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Author(s)	Horinaka, Jun Ichi; Yamanaka, Ayumi; Takigawa, Toshikazu
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Note

Rheological Properties of Concentrated Solutions of a Branched Polysaccharide Dextran in an Ionic Liquid

Jun-ichi HORINAKA^{1,†}, Ayumi YAMANAKA², and Toshikazu TAKIGAWA¹¹*Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo, Kyoto 615-8510, Japan*²*Faculty of Engineering, Kyoto University, Nishikyo, Kyoto 615-8510, Japan*

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Rheological properties of dextran solutions in 1-butyl-3-methylimidazolium acetate were examined up to the concentration (c) of $4.1 \times 10^2 \text{ kgm}^{-3}$. A high molecular weight ($\approx 2 \times 10^6$) dextran with a degree of divergence of 4 % was used. The zero-shear viscosity estimated from the flow behavior indicated that dextran chains in the solutions entangle each other at $c \geq 1.7 \times 10^2 \text{ kgm}^{-3}$. In fact the plateau modulus (G_N^0) was obtained from the G' and G'' curves for $c \geq 2.6 \times 10^2 \text{ kgm}^{-3}$. However, the anomalous results were obtained regarding entanglement of dextran chains: The molecular weight between entanglements was constant against c at 2.3×10^4 , so that a large number of entanglements per chain was expected in spite of the subtle rubbery plateau that was actually observed. It was proposed that the dextran has the main structure of long branches and each branch is densely sub-branched.

Key Words: Dextran / Branched structure / Concentrated solution / Viscoelasticity / Entanglement

1. INTRODUCTION

Dextran chain is composed of repeating glucose units having primarily $\alpha(1 \rightarrow 6)$ linkage and occasionally $\alpha(1 \rightarrow 3)$ or $\alpha(1 \rightarrow 4)$ linkage; the additional $\alpha(1 \rightarrow 3)$ or $\alpha(1 \rightarrow 4)$ linkage causes divergence, or branching, in the backbone of dextran¹⁻³. Because of this distinctive linkage, there have been a large number of experimental studies focusing on branching of dextran. So far the degrees of branching as well as the resultant conformations of dextran have been assessed by means of NMR³, X-ray scattering⁴, viscosity measurement⁵⁻⁹, sedimentation^{5, 7}, and light scattering^{7, 8}. Besides, branching is interesting from the rheological point of view. In fact, the relationship between molecular structure and viscoelasticity has been widely discussed for aqueous solutions of dextran¹⁰⁻¹². Although the results depend on the origin of dextran to some extent, it has been demonstrated that the rheological properties are significantly different from those of linear polysaccharides and compact conformations of highly-branched chains are expected.

Effects of branching on the rheological properties have been examined more extensively regarding synthetic polymers such as polystyrene and polyisoprene¹³⁻²¹. At the

present time various types of branching — star, dendrimer, and comb — can be obtained at controlled degrees of branching and molecular weights. Since these primary shapes of polymer chains are especially influential in determining the manner of entanglement and disentanglement among those chains in concentrated systems, most rheological studies on the effects of branching have been performed for the melts and concentrated solutions of branched polymers. However, to our knowledge, there have been no studies on the rheological properties of concentrated solutions of dextran where the entanglement of dextran chains becomes evidently important for the viscoelasticity.

In this study, a commercial high molecular weight dextran has been used and its concentrated solutions have been prepared by employing an ionic liquid as the solvent. Our earlier studies have shown that some ionic liquids can dissolve polysaccharides at high concentrations where the entanglement coupling can be detected as the rubbery plateau in the dynamic viscoelasticity data²²⁻²⁴. Therefore, it is expected that use of an ionic liquid for dextran enables us to examine rheological properties of the concentrated solutions including the entanglement behavior for the first time.

† Corresponding author.

