

Determination of Molecular Weight and its Distribution of Flexible Chain Polymer by Phase-Modulated Flow Birefringence Technique

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(Received 6 March 2001 • accepted 26 July 2001)

Abstract—The objective of this study is to develop a systematic method to determine molecular weight and its distribution of flexible chain polymer by birefringence experiments. Using the random walk model, birefringence Δn and orientation angle χ have been optically obtained as functions of molecular weights. To confirm the theory, polystyrene solutions with different molecular weights dissolved in polychlorinated biphenyl were experimented by the phase-modulated flow birefringence (PMFB) method. Birefringence of polystyrene solutions is proportional to $(\sum c_i M_i^{1/6})^2$, and $\cot(2\chi)$ to $(\sum c_i M_i^{1/6} / B_1 \sum c_i M_i^{-0.2})^2$. The experimental results agreed well with the theoretical predictions proposed in this study.

Key words: Flexible Chain Polymer, Polystyrene, Birefringence, Orientation Angle, Molecular Weight

INTRODUCTION

Molecular weight (MW) and its distribution (MWD) of polymers have a considerable effect on macroscopic properties of polymer, such as toughness, tensile strength, adherence and environmental resistance, etc. [Nunes et al., 1982]. There are various techniques for measuring MW, such as membrane osmometry, light scattering, ultra-centrifugation, etc., but the measurement of MWD is somewhat restricted. One of the more popular measurement techniques for MWD is gel permeation chromatography (GPC) and other is the dynamic modulus measurement which was proposed by Wu in order to measure MWD of insoluble polymers [Wu, 1985; McGroarty and Tuminello, 1990]. To investigate the conformation of flexible polymer chain, several polymer models can be considered. For instance, if one considers the flexible polymer model dissolved in θ solvent, the relationship between the polymer size represented by end-to-end distance and molecular weight can be obtained along with the ideal molecular models. For the examination of the polymer conformation in transparent polymer solutions, two optical functions of birefringence and orientation angle are often used as effective experimental means [Frattoni and Fuller, 1984]. These two functions could be also usefully applied for polymer characterization in polymer film processes [Park et al., 2001]. In order to predict the birefringence and orientation angle of polymer solutions, theory relating refractive index, which is a macroscopic property, with microscopic properties such as polarizability or molecular conformation is necessary. Park has obtained analytic expressions of rheo-optical properties given as function of shear rate in weak flow fields [Park, 1989], and Kwon showed that experimental results on the rheo-optical properties according to shear rate have agreed well with the previous analytic ones [Kwon et al., 1999]. A method determining molecular weight and its distribution from optical experi-

ments has been already reported in the previous work [Oh et al., 2000], where a rigid rod-like polymer was studied.

The polarimetry technique is one of the typical rheo-optical measurements which is popular for polymer solutions. This method is to measure the shape of polarized light through the sample. In reality, the change in light intensity caused by the modulated polarized light is measured rather than the shape of polarized light itself. In this study, as in previous works, birefringence and orientation angle were measured by the phase-modulated flow birefringence (PMFB) method [Frattoni and Fuller, 1984; Oh and Park, 1992]. PMFB method, which is one of polarimetry methods, has many merits compared with the conventional ones. It is possible to obtain quite precise and accurate experimental results within a relatively short experimental time. It is also possible to adopt this method in order to characterize polymers with different chain structures.

It is well known that MW and MWD of polymers have strong impact on physical or rheological properties of polymers. Therefore, prediction of molecular weight and its distribution of polymer is important in fields of polymer processing. We have successfully examined bimodally dispersed polymer solutions by the flow birefringence and orientation angle measurements [Oh and Park, 1992]. It was based on the fact that when the flow is removed from the flowing solution its relaxation of the orientation would mainly depend on the length of rigid polymer, i.e., the molecular weight. In order to analyze multi-modal or polydisperse distribution, a more generalized molecular model is necessary in the first place. In this study we adopt an ideal molecular model for the flexible polymer chain and investigate the rheo-optical properties as functions of its molecular weight and distribution based on this model.

