COMPUTER-AIDED PHASE MODULATED FLOW BIREFRINGENCE EXPERIMENT ON POLYSTYRENE SOLUTIONS

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Abstract — A rheo-optical experimental apparatus based on Phase Modulated Flow Birefringence (PMFB) method has been developed. This PMFB method is one of the most powerful techniques to study the rheological behaviors of a polymer system.

An useful computer-aided system which has the capability of controlling the flow dynamics, signal detections and data acquisitions for the PMFB method has been developed. Also a newly modified mathematical calculation method to obtain the birefringence with less error propagations has been established. This computerized system for PMFB technique was carefully checked by the quarter wave plate calibration procedure and was proved to be reasonable for obtaining the rheo-optical properties of the polymer liquids.

Also, with the PMFB method, an experiment for investigating the effects of molecular weight on the rheological properties of 1.5 wt% of polystyrene solutions was carried out. The experimental results were in good agreement with the general viscoelastic properties of the polymer solution and with the other experimental results reported so far.

INTRODUCTION

The flow birefringence technique has been considered as one of the most valuable experimental method suitable for the investigation of the rheological properties of polymer system. It is very useful to investigate the state of stresses in polymer melts or solutions. In a flow birefringence experiment, both the degree of optical anisotropy and the average orientation of the macromolecules under deformation are measured. These optical properties are converted to the rheological properties of polymer by using the stress-optical rule.

The main advantages of this technique lie in the possibility to obtain the more accurate measurement of the flow behaviors of the flowing polymers without moving the parts of the apparatus. In many mechanical rheometers, the principal problem arises from the inherent compliance of the force transducers used to determine the stresses, which often limits the time scales which can be investigated and can even alter the qualitative features of the results. Compared with mechanical methods [1,2], the flow birefringence method can achieve much faster response time without perturbing the flow system being studied. By using the flow birefringence method, we can take both of the

shear stress and the normal stress difference of polymer liquid in a single experiment. This make the flow birefringence method to be a very valuable tool for evaluating the molecular models in a well-defined flow field such as shear flow.

The first application of the flow birefringence phenomena for the study of polymer system is dated back to 1950's. Phillippoff et al. [3,4] reported some basic results of the flow birefringence behaviors of the dilute polymer solution. For the polymer melts in a steady shear flow field, there are many experimental results by other researchers [5-9]. Also some studies tried to obtain the time-dependent rheological properties of polymer system [10,11].

In 1979, Osaki et al. [12] developed a flow birefringence technique which can measure the time dependent behaviors of the polymer solution or melt. They have reported many valuable results that can be very well accepted by rheologists and these results play a great role to connect the flow birefringence method the analysis of the microscopic molecular behaviors. Their method, however, has some defects in the sense that the birefringence and the orientation angle of one polymer system only can be obtained by two independent experiments with different the optical train. Thus for studying the transient behavior, there exist some fatal problems of checking the zero times for the two experimental sets and the changes of the state of sam-

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ple during changing the optical train.

Recently, Frattini and Fuller [13,14] have developed the phase-modulated flow birefringence (PMFB) technique which can measure both time-dependent birefringences and the orientation angles with higher sensitivity in one experiment set. The PMFB technique is based on a modulation of the phase of polarized light prior to its interaction with the sample. The PMFB method is very accurate to measure the birefringences and orientation angles in the time-dependent region as well as the steady flow region. The other flow birefringence method which has the similar functions has been developed and it is called two-color flow birefringence (TCFB) method. But the instrumental arrangements or optical devices of the PMFB method are relatively simple compared to those of the TCFB method. Until now, this PMFB method has been accepted as the most accurate and convenient method to measure the dynamic behaviors of the polymer systems [15].

