Hydrodynamic Properties of Aqueous Dextran Solutions

Xuelin Xu,[1] Hangquan Li,[2] Zhengdong Zhang,[3] Xin Qi[3]

[1]Department of R&D and Planning, National Institute of Metrology, Beijing 100013, China
[2]College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China
[3]Division of Metrology in Chemistry, National Institute of Metrology, Beijing 100013, China

ABSTRACT: The hydrodynamic performance of aqueous dextran solutions, including the rheological and thixotropic properties, were investigated. Three kinds of dextrans with different molecular weights were employed to examine the effects of the molecular weight, concentration, temperature, and so forth on the hydrodynamic properties of aqueous dextran solutions. The results showed that an aqueous solution of a dextran with a high molecular weight of 5.223×10^5 at a high concentration of 30 wt % had pseudoplastic properties, in contrast to the conclusions of other researchers finding that aqueous dextran solutions were Newtonian liquids. The viscosity of the aqueous dextran solutions decreased with temperature, and the activation energy was calculated to be 16,849.2 J/mol with a 10 wt % dextran (weight-average molecular weight = 5.223×10^5) solution. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1523–1529, 2009

Key words: polysaccharides; rheology; solution properties

INTRODUCTION

Dextran is a bacterial polysaccharide consisting of glucose monomer,[1] which is normally derived from the bacteria *Leuconostoc mesenteroides* (strain B-512F), and usually has the structure shown in Scheme 1.[2–5] Dextrans with different weight-average molecular weight (M_w) values can be produced by hydrolysis and fractionation. Fractionation can be accomplished by size exclusion chromatography or ethanol fractionation, in which dextrans with the largest M_w values precipitate first.[6,7]

Because they are water-soluble, biodegradable, and versatile, dextrans are used extensively in many fields, such as wastewater treatment and the pharmaceutical, food, biological, cosmetic, and agricultural industries. In addition, dextrans have been widely applied in grafting and addition chemistry because they have many hydroxyl groups, which allow for a broad range of substitutions with functional groups, and dextran-based materials are highly hydrophilic and biocompatible and show low protein adsorption.[8,9]

Nowadays, the properties of dextrans, including the rheological and thixotropic properties, have aroused keen interest because of the widespread applications of dextrans. Carrasco et al.[10] found that all solutions of dextrans with molecular weights ranging from 71,500 to 531,000 and with concentrations up to 30 wt % behaved as Newtonian fluids. Nomura et al.[11] also found that the solution viscosity of dextrans with molecular weights ranging from 10^4 to 2×10^6 and concentrations ranging from 0.5 to 30 wt % to be independent of the shear stress. Tirtaatmaja et al.[12] also confirmed this point of view by employing dextrans with M_w values ranging from 40,000 to 2,000,000 and with concentrations up to 30 wt %.

In this article, we reveal an interesting phenomenon: an aqueous solution of a dextran with a high M_w of 5.223×10^5 at a concentration of 30 wt % displayed non-Newtonian behavior, which conflicted with the findings of others. However, other dextrans with lower M_w values or lower concentrations did show Newtonian behavior just like that previously described. The reason could be the long chains and the thick distribution of chains, which made the occurrence of entanglements between chains and the generation of hydrogen bonds easier than other conditions.

EXPERIMENTAL

Materials

Dextrans with different M_w values were purchased from Sigma–Aldrich Corp. (St. Louis, MO); water was three-stage-distilled before being used. NaNO$_3$ was a commercial product from Beijing Chemical
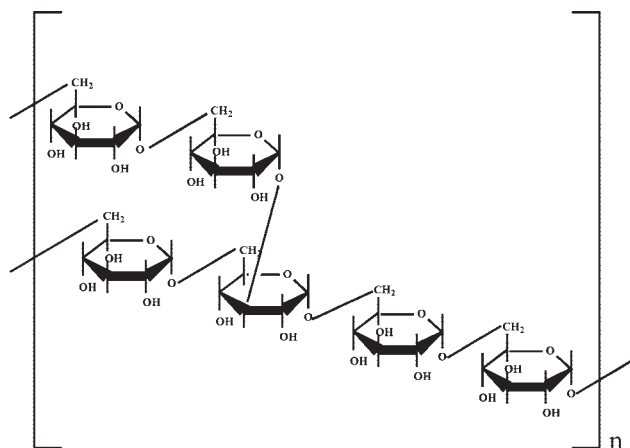
Scheme 1　Sketch of the dextran structure.

