Polymer Bulletin 22, 183–190 (1989)

Polymer Bulletin

Polydispersity effect on transient flow behavior of polystyrene solution

Tai Jun Lim and In Jae Chung*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology,
P.O. Box 131, Cheongryang, Seoul, 130-650, Korea

SUMMARY

The transient flow behavior of the binary blend of monodisperse polystyrene fractions is measured by a flow birefringence method. Both of the shear stress and first normal stress difference are obtained simultaneously in time by using a PMFB technique. The entanglements of the polymer chains significantly affect the rheological property of the binary blend in flow region. Especially, the entanglements of the high molecular weight fractions with themselves is proven to be the main source to the growth of first normal stress differences.

INTRODUCTION

The effect of the molecular weight distribution (MWD) on the rheological properties of the polymeric liquids has been one of the most important problems to be solved in polymer science. This problem is also important in the polymer industry because it is closely related to the processing of polymer materials which typically contain a range of the molecular sizes. Commercial polymers with continuous MWD are not suitable for the interpretation of the polydispersity effects because of the difficulty in measuring the various molecular weight averages. For this reason, as a simple model system, a binary blend of two well–characterized narrow MWD fractions has been used to analyze the polydispersity effect on flow behavior.

So far, however, many studies for the binary blend system are mainly concerned about the stress relaxation mechanism. [1,2] Because of the complex features of the polymer chain entanglements, the theoretical approach is very difficult for predicting some rheological properties of the binary blend. Especially, for the non–linear flow behaviors of the binary blend, any molecular theory seems to fail in predicting the rheological properties accurately. Therefore, it will be very useful to perform an experimental study on the viscoelastic properties of the binary blends in flow region in order to obtain an explicit characteristics of the MWD effect.

Many measurements of the flow behaviors have been mainly restricted to the steady state. However, for a more precise analysis of rheological properties, it is useful to measure the transient flow behaviors of the polymer system. The transient flow behaviors can give some critical information for the development of a more powerful molecular theory. Even though there have been some reports for the transient flow behaviors of the homopolymers, [3,4] only a few result [5] has been reported for the binary blends. In this study, we measured the transient behavior of the binary blend at inception, cessation and steady state of the shear flow. And an approach is performed that analyze the MWD effect on the flow behaviors with the entanglement concepts generally accepted in the stress relaxation mechanism.

EXPERIMENTAL

The flow birefringence method has proven to be an effective experimental method suitable for investigating the rheological properties of the polymeric liquids in transient

---

*To whom all correspondence should be addressed region. Among the flow birefringence methods, the phase modulated flow birefringence (PMFB) technique [6] is chosen because it has a prominent capability to measure both of the birefringence and orientation angle in real time.

Anionically polymerized linear polystyrene standards with narrow MWD (Pressure Chemical Co.) are used to make the binary blends. The polydispersity index of the PS fractions is within 1.06. Accurately weighed PS monodisperse fractions are solved in Diethyl Phthalate (DEP). The total concentration of the solution is fixed at 15 *wt%* (0.11 *g/cm*^{3}) but the composition is changed. The low and high molecular weights (*hereafter* denoted as M_1 and M_2) are 5.75×10^5 and 1.56×10^6, respectively. The weight fractions of the higher MW component (w_2) are used as 0, 0.05, 0.1, 0.2, 0.5 and 1. The molecular weight between two adjacent entanglements is estimated to be $(M_e)_{soln} = 1.4 \times 10^5$ for the test PS solution.

RESULTS AND DISCUSSION

By using the stress–optical law, the rheological properties of the polymer system can be obtained from the optical data measured by a flow birefringence method. The stress–optical law for the simple shear flow is expressed as follows:

$$\sigma_{12} = \Delta n \cdot \sin 2\chi / 2C, \quad N_1 = \Delta n \cdot \cos 2\chi / C \qquad (1)$$

where σ_{12} and N_1 is the shear stress and the first normal stress difference, respectively, and C the stress–optical coefficient.

