

# Rod-Climbing Characteristics of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Suspended Polyisobutylene/Polybutene Solution

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**ABSTRACT:** From rod-climbing rheometer measurements, we systematically investigated the normal stress values of suspended particles in polymeric liquids at low shear rates using the second-order fluid constitutional relationship. The climbing constants  $\beta$  of the suspended  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles in polyisobutylene/polybutene solutions, which exhibit Boger fluid characteristics (highly elastic, but no shear-thinning), were estimated from the rod-climbing experiment, showing that  $\beta$  increased with polymer concen-

tration and polymer molecular weight. The first normal stress difference coefficient of the suspended  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in polymeric liquids obtained from the rod-climbing rheometer was well correlated with the rheological properties measured by rotational rheometers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1548–1552, 2004

**Key words:** rod-climbing; Boger fluid; polyisobutylene; second-order fluid; rheology; suspension

## INTRODUCTION

One of the peculiar effects in non-Newtonian fluids is that of a rod-climbing phenomenon,<sup>1</sup> which is associated with nonlinear effects and normal stresses. This phenomenon does not occur in Newtonian fluids, where the stress tensor is linearly related to the rate of the strain tensor. Therefore, the rod-climbing property can be used to characterize important rheological properties for non-Newtonian, polymeric systems.<sup>2</sup> Experimentally, the rod-climbing phenomenon for various non-Newtonian fluids has been observed. Examples include not only polymer solutions but also concentrated, noncolloidal,<sup>3</sup> ferrofluids,<sup>4</sup> and biological fluids.<sup>5</sup> The theoretical analysis of rod-climbing for low rod speeds has been studied intensively. Joseph and Beavers<sup>6,7</sup> showed that the polymeric liquids used in their experiments had a second-order range (i.e., a range in which the climbing height was proportional to the square of the rod rotation speed  $\omega^2$ ). Because there is only one viscoelastic parameter, the climbing constant in the second-order fluid model showed that the parameter  $\beta$  (which depends on temperature) could be determined from measurements of the height of climb. A precise analysis of the rod-climbing phenomenon using the second-order fluid model can be used to extract important rheological parameters for

polymer solutions,<sup>8</sup> including the effects of surface tension, for the shapes of the free surface to agree better with the measured shapes.

It is a well-known fact that a mixture of polyisobutylene (PIB) and polybutene (PB), which is generally regarded as a Boger fluid, is satisfactorily described by a second-order fluid model.<sup>9–11</sup> Nonetheless, there are very few published works on particles suspended in a Boger fluid. In this study, we dispersed spherical  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles in a PIB/PB mixture and systematically examined the normal stress effect of polymeric liquids at low shear rates from the height prediction of the rod-climbing. The  $\beta$  value for particle-suspended PIB/PB solutions was processed to obtain the first normal stress difference ( $N_1$ ) using the second-order fluid model.<sup>12</sup> We will correlate  $N_1$  values obtained from these climbing constants with those measured from rotational rheometers.

## EXPERIMENTAL

### Materials and sample preparation

The PIBs used were Vistanex polyisobutylene (MM L grades obtained from Exxon/Mobil Chemicals, Baytown, TX), and the solvent was PB (900 series obtained from Daelim Chemicals, Korea), which is a chemically stable liquid with moderate to high viscosities (12–40 Pa s<sup>-1</sup>). As reported by the manufacturer, the viscosity-average molecular weights of four different grades of PIB (L-80, L-100, L-120, and L-140) were 0.99, 1.2, 1.6, and  $2.1 \times 10^6$  g/mol, respectively.<sup>13</sup> Vistanex PIBs also have been used as polymeric turbulent drag reducers<sup>14</sup> in various organic solvents.<sup>13,15,16</sup> The turbu-

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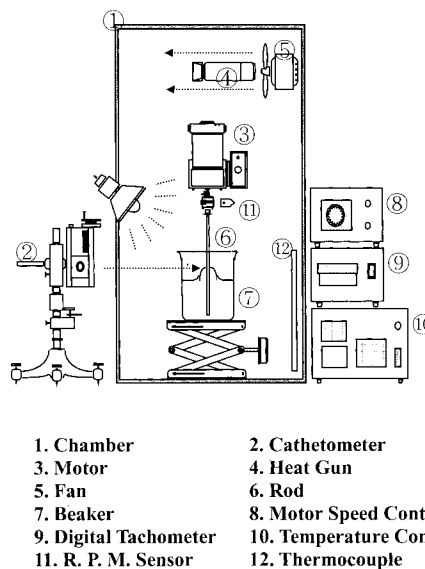
lent drag reduction phenomenon implies that the addition of a very small amount of high molecular weight polymer into a liquid can cause a drastic reduction in the frictional drag in turbulent flow.<sup>17</sup> To investigate the effect of suspended particles in a Boger fluid, we dispersed nonmagnetic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is Bayferrox 130M grade (average particle size: 0.17  $\mu$ m; specific gravity: 5.0) from Bayer AG (Leverkusen, Germany).