THEORETICAL PRINCIPLES

Optical analysis of PMFB method

The optical analysis of the PMFB method can be achieved by using the Jones calculus for the polarized light [16]. In the Jones calculus, the incident light is described by a vector, the optical component is described by a two-by-two matrix, and the outcome vector is computed by multiplying the vector by the matrix. This calculus is eminently suited to the solving of problems involving beams whose phase relations are important. When the light of which Jones vector which is expressed as $\mathbf{J}_{in}$ travels through an optical element, the Jones vector of the light leaving the optical element, $\mathbf{J}_{out}$, is given by:

$$\mathbf{J}_{out} = \underline{\underline{\mathbf{M}}}(\phi)\mathbf{J}_{in} \tag{1}$$

where $\underline{\underline{\mathbf{M}}}(\phi)$ is the Jones matrix of the optical element which is oriented so that its optic axis retains at angle ϕ relative to the reference frame.

The intensity of the light at the detector, I, is of interest in the PMFB analysis. Since the intensity of the beam is proportional to the sum of the squares of the magnitudes of the individual elements of the Jones vector, if the units of intensity or amplitude are chosen so that the proportionality constant is unity, the expression of the intensity of light is given by:

$$I = E_x^2 + E_y^2 \tag{2}$$

where E_x and E_y represent the two components of the Jones vector leaving the optical element, $\mathbf{J}_{out}$. In the cascade of the optical systems, the overall Jones matrix is obtained by multiplying the Jones matrix of each separated optical elements.

The optical train of our PMFB system is composed by polarizer, Photo Elastic Modulator (PEM), and the another polarizer called the analyzer. The oriented angles of the optical elements refer to the flow direction are 90°, 45°, and –45°, respectively. In this optical train, by using the Jones calculus, the intensity of the light at the detector is represented as follows:

$$I = (I_o/2) [1 + \cos2\chi \sin2\chi(1 - \cos \delta)\cos \delta_m$$
$$+ \cos2\chi\sin\delta \sin \delta_m] \tag{3}$$

where I_o is the light intensity on the PEM, χ is the orientation angle of the sample. The δ_m is the time varying retardation of the Photo Elastic Modulator (PEM) given by $\delta_m = A \sin \omega t$, where A is the relative phase amplitude, ω the resonant frequency of the PEM (50 kHz), and δ is the retardance of the sample.

The birefringence of the sample, Δn, is related to the retardation as follows:

$$\Delta n = - (\lambda\delta/2\pi d) \tag{4}$$

where d is the optical path length of light through the sample and λ is the wavelength of the light. The Δn is the difference between two principal values of the refractive index tensor, n_I-n_{II}, of the polymer sample in the plane normal to the direction of the light propagation.

Fourier series expansion of $\cos \delta_m$ and $\sin \delta_m$ gives [17]

$$\cos\delta_m = J_o(A) + 2\sum_{m=1}^{\infty} J_{2m}(A)\cos2m \omega t \tag{5a}$$

$$\sin\delta_m = 2\sum_{m=0}^{\infty} J_{2m+1}(A)\sin(2m+1) \omega t \tag{5b}$$

where $J_m(A)$ is the Bessel function of the first kind of order m. If the amplitude of the time varying retardance of the PEM, A, is adjusted so that $J_o(A) = 0$, then substituting (5a) and (5b) into (3) yields the intensity at the detector,

$$I = I_{dc} + I_\omega \sin \omega t + I_{2\omega}\cos 2 \omega t + \cdots \tag{6}$$

where

$$I_{dc} = I_o/2 \tag{7}$$

$$I_\omega = 2\cos2\chi\sin\delta J_1(A)I_{dc} \tag{8}$$

$$I_{2\omega} = 2\cos2\chi \sin2\chi(1 - \cos \delta)J_2(A)I_{dc} \tag{9}$$

The intensity signals of Eq.(8) and Eq.(9) are measured in a real time by using two Lock-In amplifiers tuned respectively to ω and 2ω. Here $J_1(A)$ and $J_2(A)$ are best found experimentally since Eqs.(7)-(9) are strictly valid in the limit of the perfect optical alignment and of the perfect optical component. The setting of value of A for $J_o(A) = 0$ is achieved by the PEM controller.