E-mail : horinaka.junichi.5c@kyoto-u.ac.jp

Tel: +81-75-383-2454; Fax: +81-75-383-2458

2. EXPERIMENTAL

2.1 Materials

Dextran from *Leuconostoc mesenteroides* (Sigma-Aldrich, USA) was used as received. The supplier disclosed that the molecular weight (in gmol^{-1}) of the dextran sample determined by MALLS was from 1.5×10^6 through 2.8×10^6 . To estimate the degree of branching for the dextran, $^1\text{H-NMR}$ measurement was carried out for ourselves. The ratio of hydrogens that covalently bond with C1-carbons of glucose units having $\alpha(1\rightarrow3)$ linkage to those of glucose units having $\alpha(1\rightarrow6)$ linkage was about 4 %³⁾. 1-butyl-3-methylimidazolium acetate (BmimAc; Sigma-Aldrich, USA) was selected as a solvent from several kinds of ionic liquids; preliminary tests revealed that only BmimAc gave clear solutions at high concentrations up to 40 wt%. The melting point of BmimAc was reported to be below -20°C and all the solutions examined in this study were in the liquid state. Dextran solutions in BmimAc were prepared in the following manner. The powdery dextran was added to BmimAc in a dry glass vessel preheated around 80°C , and the mixture was quickly stirred with a stainless spatula on a combined hot-plate magnetic-stirrer at 80°C for about 10 minutes followed by stirring with a stirring bar for 2–6 h. The concentration of dextran (c) ranged from 1.1×10^1 to $4.1 \times 10^2 \text{ kgm}^{-3}$ (1 to 40 wt%). In the calculation of c , $1.0 \times 10^3 \text{ kgm}^{-3}$ was assumed for the density of dextran, while a reported value of $1.055 \times 10^3 \text{ kgm}^{-3}$ at room temperature was used for BmimAc²³⁾. The dextran solutions were prepared just before the rheological measurements mentioned below.

2.2 Measurements

A commercial rheometer (ARES, now TA Instruments, USA) was used for dynamic viscoelasticity measurements with a cone-plate geometry with the diameter of 25 mm and the cone angle of 0.1 rad. The measurement temperature (T) for the solutions of $c \geq 1.6 \times 10^2 \text{ kgm}^{-3}$ ranged from 20 to 100°C . The measurement for the solutions of $c < 1.6 \times 10^2 \text{ kgm}^{-3}$ was carried out only at 40°C . The angular frequency (ω) dependence curves of the storage modulus (G') and the loss modulus (G'') were obtained in the range of ω from 0.1 to 100 s^{-1} . The amplitude of the oscillatory strain was set at 0.1 so that the linear viscoelasticity was realized.

3. RESULTS AND DISCUSSION

Figure 1 shows the master curves of G' and G'' for four dextran solutions of $c = 1.6 \times 10^2 - 4.1 \times 10^2 \text{ kgm}^{-3}$. The

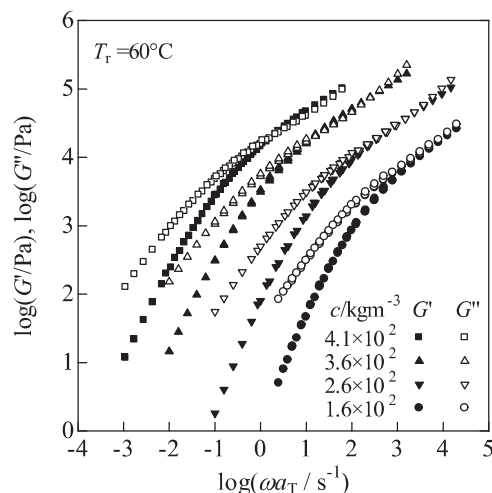


Fig. 1 Master curves of ω dependence of G' and G'' for dextran solutions of $c = 1.6 \times 10^2 - 4.1 \times 10^2 \text{ kgm}^{-3}$ at $T_r = 60^\circ\text{C}$.

