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H. J. Choi^a; H. S. Shon^{ab}; H. J. Lee^{ab}; M. S. Jhon^b

^a Department of Polymer Science and Engineering, Inha University, Incheon, Korea ^b Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA, U.S.A.

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Rheological Characterization of Polyisobutylene Solutions from Rod-Climbing Experimentation

H. J. CHOI*, H. S. SHON, H. J. LEE and M. S. JHON**

**Department of Polymer Science and Engineering, Inha University, Incheon, 402-751, Korea, **Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, U.S.A.*

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Rod-climbing constants and first-normal stress differences of polyisobutylene (PIB) solutions are obtained from rod-climbing experiments. For a low deformation rate, the polymer solution can be regarded as a second-order fluid, and the rod-climbing constant for second-order fluids is correlated with the rheological properties of the polymer solutions. The rod-climbing constants for solutions of PIB in polybutene decrease with temperature, and increase with rod size, polymer concentration, molecular weight of the polymer, and solvent viscosity. The rheological properties were measured using RMS-800, and compared with those obtained from rod-climbing experimentation.

Keywords: Polyisobutylene; second-order fluid; rod-climbing

INTRODUCTION

Manifestations of normal stress effects in non-Newtonian fluids account for the most significant phenomenological difference between non-Newtonian fluids and Newtonian fluids. The rod-climbing phenomenon is an example which illustrates this effect. During a rod-climbing experiment, a polymer solution is sheared, inducing normal stresses perpendicular to the planes of shear. The free-surface of the liquid is then deformed in the direction of the rod axis, and the fluids climb the rod. This phenomenon is

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usually referred to as the Weissenberg effect. The climb is associated with nonlinear viscoelastic effects and normal stresses, which do not exist in Newtonian fluids, where the stress is linearly related to the gradient of the velocity [1]. Therefore, in Newtonian fluids, the liquid near the rotating rod is pushed outward by centrifugal force, and the characteristic dip in the liquid surface near the rotating shaft results.

The most intensive studies in this area have been carried out by Joseph and co-workers [2–6]. Joseph and Fosdick [2] developed a systematic construction for the shape of the free surface above a rheologically simple fluid resulting from a perturbation from a state of rest. This construction gives a quantitative theory of rod-climbing when cylinder speeds are low. Furthermore, Joseph *et al.* [3], as well as Beavers and Joseph [4] show that it is necessary to retain the effects of surface tension in order for the shapes of the free surface to agree with measured shapes.

The qualitative and precise analysis of rod-climbing phenomena for viscoelastic polymer solutions can be used to characterize important rheological parameters of polymer solutions [3,4]. This includes the elasticity of polymer solutions, which is obtained from the climbing constant β and first normal stress difference N_1 . With the second-order fluid model, the rheological properties are obtained as a function of second-order parameters. The results of rod-climbing experiments, combined with the coefficients of a second-order fluid model, are correlated with the first (Ψ_1) and second (Ψ_2) normal stress difference coefficients.

A mixture of polyisobutylene (PIB) and polybutene (PB), which is generally considered to be a second-order fluid, was chosen for this study [7,8]. The rod-climbing constants for various experimental conditions of polymer concentration, solvent viscosity, molecular weight of the polymer, rod-size, and temperature were investigated. The Ψ_1 's (or N_1 's) obtained from RMS-800 measurements of the PIB solutions were compared with those obtained from rod-climbing experiments. In comparison with other experimental methods, obtaining Ψ_1 (or N_1) from this method is relatively simple.

THEORETICAL BACKGROUND

The climbing property of non-Newtonian fluids can be used to characterize the rheological parameters of the sample fluids. The most important parameter is the constant β . As shown in Kaye [9], as well as by Joseph and

Fosdick [2], β is proportional to the height of climb in a slow steady flow. The shape of the free surface from a perturbation method is found to be expressed in the following form [2],

$$h(r, \omega) = h_0(r) + h_2(r)\omega^2 + O(\omega^4) \quad (1)$$

where ω is the angular frequency of the rotating rod, $h_0(r)$ is the static rod climb (which is independent of ω), and the higher order term $O(\omega^4)$ is neglected. Considering the effect of surface tension, the height rise function $h_2(r)$ is obtained from the following equations:

$$\frac{\sigma}{r}(\text{r}h_2')' - \rho gh_2 = -2\frac{a^4}{r^4}(3\alpha_1 + 2\alpha_2) + \frac{\rho a^4}{2r^2}, \quad (2)$$