For the PS–DEP system, the stress–optical coefficient was obtained from Eq.(1) by measuring birefringence(Δn) from PMFB and shear stress σ_{12} from the Rheometrics Mechanical Spectrometer (Model RMS–800). For the PS–DEP system, the C is measured as $(-2.1 \pm 0.1) \times 10^{-9}$ Pa^{-1} as shown in Fig.1, and the C value does not changed with w_2–variation, which agrees with the general concept that the C is the function of the temperature and the kind of solvent but independent of the MW and MWD. [7]

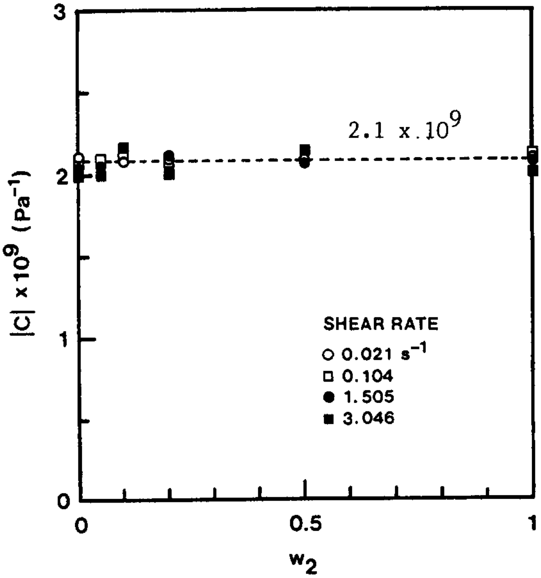

Fig.1 Stress–optical coefficients of the PS–DEP solutions.

Table I Rheological Characteristics of PS samples

w_2	η_0 (Pa·s)	J_e (Pa^{-1})	τ (s)
0	1.60×10^3	9.88×10^{-4}	1.58
0.05	2.34×10^3	1.02×10^{-3}	2.38
0.1	3.17×10^3	9.76×10^{-4}	3.10
0.2	3.79×10^3	1.17×10^{-3}	4.43
0.5	9.66×10^3	1.24×10^{-3}	12.0
1.0	3.17×10^4	1.13×10^{-3}	35.7

For the entangled polymer systems, the product of the longest relaxation time (τ) and the shear rate (κ) is an important parameter for the rheological properties [4]. Table I shows the rheological characteristics of the PS solutions used in this study. Here, since it is not possible to accurately determine the value of the τ [8], this value of is approximately obtained by the product of zero–shear rate viscosity (η_0) and the steady state compliance (J_e) determined from the steady state measurements.

Inception of Shear Flow

The transient behaviors in the inception of shear flow can be analyzed by the stress growth functions expressed as follows:

$$\hat{\eta}(\kappa,t) = \hat{\sigma}_{12}(\kappa,t)/\kappa, \quad \hat{\Psi}_1(\kappa,t) = \hat{N}_1(\kappa,t)/\kappa^2 \tag{2}$$

where $\hat{\eta}(\kappa,t)$ and $\hat{\Psi}_1(\kappa,t)$ denote the shear stress and first normal stress difference growth function, respectively.

The transient behaviors of the $\hat{\eta}(\kappa,t)$ and $\hat{\Psi}_1(\kappa,t)$ for the binary blends are represented in Fig.2. For the low values of w_2, the $\hat{\eta}(\kappa,t)$ does not show any great changes with respect to that of M_1 component, but at higher w_2–values such as 0.5 and 1 the distribution of $\hat{\eta}(\kappa,t)$ have some distinct higher values. This phenomena show that the entanglements between the M_1 and M_2 polymer chains are much affected by the M_2 component. The growing rate of the $\hat{\Psi}_1(\kappa,t)$ at the start of the shear flow is larger than that of the $\hat{\eta}(\kappa,t)$. As expected, the M_1 component goes to the steady state more rapidly than the M_2 component according to $\hat{\eta}(\kappa,t)$ and $\hat{\Psi}_1(\kappa,t)$.

In the inception of the shear flow, the elapsed time, t_{ss}, of the growth function to reach the steady state is simple but useful time scale for the analysis of transient behaviors. For more precise analysis of the characteristic time scales, a molecular theoretical viewpoint is helpful. The blending effect on the time t_{ss} elapsed until the steady state is shown in Fig.3. The t_{ss} from the data of $\hat{\eta}(\kappa,t)$ shows monotonically increasing pattern with w_2 at low shear rate of 0.063 s^{-1}, but a rapid increase for $w_2 = 1$ at higher shear rate in Fig.3–(a). The latter seems to occur due to the "overshoot" in $\hat{\eta}(\kappa,t)$. On the other hand, as represented in Fig.3–(b), the "overshoot" phenomena of the $\hat{\Psi}(\kappa,t)$ does not observed for the same conditions. The t_{ss} obtained from $\hat{\Psi}_1(\kappa,t)$ data shows almost the same value up to about 0.1 of w_2.