THEORY

For the prediction of optical properties of a polymer solution, microscopic properties such as molecular polarizability and conformation should be considered. Many polymers can be treated as

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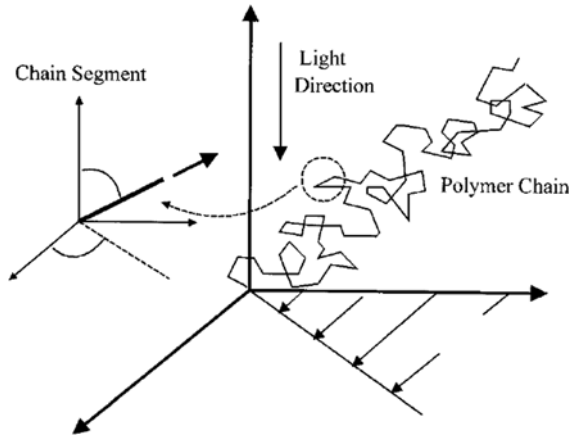


Fig. 1. Kuhn-Grun model of a flexible polymer chain. In a laboratory frame, light is transmitted perpendicularly to the shear flow field through a polymer solution.

a flexible polymer chain but they exhibit more complex circumstances than the rigid rod polymers do. Janeschitz-Kriegl [1969] proposed a model to examine the optical anisotropy of a flexible polymer chain, which is pictured in Fig. 1. A flexible polymer chain is modeled as a sequence of N segments that are attached through freely rotating joints. Each segment has a length a . When the incident light is traversing along the z axis, each segment can be taken to have a uniaxial polarizability, α_{ij}^s , of the following form in a frame coaxial with its principal directions.

$$\alpha_{ij}^s = \begin{bmatrix} \alpha_2 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_1 \end{bmatrix} = \begin{bmatrix} \alpha_a & 0 & 0 \\ 0 & \alpha_a & 0 \\ 0 & 0 & \alpha_z \end{bmatrix} + \frac{1}{3} \Delta \alpha E_{ij}, \quad (1)$$

where α_a , $\Delta \alpha$ and E_{ij} are as follows.

$$\begin{aligned} \alpha_a &= (2\alpha_2 + \alpha_1)/3, \\ \Delta \alpha &= \alpha_1 - \alpha_2, \\ \text{and } E_{ij} &= \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix}. \end{aligned} \quad (2)$$

Polarizability, α_{ij}^s , obtained in the frame of a polymer segment should be expressed in the laboratory frame. When the unit vector u_i of the principal direction of a segment is oriented at the polar and azimuthal angles θ , ϕ in the laboratory frame, as follows,

$$u_i = (s_\theta c_\phi, s_\theta s_\phi, c_\theta), \quad (3)$$

where the shorthand $s_\theta = \sin \theta$ and $c_\theta = \cos \theta$ are used, α_{ij}^s can be transformed into the polarizability tensor α_{ij}^L in the laboratory frame using a rotation tensor T_{ij} .

$$\begin{aligned} \alpha_{ij}^L &= T_{ki}^{-1} \alpha_{kl}^s T_{lj} = \begin{bmatrix} s_\phi & c_\phi c_\theta & s_\theta c_\theta \\ -c_\phi & c_\theta s_\phi & s_\theta s_\phi \\ 0 & -s_\theta & c_\theta \end{bmatrix} \cdot \begin{bmatrix} \alpha_2 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_1 \end{bmatrix} \cdot \begin{bmatrix} s_\phi & -c_\phi & 0 \\ c_\phi c_\theta & c_\theta s_\phi & -s_\theta \\ s_\theta c_\phi & s_\theta s_\phi & c_\theta \end{bmatrix} \\ &= \alpha_2 \delta_{ij} + \Delta \alpha \begin{bmatrix} s_\theta^2 c_\phi^2 & s_\theta^2 c_\phi s_\phi & c_\theta s_\theta c_\phi \\ s_\theta^2 c_\phi s_\phi & s_\theta^2 s_\phi^2 & c_\theta s_\theta s_\phi \\ c_\theta s_\theta c_\phi & c_\theta s_\theta s_\phi & c_\theta^2 \end{bmatrix} = \alpha_2 \delta_{ij} + \Delta \alpha (u_i u_j) \end{aligned} \quad (4)$$