$$\text{with } h_2' = 0, \text{ and } h_2(r) \rightarrow 0 \text{ as } r \rightarrow \infty,$$

where σ is the surface tension, a is the radius of the rotating rod, ρ is the density of the liquid, g is the gravitational acceleration, and the prime denotes the derivative with respect to r . In addition, α_1 and α_2 are the parameters in the second-order approximation of stress tensor τ in the fluid. $T = -P\delta + \tau$ where $\tau_{(n)} = \tau_1 + \tau_2 + \dots + \tau_{(n)} + \dots$ for any simple non-Newtonian fluid. Here, $\tau_1 = \mu A_1$ for the linear, or Newtonian, approximation: and τ_2 is given by:

$$\tau_2 = \alpha_1 A_1 + \alpha_2 A_1^2, \quad (3)$$

where A_1 is Rivlin-Ericksen kinematic tensor of degree 1, and the expression $\tau_{(2)} = \tau_1 + \tau_2$ is termed the extra stress of a fluid of grade two.

The first-order solution for the simple fluid is exactly the same as that for a Newtonian fluid. The two-parameter expansion procedure is adopted, and the second-order solution is obtained as follows

$$h(a, \omega) \approx h_0(a) + \frac{4\pi^2 a}{\sigma(S)^{1/2}} \left[\frac{4(3\alpha_1 + 2\alpha_2)}{4 + \kappa} - \frac{\rho a^2}{2 + \kappa} \right] \frac{\omega^2}{2} \quad (4)$$

where $\kappa = a(S)^{1/2}$ and $S = \rho g/\sigma$.

From Equation (4), and the observation that values of h vary linearly with ω^2 in the rod-climbing experiment, β can be calculated with the known values of σ and $(dh/d\omega^2)_{\omega \rightarrow 0}$ as follows [3]:

$$\beta = \frac{4 + \kappa}{4} \left[\frac{\sigma(S)^{1/2}}{2a\pi^2} \left(\frac{dh}{d\omega^2} \right)_{\omega \rightarrow 0} + \frac{\rho a^2}{2 + \kappa} \right]. \quad (5)$$

In addition, the climbing constant β is related to the rheological properties of the fluid by:

$$\beta = 3\alpha_1 + 2\alpha_2. \quad (6)$$

The constants α_1 and α_2 are related to the zero shear values of the first and second normal stress differences N_1 and N_2 by the following equations:

$$\begin{aligned} N_1 &= -2\alpha_1 \dot{\gamma}^2 \equiv \Psi_1 \dot{\gamma}^2 \\ N_2 &= (2\alpha_1 + \alpha_2) \dot{\gamma}^2 \equiv \Psi_2 \dot{\gamma}^2 \end{aligned} \quad (7)$$

where $\dot{\gamma}$ is the shear rate, $\alpha_1 = -\Psi_1/2$ and $\alpha_2 = \Psi_1 + \Psi_2$.

Therefore, from these relations, β is expressed as follows [6],

$$\beta = 3\alpha_1 + 2\alpha_2 = \Psi_1/2 + 2\Psi_2 \quad (8)$$

For many polymeric systems, it is well known that Ψ_2 is negative and has an absolute value much smaller than that of Ψ_1 . For simplicity, the approximation $\Psi_2/\Psi_1 \approx -0.1$ [6] is made, and Equation (8) becomes

$$\beta = 0.3\Psi_1. \quad (9)$$

Thus, from the measured values of the rod climbing heights, the value of β is determined, and Ψ_1 can then be obtained from Equation (9).

EXPERIMENTAL

High-molecular-weight PIBs of different concentrations and molecular weights in low-molecular-weight PB were prepared for the rod-climbing experiments. The PIBs (Vistanex, MM grades L-80, L-100, L-120 and L-140, Exxon Chemicals) are highly paraffinic hydrocarbon polymers, composed of long straight-chain molecules terminally unsaturated. Due to their molecular structure, PIBs are relatively inert and resistant to chemical and oxidative attack, but are soluble in hydrocarbon solvents. PBs (Daelim Chemicals, Korea) are chemically stable liquids with moderate to high viscosities (120 ~ 400 cP). Additionally, PBs do not form residues when they are either volatilized or thermally decomposed, at sufficiently high temperatures.

