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Linear Viscoelasticity of Polystyrene Solution Having a Wide Molar Mass Distribution around the Coil Overlap Concentration

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Linear viscoelastic behavior for solutions of polystyrene (PS) having broad molar mass distribution (MMD) in tricresyl phosphate (TCP), which is a good solvent, was investigated at concentrations, c , around the coil-overlapping-concentration, c^* . GPC measurement indicated that molar mass distribution of sample was close to most probable distribution. Below c^* , the viscoelastic behavior was described well with the Rouse-Zimm (RZ) theory if considered molar mass distribution. On the other hand, at concentrations around the c^* , the viscoelastic behavior was not described by the RZ mode alone and the additional long-time (LT) modes were needed, similarly to the case of monodispersed molar mass distribution system. This implies that the LT modes are originated by the inter-molecular interaction. Compared with the monodispersed system, magnitude of the LT modes showed the same c dependence, being proportional to c^2 while the relaxation time of the LT mode showed a different c dependence. Owing to the broad MMD and the LT term, the viscoelastic spectra have the broad terminal flow relaxation time distribution but still can be apparently fit with the Rouse-Zimm (RZ) theory, resulting that the apparent molar mass, M_w^{app} , is higher molar mass than the real molar mass depending at concentrations of $c > c^*$. At $c / c^* = 2.9$, M_w^{app} was estimated at 4.1 times larger than the true molar mass. By considering the LT terms, the molar mass can be estimated by fitting with the Rouse-Zimm (RZ) term.

Key Words: Linear viscoelasticity / Polystyrene / Semidilute solution / Molecular weight / Rouse-Zimm model

1. INTRODUCTION

Linear viscoelastic properties and molecular dynamics of polymeric systems have long been studied by many researches.¹⁻³⁾ However, most of the rheological studies concern the solutions in dilute regime or well entangled regime. Systematic studies around the coil-overlapping concentration are quite limited.⁴⁻⁶⁾

Linear viscoelastic properties of dilute polymer solutions were well described by the bead-spring model.¹⁾ The earliest and basic theory using the bead-spring model is called as the Rouse theory⁷⁾, which ignore hydrodynamic interaction between beads. The Zimm theory considers the hydrodynamic interaction.⁸⁾ According to these theories, the complex modulus, G^* , which is expressed by the storage modulus, G' , and the loss modulus, G'' , is represented as a function of angular frequency, ω :

$$G^* = G' + iG'' = \frac{cRT}{M} \sum_{p=1}^N \frac{i\omega\tau_p}{1 + i\omega\tau_p} + i\omega\eta_s \quad (1)$$

$$\tau_p = \frac{\tau_{\text{RZ}}}{p^k} \quad (2)$$

were, c is the polymer concentration, R gas constant, T temperature, M the molar mass and η_s the solvent viscosity. The relaxation time, τ_p , is the Rouse-Zimm relaxation time of the p -th normal mode with τ_{RZ} the longest Rouse-Zimm relaxation time. G^* represented by eqs 1 and 2 shows the power-law behavior with an exponent of $1/k$ in $\omega \geq \tau_{\text{RZ}}^{-1}$ region. The exponent, k , is the parameter determined by the hydrodynamic interaction. For the case of θ condition, $k = 2$ corresponds to the free-draining limit (the Rouse model) while $k = 1.5$ does to the non-free-draining limit (Zimm model). The Zimm theory successfully describes the limiting behavior of polymers in θ solvents in the infinite dilution.¹⁾

In good solvents, the exclude volume effect should be considered. Experimentally, G^* data in the infinite dilution limit can be fitted with eqs. 1 and 2 with appropriate choice

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of value of k . However, both the Rouse and Zimm models assume the Gaussian chain statistics, and therefore both of them is not adequate to apply to good solvent systems, where the chain statistics cannot be represented by Gaussian statistics due to the excluded volume effect. Later Doi and Edwards successfully explained the viscoelastic behavior of linear polymers in good solvents with the scaling theory considering the excluded volume potential.⁹⁾ This theory gave a scaling relation to connect the relaxation property with intrinsic viscosity – molar mass.