Reagents Co. (Beijing, China); 0.25- and 0.45-μm filters were acquired from Whatman (Maidstone, UK).

M_w and weight-average molecular weight/number-average molecular weight (M_w/M_n) measurement

Dextrans used in this article were supplied by Sigma–Aldrich as candidates for molecular weight reference materials. The samples were dissolved in a mobile phase to get transparent solutions of different concentrations. The mobile phase was a $0.1N$ NaNO$_3$ aqueous solution that had been treated with a 0.25-μm filter in case any impurity existed in it. To minimize undesired effects on the determination of M_w and the polydispersity index (M_w/M_n), the operating process had to be exactly the same in the preparation of the mobile phase and dextran solutions. Finally, each dextran solution was further filtered through a 0.45-μm filter before it was injected into the pump of a multi-angle laser light scattering (MALLS) apparatus (Dawn DSP, Wyatt Technology Co., Santa Barbara, CA).

M_w and M_w/M_n values of dextrans were measured by gel permeation chromatography (GPC) combined with MALLS equipped with a He–Ne laser ($\lambda = 690$ nm; Dawn DSP, Wyatt Technology) over the angular range of 49–135° at 25 ± 1°C.

Hydrodynamic properties of the aqueous dextran solutions

The study of the rheological and thixotropic properties of the aqueous dextran solutions was conducted on an ARES-RFS III rheometer (TA Instruments, New Castle, DE). The test temperature was controlled at 25 ± 1°C. The clamping fixtures used in the tests were as follows: coaxial cylinders for the

TABLE I
M_w and M_w/M_n Values of Dextran

Dextran	M_w	M_w/M_n
D10	1.090×10^5	1.332
D25	2.694×10^5	1.367
D50	5.223×10^5	1.450

10 wt % solutions and parallel plates for the 30 wt % solutions.

RESULTS AND DISCUSSION

Measurement of M_w and M_w/M_n

Three kinds of dextrans, D10, D25, and D50, were employed, which had different nominal M_w values of 1×10^5, 3×10^5, and 5×10^5, respectively. To accurately investigate the effect of M_w on the mobile properties of the aqueous solutions, M_w and M_w/M_n were determined.

First, different amounts of dextran D10 were dissolved in three-stage-distilled water to get a series of aqueous dextran solutions, the concentrations of which were 1, 2, 3, 4, and 5 mg/mL. The dn/dc value of D10 was determined by GPC to be 0.146 mL/g. Then, M_w and M_w/M_n of D10 were measured by MALLS combined with GPC, and the results are shown in Table I.

The M_w and M_w/M_n values of D25 and D50 were measured with the same process, and their data are also listed in Table I.

Table I shows that all the dextrans used had narrow molecular weight distributions. It can be concluded that the experimental results on the effect of M_w on the mobile properties were believable.

Rheological properties of the aqueous dextran solutions

Effect of the solution concentration on the rheology

A 30 wt % D50 aqueous solution was tested with the ARES-RFS III rheometer. The shear rate was increased gradually from 0.02 to 1000 s^{-1} to get 25 measurements, each lasting for 30 s. The results are shown in Figure 1. When the shear rate increased, the viscosity of the solution decreased, and this indicated that the solution had shear-thinning characteristics.

The dextrans used in this experiment were derived from the bacteria *L. mesenteroides* (strain B-512F), and the structure of this dextran is shown in Scheme 1.