A low viscosity solution of PIB was prepared by dissolving the desired amount of PIB (cut into small pieces) into a cosolvent, reagent grade

toluene. The solution was then continuously stirred in a sealed-glass flask for at least 48 h. This solution was then mixed with 1,000mL PB, and subsequently placed on a magnetic stirring heating plate at $30 \pm 0.2^\circ\text{C}$ for 48 h (a low rotation speed was used to minimize degradation). The complete removal of toluene from the solution was achieved by placing the solution in a vacuum oven. A nonshear thinning solution (often termed Boger fluid) consisting of PIB and PB was obtained [10].

The rod-climbing apparatus consists of a rod inserted vertically into a jar of PIB-PB fluid. The rod was driven vertically by an electrostatic servomotor (Sunmi Tech. Co., Seoul, Korea) with a control system to maintain constant speed under varying torque conditions. The apparatus can accommodate rods of diameters up to 1.2 cm. This limitation of rod diameter is imposed by the requirement that the diameter of the fluid container (12 cm) should be 10 times that of the rod diameter in order for the unbounded fluid approximation to be valid. The rod-climbing apparatus was enclosed in a thermostatic container and placed in a temperature controlled chamber accurate to 0.2°C . The rod and climbing fluid are viewed through the front of the chamber.

The angular speed of the rod was fixed for each experiment, and measured using a digital tachometer with an accuracy of 0.5 rpm. The climbing height of the fluid was then measured using a cathetometer (Gaertner Scientific Co., Chicago, USA), with a reproducibility of 0.001 cm.

RESULTS AND DISCUSSION

Figure 1 shows shear viscosity as a function of shear rate for different concentrations of L-80 PIB in PB. Figure 2 shows the first-normal stress difference of the test fluids as a function of shear stress using a RMS-800 with couette device (Rheometrics, Piscataway, USA). From Figures 1 and 2, it is found that the PIB-PB solutions (Boger fluids [11]) show second-order fluid behavior with high time-independent values of viscosity and elasticity.

For second-order fluids, the upper convected Maxwell model has been applied to characterize the rheological properties. N_1 is then obtained with a relaxation time λ as follows [12,13]:

$$N_1 = 2\eta\lambda\dot{\gamma}^2. \quad (10)$$

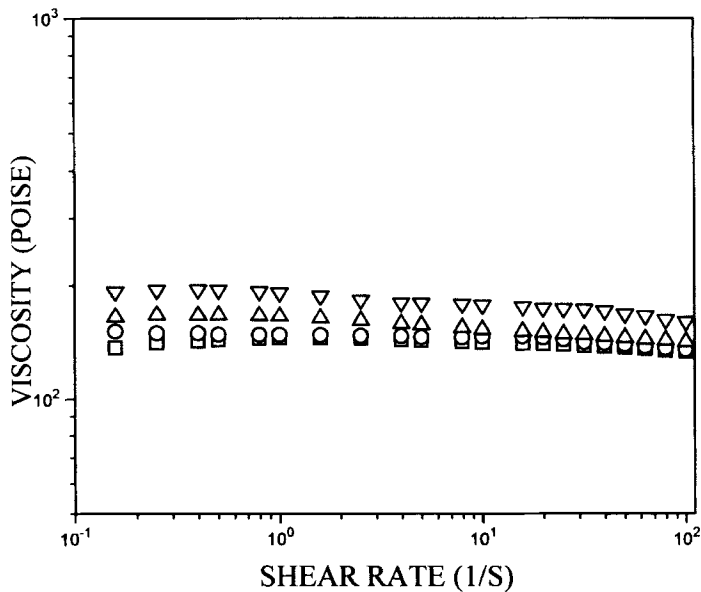


FIGURE 1 Viscosity vs. shear rate for L-80 PIB in PB at 30°C. (\square : 0.2% w/w, \circ : 0.4% w/w, \triangle : 0.6% w/w, ∇ : 0.8% w/w).