Let β_1 and β_2 be defined as follows.

$$\beta_1 = 2(I_\omega/I_{dc})J_1(A) \tag{10}$$

$$\beta_2 = (I_{2\omega}/I_{dc})J_2 \ (A) \qquad (11)$$

Then β_1 and β_2 give two equations in the two unknowns, δ and χ:

$$\cos 2\chi \sin \delta = \beta_1 \qquad (12)$$

$$\sin 4\chi \ (1 - \cos \delta) = \beta_2 \qquad (13)$$

Elimination of δ from Eqs.(12) and (13) results in an analytic expression for χ:

$$\cos \{4\chi - \tan^{-1}(\beta_1/\beta_2^2)\} = \frac{2\beta_1^2 - \beta_2^2}{2(\beta_1^4 + \beta_2^2)^{1/2}} \qquad (14)$$

And the retardation of the sample can be calculated directly from β_1 and β_2 by some simple mathematical calculations:

$$\delta = 2\sin^{-1}\sqrt{(B/2)} \qquad (15)$$

$$\text{where } B = \frac{4\beta_1^2 + 2\beta_2^2 - 2\beta_1^2\sqrt{(4 - 4\beta_1^2 - \beta_2^2)}}{4\beta_1^2 + \beta_2^2}$$

By comparing our retardation calculation scheme with that of Frattini [14] in which δ is obtained from the measuring value of the χ, our scheme has a advantage to be able to remove the error propagations during the δ-calculation from the measured χ. Through these steps, we can obtain simultaneously both the flow-induced birefringence and orientation angle of the polymer solution in a real time.

The stress-optical rule

The rheological application of the flow birefringence method is based on the stress-optical rule, which states that the deviatoric components of the refractive index tensor are linearly proportional to those of the stress tensor. That is, this rule links the stress field and the optical anisotropy caused by the flow. This rule postulates that the stress tensor and the refractive index tensor are linearly related as follows:

$$\underline{n} + n_a\underline{I} = C\ (\underline{\sigma} + p\underline{I}) \qquad (16)$$

where n_a is the mean refractive index of the system, $\underline{\sigma}$ is the stress tensor, p is the isotropic pressure on polymer system and C is the stress-optical coefficient.

For a simple shear flow, an optical anisotropy of the polymer liquid with respect to the light beam directed along the flow direction is described by the amount of birefringence Δn and the extinction angle χ. Here $\Delta n\ (= n_I - n_{II})$ is the difference of the principal refractive indices between the directions of the stretch and perpendicular to it. Also the extinction angle χ is the angle between the flow direction and one of the principal axes which makes an angle less than $45°$. For the simple shear flow, the following expressions of the shear stress and the first normal stress difference of polymer system can be obtained:

$$\Delta n \sin 2\chi = 2C\ \sigma_{12} \qquad (17)$$

$$\Delta n \cos 2\chi = C\ (\sigma_{11} - \sigma_{22}) \qquad (18)$$

This stress-optical rule shows that the ratio of the amount of birefringence to the difference between the corresponding principal stresses is a constant independent of the shear rate and the time. The validity of the stress-optical rule has been confirmed for a few types of the time-dependent flow [8,12,15] as well as the steady shear flow [6,7] of polymer liquids. In general, the stress-optical rule is accepted for the simple flow up to moderate shear rate regions.

DEVELOPMENT OF PMFB APPARATUS

Optical train

A block diagram of the instruments and its optical train is shown schematically in Fig. 1. The light source is a 2 mW He-Ne laser of which wavelength is 632.8 nm. This monochromated light is linearly polarized with $90°$ to the flow direction by a high quality, Glan-Thompson crystal polarizer. The linearly polarized light then passes through a Photoelastic Modulator (Hinds International, Model PEM-80) which oriented at $45°$ with the flow direction.