Dextran sample D50, with a high M_w value of 5.223×10^5, was a typical long-chain polymer. In its aqueous solution, physical entanglement easily took place between chains or inside a chain, resulting in
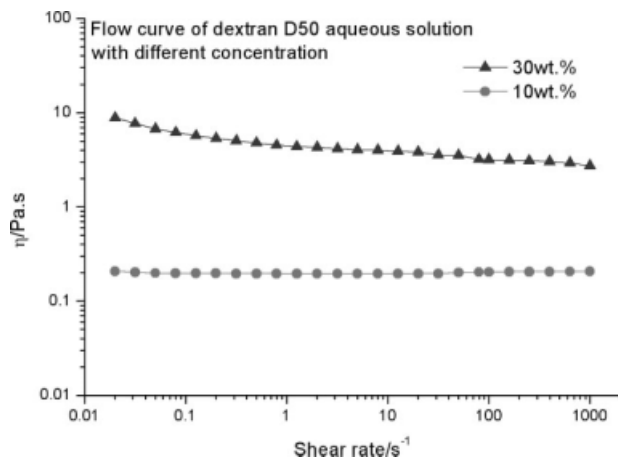
Figure 1 Effect of the solution concentration on the rheological properties.

dextrans in a condition of chain assembly. Therefore, the solution had a high viscosity. When the shear rate increased, the distribution condition of the dextran changed, some of the tangles between chains opened, and the viscosity of the solution decreased.

This observation was different from conclusions drawn by others.[10–12] The reason was supposed to be the difference in the molecular lengths of the dextran samples used in the experiments. Actually, there were big differences in the structures of dextrans from different corporations or from different batches from the same corporation. Conflicting data on the branch lengths implied that the average branch length was less than three glucose units.[13,14] However, other methods indicated that branches had more than 50 glucose units.[15,16] For the dextran with short side chains, the chain length was greater than of the dextran with the same M_w but longer side chains. Therefore, for those dextrans with long backbone chains, the entanglement of chains more easily took place than for those with short backbone chains.

Furthermore, all the oxygen atoms, being inside circles and acting as bridge connections, could act as hydrogen accepters, and hydrogen atoms on the hydroxide groups could be hydrogen donors,[17] so there were some hydrogen bonds inside a chain and between chains. As the shear rate increased, some of the hydrogen bonds were broken, the assembling conditions of the chains changed, the viscosity of the solution decreased, and this resulted in shear thinning of the solution.

A 10 wt % D50 aqueous solution was subjected to the same test; the results (in Fig. 1) showed that the viscosity of the solution did not change with the shear rate. That is, the solution showed the properties of a Newtonian fluid. The reason was that with the reduction of the solution concentration, the distribution of D50 chains began thinning, and the distance between the chains increased. Possibilities of chain collision, physical tangles, and hydrogen-bond generation were reduced. As we know, a dilute polymer aqueous solution performs as a Newtonian fluid. The D50 aqueous solutions with concentrations of 10 and 30 wt % were subjected to FTIR analysis; the results are shown in Figure 2. The FTIR spectra demonstrated that the absorption peak corresponding to the O—H stretching vibration decreased from 3394.157 to 3386.444 cm^{-1} with the solution concentration increasing from 10 to 30 wt %, and this indicated the generation of more hydrogen bonds.[18,19]

For a Newtonian fluid, a pseudoplastic fluid, and a swelling fluid, the relation between the shear stress (τ) and shear rate (γ) can be expressed by the power-exponent equation:[20,21]

$$\tau = K\gamma^n$$

where K is the consistency factor and n is the non-Newtonian index.

This equation can be transformed into the following formula: $\lg \tau = \lg K + n \lg \gamma$. Plotting $\lg \tau$ as a function of $\lg \gamma$, we can take the n value the slope of the curve. For a pseudoplastic fluid, $n < 1$; for a Newtonian fluid, $n = 1$; and for a swelling fluid, $n > 1$.