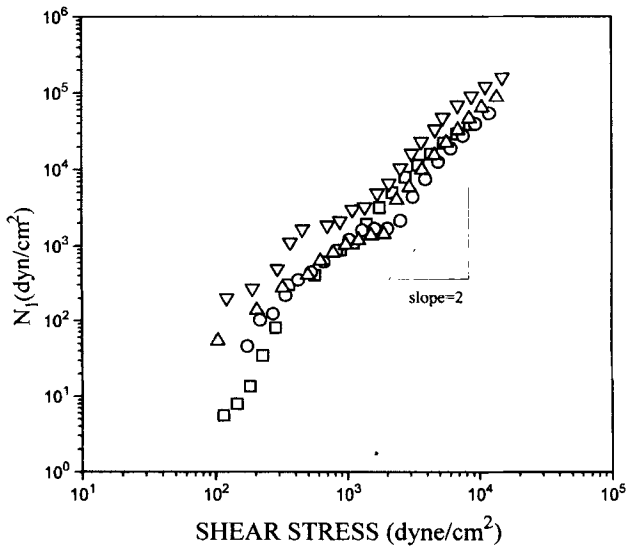


FIGURE 2 First-normal stress difference N_1 vs. shear stress for L-80 PIB in PB at 30°C. (\square : 0.2% w/w, \circ : 0.4% w/w, \triangle : 0.6% w/w, ∇ : 0.8% w/w).

Therefore, over most of the available shear rates, N_1 exhibits a quadratic dependence on $\dot{\gamma}$, as shown in Figure 2. Similar behaviors are observed for various second-order fluids, such as PIB in a solvent of PB and kerosene [12–14], as well as polyacrylamide in mixtures of glycerine and water [15,16]. Additionally, Figure 3 gives a plot of $N_1/\dot{\gamma}_2 (= \Psi_1)$ vs. stress. Ψ_1 increases slightly with increasing PIB concentration, and is almost independent of the shear stress. This plot permits a more direct comparison with the data on β .

Figure 4 shows the rod-climbing height h versus ω^2 for four different concentrations of PIB-PB. Higher polymer concentrations (i.e., higher elasticity) exhibit higher rod-climbing heights. The relationship between β and concentration can be considered from the theory developed by Brunn [17], who adopted Brinkman's analysis for the dumbbell model polymer in a second-order fluid. The material functions (η , Ψ_1 and Ψ_2) obtained by Brunn are:

$$\eta = \eta_s(1 + c[\eta] + 0.5(c[\eta])^2),$$

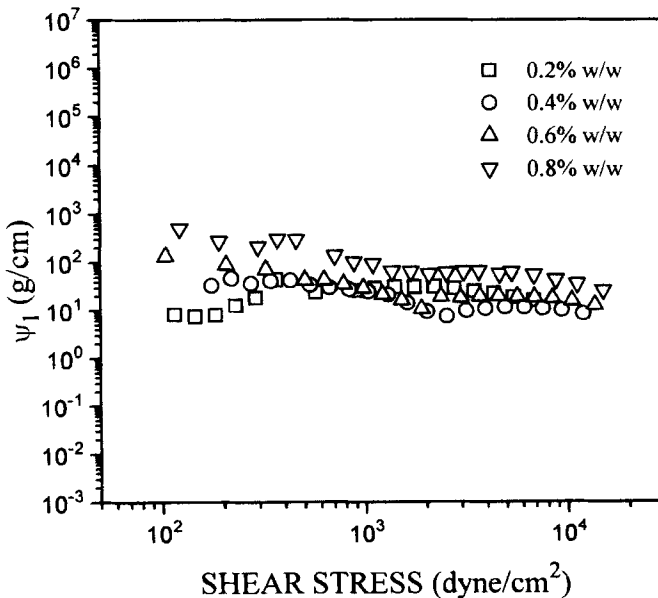


FIGURE 3 $N_1/\dot{\gamma}(= \Psi_1)$ vs. shear stress for L-80 PIB in PB at 30°C.