The modulated beam is then transmitted through the sample contained in a Couette flow cell. The flow cell is a coaxial cylinder pair with the inner cylinder being the stator and the outer cylinder the rotor and it is coupled to the motor driver through an electro-magnetic clutch/brake module, C/B. The outer cylinder is accurately rotated by a stepping motor through a timing pulley and belt assembly. For a precise motion control and synchronization with the data acquisition unit, a stepping motor/drive and an indexer, and an
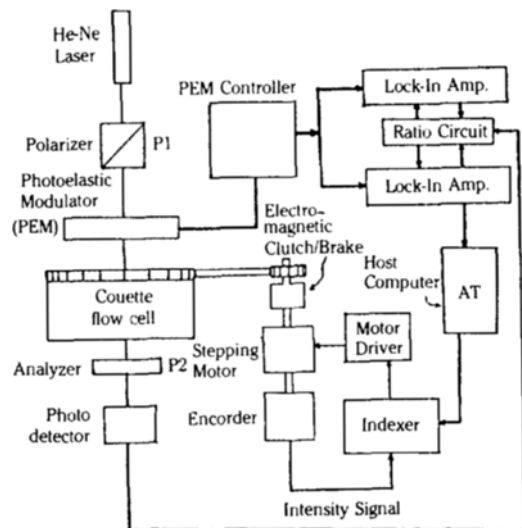

Fig. 1. Schematic diagram of PMFB system.

encoder are used to rotate the Couette flow cell. The indexer (CompuMotor Model 3000) receives the hgih-level command languages from the host computer (IBM PC/AT). By interpreting these commands and generating the necessary pulse signals, the indexer controls the acceleration of the flow and the flow directions.

After passing through the sample, the beam travels through a second polarizer, called the analyzer. The relative orientations of the optical components are as follows; the polarizer, P1, is perpendicular to the flow direction (90°), the PEM is at 45°, and the analyzer, P2, is at –45° with respective to the flow direction. Following the analyzer the beam is falling onto the photodetector (United Detector Technology, PIN-10D) after being filtered by a narrow band interference filter (Oriel, Model 53935). This filter allows to easily isolate wavelength regions of interest (around peak wavelength: 632 nm) from the ambient light which may causes the offset problem. With the Fourier decomposition of the intensity signals at the detector, the information to be obtained from each signals includes the mean intensity I_{dc}, the first harmonic, I_ω, and the second harmonic, $I_{2\omega}$. As described previously, the two ratios I_ω/I_{dc} and $I_{2\omega}/I_{dc}$ provide sufficient information to obtain the birefringence and average orientation angle of the sample.

Detection and Data Acquisition

As shown in Fig. 2, we have performed a signal processing during the experiment to determine the flow birefringences and the orientation angles of the

Fig. 2. Diagram of the signal detection and data acquisition system.

sample in the simple shear flow. The light intensities detected as a form of current signals at the photodiode go into the pre-amplifier (D1). The output full intensity signal from J1 port is fed into two Lock-In amplifiers (Stanford Research System Inc. Model: SR510), 1f and 2f. They are both received the same reference signal from the PEM controller and the reference phase differences of the 1f- and 2f-amplifier are set to 0° and 90°, respectively. Then the output signals from two Lock-In amplifiers (I_ω, $I_{2\omega}$) is fed back to the ratio circuits and these analog signals provide two ratio components R_ω (I_ω/I_{dc}) and $R_{2\omega}$ ($I_{2\omega}/I_{dc}$). Determining the R_ω and $R_{2\omega}$ by the electrical circuit is accurately synchronous with time rather than by the digital dividing method. The R_ω and $R_{2\omega}$ are converted to the corresponding digital signals by an A/D converter with 13 bit resolution. These digital signals are then read by the host computer and finally the Δn and χ are obtained. All of the data acquisitions and process controls are performed by a program written in Compiled Basic language.

Since all of the computer controls for stepping motor and data acquisition system are achieved simultaneously, our PMFB experiment including data processing does not takes longer than two minutes in each experiment.

Calibration steps

Once the optical devices has been aligned, some calibration steps of the apparatus should be performed. This calibration steps are for satisfying $J_o(A) = 0$ and for determining the values of $J_1(A)$ and $J_2(A)$ experimentally by inserting a known-retardation optical component (quarter-wave plate) into the sample part. A typical alignment for the calibration step is as follows:

$$\text{Laser} - \text{Polarizer} - \text{PEM} - \text{QWP} - \text{Analyzer} - \text{Detector}$$
$$\qquad\qquad 90° \quad\ 45° \quad\ \theta \qquad\ -45°$$