With this method, the n values of 30 and 10 wt % D50 solutions were obtained, and the results are shown in Figure 3(A,B). For the 30 wt % solution, n was 0.9092, showing a pseudoplastic property. When the solution concentration was reduced to 10 wt %, the n value increased to 0.9980, very close to 1, and the solution behaved as a Newtonian fluid. This was fully consistent with our observation from Figure 1: the D50 aqueous solution showed shear thinning at a high concentration and was Newtonian at a low concentration.
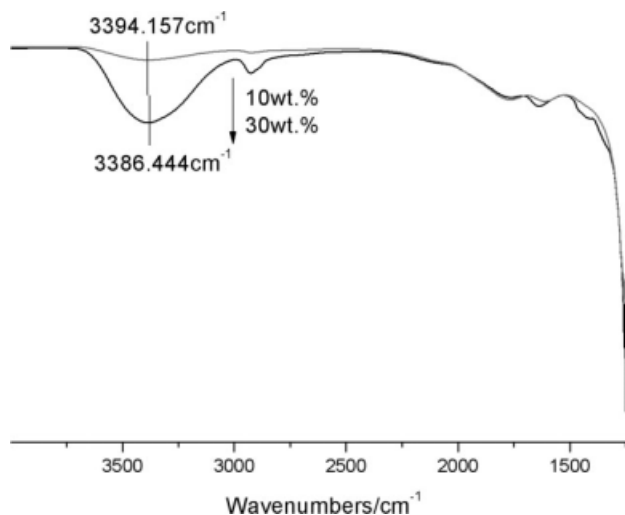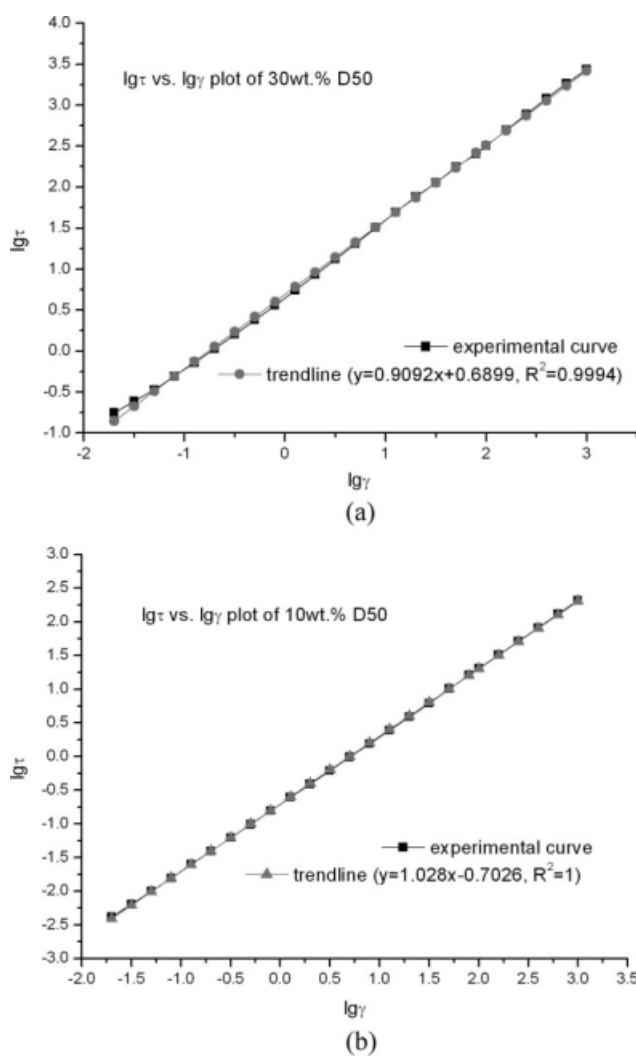

Figure 2 FTIR spectra of the D50 aqueous solution.

Figure 3 Relation between the shear stress (τ) and shear rate (γ).

Moreover, the n values of the D10 and D25 aqueous solutions at concentrations of 10 and 30 wt % were calculated, and the results are shown in Table II. The n values of the aqueous dextran solutions were reduced in two ways: increasing the molecular weight of the dextran sample at the same solution concentration and increasing the solution concentration for the same sample of dextran, except for D10.

Effect of M_w on the rheological properties

The rheological properties of three kinds of dextrans with different M_w values were investigated at a concentration of 30 wt %. The results are shown in Figure 4(A). From this figure, two conclusions can be drawn: the viscosity of the solutions with the same concentration increased with M_w, and along with the increase in M_w, the fluid types of the solution changed from Newtonian at a low M_w to pseudoplastic at a high M_w.