In the binary blends of two monodisperse MW polymer components, the entanglements of the high MW fractions with themselves begin at a critical weight fraction (w_c) below which the binary blend behaves as the dilute solution of the high MW component dissolved in low MW component. The w_c can be approximately expressed as follows [9]:

$$(w_c)_{soln} = (M_c)_{soln} \,/\, M_2 \tag{3}$$

where $(M_c)_{soln}$ is the characteristic MW of the concentrated solution. In this study,

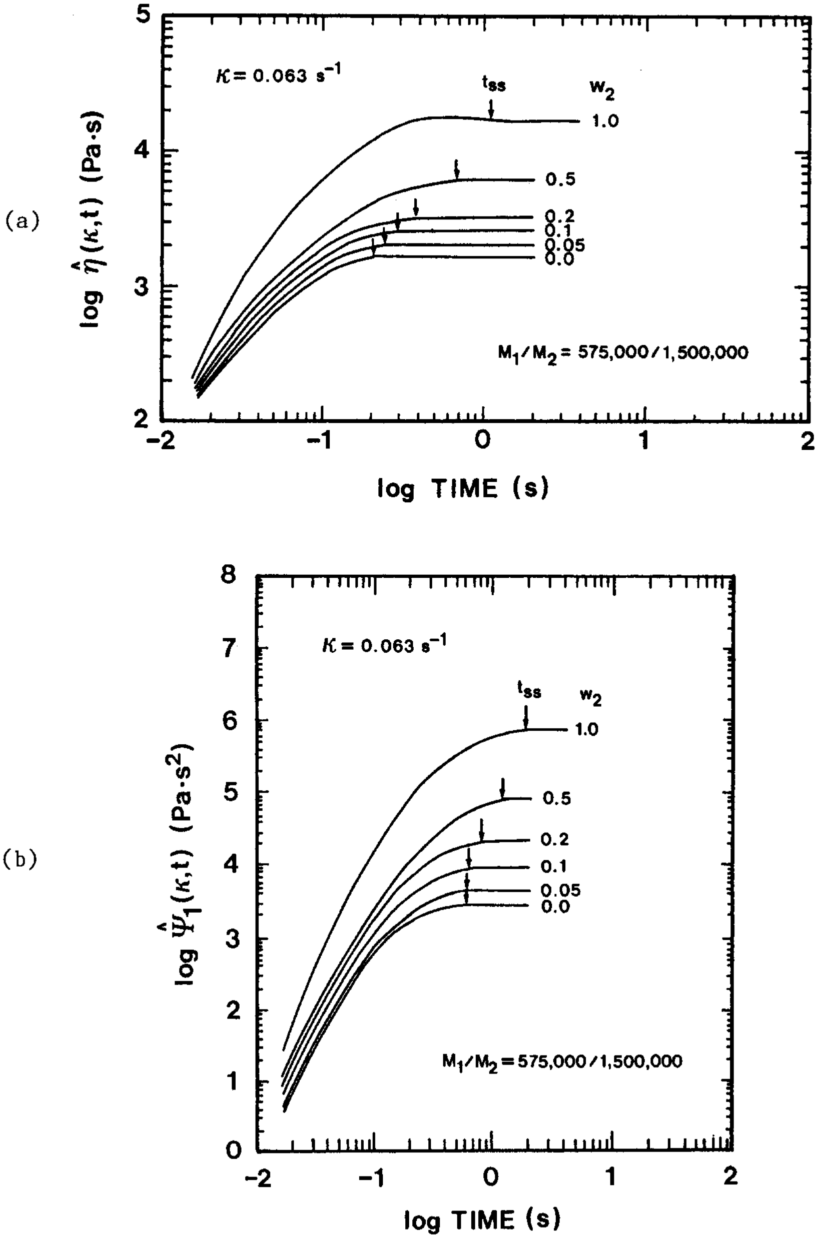

Fig.2 Stress growth functions of the inception of shear flow

(a) Shear stress growth function

(b) Normal stress difference growth function

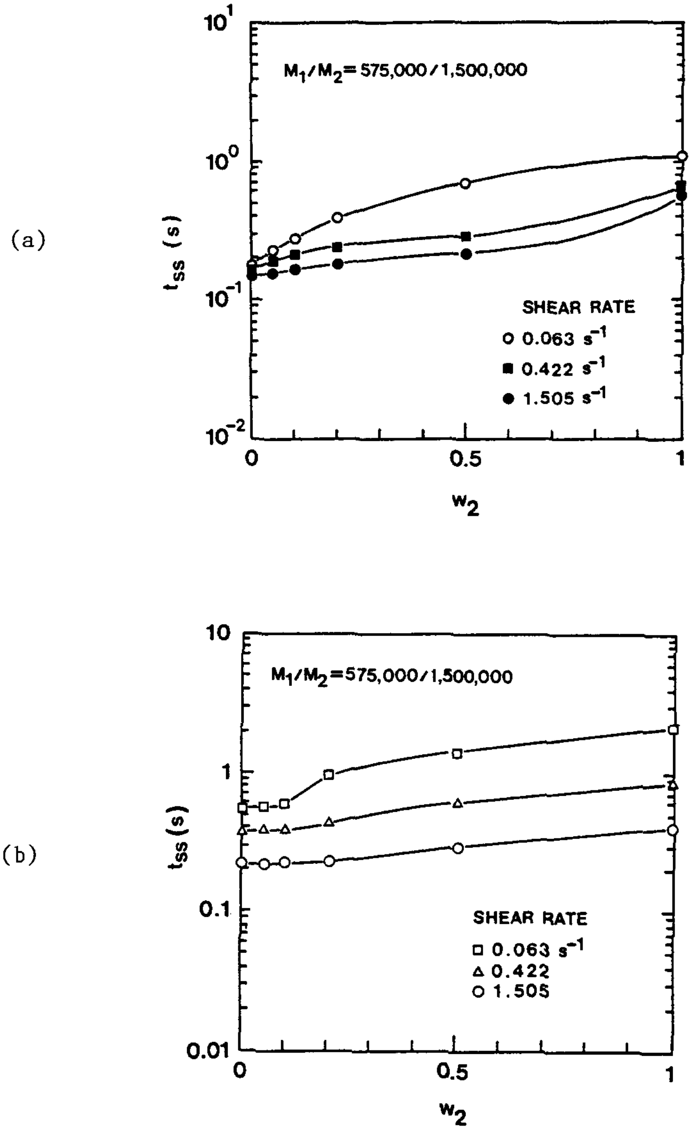

Fig.3 Distribution of the steady state reaching time (t_{ss})