Then, the output intensity at the detector is given by the Jones calculus for the above optical train:

$$I/I_o = I_{dc} + I_\omega \sin \omega t + I_{2\omega} \cos 2\omega t + \cdots \qquad (19)$$

where

$$I_{dc}/I_o = (1/2) \left[1 + 1/2 J_o (A) \sin 4\theta\right] \qquad (20)$$

$$I_\omega/I_o = J_1 (A) \cos 2\theta \qquad (21)$$

$$I_{2\omega}/I_o = (1/2) J_2 (A) \sin 4\theta \qquad (22)$$

As the Eq.(20) indicates, I_{dc} signal is a constant when $J_o(A) = 0$. We can adjust the value of A until the point that I_{dc} signal shows a constant value with any rotation angle of QWP. This setting procedure has the advantage that at this point the I_{dc} signal forming the denominator in the ratio circuits does not have any dependence on the optical anisotropy of the sample. The results of $J_o(A)$ calibration in our apparatus are shown in Fig. 3.
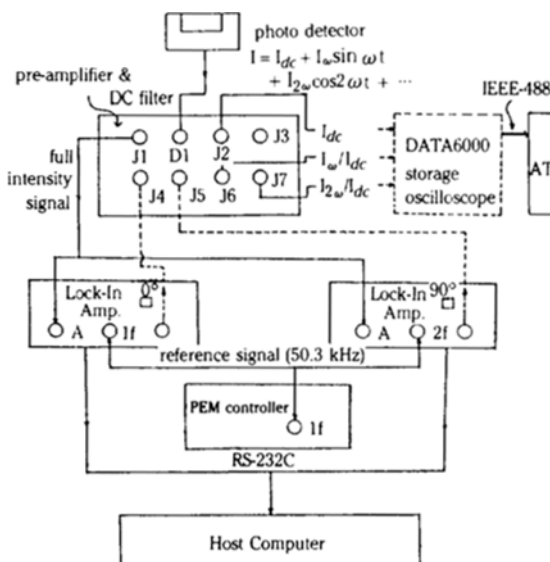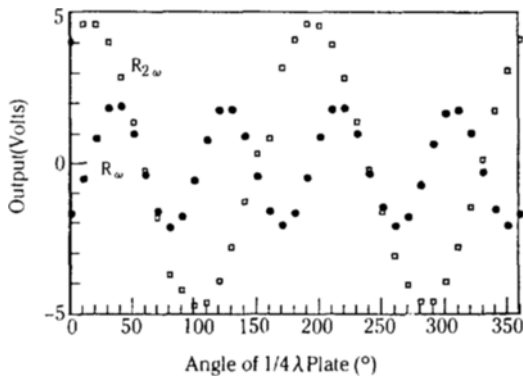
Fig. 3. Typical results of determination of $J_1(A)$ and $J_2(A)$.

When $J_d(A) = 0$, rearranging the Eqs.(21) and (22) yields,

$$R_\omega = I_\omega / I_{dc} = 2J_1(A)\cos 2\theta \qquad (23)$$

$$R_{2\omega} = I_{2\omega} / I_{dc} = J_2(A)\sin 4\theta \qquad (24)$$

In principle, the ideal values of the Bessel functions $J_1(A)$ and $J_2(A)$ should have the following values at the point $J_d(A) = 0$ are $J_1(A) = 0.519$ and $J_2(A) = 0.432$, respectively. We used, however, experimentally determined values of $J_1(A)$ and $J_2(A)$ to obtain Δn and χ because these values contain the compensations of the non-ideal properties of the optical components and the imperfect alignments. Therefore, after the calibration steps, the signals of R_ω and $R_{2\omega}$ from the ratio circuit only have the information of the polymer sample without affected by the optical train. As it should be, the two ratio signals are simple sinusoidal functions with peak-to-peak values of $4J_1(A)$ and $2J_2(A)$. Typical results are shown in Fig. 3.