In the above, δ_{ij} is Kronecker delta. Contribution of α_{ij}^L to the laboratory frame may be divided into the polarizabilities parallel, α_p , and perpendicular, α_r , to the z -axis of the light direction.

$$\alpha_p = \alpha_2 + \Delta \alpha c_\theta^2, \quad (5)$$

$$\alpha_r = \alpha_2 + \Delta \alpha s_\theta^2 c_\phi^2. \quad (6)$$

The polarizability of the entire chain is the summation of this polarizability over all the segments.

$$\langle \alpha_{ij} \rangle = N \alpha_2 I_{ij} + N \Delta \alpha \langle u_i u_j \rangle, \quad (7)$$

where the angular brackets $\langle \rangle$ represent the average over an orientation distribution function $\Psi(\theta, \phi; r)$, which describes the probability of a particular orientation of each segment. We use the following distribution function for the random walk model which Kuhn and Grun derived.

$$\Psi(\theta, \phi; R_e) = A \exp\left(\frac{3R_e}{Na} \cos \theta\right). \quad (8)$$

Here A is a normalization constant and R_e is the end-to-end distance of a polymer chain, given by

$$R_e = N \frac{\int_0^{2\pi} d\phi \int_0^\pi \Psi a \cos \theta \sin \theta d\theta}{\int_0^{2\pi} d\phi \int_0^\pi \Psi \sin \theta d\theta}. \quad (9)$$

R_e/Na is simply obtained in the form of Langevin function $L(k)$ defined as

$$R_e/Na = L(k) = \coth(k) - 1/k, \quad k = 3R_e/Na. \quad (10)$$

Use of the Kuhn and Grun's distribution function gives averaged contributions of polarizability, $\langle \alpha_p \rangle$ and $\langle \alpha_r \rangle$, for the entire chain.

$$\langle \alpha_p \rangle = N \alpha_2 + 2N \Delta \alpha \left(\frac{1}{3} - \frac{L(k)}{k} \right), \quad (11)$$

$$\langle \alpha_r \rangle = N \alpha_2 - N \Delta \alpha \left(\frac{1}{3} - \frac{L(k)}{k} \right).$$

When $3R_e/Na \ll 1$, Langevin function can be approximated as a polynomial by Taylor series expansion.

$$\frac{L(k)}{k} = \frac{1}{3} - \frac{1}{5} \left(\frac{R_e}{Na} \right)^2 + O\left(\left(\frac{R_e}{Na} \right)^4 \right). \quad (12)$$

Finally, using the above approximation, polarizability of the entire chain, $\Delta \gamma$, is given as follows.

$$\Delta \gamma = \langle \alpha_p \rangle - \langle \alpha_r \rangle = \frac{3}{5} N \Delta \alpha \left(\frac{R_e}{Na} \right)^2. \quad (13)$$

Optical properties of a polymer solution can be examined through two optical functions, birefringence Δn and orientation angle χ . Refractive index tensor n_{ij} in the frame of a polymer segment is expressed in the similar way as follows, corresponding to Eq. (1).

$$n_{ij} = n_a \delta_{ij} + \frac{1}{3} (n_1 - n_2) E_{ij}. \quad (14)$$

Here n_a is $(2n_2 + n_1)/3$ and n_1 , n_2 represent the refractive indices with respect to polymer axes x_1 and x_2 , respectively. A qualitative derivation of difference of refractive indices, $n_1 - n_2$, was given in the previous work, which was derived using the Lorentz-Lorenz formula

for the isotropic material.

$$n_1 - n_2 = \frac{2\pi(n_a^2 + 2)^2}{9n_a} c \Delta\gamma. \quad (15)$$

Refractive index tensor $\langle n_{ij} \rangle$ of the entire chain to the laboratory frame is given corresponding to Eq. (7).

$$\langle n_{ij} \rangle = N\alpha_i I_{ij} + N(n_1 - n_2) \langle u_i u_j \rangle. \quad (16)$$