master curves were made by applying the time (angular frequency)-temperature superposition principle to the G' and G'' curves at each T with the reference temperature (T_r) of 60°C . The horizontal shift factor is designated by a_T . As demonstrated in the figure, the superposition principle holds well for all the solutions of c ranging from 1.6×10^2 to $4.1 \times 10^2 \text{ kgm}^{-3}$. On each pair of master curves the flow region is observed at low ωa_T ; actually, the relation $G' \propto \omega^2$ cannot be identified for $c \geq 3.6 \times 10^2 \text{ kgm}^{-3}$ within the experimental conditions, while all the G'' curves show the terminal behavior of $G'' \propto \omega$.

To examine the effect of entanglement in the solutions, the zero-shear viscosity (η_0) has been estimated at 40°C from the dynamic viscoelasticity measurement by using the equation

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega} \quad (1)$$

and is double-logarithmically plotted against c in Fig. 2. The c -dependence of η_0 can be characterized by two slopes as drawn in the figure: 1.7 for $c \leq 5.3 \times 10^1 \text{ kgm}^{-3}$ and 12 for $c \geq 2.6 \times 10^2 \text{ kgm}^{-3}$. Then the critical concentration (c_c) for the dextran solutions can be determined to be $1.7 \times 10^2 \text{ kgm}^{-3}$ as the intersection of the slopes. It is noted that c_c is several times higher than the threshold of chain overlap (c^*). For comparison, the c -dependence of η_0 for cellulose solutions in 1-butyl-3-methylimidazolium chloride (BmimCl; Aldrich, USA) is shown in Fig. 3(a); c ranges from 1.1×10^1 to $2.1 \times 10^2 \text{ kgm}^{-3}$ and details of the rheological measurement have been explained in our previous paper²²⁾. It should be emphasized that cellulose is a typical linear polysaccharide. The c -dependence of η_0 can be similarly fitted by two solid lines with the slopes of 1.7 and 9 as represented in the figure, and accordingly $c_c = 9.8 \times 10^1 \text{ kgm}^{-3}$ can be determined. The lower slopes of 1.7 are the same for the dextran and cellulose

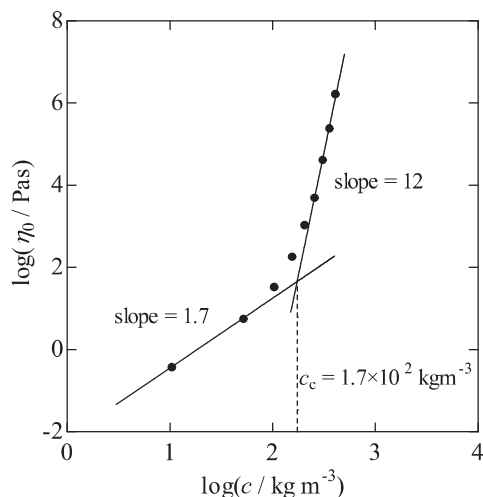


Fig. 2 Double-logarithmic plot of η_0 against c for dextran solutions of $c = 1.1 \times 10^1 - 4.1 \times 10^2 \text{ kgm}^{-3}$ at 40°C . Two solid lines are drawn to fit the data points at low and concentrated regions and c_c is determined as the intersection.

solutions, although the slope might be slightly higher compared with the terminal c -dependence of η_0 in the dilute region, which is typically unity. On the other hand, the higher exponent 12 for the dextran solutions is significantly larger than those for the concentrated solutions of cellulose. Stronger c -dependence of η_0 for a star-branched polymer than linear one has been reported regarding concentrated solutions of polyisoprene likewise¹³⁾. The strong c -dependence of η_0 is probably a characteristic of concentrated solutions of branched polymers. It is well known that c_c corresponds to the beginning of entanglement coupling between polymer chains in polymer solutions. In fact the cellulose solution of $c = 1.1 \times 10^2 \text{ kgm}^{-3}$ examined in our earlier study have exhibited an obvious rubbery plateau in the G' curve implying the entanglement coupling²²⁾. Furthermore, Fig. 3(b) demonstrates that there is no rubbery plateau for the cellulose solution of $c = 5.4 \times 10^1 \text{ kgm}^{-3}$, which is slightly below c_c . In this context it is expected that the dextran chains well entangle each other above $c = 1.7 \times 10^2 \text{ kgm}^{-3}$.