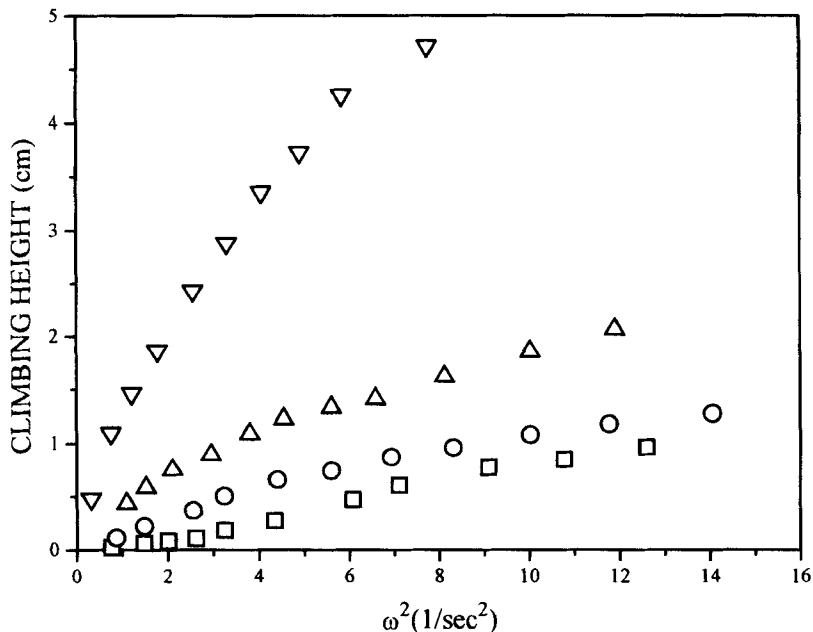


FIGURE 4 Effect of polymer concentration for L-80 PIB in PB on rod-climbing height using a 1.0-cm diameter rod at 30°C. (\square : 0.2% w/w, \circ : 0.4% w/w, \triangle : 0.6% w/w, ∇ : 0.8% w/w).

$$\Psi_1 = \frac{2M\eta_s^2[\eta]^2c}{RT}(1+1.25c[\eta]), \quad (11)$$

$$\text{and } \Psi_2 = \frac{-0.25M\eta_s^2[\eta]^3c^2}{RT}.$$

Inserting Equation (11) into Equation (8), we obtain

$$\beta = \frac{M\eta_s^2[\eta]^2c(1+0.75c[\eta])}{RT}. \quad (12)$$

Equation (12) shows that the rod-climbing height increases with increasing polymer concentration and solvent viscosity. Experimentally the rod-climbing height was observed to increase with solvent viscosity η_s and the square of the η_s in agreement with Equation (12). Rearranging Equation (12), the following equation can be obtained:

$$\frac{\beta}{\eta_s^2 c} = B(1 + 0.75c[\eta]) \quad (13)$$

where B , a constant at given temperature and molecular weight, is $M[\eta]^2/RT$. Equation (13) suggests a linear correlation between $\beta/\eta_s^2 c$ and c , as shown in Figure 5. Table I displays the measured values for climbing constants, zero shear viscosities and first normal stress difference coefficients for various concentrations of L-80 PIB in PB at 30°C. The climbing constants and the first-normal stress difference coefficients are obtained

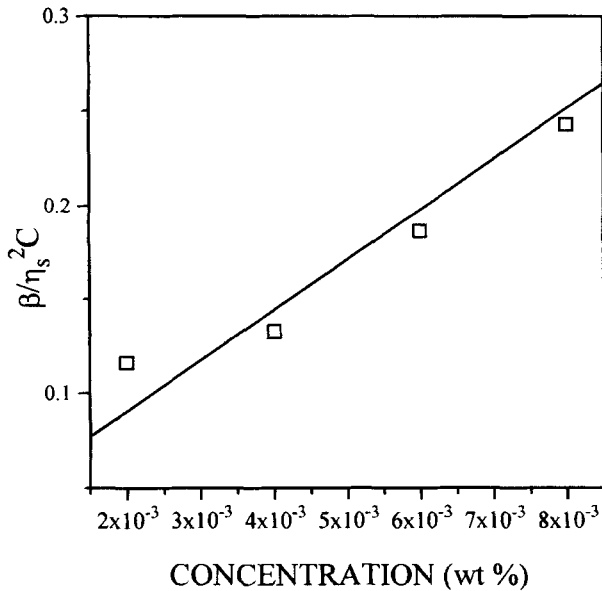


FIGURE 5 $\beta/\eta_s^2 C$ vs. concentration for L-80 PIB in PB at 30°C

TABLE I Experimental results for different concentrations of L-80 PIB in PB at 30°C with $D = 1.0$ cm rod.

Conc. (% w/w)	$(dh/d\omega^2)_{\omega \rightarrow 0}$ [cm \diamond s ²]	β [g/cm]	Zero shear viscosity [Poise]	Ψ_1 [g/cm]
0.2	0.141	6.4	139.0	21.3
0.4	0.324	14.6	150.0	48.7
0.6	0.687	30.8	165.7	102.7
0.8	1.198	53.5	193.0	178.3

from the rod-climbing experiments and the zero shear viscosities are measured using a RMS-800.

The rod-climbing experiment was also performed for different PIB molecular weights. For 0.2% w/w of four different molecular weight samples of PIB in PB, the climbing constant increases with increasing molecular weight, as shown in Figure 6.