Above refractive index tensor can be decomposed into components parallel and perpendicular to the plane normal to the light direction in a given system. When the light is traversing along z axis, the birefringence Δn , the difference in the eigenvalues of the real part of refractive index tensor and orientation angle χ , defined in the laboratory frame are given as follows:

$$\tan(2\chi) = \frac{2\langle u_x u_y \rangle}{\langle u_x^2 \rangle - \langle u_y^2 \rangle}, \quad (17)$$

$$\Delta n = (n_1 - n_2) [(\langle u_x^2 \rangle - \langle u_y^2 \rangle)^2 + 4\langle u_x u_y \rangle^2]^{1/2}. \quad (18)$$

Because average polarizabilities are determined from the end-to-end distance of a flexible polymer chain, it is necessary to analyze molecular weight and its distribution of a polymer. Δn and χ for the polydisperse solution are written into

$$\tan(2\chi) = \frac{2\sum c_i \Delta\gamma_i \langle u_x u_y \rangle_i}{\sum (c_i \Delta\gamma_i \langle u_x^2 \rangle_i - c_i \Delta\gamma_i \langle u_y^2 \rangle_i)}, \quad (19)$$

$$\Delta n = \frac{2\pi(n_a^2 + 2)^2}{9n_a} [\sum c_i \Delta\gamma_i (\langle u_x^2 \rangle - \langle u_y^2 \rangle)^2 + 4(\sum c_i \Delta\gamma_i \langle u_x u_y \rangle^2)]^{1/2} \quad (20)$$

Here i is a summation index for different polymer chain sizes and c_i the number of macromolecules per unit volume of polymer solution. By substituting the result of $\Delta\gamma$ of Eq. (13) into above equations, we finally obtain

$$\tan(2\chi) = \frac{2\sum (c_i/N_i) \langle R_x R_y \rangle_i}{\sum (c_i/N_i) (\langle R_x^2 \rangle_i - \langle R_y^2 \rangle_i)}, \quad (21)$$

$$\Delta n = \frac{2\pi(n_a^2 + 2)^2}{15a^2 n_a} \Delta\alpha [\sum (c_i/N_i) (\langle R_x^2 \rangle - \langle R_y^2 \rangle)^2 + 4(\sum (c_i/N_i) \langle R_x R_y \rangle^2)]^{1/2} \quad (22)$$

$R_x = R_e u_x$ and $R_y = R_e u_y$ are used instead of u_x and u_y . To obtain the expressions for $\langle R_x^2 \rangle - \langle R_y^2 \rangle$ and $\langle R_x R_y \rangle$, we consider two typical models for a flexible polymer. First one is the Rouse model [Zimm, 1956], in which N beads and $N-1$ springs are freely jointed. This model does not include either the excluded volume interaction or the hydrodynamic interaction.

$$\langle R_x^2 \rangle - \langle R_y^2 \rangle = 0.4\epsilon^2/\mu, \quad 2\langle R_x R_y \rangle = \epsilon/\mu. \quad (23)$$

$$\epsilon = M[\eta]\eta_0\gamma/RT, \quad \mu = (3/2)R^2. \quad (24)$$

Here M is molecular weight of a segment, $[\eta]$ and η_0 are the intrinsic viscosity and the solvent viscosity, and γ is the shear rate. R is the gas constant and T is the absolute temperature. If we adopt the Rouse-Zimm model in order to take into account the hydrodynamic interactions between segments, the results are

$$\langle R_x^2 \rangle - \langle R_y^2 \rangle = 0.2\epsilon^2/\mu, \quad 2\langle R_x R_y \rangle = \epsilon/\mu. \quad (25)$$

Detailed calculations for $\langle R_x^2 \rangle - \langle R_y^2 \rangle$ and $\langle R_x R_y \rangle$ are well explained in the paper of Peterlin [1963]. Eqs. (23) and (25) can be written into a general form,

$$\langle R_x^2 \rangle - \langle R_y^2 \rangle = p\epsilon^2/\mu, \quad 2\langle R_x R_y \rangle = \epsilon/\mu, \quad (26)$$

where p has a value between 0 and 1. Use of Eq. (26) gives $\tan(2\chi)$ and Δn expressed in terms of molecular weight and intrinsic viscosity.