In dilute regime with finite concentration, the viscoelastic behavior is modified from the limiting behavior in the infinite dilution. This is because the inter-chain interaction affects the molecular chain dynamics. Such interactions result in the screening of the excluded volume effect and the hydrodynamic interaction. As a result, dynamic modulus approaches to Rouse-like behavior. As for the effect of finite concentration, Muthukumar and Freed theoretically considered the effect of hydrodynamic screening.¹⁰⁾ Osaki et al. studied viscoelastic behaviors of the flexible polymer in the good solvent at finite concentration experimentally. According to them, when the concentration is close to the overlap concentration, c^* , the complex modulus can be described by the sum of Rouse-Zimm (RZ) term and an additional term (called as long-time (LT) term). The LT term was considered that corresponds to the mode of interaction of constraint among polymer chain coils. At the more concentrated regions, the interaction is represented entanglement among polymer chains. However, the concentration dependence of the relaxation time of the LT term was different from those for the entangled system. Marrucci et al. attributed to the LT term to anisotropic diffusivity which mimics the effect of topological interactions arising in polymeric solutions in the vicinity of the overlap concentration.⁶⁾

In the previous study, the LT mode was studied for only monodispersed molar mass polymer in the good solvent. In the θ solvent systems, the similar LT mode was observed. However, the details of the LT mode were not brought out for various systems. Therefore, in order to understand the viscoelastic behavior at the finite concentration, various systems should be examined. In this study, we consider the effect broad molar mass distribution (MMD) on linear viscoelasticity in finite concentration regime. The concentration dependence of the LT mode was compared with one of the system having monodispersed molar mass distribution. We will show that the LT mode might have the broad relaxation time distribution for polymers having broad MMD,

2. EXPERIMENTAL

2.1 Materials

Measurements were carried out for polystyrene (PS) solutions in tricresyl phosphate (TCP). PS with broad MMD, Toporex GP550-51, was supplied from Mitsui Toatsu Chemicals Co., Ltd. The molar mass was characterized by a measurement of gel permeation chromatography (GPC). The result is shown by the mass-fraction, w_M , in Figure 1. The weight-average molar mass, M_w , was $2.46 \times 10^5 \text{ g mol}^{-1}$ and the number-average molar mass, M_n , was $1.28 \times 10^5 \text{ g mol}^{-1}$. According to Figure 1, MMD resembles the most probable distribution ($M_w / M_n = 2$). TCP is a good solvent for PS. PS and TCP were homogeneously mixed with the addition of dichloromethane, and the latter was removed completely at 353 K and lower pressure. The test solutions having various PS concentration, c , are described in Table I.

The specific viscosity of polymers with broad MMD in various solvents can be expressed by a universal function of

Fig. 1. The mass-fraction plotted against molar mass for the PS sample measured by GPC. The fitting curve was represented the summation of two terms of most probable distribution functions. As a comparison, a most probable distribution function at $M_n = 1.28 \times 10^5 \text{ g mol}^{-1}$ was displayed.

Table I. Sample codes, concentrations, viscoelastic parameters and the apparent molar masses at 283 K.

Sample Code	$c/\text{g cm}^{-3}$	$10^2 \eta_{RZ}/\text{s}$	$10^2 G_{LT}/\text{Pa}$	$10^2 \eta_{LT}/\text{s}$	$10^{-5} M_w^{\text{app}}/\text{g mol}^{-1}$
PS/TCP-28	0.28	120	83	2000	—
PS/TCP-14	0.14	3.5	16	25	10
PS/TCP-10	0.10	1.0	75	6.0	7.7
PS/TCP-7	0.070	0.54	4.0	2.0	5.4
PS/TCP-4	0.040	0.36	1.5	0.60	4.2
PS/TCP-3	0.030	0.33	1.0	0.17	2.8
PS/TCP-2	0.020	0.27	—	—	2.5

$c[\eta]$.^{11,12)} Here, $[\eta]$ is the intrinsic viscosity. Considering these experimental results and Einstein's viscosity equation, we defined coil-overlapping concentration, c^* , as $c^* = 2.5 / [\eta]$ in this study. $[\eta]$ for the present PS sample was estimated with the Mark-Houwink-Sakurada equation determined for the PS/TCP system.¹³⁾

$$[\eta] = KM_v^\alpha = 7.2 \times 10^{-3} M_v^{0.72} \quad (3)$$

The viscosity-average molar mass, M_v , for the present sample was determined to be $2.22 \times 10^5 \text{ g mol}^{-1}$ with GPC data by using the relationship, $M_v = (\sum N_i M_i^{\alpha+1} / \sum N_i M_i) / \alpha$ with the value of $\alpha = 0.72$ in eq. 3. Here, N_i and M_i represent the number and molar mass of the i th polymer respectively. The determined c^* was 0.049 g cm^{-3} for the present PS sample.

