

NOTE

Entanglement network of agarose in various solvents

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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 cellulose¹ 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, that is, 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 because of 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, Cleveland, OH, USA) was used without further purification. FA (Wako, Osaka, Japan) and MFA (Aldrich, St Louis, MO, USA) were used as received. The ionic liquid BmimCl (Aldrich) 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 $\sim 80^\circ\text{C}$. Then, the vessel was sealed and left on the hot plate for complete melting. The concentration of agarose (c) was 1.0×10^2 or $2.0 \times 10^2 \text{ kg m}^{-3}$, that is, ca 10 or 20 wt %. In the calculation of c , $1.0 \times 10^3 \text{ kg m}^{-3}$ was assumed for the density of agarose, and 1.14×10^3 , 1.00×10^3 and $1.08 \times 10^3 \text{ kg m}^{-3}$ were used for the densities of FA,¹⁴ MFA¹⁴ 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, New Castle, DE, 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 FA¹⁴ and MFA¹⁴ are reported to be 2.6 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– 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 1a the master curves of the ω dependence of the dynamic viscoelastic functions (G' and G'') for the BmimCl and FA solutions of agarose at $c = 100 \text{ kg m}^{-3}$. 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°C for both solutions. For the FA solution, the dynamic viscoelasticity measurements were taken in the T -range of 5– 20°C . The master curves were prepared initially at 20°C , and then the master curves were shifted so that $T_r = 80^\circ\text{C}$ 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 $\log \omega a_T$ of 2.2–4.7. 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

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

where R is the gas constant. It should be noted that M_e in the above equation should be in kg mol^{-1} . For the BmimCl solution at $c=100 \text{ kg m}^{-3}$, we have a G_N^0 of $1.2 \times 10^4 \text{ Pa}$ 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, that is, 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 1b shows the same data as Figure 1a, 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 $c=100 \text{ kg m}^{-3}$ 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 $c=100 \text{ kg m}^{-3}$, 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 $c=100 \text{ kg m}^{-3}$ are shown in Figure 2. It should be noted that a_T here is the shift factor from T_r (80°C) even for the FA solutions; namely, the original shift factor was modified so that at

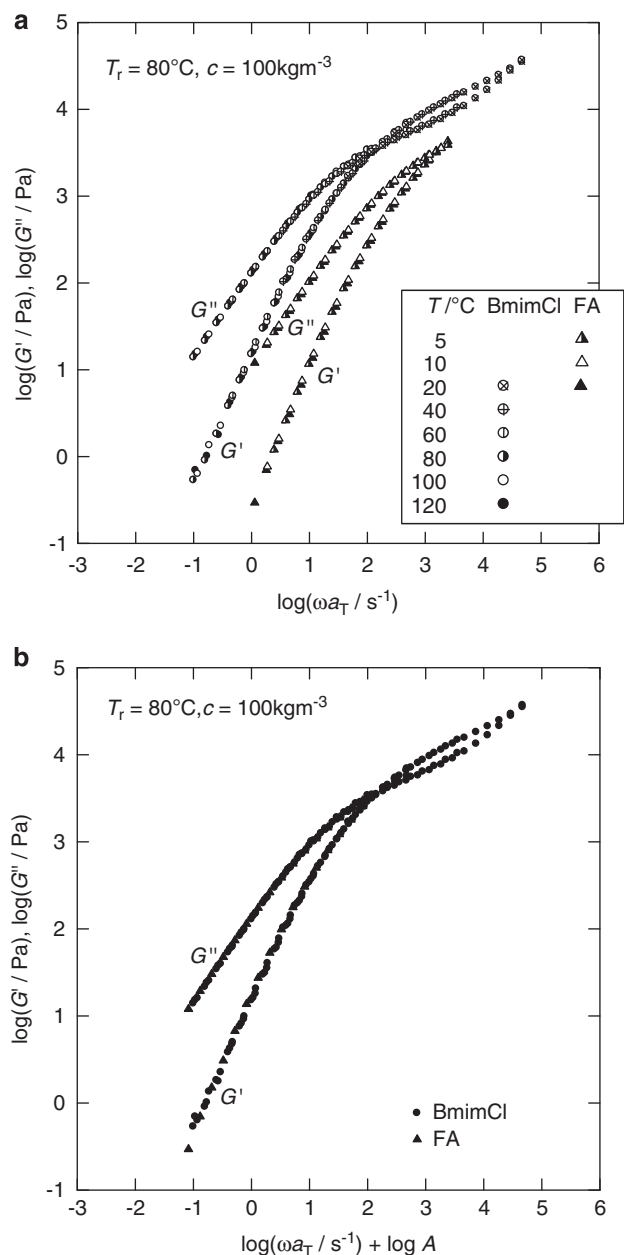


Figure 1 (a) Master curves of the ω -dependence of G' and G'' for the 1-butyl-3-methylimidazolium chloride (BmimCl) and formamide (FA) solutions of agarose at $c=100 \text{ kg m}^{-3}$. The reference temperature, T_r , is 80°C . (b) The FA curves are horizontally shifted by the parameter A .