$$\tan(2\chi) = \frac{RT \sum (c_i/N_i^2) M_i [\eta]_i}{p\eta_0 \sum (c_i/N_i^2) M_i^2 [\eta]_i^2} \gamma^{-1}, \quad (27)$$

$$\Delta n = \frac{4\pi(n_a^2 + 2)^2}{45RTn_a a^4} \Delta\alpha \left\{ \sum (c_i/N_i^2) M_i [\eta]_i^2 + \left[\frac{2p\eta_0 \gamma}{3RT} \sum (c_i/N_i^2) M_i^2 [\eta]_i^2 \right]^2 \right\}^{1/2} \gamma \quad (28)$$

The number of segments N and intrinsic viscosity $[\eta]$ are replaced by the following model equations, which are all the functions of the average molecular weight.

i) Rouse model,

$$[\eta] = N_a N^2 \zeta / 36M\eta_0. \quad (29)$$

ii) Rouse-Zimm model in the θ solvent,

$$[\eta] = 0.425N_a N^{3/2} a^3 / M. \quad (30)$$

iii) Rouse-Zimm model in the good solvent

$$[\eta] = N_a N^{1/2} a^3 / M. \quad (31)$$

By using the above equations of (29)-(31), $\tan(2\chi)$ and Δn are finally expressed in the following form.

$$\tan(2\chi) = B_1 \left[\frac{\sum (c_i M_i^d)}{\sum (c_i M_i^f)} \right] \gamma^{-1}, \quad (32)$$

$$\Delta n = B_2 [(\sum c_i M_i^g)^2 + (B_3 \sum c_i M_i^e)^2 \gamma^2]^{1/2} \gamma \quad (33)$$

Here B_1 , B_2 , B_3 , d , e , f , and g are adjustable parameters independent on molecular weight and are determined by the corresponding molecular model. These are given in Table 1.

Table 1. Adjustable parameters on birefringence and orientation angle in Eqs. (32) and (33)

	Rouse model	Rouse-Zimm model in the θ solvent	Rouse-Zimm model in the good solvent
B_1	$\frac{36RT}{pN_a a^2 \zeta}$	$2.35 \frac{RT}{p\eta_0 N_a a^3}$	$\frac{RT}{p\eta_0 N_a a^3}$
B_2	$\frac{\pi(n_a^2 + 2)^2 \Delta\alpha N_a \zeta}{405RTn_a a^2 \eta_0}$	$0.119 \frac{(n_a^2 + 2)^2 \Delta\alpha N_a}{RTn_a a}$	$\frac{4\pi(n_a^2 + 2)^2 \Delta\alpha N_a}{45RTn_a a}$
B_3	$\frac{pN_a a^2 \zeta}{54RT}$	$0.283 \frac{p\eta_0 N_a a^3}{RT}$	$0.283 \frac{p\eta_0 N_a a^3}{RT}$
d	0	-0.5	-0.2
e	2	1	1.6
f	0	-0.5	-0.2
g	2	1	1.6

Table 2. Code name of polystyrene solutions used in this study

M.W.	Weight concentration	
	500 ppm	1,000 ppm
(1) 20,000,000	PS1L	PS1H
(2) 7,600,000	PS2L	PS2H
(1)+(2)	PSCL	PSCH

EXPERIMENTAL

To measure birefringence and orientation angle of polymer solutions, phase-modulated flow birefringence (PMFB) experiments were performed. The PMFB method has been proven to be a valuable tool for evaluating molecular models of polymer solutions in well-defined flow fields. This technique is capable of measuring both the flow-induced birefringence and average orientation angle simultaneously, which has been reported in detail for the bimodal polymer solutions in a previous paper by Oh and Park [2000]. A flow cell of coaxial cylinders was used in the experiments to make a stable shear flow.

Polymer solutions used in PMFB experiments have some general restrictions. To avoid light scattering, the polymer size should be smaller than the wavelength of the light source. Polymer solutions should be clear to neglect any dichroism and have little or no form birefringence due to the difference in refractive indices between polymer and solvent. Polystyrene (Polysciences, Inc.) is selected as a model of the flexible polymer chain which can be dissolved in polychlorinated biphenyl (PCB). They possess very small polydispersity indices less than about 1.1 that they could be considered as monodisperse ones. Since PCB has a high viscosity, a stable shear flow field is easily obtained in case of the dilute polymer solutions. All experiments were performed at room temperature of about 20 °C. Sample solutions used in this study are summarized in Table 2. Especially, sample solutions were carefully weighed in order to minimize any errors in the analysis.