As M_w increased, physical tangles of chains and inter/inner hydrogen bonds easily took place. For dextrans with a high molecular weight, the viscosity of the solution at a low shear rate was bigger; as the shear rate increased, the tangles were opened, and the hydrogen bonds were broken. Therefore, the solution showed pseudoplastic properties. For dextrans with a low molecular weight, the chains were generally short; the effect of the physical tangles and the hydrogen bonds was not obvious. Therefore, the viscosity of the solution did not decrease with the shear rate. The calculation of n supported the conclusion [see Fig. 4(B)]: the n values of D50, D25, and D10 increased gradually, and non-Newtonian behavior gradually weakened.

When the concentration of the solutions decreased to 10 wt %, the effect of M_w on the rheological properties was investigated again. The results [Fig. 4(C)] showed that all three kinds of dextran solutions approximately behaved as Newtonian fluids. This was due to the low concentration of the solution. At a low concentration, the effect of physical tangles between molecular chains and hydrogen bonds became smaller than at a high concentration. Therefore, the solution expressed Newtonian properties.

Figure 4(A,C) shows that for all the solution concentrations and for all the dextrans, the viscosity values of the solutions were stable at the shear rate of 2 s^{-1}. To investigate the effects of M_w and the concentration on the viscosity of the solutions, the viscosity values at 2 s^{-1} were taken from the aforementioned experimental data, and the viscosity–M_w curve was obtained, as shown in Figure 4(D), which includes experimental data for two other dextran samples with molecular weights of 4.258×10^3 and 1.340×10^4. The same two conclusions were drawn: for a given dextran, the viscosity of the solutions increased with the concentration, and at the same concentration, the viscosity of the solutions increased with M_w.

Effect of temperature on the rheological properties of the solutions

A 10 wt % D50 aqueous solution was employed to investigate the effect of temperature on the rheological properties. From 25 to 65°C, five measurements were taken; the results are shown in Figure 5(A).

TABLE II
n Values of the Aqueous Dextran Solutions

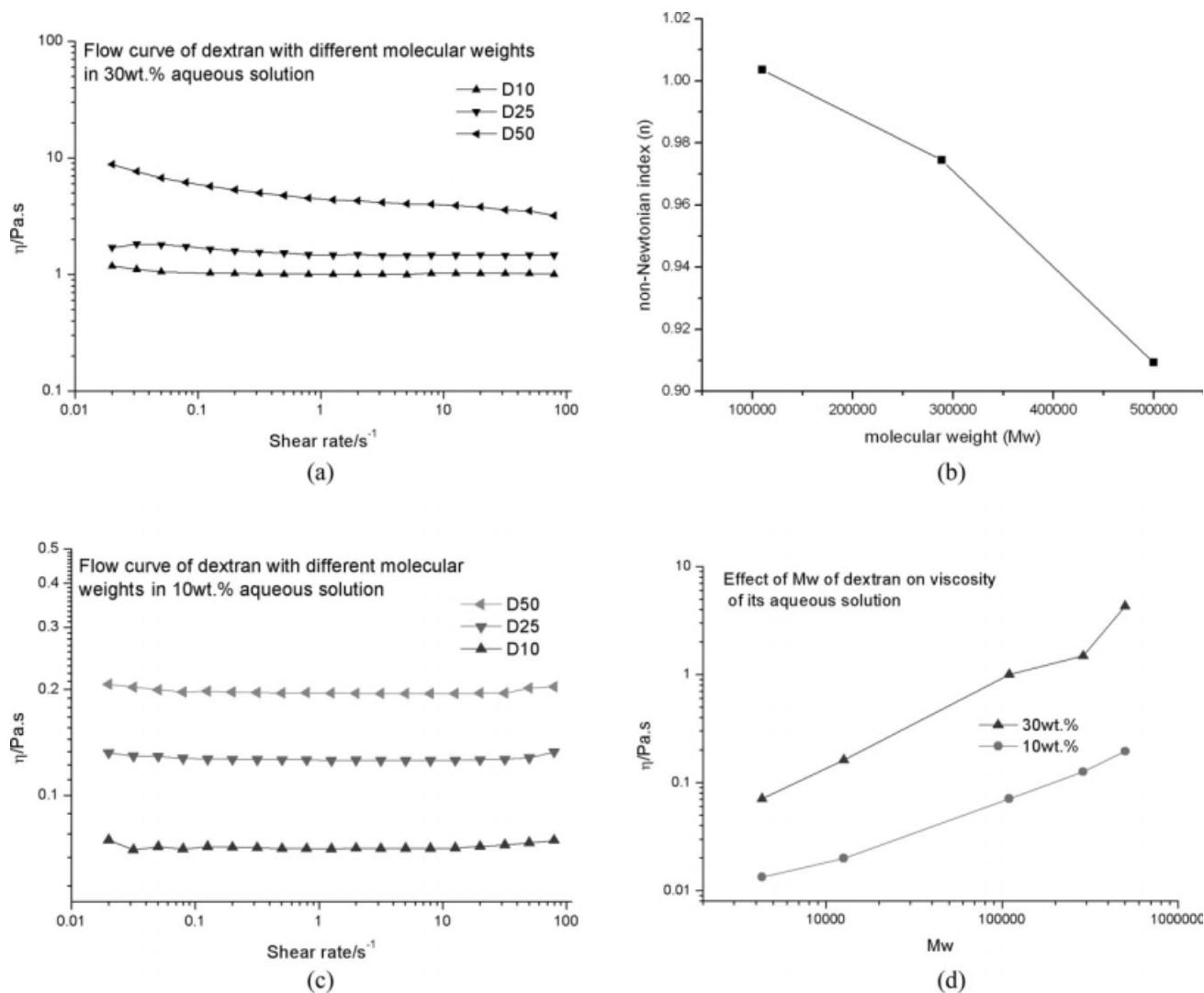| Dextran	n	
	10 wt %	30 wt %
D10	1.0017	1.0035
D25	0.9987	0.9744
D50	0.9980	0.9323

