figure 2. It should be noted that a_T here is the shift factor from T_r (80 ^{o}C)

even for the FA solutions; namely, the original shift factor was modified so that at 80 ^{o}C $\log a_T =$

0. The data points for the FA solution fall on a single line, indicating that the T-dependence of a_T

can be well described by an Arrhenius-type equation. The plots of $\log a_T$ vs. T^{-1} for the BmimCl

solution can also be approximated by a single line.

Figure 3 shows the master curves of G' and G'' of agarose in BmimCl, FA and MFA at

$c = 200$ kgm^{-3}. The master curves for BmimCl cover a wide range of ωa_T compared with the

others due to the wider T-range of the measurements. For the plateau zone, we have a G_N^0 of

5.2×10^4 Pa, leading to an M_e of 1.1×10^4 at $c = 200$ kgm^{-3}. This M_e value is roughly half of that

(2.4×10^4) for the solution at $c = 100$ kgm^{-3}. The master curves for the FA and MFA solutions (FA

and MFA curves, respectively) overlapped well with each other, and the flow zone and the onset

of the plateau zone are observed for these curves, as in the case of the FA curves at $c = 100$

kgm^{-3}. In addition, the intersections of G' and G'' for the FA and MFA curves are identical in

height to that of the BmimCl curve, suggesting that G_N^0 is the same for these solutions, and

therefore, it is expected that all three solutions will have the same value of M_e. Again, M_e is

independent of the solvent species.

The plots of a_T versus T^{-1} are shown in Figure 4. Here, a_T is the shift factor from T_r (80

^{o}C) for all solutions; namely, the original shift factor was modified so that at 80 ^{o}C, log $a_T = 0$

for the FA and MFA solutions. It is interesting that the data points for the FA and MFA solutions

fall on a single line, indicating that the T-dependence of a_T can be well described by the same

Arrhenius-type equation.

CONCLUSION

The rheological properties of concentrated solutions of agarose having two different

concentrations were compared. Two organic solvents formamide and N-methylformamide, and

an ionic liquid BmimCl were used as the solvents. The ω-dependence curves of G' and G'' for

these solvents overlapped well only after a horizontal shift was introduced. The good agreement

in the curves indicates that the entanglement properties of the agarose chains are similar

regardless of the solvent. The small $M_{e,melt}$ for polysaccharides can be attributed to the network

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of polysaccharide chains, not to the network formed by the ionic liquid molecules.

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Figure Legends

Figure 1   (a) Master curves of the ω-dependence of G' and G'' for the BmimCl and FA solutions of agarose at $c = 100$ kgm^{-3}. The reference temperature, T_r, is 80 ^{o}C. (b) The FA curves are horizontally shifted by the parameter A.

Figure 2   Shift factor a_T plotted against T^{-1} for the BmimCl and FA solutions of agarose at $c = 100$ kgm^{-3}. The reference temperature, T_r, is 80 ^{o}C.

Figure 3   Master curves of the ω-dependence of G' and G'' for the BmimCl, FA and MFA solutions of agarose at $c = 200$ kgm^{-3}. The reference temperature, T_r, is 80 ^{o}C.

Figure 4   Shift factor a_T plotted against T^{-1} for the BmimCl, FA and MFA solutions of agarose at $c = 200$ kgm^{-3}. The reference temperature, T_r, is 80 ^{o}C.
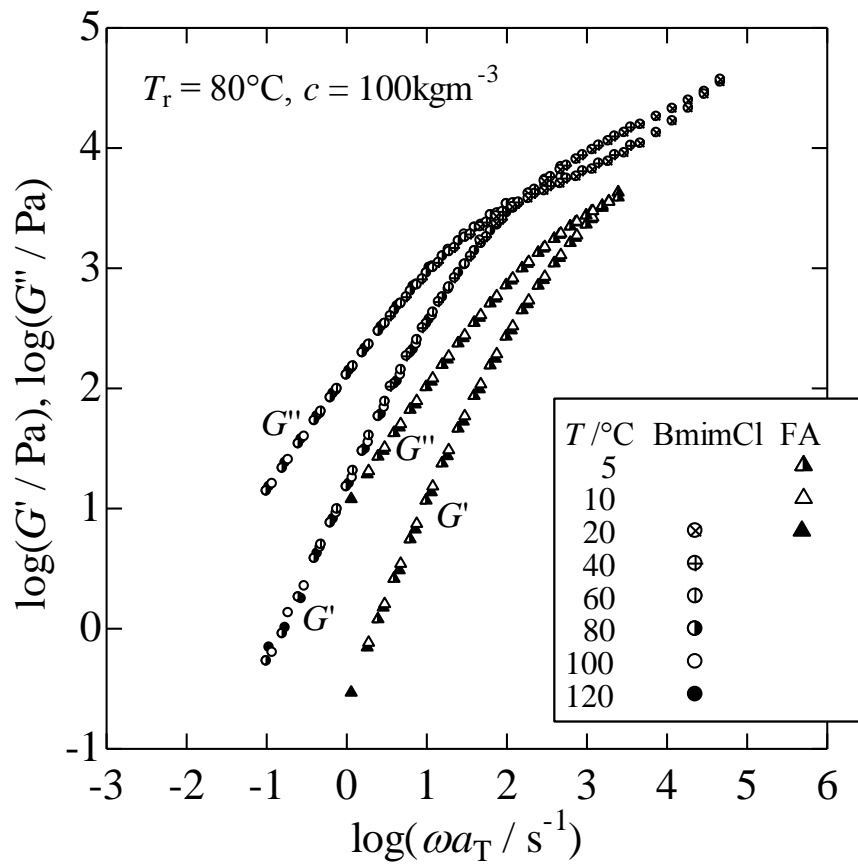
Fig. 1(a)