Now discussion is focused on the higher ωa_T region of the G' and G'' curves in Fig. 1. The G' and G'' curves for $c = 1.6 \times 10^2 \text{ kgm}^{-3}$ converge and increase with ωa_T with the same slope (n) of $1/2$, which appears quite similar to the G' and G'' curves for the cellulose solutions shown in Fig. 3(b). On the G' and G'' curves for $c \geq 2.6 \times 10^2 \text{ kgm}^{-3}$, where the entanglements occur, the same power law behavior with $n = 1/2$ is observed at high ωa_T , and the relation $G' > G''$ becomes clear as c increases in the power law region²⁵⁾. Although the relation $G' > G''$ with $n = 1/2$ violates in principle the Kramers-Kronig relation between G' and G'' , this may originate from the entanglements between dextran chains. We have no idea for appropriate estimation of the number of

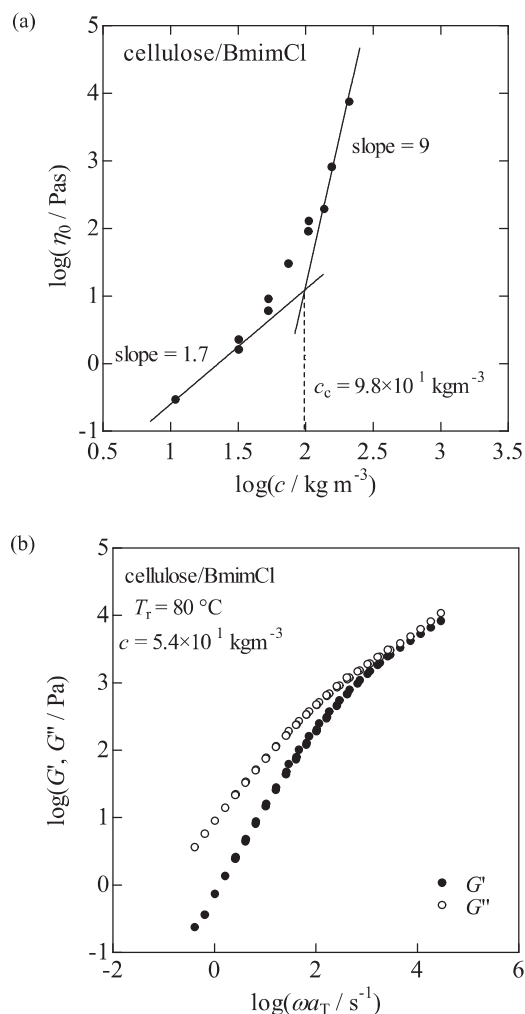


Fig. 3 (a) Double-logarithmic plot of η_0 against c for cellulose solutions in BmimCl of $c = 1.1 \times 10^1 - 2.1 \times 10^2 \text{ kgm}^{-3}$. Two solid lines are drawn to fit the data points at low and concentrated regions and c_c is determined as the intersection. (b) Master curves of ω dependence of G' and G'' for cellulose solution of $c = 5.4 \times 10^1 \text{ kgm}^{-3}$.