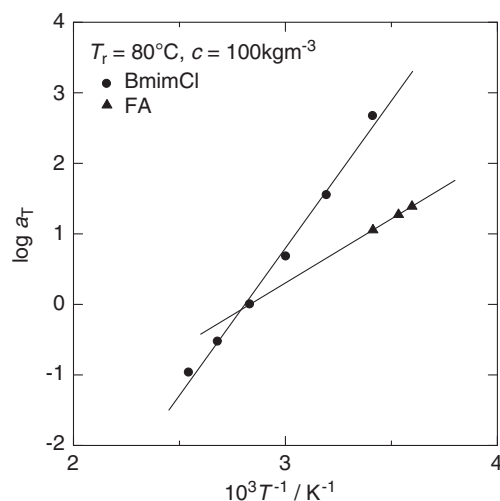


Figure 2 Shift factor a_T plotted against T^{-1} for the 1-butyl-3-methylimidazolium chloride (BmimCl) and formamide (FA) solutions of agarose at $c=100 \text{ kg m}^{-3}$. The reference temperature, T_r , is 80°C .

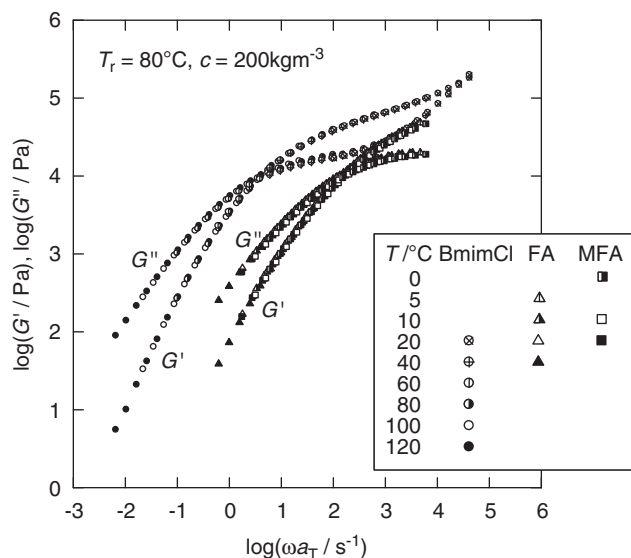


Figure 3 Master curves of the ω -dependence of G' and G'' for the 1-butyl-3-methylimidazolium chloride (BmimCl), formamide (FA) and *N*-methylformamide (MFA) solutions of agarose at $c=200\text{ kg m}^{-3}$. The reference temperature, T_r , is 80°C .

80°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 $\log a_T$ versus 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 $c=200\text{ kg m}^{-3}$. The master curves for BmimCl cover a wide range of ωa_T compared with the others because of the wider T -range of the measurements. For the plateau zone, we have a G_N^0 of $5.2 \times 10^4\text{ Pa}$, leading to an M_e of 1.1×10^4 at $c=200\text{ kg m}^{-3}$. This M_e value is roughly half of that (2.4×10^4) for the solution at $c=100\text{ kg m}^{-3}$. 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 $c=100\text{ kg m}^{-3}$. 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°C) for all solutions; namely, the original shift factor was modified so that at 80°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 FA and MFA, 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

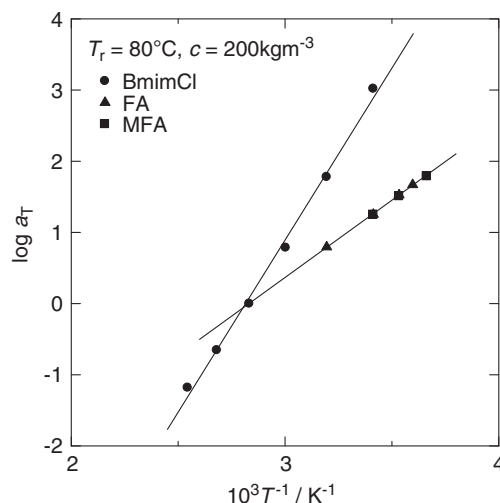


Figure 4 Shift factor a_T plotted against T^{-1} for the 1-butyl-3-methylimidazolium chloride (BmimCl), formamide (FA) and *N*-methylformamide (MFA) solutions of agarose at $c=200\text{ kg m}^{-3}$. The reference temperature, T_r , is 80°C .

the agarose chains are similar regardless of the solvent. The small $M_{e,\text{melt}}$ for polysaccharides can be attributed to the network of polysaccharide chains, not to the network formed by the ionic liquid molecules.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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