(a) t_{ss} for $\hat{\eta}(\kappa,t)$ (b) t_{ss} for $\hat{\Psi}_1(\kappa,t)$

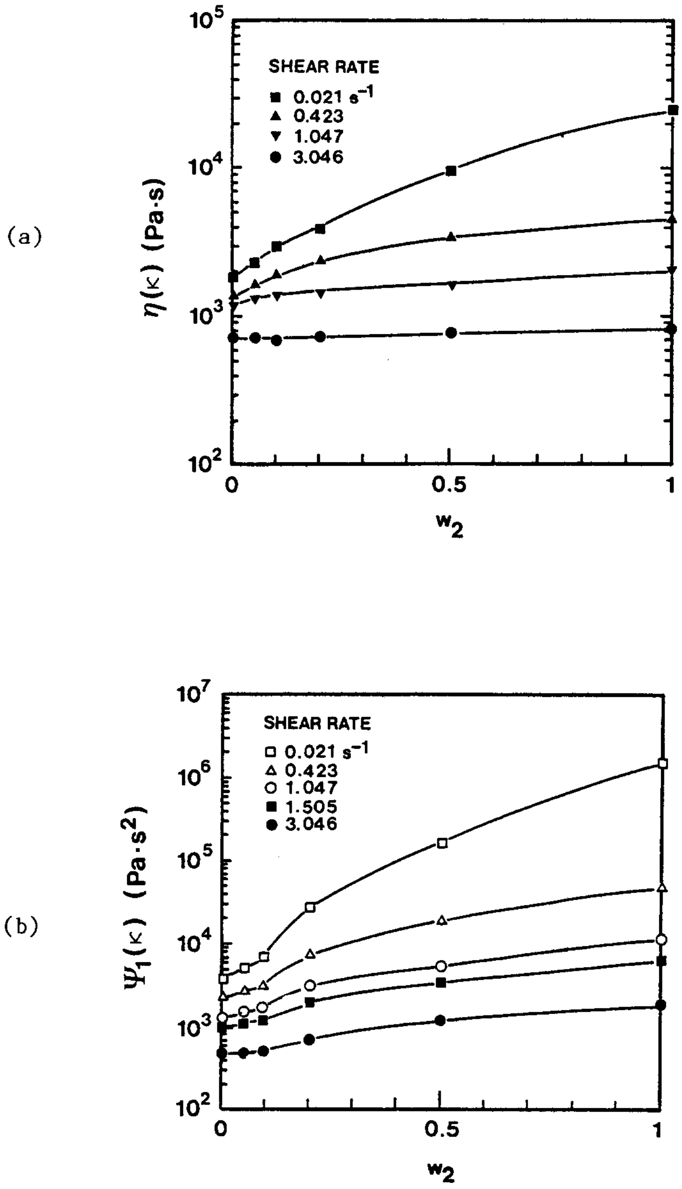

Fig.4 MWD effect on the steady state rheological properties

(a) Shear viscosity (b) Normal stress difference coefficient

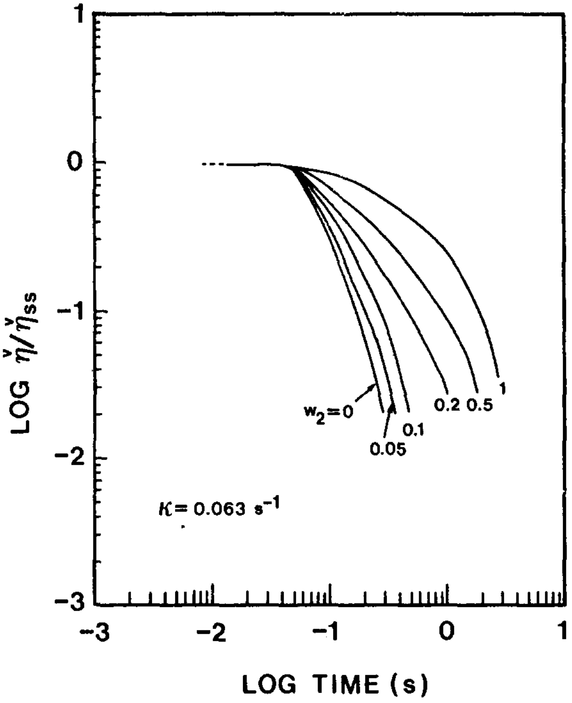

Fig.5 Shear stress decay function. $\check{\eta}(\kappa,t)$ is normalized by the corresponding steady–state value

the w_c is estimated to be 0.15. For $w_2<w_c$, there exist no entanglement between M_2 components. In this case, t_{ss} obtained from $\Psi_1(\kappa,t)$ data does not significantly change with w_2–variation. In the region of $w_2>w_c$, however, the entanglements between the molecular chains of M_2 components increase and make the first normal stress difference to increase with the w_2. From these results, it can be thought that the entanglements of the high MW fractions with themselves are the main cause for the growth of first normal stress difference.

Steady State and Cessation of Shear Flow

The shear viscosity, $\eta(\kappa) \equiv \sigma(\kappa)/\kappa$, and first normal stress difference coefficient, $\Psi_1(\kappa) \equiv N_1(\kappa)/\kappa^2$, in steady shear flow are represented in Fig.4. At low shear rate the $\eta(\kappa)$ increases monotonically with increase of the w_2. On the other hand, the blending effect on the $\eta(\kappa)$ is not shown at high shear rate. However, for the $\Psi_1(\kappa)$ some blending effect is still observed at high shear rate region. As mentioned in above section, small increment of the $\Psi_1(\kappa)$ is also observed at $w_2<w_c$ region.