entanglements for such power law systems probably due to the constraint release, but we fortunately found that the $\tan\delta$ vs ωa_T curves from experiments show a minimum in the power law region. Therefore, we define “rubbery plateau modulus (G_N^0) for the power law systems” according to the conventional method; namely, G_N^0 corresponds to the G' value at ωa_T where the $\tan\delta = G''/G'$ vs. ωa_T curve attained the minimum in the rubbery plateau region²²⁾. For example, G_N^0 for the dextran solution of $c = 4.1 \times 10^2 \text{ kgm}^{-3}$ is determined to be $4.7 \times 10^4 \text{ Pa}$, as illustrated in Fig. 4. Then the analogy between the entangled network of polymer chains and the cross-linked network of rubber provides the following equation

$$G_N^0 = \frac{10^3 cRT}{M_e} \quad (2)$$

where M_e is the molecular weight between entanglements and R is the gas constant²⁶⁻²⁸⁾. Basically, G_N^0 should be estimated by integration over the terminal relaxation peak of G'' ²⁷⁾, but

there are several approximated methods to estimate the value of G_N^0 other than that employed in this study: Details have been widely discussed for well-entangled linear polymers²⁹. Use of a dextran sample with higher molecular weight might enable us to make comparable discussion even for the branched polysaccharide, although no such a sample is available at the present time.

Figure 5 shows the double-logarithmic plot of G_N^0 vs. c . As plotted in the figure, two measurements have been made at each concentration to confirm the reproducibility of the data. An obvious relation $G_N^0 \propto c$ has been obtained as indicated by the broken line. According to the well-established relation $M_e \propto c^{-1}$ for concentrated polymer solutions^{30, 31}, eq 2 provides a $G_N^0 \propto c^2$ relation, implying that the result for a branched polysaccharide dextran obtained in this study is totally different from the ordinary cases. In Fig. 6, the apparent values of M_e for the dextran calculated by using eq 2 are plotted against c . As naturally expected, M_e for the dextran is constant against c at $M_e = 2.3 \times 10^4$. As far as we know, M_e that is independent of c has not been reported yet for polymer solutions. Moreover, it should be noted that the number of entanglements included in a single dextran chain becomes about 100 by a simple calculation with M and the obtained M_e . This large number seems inconsistent with the appearance of the rubbery plateau in the G' and G'' curves in Fig. 1. It is impossible at the present stage to clarify the reason for these results, but a specific branched structure of high molecular weight dextran is probably responsible for the anomalous entanglement. As described in the experimental section, the dextran chain contains about 4 % of divergent point on the glucose unit basis. Since this frequency of divergence is close to that of other dextran samples, it is certain that our dextran has a

typical chain structure of high molecular weight dextran. It has been reported in earlier studies that a dextran chain takes a branched structure and tends to form a sphere as a whole having a high density of segments inside^{10, 11}. The topological feature of branching as well as the high density would tend to prevent the dextran chains from interpenetrating; consequently, the effective concentration of dextran involved with entanglement maintains a certain value regardless of c , while the number density of entangled chains, which determines the level of G_N^0 , increases in proportion to c . It is expected that the difficulty of interpenetration due to branched structure has great importance in entanglement of dendrimers in the similar way. In fact melt rheology for a dendritically-branched polystyrene with the molecular weight of $\sim 10^6$ shows no definitive evidence of entanglement²⁰.

Although the subtle rubbery plateau caused by branched structure is somewhat similar between dextran chain and

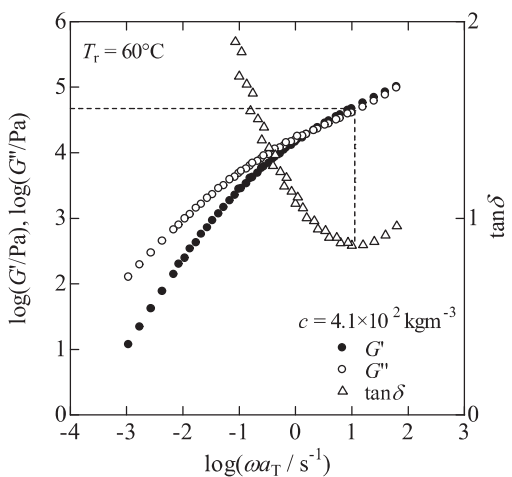


Fig. 4 Illustration of estimating G_N^0 for the dextran solution. Master curves of ω dependence of G' and G'' for the solution of $c = 4.1 \times 10^2 \text{ kgm}^{-3}$ are given together with the $\tan \delta$ curve in the rubbery plateau region. The broken lines indicate the minimum of $\tan \delta$ and the level of G_N^0 .