Figure 4 Effect of M_w on the rheological properties of the solutions.

The viscosity of the solution decreased with temperature.

Using the Kurata–Stockmayer–Fixman, Berry, and Inagaki–Suzuki–Kurata methods, Efkan and Ali[22] found that in ethylene glycol, with increasing temperature, the tangles between chains of dextran shrank, and the root-mean-square end-to-end distance was shortened. Besides, when the temperature increased, the thermal motion of molecules intensified, and the molecular interaction weakened. Therefore, it was not too difficult to understand the phenomenon of the viscosity of the solution decreasing with temperature.

As we know, the viscosity of the solution (η) and the temperature (T) meet in the following equation:

$$\eta = \eta_0 \times e^{\Delta E/RT}.$$

where η_0 is the initial viscosity, ΔE is the activation energy, and R is the universal gas con-

stant. After a transformation, the equation can be changed into

$$\ln\eta = \ln\eta_0 + \Delta E/RT.$$

By making a plot of ln η as a function of $1/T$ and then performing line fitting, we found that the slope of the line was $k = \Delta E/R$. Figure 5(B) shows that the fitting situation was very good: the fitting coefficient was 0.9925, and the slope of the line (k) was 2028.6. In addition, ΔE was calculated to be 16,865.8 J/mol.

Moreover, by the same process, ΔE of the 30 wt % D50 aqueous solution was determined to be 17,180.1 J/mol, a little higher than that of the 10 wt % solution, and this could be interpreted as the formation of more tangles and generation of more hydrogen bonds between chains.