Materials

The samples investigated are solutions of polystyrene in diethyl phthalate (DEP). Polystyrene samples of the narrow molecular weight distribution are supplied by Pressure Chemical Co.. The sample codes and the molecular weights are listed in Table 1. Since we has concerned only about the molecular weight effects on the rheological properties of the PS solutions, the wide ranges of the molecular weights were used in

Table 1. Molecular weights and sample codes of 1.5 wt% PS solutions in DEP

PS code	M_w	M_w/M_n*
M2	2.0×10^3	1.06
M90	9.0×10^4	1.04
M900	9.0×10^5	1.04

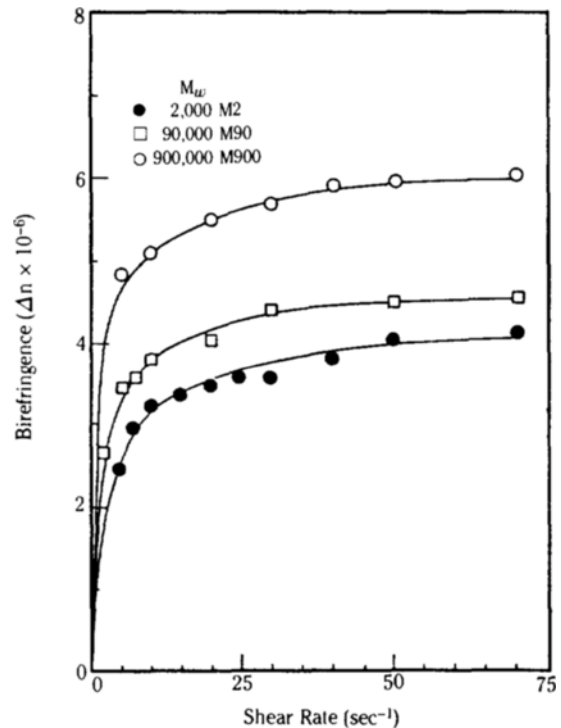* data according to the manufacturer

Fig. 4. Flow birefringence of PS solution in DEP (conc. = 1.5 wt%).

this study.

RESULTS AND DISCUSSION

The birefringence distributions with the shear rates of the PS solutions subjected to steady simple flow is shown in Fig. 4. The magnitude of the birefringence increased with the molecular weight of the sample, always maintaining the "saturation form" with the shear rates.

The distribution of orientation angles which directly shows the conformations of the polymer chain in the flow field is shown in Fig. 5. Same as the results of other researchers, our PMFB system can obtain orientation angles which does not exceed the 45° which can be shown for the Newtonian fluids. The orientation angles are decreased with the molecular weights.

Our samples of 1.5 wt% PS solution can be considered as the semi-dilute region because the critical concentration of the samples in which the polymer chains begin to overlap with each other [18] is proved to be below for that of the concentrated solution in all ranges of the molecular weights. In general, for a semi-dilute polymer solution, the linear stress-optical rule described in the above section can be accepted [18]. Thus, in this paper, we obtained the shear stress σ_{12}
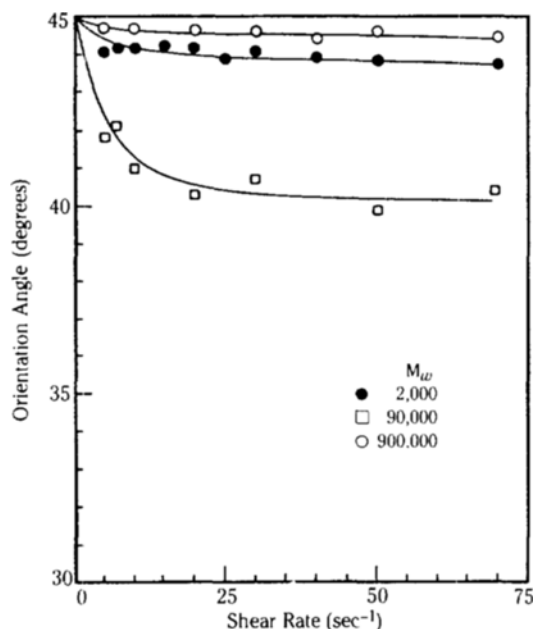
Fig. 5. Distribution of orientation angles of PS solution in DEP (conc. = 1.5 wt%).

Fig. 7. Normal stress difference distribution with shear rate of PS solution (conc. = 1.5 wt%).

and the normal stress difference σ_{11}-σ_{22} calculated from the data of Δn and χ by assuming $C = 5.8 \times 10^{-9}$ Pa^{-1}, which was reported by Osaki et al. [12].