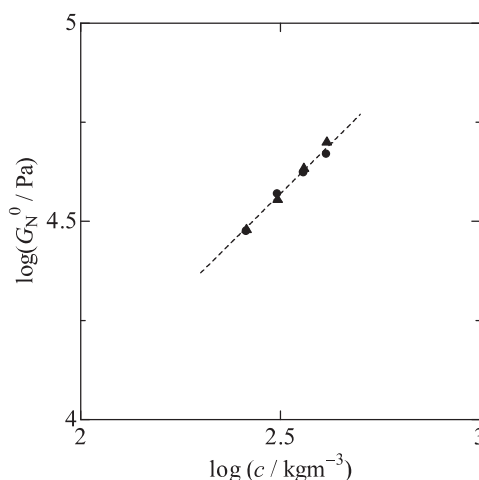


Fig. 5 Double-logarithmic plot of G_N^0 against c for dextran in the solutions of $c = 2.6 \times 10^2 - 4.1 \times 10^2 \text{ kgm}^{-3}$. The broken line is the best fit one with a slope of unity.

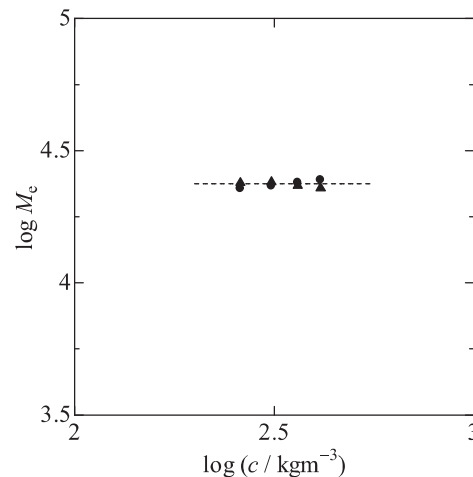


Fig. 6 Double-logarithmic plot of M_e against c for dextran in the solutions of $c = 2.6 \times 10^2 - 4.1 \times 10^2 \text{ kgm}^{-3}$. The broken line is the best fit one with a slope of zero.

polystyrene dendrimer, the terminal flow behavior seems different from each other. For the dendritically-branched polystyrene, it has been claimed that there appears an inflection point of the relaxation curves in the flow region perhaps due to structural relaxation associated with whole particle movement of polymers²⁰). Similar terminal slow relaxation has been reported for star polymers with large number of short arms, whose behavior is analogous to colloids¹⁶). As for our dextran, however, no such inflection nor slow relaxation can be found in the flow region, as demonstrated in Fig. 1. It is also known regarding star polymers that a group of stars which have small number of arms or very long arms show terminal dynamics mainly controlled by the arm relaxation¹⁶). The terminal relaxation behavior of our dextran seems similar to the latter case of star polymers. Accordingly, it might be possible to propose that the dextran consists of long branches as a whole and each branch has a highly sub-branched structure.

4. CONCLUSION

Dynamic viscoelasticity of concentrated solutions of high molecular weight dextran in BmimAc has been examined. It has been revealed that the rubbery plateau is not so obvious in the master curves of G' and G'' even at the highest concentration of $4.1 \times 10^2 \text{ kgm}^{-3}$. Differing from the ordinary rheological behavior of concentrated solutions of linear polymers, $G_N^0 \propto c$ and $M_e \propto c^0$ relations have been obtained with respect to the chain entanglement. A long-branched plus densely-sub-branched structure of dextran chain could explain the anomalous rheological behavior.