Thixotropic properties of the solutions

That a solution is thixotropic means that the viscosity of the solution decreases because of stress and
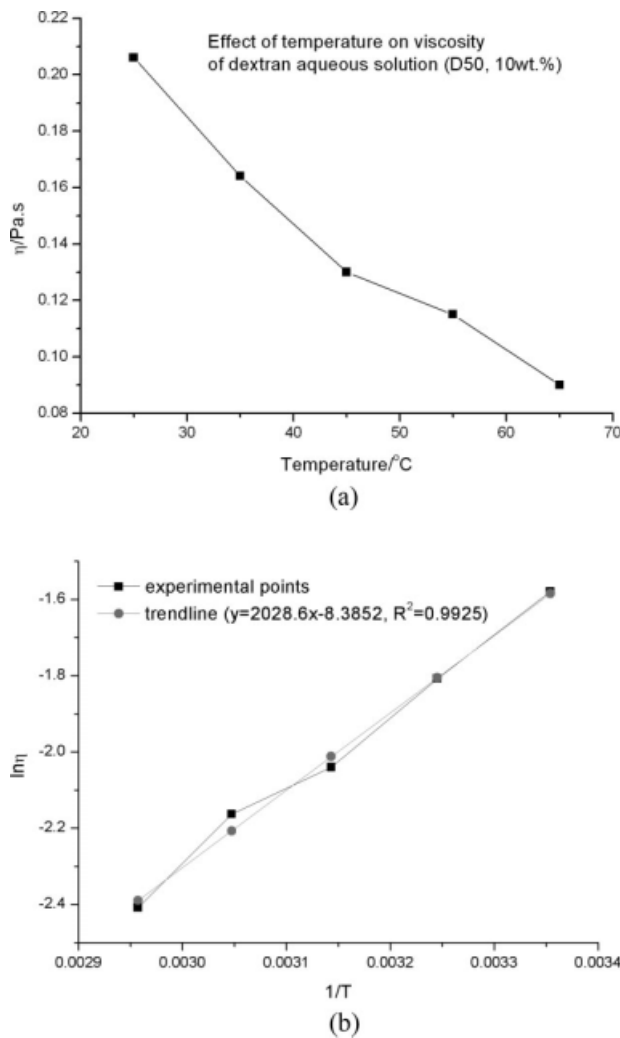
Figure 5 Effect of temperature on the rheological properties of the solution.

can be gradually restored when the stress has been withdrawn. The reason for thixotropy is the rate difference between the breakage and restoration of the inner molecular structure. Those molecules that meet a block during structure restoration are more likely to have this property. The thixotropic properties of solutions are often characterized by testing of the thixotropic loop: the larger the area of the thixotropic loop, the greater the thixotropy.

Figure 6(A) shows the viscosities of three kinds of dextrans with different M_w values in 10 wt % aqueous solutions. The maximal shear rate was 10 s^{-1}, and the time of the shear rate was 120 s. The results showed that none of the dextran samples formed a thixotropic loop, indicating that the dextran samples used in the experiments did not deform. In addition, the viscosity change caused by the difference in M_w can be found in this figure: the higher M_w was, the greater the viscosity of the solution was. This supported the aforementioned results again.

As the concentration of the solution increased to 30 wt %, as in Figure 6(B), the D10 and D25 solutions still did not form thixotropic loops. However, for D50, the situation changed: the rising and declining curves of the shear rate did not agree well and were not straight. This meant that the deformation of D50 molecules was restricted in the 30 wt % aqueous solution. With a high concentration and high M_w, the chains were more prone to tangle and form intermolecular hydrogen bonds. In the deformation process, the aforementioned structure was destroyed, and it was difficult for the chains to be restored to the previous level. Of course, during this process, the high viscosity impeded the movement of molecules, and this promoted the formation of thixotropy.

CONCLUSIONS

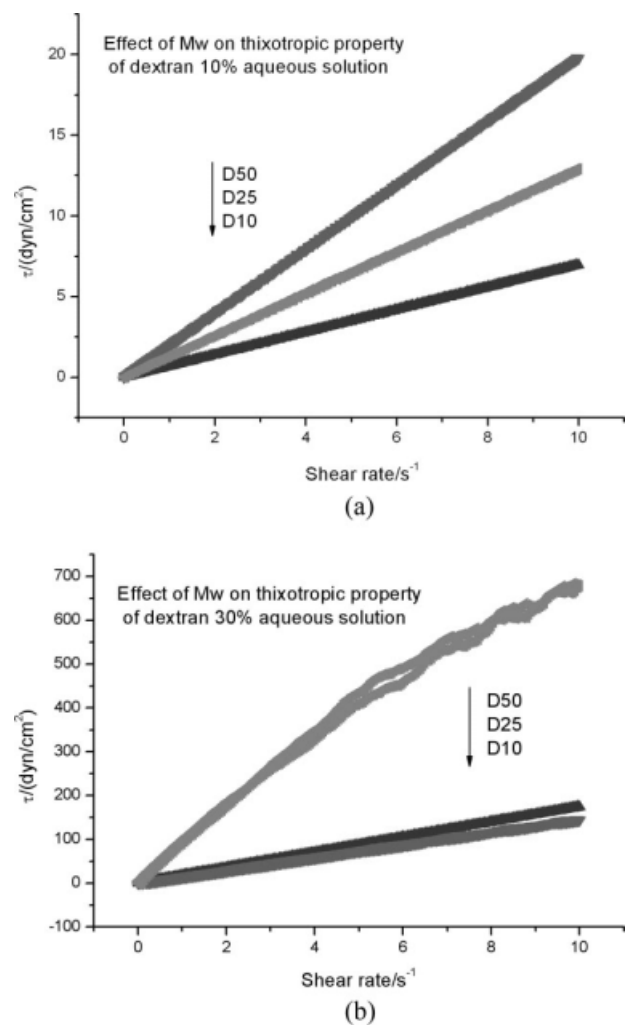The hydrodynamic properties of aqueous dextran solutions were investigated. At a high concentration