Figure 7 shows the rod-climbing heights for 0.2% w/w L-140 PIB in PB versus the square of the rotational speed of the rod for three different rod sizes. As expected, the rod-climbing height increases with rotational speed and rod size. Since β is almost identical for the several rod sizes (smaller than R_c), a rod size of 1.0cm was arbitrarily selected for use in the experiment. When surface tension is neglected, $h_2(r)$ in Equation (1) can be represented as follows:

$$h_2(r) = \frac{4\pi^2}{\rho g} \left[\frac{2a^4}{r^4} \beta - \frac{\rho a^4}{2r^2} \right]. \quad (14)$$

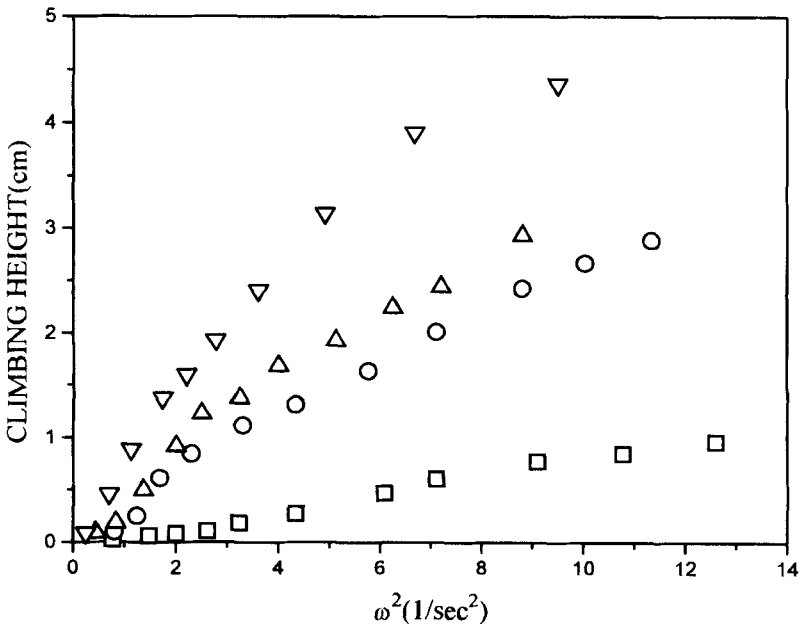


FIGURE 6 Effect of polymer molecular weight on rod-climbing height using a 1.0-cm diameter rod with 0.2% PIB in PB at 30°C. (□ : L-80, ○ : L-100, △ : L-120, ▽ : L-140).

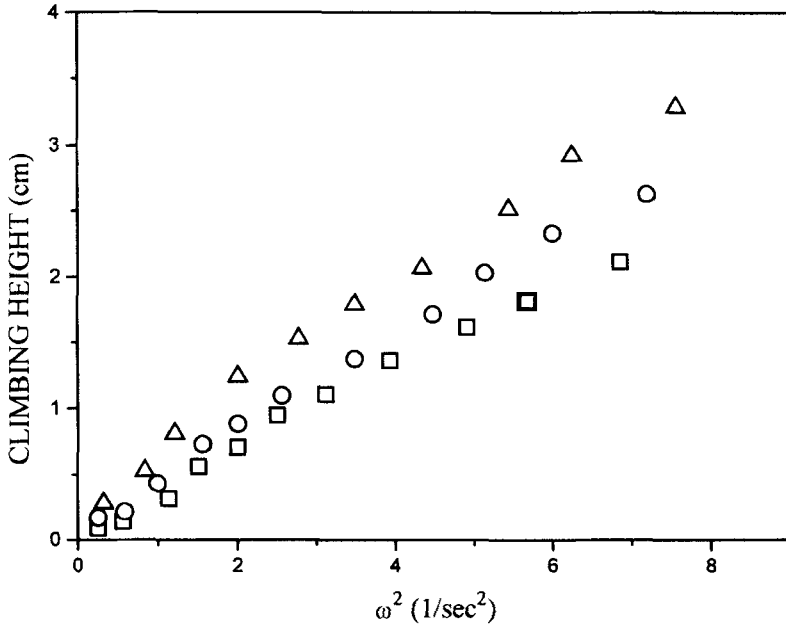


FIGURE 7 Effect of rod size on rod-climbing height for 0.2% w/w L-140 PIB in PB at 30°C. (□ : 9mm, ○ : 10mm, △ : 12mm).