$T_r = 80°C$, $c = 100 \mathrm{kgm}^{-3}$
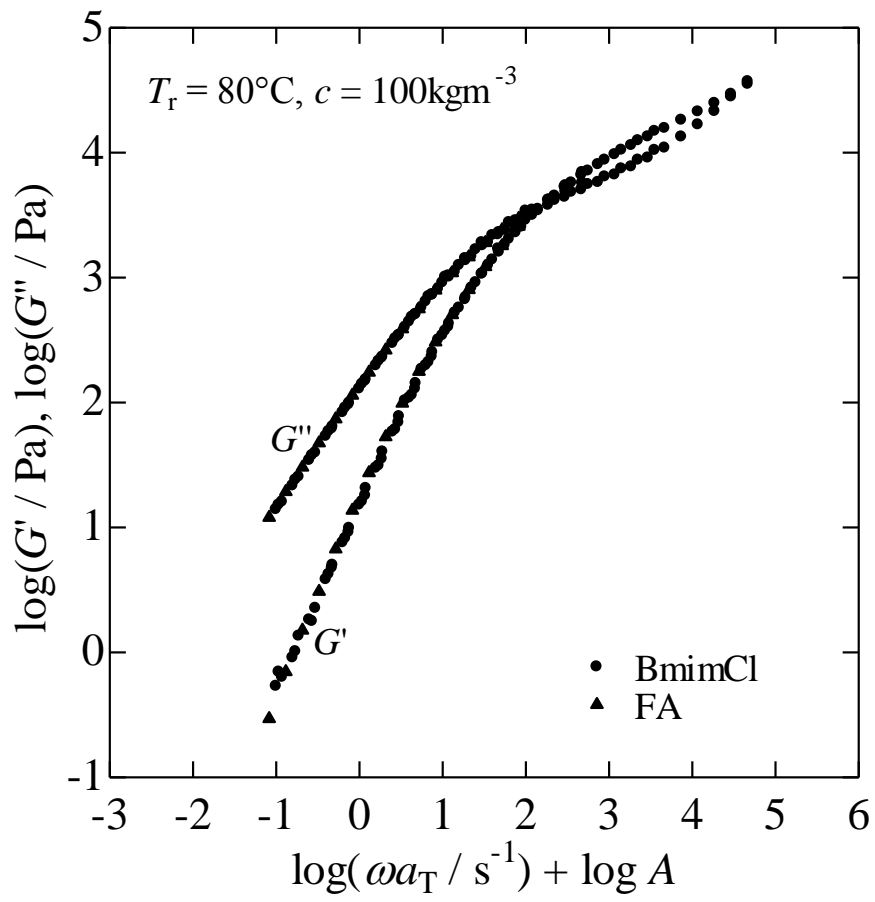
G''

G'

● BmimCl
▲ FA

$\log(G' / \mathrm{Pa})$, $\log(G'' / \mathrm{Pa})$

$\log(\omega a_T / \mathrm{s}^{-1}) + \log A$

Fig. 1(b)

Fig. 2

The plot shows $\log(G'/\mathrm{Pa})$, $\log(G''/\mathrm{Pa})$ on the vertical axis versus $\log(\omega a_\mathrm{T}/\mathrm{s}^{-1})$ on the horizontal axis.

$T_\mathrm{r} = 80°C$, $c = 200\,\mathrm{kgm}^{-3}$

T /°C	BmimCl	FA	MFA
0			⬓
5		△	
10		▲	☐
20	⊗	△	■
40	⊕	▲	
60	⊖		
80	◑		
100	○		
120	●		

Fig. 3

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Fig. 4