2.2 Measurements

Standard rheometers (ARES and ARES-G2; TA instrument) was used for all the rheological measurements. Parallel plate fixtures with 25 mm and 8 mm diameter were employed. Complex shear modulus was measured at isothermal conditions in the temperature range from 223 to 343 K and the data were reduced to a reference temperature, 283 K. In order to obtain the composite curve, the horizontal shift factor, a_T , was determined by comparison of loss tangent, $\tan \delta = G'' / G'$, at various temperature. For construction of composite curves for G' and G'' , a small vertical shift factor, b_T , being proportional to the absolute temperature, T , was used. Temperature dependence of density of solution, $(d\rho/dT) / \rho \sim 10^{-4}$ was ignored for calculation of b_T .

3. RESULTS AND DISCUSSION

3.1 Complex Modulus

Figure 2 displays the composite curve of complex modulus for PS/TCP-2. The high frequency region corresponds to the glass-to-rubber transition zone and the low frequency region does to the terminal flow region which is characterized with $G' \sim \omega^2$ and $G'' \sim \omega$. In the frequency region of $4 < \log(\omega a_T / \text{s}^{-1}) < 7$, a power-law behavior as expressed below was observed for G' .

$$G' = a\omega^{1/2} \quad (4)$$

Here, the parameter a is a constant depending on temperature. The same power-law was anticipated for G'' around $\log(\omega a_T / \text{s}^{-1}) = 3$. However, this power-law region was not clear because G'' involves large contribution of solvent viscosity, $\sim \eta\omega$. Since the solvent is a glass forming material, the solvent contribution to modulus can be described with the glassy modulus, G_G^* .

$$G^* = G_p^* + G_G^* \quad (5)$$

Here, G_p^* is polymer component. For $\log(\omega a_T / \text{s}^{-1}) < 8$, the glassy modulus may be simplified as follows.

$$G_G^* = G'_G + iG''_G = m\omega^2 + in\omega \quad (6)$$

Here, the values of $m / \text{Pas}^2 = 1.40 \times 10^{-10}$ and $n / \text{Pas} = 1.86 \times 10^{-1}$ were applied. The value of n is close to the value of the viscosity of TCP, η_s . However, these values have slight disagreement, because the solvent dynamics is modified by the PS chain.

As the case of solution having the lowest concentration ($c = 0.020 \text{ g cm}^{-3}$), G_p^* at frequencies $\log(\omega a_T / \text{s}^{-1}) < 2.5$ could be described with the RZ theory. The RZ term, G_{RZ}^* , is described with the following equation.

$$G_{RZ}^* = G'_{RZ} + iG''_{RZ} = \sum_{M=0}^{\infty} \left(x_M \frac{cRT}{M} \sum_{p=1}^N \frac{i\omega\tau_p}{1 + i\omega\tau_p} \right) \quad (7)$$

Here, x_M is the molar fraction having molar mass, M . x_M is determined by the fitting curve in Figure 1. The fitting parameters are k , N , and τ_{RZ} . The value of N differs depending on the value of M as $N = M / M_s$. Here, M_s is the molar mass of the viscoelastic segment.¹⁴⁻¹⁷⁾ According to the study of PS solutions, M_s were estimated at $5000 - 8000 \text{ g mol}^{-1}$. We applied $M_s = 5000 \text{ g mol}^{-1}$. τ_{RZ} was determined by the fitting at the power-law region with the horizontal shift. For the value of a power, $k = 2$ was applied because a good fit was attained at power-law region for the all concentrations. According

Fig. 2. The squares represent complex modulus for PS/TCP-2 at 283 K. The filled marks represent G' and the unfilled marks represent G'' . The circles represent G_p^* , which is estimated by eq. 6. The solid and dashed lines represent G_p^* , which was calculated by eq. 7.

to the theory of Doi and Edwards for dilute solutions, in the infinite dilution limit, the value of k is related to the chain dimension exponent, α . Using this value, we obtain $k = 0.72 + 1 = 1.72$. However, for $c \geq 0.020 \text{ g cm}^{-3}$, $k = 2$ gave a better fitting result. The resulting fitting curves are shown in Figure 2. This indicates that the hydrodynamic interaction was screened for the system of $c \geq 0.020 \text{ g cm}^{-3}$. We note that the additional low mode was not necessary for 0.020 g cm^{-3} solution. Thus we conclude that for solution $c \geq 0.020 \text{ g cm}^{-3}$, G^* can be quantitatively described with the Rouse theory and the glassy solvent contribution.