Figure 6 Effect of M_w on the thixotropic properties of the solution.

of 30 wt %, D50, whose M_w was 5.223×10^5, behaved as a pseudoplastic fluid, and this conflicted with the findings by other scientists,[10–12] whereas the rest of the experimental results from rheological tests with a low M_w value or a low concentration agreed very well with others' results; that is, the aqueous solutions expressed Newtonian properties. In thixotropic property tests, most dextran solutions did not form a thixotropic loop, except for the 30 wt % solution of D50.

References

1. Santos, M.; Jose, T.; Rodrigues, A. Biochem Eng J 1999, 4, 177.
2. Lapasin, R.; Pricle, S. Rheology of Industrial Polysaccharides, Theory and Applications; Aspen: Gaithersburg, MD, 1999; p 35.
3. Rankin, J. C.; Jeanes, A. J Am Chem Soc 1954, 76, 4435.
4. Walther, K. A.; Brujic, J.; Li, H.; Fernández, J. M. Biophys J 2006, 90, 3806.
5. Oyaizu, K.; Yamaguchi, A.; Hayashi, T.; Nakamura, Y.; Yoshii, D.; Ito, Y.; Yuasa, M. Polym J 2006, 38, 343.
6. Granath, K. A.; Flodin, P. Makromol Chem 1961, 48, 160.
7. Ingelman, B.; Halling, M. S. Ark Kemi 1949, 1, 61.
8. Hiemstra, C.; Leonardus, J. V. D. A.; Zhong, Z. Y.; Dijkstra, P. J.; Jan, F. Macromolecules 2007, 40, 1165.
9. Krishnamoorthi, S.; Mal, D.; Singh, R. P. Carbohydr Polym 2007, 69, 371.
10. Carrasco, F.; Chornet, E.; Overend, R. P.; Costa, J. J Appl Polym Sci 1989, 37, 2087.
11. Nomura, H.; Koda, S.; Hattori, F. J Appl Polym Sci 1990, 41, 2959.
12. Tirtaatmadja, V.; Dunstan, D. E.; Boger, D. V. J Non-Newtonian Fluid Mech 2001, 97, 295.
13. Lindberg, B.; Svensson, S. Acta Chem Scand 1968, 22, 1907.
14. Larm, O.; Lindberg, B.; Svenssson, S. Carbohydr Res 1971, 20, 39.
15. Bovey, F. A. J Polym Sci 1959, 35, 167.
16. Senti, R. F.; Hellman, N. N.; Ludwig, N. H.; Babcock, G. E.; Tobin, R.; Glass, C.; Lamberts, B. J Polym Sci 1955, 17, 527.
17. Vinogradov, S. N.; Linnell, R. H. Hydrogen Bonding; Van Nostrand Reinhold: New York, 1971; p 250.
18. Maillo, J.; Pages, P.; Vallejo, E.; Lacorte, T. Eur Polym J 2005, 41, 753.
19. Su, Y. C.; Kuo, S. W.; Yei, D. R.; Xu, H. Y.; Chang, F. C. Polymer 2003, 44, 2187.
20. Maglione, R.; Ferrario, G. Oil Gas J 1996, 94, 63.
21. Naimi, M.; Hasnaoui, M.; Platten, J. K. Eng Comput 2000, 17, 638.
22. Efkan, Ç.; Ali, G. Eur Polym J 2002, 36, 2143.