In order to obtain the rod-climbing height, the right-hand-side of Equation (14) must be positive. This relation provides the criteria for selecting the appropriate rod size since the free surface only rises if $r^2 < (4\beta/\rho)$ for small ω [18]. For this reason, it is better to use rods with a small diameter in the rod-climbing experiments.

Figure 8 shows the effect of temperature on the rod-climbing height with 0.2% w/w L-140 PIB in PB. In this experiment, the three temperatures of the polymer were maintained within 0.2°C. As predicted, the rod-climbing height decreases with increasing temperature. Beavers and Joseph [4] show that climbing heights of the polymer exhibit a bell-shaped profile at the rod which is largely influenced by the temperature of the fluid. They also show that as the rotational speed is increased to very high values (50rev/s), the rod-climbing height decreases and experiences inertia-dominated depression of the free surface. This depression of the free surface at high speeds may be caused by viscous heating near the rod. Small changes in temperature may cause noticeable changes in the value of β . For example, Beavers and Joseph [4] found that at STP:

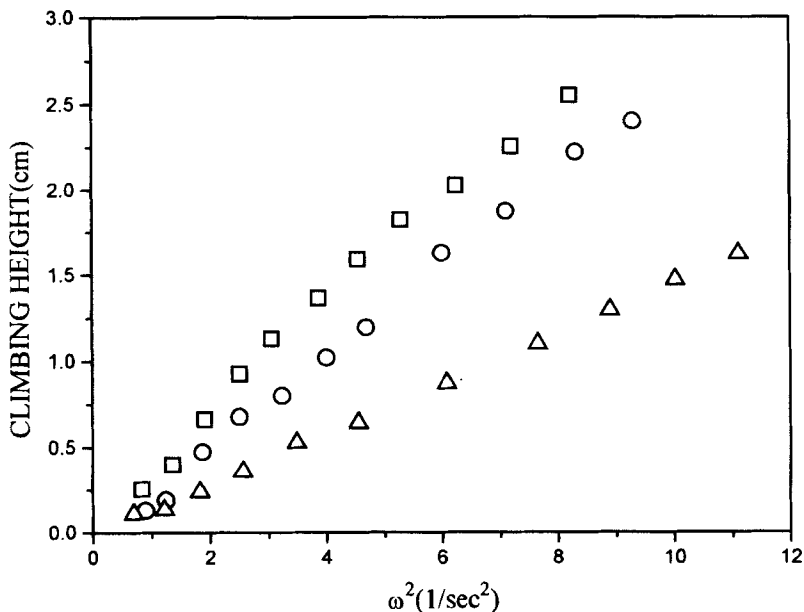


FIGURE 8 Effect of experimental temperature on rod-climbing height for L-100 PIB 0.2% w/w in PB using a 1.0 cm diameter rod. (□ : 25°C, ○ : 30°C, △ : 35°C).

$$\beta = 20 \exp(-0.115 T) \text{ g/cm for } 25^\circ\text{C} < T(^{\circ}\text{C}) < 50^\circ\text{C} \quad (15)$$

which empirically relates temperature to β .

The rheological properties were also measured with a mechanical spectrometer (RMS-800) in couette mode, at 30°C. The N_1 and η were measured for PIB-PB systems. The N_1 values obtained from the rod-climbing experiments were found to agree relatively well with those measured using from the RMS-800 rheometer. When these results are replotted to characterize the relation between $N_1/\dot{\gamma}_2 (= \Psi_1)$ and stress, as shown in Figure 9, consistency of Ψ_1 in both measurements can be observed. It also indicates that Ψ_1 is independent of the shear stress. This can be compared with the result which Joseph *et al.* [18] obtained for PIB in decalin. They studied the first-normal stress difference for two different molecular weight samples of PIB in decalin. They also attempted to compare the values computed from the rod-climbing constant with those obtained from the Rheometrics rheometer, at the lowest shear rates. However, the limiting values of the Ψ_1 are inconsistent with corresponding values measured using a rheometer for