3.2 Complex Modulus at Finite Concentration

Figure 3 compares the storage modulus G' for PS/TCP solution at various c . Here, the complex modulus was reduced with c . Furthermore, the spectra were shifted x times along horizontal axes as based PS/TCP-4 in order to reduce to the iso-frictional state. This means the proportional coefficient, a/c , in eq. 4 was reduced to same value. In the Rouse theory, the value of a is related to the longest Rouse relaxation time, τ_R .

$$a = \frac{1.11cRT}{M} \tau_R^{1/2} \quad (8)$$

$$\tau_R = \frac{b^2 N^2 \zeta}{6\pi k_B T} \quad (9)$$

Here, b , N , ζ , and k_B are the end-to-end distance of subchain, the number of subchain per polymer chain, the friction coefficient of subchain, and Boltzmann constant, respectively.

Fig. 3. Reduced storage modulus, $G' b_T^{-1} c^{-1}$, plotted against the reduced angular frequency at 283 K. The frequency axis was reduced by the shift factor, x , for iso-frictional state. The fitting curve represent the RZ term. Here, $10^{-3} \text{ m}^2 \text{ s}^{-2} = \text{Pa g}^{-1} \text{ cm}^{-3}$.

Thus, with this reduction, all the solution has the same value of the Rouse relaxation time.

As shown in Figure 3, at low concentrations ($c \leq 0.030 \text{ g cm}^{-3}$), the terminal relaxation times are independent of c . On the other hand, at $c \geq 0.040 \text{ g cm}^{-3}$, the solutions show additional relaxation modes at low frequencies. These additional modes would be correspond to the LT term reported in the previous study for PS solution having narrow molar mass distribution. In the following we estimate the LT term by subtracting the RZ term from the experimental data. As shown in Figure 2, at high frequencies the glassy modulus was observed. For the precise estimation of the LT term, we also subtracted the glassy contribution. In the following section, we discuss the LT term.

3.3 The LT Term

As explained earlier, at finite concentrations $c \geq 0.030 \text{ g cm}^{-3}$, the LT term is necessary for describing the complex modulus. Figure 4 shows the LT component for PS/TCP-4. In the high frequency region, the fitting curve did not agree with the experimental result. This is because the reduction of the glassy component was not appropriate strictly. However, the behavior in the high frequency region does not affect the LT mode because the behavior in the high frequency region reflects the local mode of the polymer and the solvent. Therefore, the disagreement in the high frequency region is negligible in this study. On the other hand, the disagreement in the terminal relaxation region is significant. This disagreement

Fig. 4. Circles represent G^* subtracted the glassy mode. Lines represent the RZ term, which was fitted with $G^* - G_G^*$ at the power law region. Squares represent the LT term, which was calculated by $G_{LT}^* = G^* - G_G^* - G_{RZ}^*$.

indicates the existence of the long time mode. The LT mode was estimated by subtraction G_{RZ}^* from $G^* - G_{\text{G}}^*$. At $c = 0.020 \text{ g cm}^{-3}$, G_{LT}^* could be negligible because $G^* - G_{\text{G}}^*$ corresponded to G_{RZ}^* as seen in Figure 2 and 3. Figure 4 displays the LT mode for PS/TCP-4. In the case of the system having monodispersed molar mass distribution, the LT term is expressed by a single Maxwell model. However, the LT term in this study was expressed a broad relaxation mode. Furthermore, the higher concentration system had the broader LT mode. This is because of the broad MMD of PS. The relaxation modulus, G_{LT} , and the relaxation time, τ_{LT} , of the LT mode was defined as displayed in Figure 4.

3.4 The Concentration Dependence of the LT Term

The concentration dependence of the characteristic parameters, G_{LT} and τ_{LT} for the LT term was shown in Figure 5. Here, a reduced modulus, $G_{\text{LT}}M_w / cRT$, and a reduced relaxation time, $\tau_{\text{LT}} / \tau_{\text{RZ}}$, are plotted against a reduced concentration, c / c^* . In Figure 5, the solid and dashed lines represented approximated curves for $G_{\text{LT}}M_w / cRT$ (eq 9) and $\tau_{\text{LT}} / \tau_{\text{RZ}}$ (eq 10) respectively.

$$\frac{G_{\text{LT}}M_w}{cRT} = 0.50 \frac{c}{c^*} \quad (10)$$

$$\frac{\tau_{\text{LT}}}{\tau_{\text{RZ}}} = 2.2 \left(\frac{c}{c^*} \right)^{1.2} \quad (11)$$

For the LT term, the modulus was proportional to c^2 so that the term vanished faster than the RZ term as the concentration