The shear stress decay functions, $\check{\eta}(\kappa,t) \equiv \check{\sigma}_{12}(\kappa,t)/\kappa$, for the cessation of shear flow are plotted in Fig.5. Here, the $\check{\eta}(\kappa,t)$ is normalized by the corresponding steady state value, $\check{\eta}_{ss}$ for each blends. As the w_2 increases, the shear stresses produced by the flow relax more slowly. However, the time at which the departure from the steady state value begins is same for all blends.

REFERENCES

1. H.Watanabe, T.Sakmoto, and T.Kotaka, macromol., 20, 530 (1987).
2. H.Y.Kim and I.J.Chung, J. of Polym. Sci.: Phys. Ed., 25, 2039 (1987).
3. K.Osaki, N.Bessho, T.Kojimoto, and M.Kurata, J. of Rheol., 23, 617 (1979).
4. E.V.Menezes and W.W. Graessley, Rheol. Acta, 19, 38 (1980).
5. M. Kinouchi, M. Takahashi, T. Masuda and S. Onogi, J. Soc. Rheol. Japan, 4, 25 (1976).
6. P.L.Frattini and G.G. Fuller, J. of Rheol., 28, 61 (1984).
7. M.Doi and S.F.Edwards, "The Theory of Polymer Dynamics," Clarendon Press, 222 (1986).
8. D.S. Pearson, A.D. Kiss, L.J. Fetters, and M. Doi, J. of Rheol., 33, 517 (1989).
9. W.W.Graessley, "The Entanglement Concept in Polymer Rheology," Adv. Polym. Sci., 16, 50 (1974).

Accepted July 6, 1989 S