RESULTS AND DISCUSSION

In the theory, two optical functions, birefringence Δn and orientation angle χ , have been expressed in terms of molecular weight and its distribution. Using these results, birefringence and orientation angle obtained from PMFB experiments were examined on the shear flow field, with various concentrations and polymer molecular weights.

Fig. 2 shows the shear rate dependence of birefringence of polystyrene solutions. PMFB experiments are often experimented in dilute solutions in order to exclude the hydrodynamic interactions in concentrated solutions. In the experiments of Fig. 2, polystyrenes were dissolved in PCB at concentrations of 500 and 1,000 ppm (Sample Code Names, PS1L and PS1H). Birefringence is proportional to square shear rate, $\dot{\gamma}^2$ up to the strength of 200 sec⁻¹ experimented. Two series of birefringence curves with different concentrations coincide with each other if Δn is normalized with its concentration. This proportionality of birefringence to the concentration means that these concentrations are in the limit of hydrodynamically dilute regime.

March, 2002

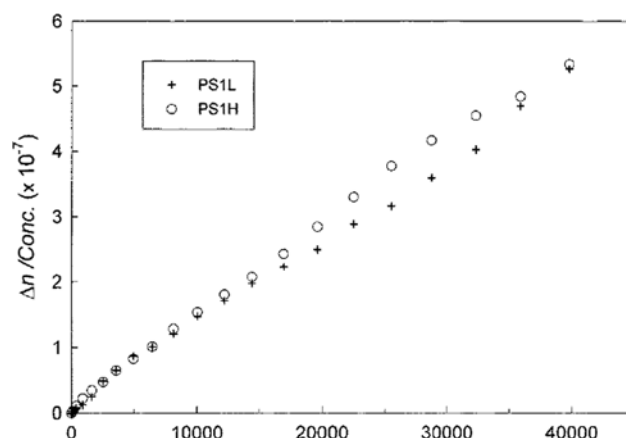


Fig. 2. Steady state flow birefringence plotted as a function of the square of shear rate, $\dot{\gamma}^2$, for polystyrene solutions of different concentrations (MW=20×10⁶; ● for PS1L and ○ for PS1H).

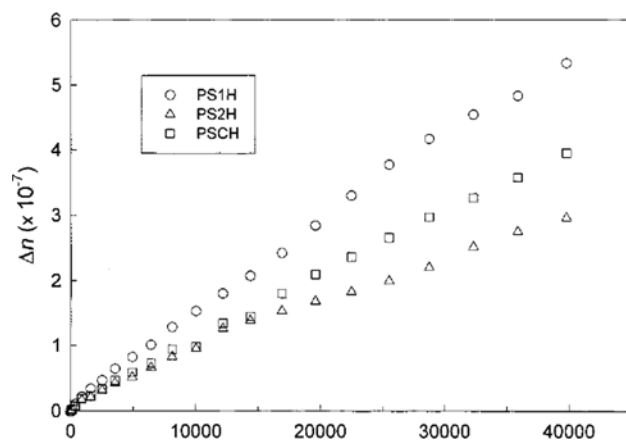


Fig. 3. Molecular weight dependences of birefringence for polystyrene solutions with different Molecular weights (○ for PS1H of MW=20×10⁶, △ for PS2H of MW=7.6×10⁶, and ◇ for PSCH of equal weight ratio of PS1H and PS2H).

Effects of molecular weight on Δn are shown in Fig. 3. Solutions PS1H and PS2H, which have polydispersities less than about 1.1, can be assumed to be monodisperse. Solution PSCH stands for a sample mixed with PS1H and PS2H by the weight ratio of 1 : 1. Solution PSCH was prepared to examine the bimodal system. In all cases, birefringence is in proportion to $\dot{\gamma}^2$.