Fig. 5. The concentration dependence of the parameters for the LT term. A reduced modulus, $G_{\text{LT}}M_w / cRT$ (circles), and a reduced relaxation time, $\tau_{\text{LT}} / \tau_{\text{RZ}}$ (squares), are plotted against the a reduced concentration, c / c^* .

decreased. This behavior was observed in the previous report. Here, to be scaled with the exponent of 2 indicated that the term originated in the intermolecular interaction. This behavior denoted the same tendency of the entanglement of polymers. The coefficient, 0.50, in this result was about two times larger than the result for the system having monodispersed molar mass. If M_n was applied for eq 10 instead of M_w , the coefficient was nearly equal. This indicates the modulus of the LT term can be reduced the molar-fraction.

For the relaxation time of the LT term, the concentration dependence of $\tau_{\text{LT}} / \tau_{\text{RZ}}$ was different from the system having monodispersed molar mass. In the monodispersed molar mass system, τ_{LT} was 4 – 5 times longer than τ_{RZ} independently of the concentration and molar mass. On the other hand, in the broad MMD system, τ_{LT} was proportional to $c^{1.2}$ in the iso-frictional state. For entangled polymer solutions, the concentration dependence of the relaxation time is proportional to $c^{3.4}$ at $c \leq 0.1 \text{ g cm}^{-3}$ in the iso-frictional state. Although the c dependence of τ_{LT} was not stronger than those of entangled systems, this dependence indicates that the LT term was not contributed by only the constraint or friction among polymer chain coils but also the entanglement-like interaction among polymer chains. In other words, when the sample had the broad MMD, long chains developed the intermolecular interaction similar to entanglement.

3.5 The Appearance Molar mass, M_w^{app}

As shown earlier, for the MMD systems, the LT modes had the broad relaxation time distribution compared with the monodispersed molar mass system. This means that if the LT modes are not considered then the Rouse-Zimm fitting at finite concentration regime gave an apparently higher molar mass than the real molar mass. In order to discuss this more quantitatively, we fit data with only the Rouse-Zimm term and estimated apparent molar mass, M_w^{app} , for solutions having $c/\text{g cm}^{-3} < 0.14$. Figure 6 displays an example of fitting with the RZ term. We note that the data at $c/\text{g cm}^{-3} < 0.14$ are well described with only the Rouse-Zimm term if the most probable molar mass distribution is assumed.

In Figure 7, the concentration dependence of M_w^{app} was depicted. Figure 7 clearly shows that if the LT term was ignored, then the higher molar mass was obtained. At $c / c^* = 2.9$, the molar mass was estimated at 4.1 times larger than the molar mass determined by GPC. Thus for semi-dilute solution of $c / c^* > 1$, the LT term should be considered to estimate the molar mass from viscoelastic data.

Fig. 6. The result of the fitting for $G^* - G_G^*$ with the only RZ term having the appearance molar mass. G_{RZ}^* was calculated by eq 7.

Fig. 7. The concentration dependence of the appearance molar mass, M_w^{app} . M_w^{app} was reduced the real molar mass.

4. CONCLUSION

For PS/TCP solutions, the viscoelastic behavior was investigated at concentrations around the coil-overlapping-concentration. We used PS having a broad MMD as a sample. At $c = 0.02 \text{ g cm}^{-3}$, the viscoelastic behavior described by the Rouse-Zimm theory. However, at higher concentrations ($c \geq 0.03 \text{ g cm}^{-3}$), the intermolecular interaction mode could not be negligible in the long time region. This appearance of the LT mode had reported for the monodispersed molar mass PS in TCP yet. The concentration dependence of the modulus, G_{LT} , was consistent with the previous report, which was proportional to c^2 . On the other hand, the different concentration dependence was observed for the relaxation time of the LT mode, τ_{LT} . When the MMD was

broad, this dependence described as $\tau_{LT} \sim c^{1.2}$. This indicated the intermolecular interaction could be described by the entanglement-like behavior.

Because the LT mode had broad relaxation time distribution for the broad MMD, the viscoelastic spectra have broad terminal flow relaxation time distribution. Therefore, it seems that the viscoelastic spectrum have higher molar mass than the real molar mass. The apparent molar mass, M_w^{app} , was estimated by the fitting with the G_{RZ}^* . At $c / c^* = 2.9$, the molar mass was estimated at 4.1 times larger than the real molar mass. At the finite concentration region, when the molar mass is estimated by linear viscoelastic measurement, the LT term should be considered.

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