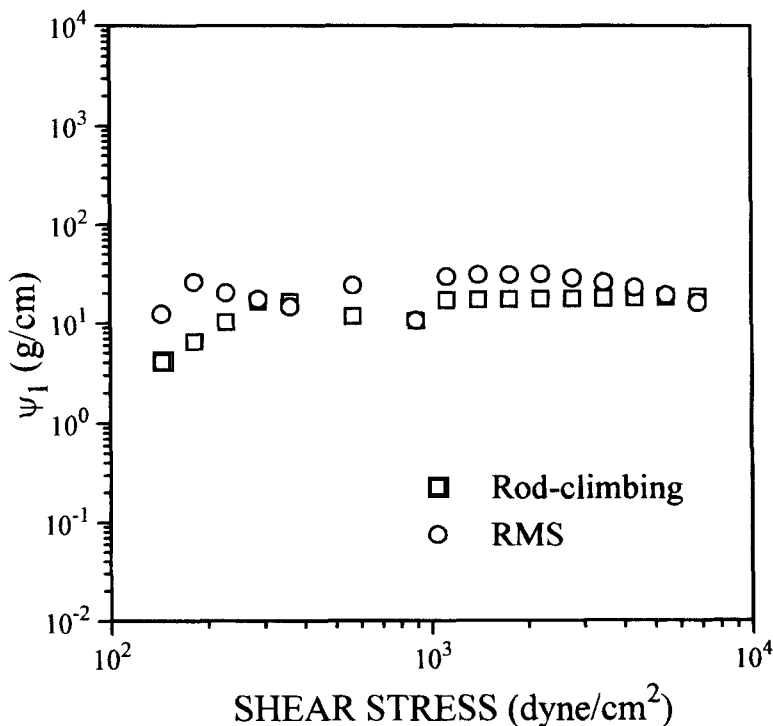


FIGURE 9 Comparison of Ψ_1 from RMS-800 to Ψ_1 from rod-climbing experiment for 0.2% w/w L-80 PIB in PB at 30°C. (○ : RMS-800, □ : Rod-climbing).

their polymer solutions of PIB in decalin. This inconsistency might come from the fact that their sample is not a second-order fluid since it shows the shear-thinning behavior.

CONCLUSIONS

Climbing constants β and first normal stress differences N_1 of PIB-PB system were investigated, and the correlation between β and N_1 of the polymer solutions was found. The N_1 values computed from the rod-climbing experiments agreed with those measured with the RMS-800 rheometer. The β and N_1 were found to decrease with temperature, but increase with rod size, polymer concentration, solvent viscosity, and molecular weight of PIB.

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References

1. R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids*; Wiley: New York, 1987; 2nd ed., Vol. 1.
2. D. D. Joseph and R. L. Fosdick, *Arch. Rat. Mech. Anal.*, **49**, 321 (1973).
3. D. D. Joseph, G. S. Beavers, and R. L. Fosdick, *Arch. Rat. Mech. Anal.*, **49**, 381 (1973).
4. G. S. Beavers and D. D. Joseph, *J. Fluid Mech.*, **69**, 475 (1975).
5. H. H. Hu, O. Riccius, K. P. Chen, M. Arney, and D. D. Joseph, *J. Non-Newtonian Fluid Mech.*, **35**, 287 (1990).
6. G. A. Nuñez, G. S. Ribeiro, M. S. Arney, J. Feng, and D. D. Joseph, *J. Rheol.*, **38**, 1251 (1994).
7. H. J. Choi, Ph. D. Dissertation, Carnegie Mellon University, Pittsburgh, PA, 1987.
8. H. J. Choi, D. C. Prieve, and M. S. Jhon, *J. Rheol.*, **31**, 317 (1987).
9. A. Kaye, *Rheol. Acta*, **12**, 207 (1972).
10. D. V. Boger and H. Nguyen, *Polym. Eng. Sci.*, **18**, 1037 (1978).
11. L. M. Quinzani, D. H. McKinley, R. A. Brown, and R. C. Armstrong, *J. Rheol.*, **34**, 705 (1990).
12. D. M. Binding, D. M. Jones, and K. Walters, *J. Non-Newtonian Fluid Mech.*, **35**, 121 (1990).
13. M. E. Mackay and D. V. Boger, *J. Non-Newtonian Fluid Mech.*, **22**, 235 (1987).
14. G. Prilutski, R. K. Gupta, T. Sridhar, and M. E. Ryan, *J. Non-Newtonian Fluid Mech.*, **12**, 233 (1983).
15. R. J. Binnington and D. V. Boger, *Polymer Eng. Sci.*, **26**, 133 (1986).
16. L. Choplin, P. J. Carreau, and A. Ait Kadi, *Polymer Eng. Sci.*, **23**, 459 (1983).
17. P. Brunn, *J. Rheol.*, **24**, 263 (1980).
18. D. D. Joseph, G. S. Beavers, A. Cers, C. Dewald, A. Hoger, and P. T. Than, *J. Rheol.*, **28**, 325 (1990).