Theoretical expression on birefringence obtained by using the Rouse-Zimm model in the good solvent is now considered. From the experimental results of birefringence proportional to $\dot{\gamma}^2$, it can be said that $\sum c_i M_i^{0.2} \ll B_3 \sum (c_i M_i^{1.6})^2 \dot{\gamma}^2$ in Eq. (33). Thus it may be simplified as follows.

$$\Delta n \propto (\sum c_i M_i^{1.6}) \dot{\gamma}^2 \quad (34)$$

In analyses of effects of molecular weight on Δn , it is convenient to replace the number concentration c by the weight concentration C . Eq. (34) can be rewritten by expressing $\sum C_i M_i^{1.6}$ as $\overline{M}^{1.6}$. Then Eq. (33) becomes

$$\Delta n = B_2 B_3^{1/2} \overline{M}^{1.6} \dot{\gamma}^2 \quad (35)$$

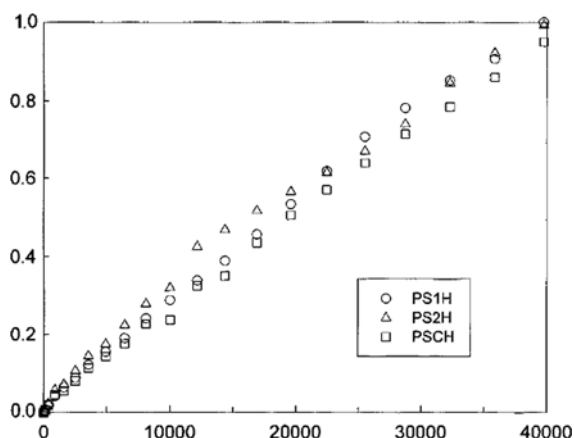


Fig. 4. Plot of $\Delta n/M^{1.6}$ normalized by a maximum value of experimented PS1H data.

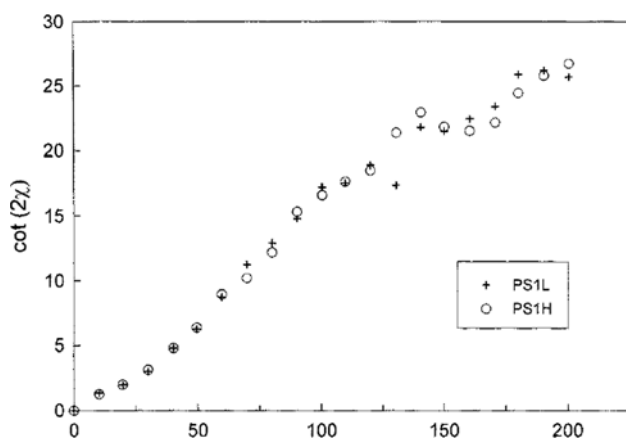


Fig. 5. $\cot(2\chi)$ versus shear rate γ for polystyrene solutions of MW $=20 \times 10^6$ at different concentrations (● for PS1L and ○ for PS1H).

$\Delta n/M^{1.6}$ vs. γ^2 was plotted in Fig. 4 on PS solutions having different MW and MWD. Single master curve of birefringence to γ^2 could be obtained as shown. In the figure, birefringence results were normalized by maximum values of PS1H solution. It can be conclusively said that the Rouse-Zimm model in the good solvent represents well the birefringence of PS solutions.

Fig. 5 shows experimental results of orientation angle χ corresponding to above birefringence results. $\cot(2\chi)$ is independent on the polymer solution's concentration and is proportion to shear rate γ , which is coincident with Eq. (32). The slope of $\cot(2\chi)$ to γ in the Figure is $\sum c_i M_i^{1.6} / B_1 \sum c_i M_i^{-0.2}$ according to Eq. (32). Here B_1 is a constant independent on molecular weight and solution's concentration.

Effect of molecular weight on the orientation angle is seen in Fig. 6. The orientation angle χ converges to the shear flow direction of 0° as the flow becomes strong. In experiments using different molecular weights, $\cot(2\chi)$ depends linearly on shear rate γ . In cases of monodisperse solutions of PS1H and PS2H, $\cot(2\chi)$ is proportional to $M^{1.6}$, and in case of using the bimodal solution of PSCH, proportional to $\sum c_i M_i^{1.6} / \sum c_i M_i^{-0.2}$. Therefore, all the results seen in the figure are well agreed with a single master curve normalized by maximum values of PS1H solution.