By the stress-optical rule, the obtained results of σ_{12} and σ_{11}-σ_{22} are shown in Fig. 6 and Fig. 7. The distributions of σ_{12} with the shear rate does not show any overshoot pattern in all ranges of the molecular weight in our study. But σ_{12} increased with the molecular weights.

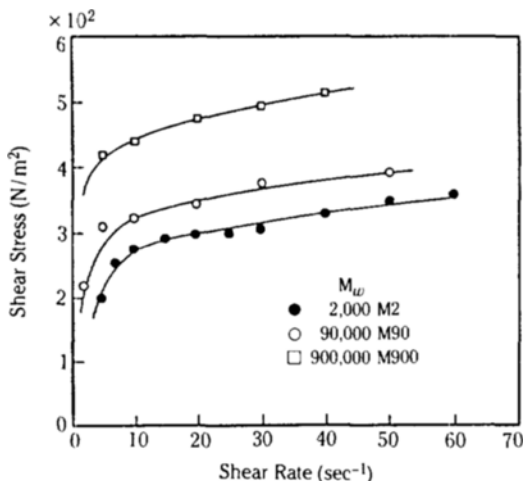As shown in Fig. 7, the σ_{11}-σ_{22} of high molecular

weight M90 shows very large values compared with M2 or M900. This shows the large dependence of σ_{11}-σ_{22} on the molecular weights.

In this paper, we did not contain the results of other researchers, but our data were confirmed to be reasonable by surveying their literatures. Also we centered our attention on the general patterns of flow birefringences and orientation angles because of the lack of the rheo-optical data of semi-dilute polystyrene solution.

CONCLUSIONS AND FUTURE WORKS

To investigate the simultaneous behavior of the flow birefringence and the orientation angle of the polymer solution, a computer-aided controlling and data acquisition system for PMFB technique has been developed. This optical technique is capable of obtaining fast responses of the optical properties of polymer materials.

Also we have developed a new method for a calculation of the orientation angle and the birefringence directly from the Lock-In amplifiers signals, which has been proved to be a more accurate method with less error propagations.

A study has carried out which using the 1.5 wt% of PS solution for confirming the usefulness of the PMFB technique and for investigating the molecular weight effect on the rheological properties of the PS solution.

The distribution of the birefringence and the orien-

Fig. 6. Shear stress distribution with shear rate of PS solution (conc. = 1.5 wt%).

tation angle showed the general accepted patterns of the previous mechanical or optical results. The behaviors of the normal stress difference showed a large dependence on the molecular weights. In the region of the concentrations and the molecular weights which considered in our study, there was no overshoot phenomena in the shear stress and the normal stress difference.

Although the experiments were only confined to the steady state simple shear flow, it would be recommendable to study the rheological properties of the polymer liquids in the transient state and oscillatory shear flow for further researches. An accurate measurement of the transient behaviors of polymer liquids will be necessary to develop the molecular theories for predicting rheological properties of the polymer materials.

In addition, it will be interesting to study the combined effect on the various polymer materials in which external electric or magnetic fields are superimposed on shear fields.

ACKNOWLEDGEMENT

NOMENCLATURE

A   : Amplitude of time-varying retardance of the Photoelastic Modulator
C   : Stress-optical coefficient
I_{dc} : Mean intensity signal
I_ω : Intensity of the first harmonic component
$I_{2\omega}$: Intensity of the second harmonic component
$J_0(A)$: Bessel function of the first kind of order 0
$J_1(A)$: Bessel function of the first kind of order 1
$J_2(A)$: Bessel function of the first kind of order 2
R_ω : Ratio signal intensity with first harmonic component
$R_{2\omega}$: Ratio signal intensity with second harmonic component
d   : Optical path length
Δn : Birefringence

δ : Retardance of the polymer sample
δ_m : Time-varying retardance of the Photoelastic Modulator
χ : Orientation angle
λ : Wavelength of the light
$\underline{\sigma}$: Stress tensor
ω : Resonance frequency of the PEM

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