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REFERENCES

- Rankin JC, Jeanes A, *J Am Chem Soc*, **76**, 4435 (1954).
- Dimler RJ, Wolff IA, Sloan JW, Rist CE, *J Am Chem Soc*, **77**, 6568 (1955).
- Liamas-Arriba MG *et al.*, *Food Hydrocolloids*, **89**, 613 (2019).
- Garg SK, Stivala SS, *J Polym Sci Polym Phys Ed*, **16**, 1419 (1978).
- Wales M, Marshall PA, Weissberg SG, *J Polym Sci*, **10**, 229 (1953).
- Wales M, Marshall PA, Rothman S, Weissberg SG, *J Polym Sci*, **10**, 353 (1953).
- Senti FR *et al.*, *J Polym Sci*, **17**, 527 (1955).
- Basedow AM, Ebert KH, *J Polym Sci Polym Sympo*, **66**, 101 (1979).
- Antonioni E, Buitrago CF, Tsianou M, Alexandridis P, *Carbohydr Polym*, **79**, 380 (2010).
- Sabatie J, Choplin L, Moan M, Doublier JL, Paul F, Monsan P, *Carbohydr Polym*, **9**, 87 (1988).
- Sabatie J, Choplin L, Doublier JL, Arul J, Paul F, Monsan P, *Carbohydr Polym*, **9**, 287 (1988).
- Tirtaatmadja V, Dunstan DE, Boger DV, *J Non-Newtonian Fluid Mech*, **97**, 295 (2001).
- Graessley WW, *Am Chem Res*, **10**, 332 (1977).
- Ohta Y, Masuda T, Onogi S, *Polym J*, **18**, 337 (1986).
- Fetters LJ, Kiss AD, Pearson DS, Quack GF, Vitus FJ, *Macromolecules*, **26**, 647 (1993).
- Pakula T, Vlassopoulos D, Fytas G, Roovers J, *Macromolecules*, **31**, 8931 (1998).
- Watanabe H, *Prog Polym Sci*, **24**, 1253 (1999) and references therein.
- Yamamoto T, Ohta Y, Takigawa T, Masuda T, *Nihon Reoroji Gakkaishi*, **30**, 129 (2002).
- Watanabe H, Matsumiya Y, Inoue T, *Macromolecules*, **35**, 2339 (2002).
- Dorgan JR, Knauss DM, Al-Muallem HA, Huang T, Vlassopoulos D, *Macromolecules*, **36**, 380 (2003).
- van Ruymbeke E, Orfanou K, Kapnistos M, Iatrou H, Pitsikalis M, Hadjichristidis N, Lohse DJ, Vlassopoulos D, *Macromolecules*, **40**, 5941 (2007).
- Horinaka J, Yasuda R, Takigawa T, *J Polym Sci B Polym Phys*, **49**, 961 (2011).
- Horinaka J, Urabayashi Y, Takigawa T, Ohmae M, *J Appl Polym Sci*, **130**, 2439 (2013).
- Horinaka J, Chen K, Takigawa T, *Rheologica Acta*, **57**, 51 (2018).
- Holmes LA, Kusamizu S, Osaki K, Ferry JD, *J Polym Sci A2*, **9**, 2009 (1971).
- Onogi S, Masuda T, Kitagawa K, *Macromolecules*, **3**, 109 (1970).
- Ferry JD, "Viscoelastic Properties of Polymers", 3rd ed, (1980), John Wiley & Sons Inc, NY.
- Doi M, Edwards SF, "The Theory of Polymer Dynamics", (1986), Clarendon, Oxford.
- Liu C, He J, van Ruymbeke E, Keunings R, Bailly C, *Polymer*, **47**, 4461 (2006).
- Bhattacharjee PK, Oberhauser JP, McKinley GH, Leal LG, Sridhar T, *Macromolecules*, **35**, 10131 (2002).
- Huang Q, Mednova O, Rasmussen HK, Alvarez NJ, Skov AL, Almdal K, Hassager O, *Macromolecules*, **46**, 5026 (2013).