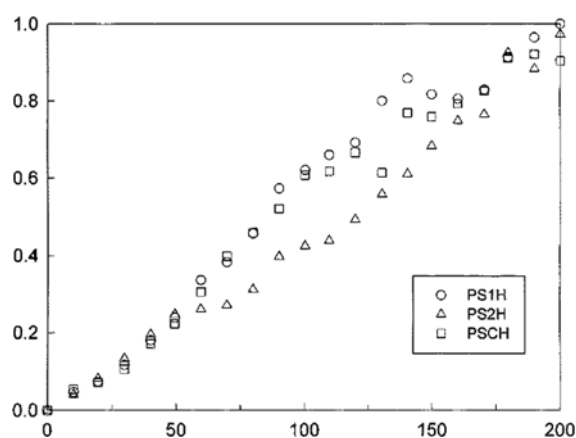


Fig. 6. Plot of $\cot(2\chi)/(M^{1.6}/M^{-0.2})$ normalized by a maximum value of experimented PS1H data.

CONCLUSION

On the polymer solution with a flexible chain, effects of molecular weight on two optical functions, birefringence and orientation angle, were investigated. Birefringence and orientation angle having the following dependence of molecular weight were derived for the Rouse-Zimm model in the good solvent.

$$\Delta n \propto [(\sum c_i M_i^{-0.2})^2 + (B_3 \sum c_i M_i^{1.6})^2 \gamma^2]^{1/2} \gamma \quad (36)$$

$$\cot(2\chi) \propto [\sum c_i M_i^{1.6} / \sum c_i M_i^{-0.2}] \gamma \quad (37)$$

In order to confirm the above theory obtained from the flexible chain model, dilute polystyrene solutions with ultrahigh molecular weight were experimented and the following results were obtained. Birefringence showed linear increment on the concentration and proportionality to the shear rate. Results of the birefringence showed the molecular weight dependence according to the theory and were superimposed on a master curve. Orientation angle was independent on the concentration of solutions, of which results coincided with the theory. In conclusion, it can be said that the method examining the molecular weight and its distribution of polymer solutions with flexible chain was established theoretically and experimentally, and polystyrenes used in this experiments obey well the Rouse-Zimm model in a good solvent. This paper was supported by Woosuk University.

NOMENCLATURE

A	: integration constant in orientation distribution function $\Psi(\theta, \phi, r)$
a	: a segment length of Kuhn and Grun's flexible polymer chain model
B_1, B_2, B_3	: adjustable parameters in Table 1
c, C	: number and weight concentration of polymer solution
c_θ	: $\cos\theta$
d, e, f, g	: adjustable parameters in Table 1
I_{ij}	: unit tensor
$L(k)$: Langevin function
M	: molecular weight
N	: number of segments of Kuhn and Grun's flexible poly-

	mer chain model
N_A	: Avogadro number
n_{ij}	: refractive index tensor
n_1, n_2	: refractive index of principal directions in polymer segment frame
n_o	: $(2n_2 + n_1)/3$
R	: gas constant
R_e	: end-to-end distance of flexible polymer chain
R_x, R_y	: x- and y-component of end-to-end distance of flexible polymer chain
s_θ	: $\sin\theta$
T	: temperature
T_{ij}	: rotation tensor
u_i	: unit vector of i -th segment of flexible polymer chain model
x_i	: polymer segment axes

Greek Letters

α	: polarizability
$\alpha_{ij}^L, \alpha_{ij}^S$: polarizability tensors in lab. frame and polymer segment
α_l, α_r	: polarizabilities parallel and perpendicular to the light direction
γ	: shear rate
$\Delta\alpha$: difference between principal polarizabilities α_1 and α_2
Δn	: birefringence
δ_{ij}	: Kronecker delta
η_s	: solvent viscosity
$[\eta]$: intrinsic viscosity
ζ	: friction factor of a polymer
χ	: extinction angle of polymer solution
Ψ	: orientation distribution function
$\langle \rangle$: average over orientation distribution function Ψ

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