The Newtonian solvent PB was made to be viscoelastic by dissolving a small amount of high molecular weight PIB in reagent-grade toluene, a volatile and good solvent for both PIB and PB. Note that PIB is compatible with PB, although it is difficult to dissolve PIB in PB without using a cosolvent. The small pieces of PIB were dissolved in toluene by a magnetic stirring bar in a sealed glass flask for a minimum of 72 h. The solution of PIB in toluene was then mixed with PB in a 1000-mL beaker, with occasional stirring with a glass stick for a minimum of 3 days. A low-speed rotation was maintained to minimize the degradation of high molecular weight PIB molecules. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was oven dried and finely sieved before use.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles were then suspended in the PIB/PB/toluene solution, which has a sufficiently low solution viscosity to uniformly disperse particles. To prepare a highly viscoelastic solution, the cosolvent toluene was then removed as completely as possible, using a rotary evaporator and a vacuum oven.

### Measurements

The rod-climbing apparatus consisted of a rod vertically inserted into a jar of the test fluid. The fluid was contained in a circular glass vessel. The rod was driven by an electrostatic dc servomotor with a feedback control system (Sun Mi Technology Co. SMS 20, Korea) to maintain constant speed under varying torques. The motor and rod were connected by a chuck. This rod-climbing apparatus was then enclosed in a thermostatically controlled container. (This system maintained the temperature accurately to within 0.1°C.) The schematic representation of the apparatus is shown in Figure 1. The angular speed of the rod was measured by means of a digital tachometer (Han-young SM3, Korea) with an accuracy of 0.1 rpm and fixed at a constant angular speed for each height-measuring step. The climb height of the fluid was then measured using a cathetometer (Gaertner Scientific Corp. Serial No. 7081-p, Skokie, IL). Measurements of the climb height were reproducible to within  $\pm 0.001$  cm.

Various experimental conditions such as different polymer molecular weights and polymer concentrations were applied. We also measured rheological properties ( $\eta$ ,  $G'$ ,  $G''$ , and  $N_1$ ) of the suspended particles in PIB/PB solutions using rotational rheometers



**Figure 1** Schematic representation of a rod-climbing rheometer.

(Physica MC-120, Stuttgart, Germany and ARES, Rheometrics, Piscataway, NJ) at 30°C.

### RESULTS AND DISCUSSION

The climbing constant was derived from the perturbation,<sup>7,18</sup> and the free surface is expressed as a function of both radial position ( $r$ ) and a rotational speed as follows:

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

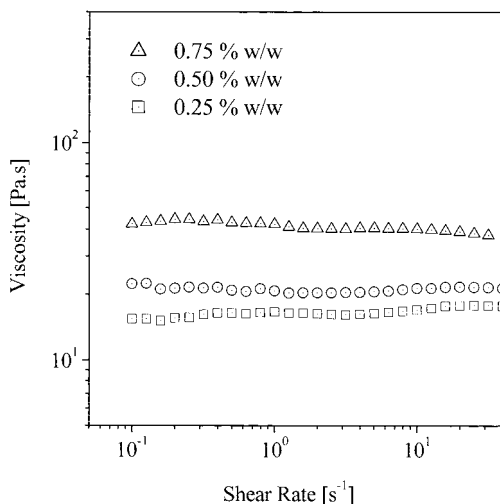
where  $\omega$  is the angular speed of the rotating rod (rev/s),  $h_0(r)$  is the static rod climb height, and the higher-order term  $o(\omega^4)$  can be neglected. With the surface tension ( $\sigma$ ) of the polymeric fluid, the height rise function of rod size  $r = a$  is more explicitly obtained as<sup>2,6,7</sup>

$$h(a, \omega) \cong h_0(a) + \frac{4\pi^2 a}{\sigma\sqrt{S}} \left( \frac{4\beta}{4 + \kappa} - \frac{\rho a^2}{2 + \kappa} \right) \frac{\omega^2}{2} \quad (2)$$

where  $\kappa = a(S)^{1/2}$ ;  $S = \rho g / \sigma$ , where  $\rho$  is the density of the liquid and  $g$  is the gravitational acceleration; and  $h_0(a)$  is a static climb height before applying rotation. In eq. (2),  $\beta$  is the climbing constant, which is related to the parameters of a simple fluid of grade two or is related to the first and second normal stress difference coefficients at zero shear rate<sup>2,12</sup>:

$$\beta = 3\alpha_1 + 2\alpha_2 = \frac{\Psi_1}{2} + 2\Psi_2 \quad (3)$$

where  $\Psi_1$  and  $\Psi_2$  are the first and second normal stress difference coefficients, respectively;  $\alpha_1$  and  $\alpha_2$



**Figure 2** Viscosity versus shear rate for three different polymer concentrations (PIB L-100, 0.25, 0.50, and 0.75% w/w) in PB/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (0.03 v/v) at 30°C.

are coefficients characterizing material properties, which correspond to those from the retarded-motion expansion.<sup>19,20</sup>

From the observation of the climbing height  $h$  with different  $\omega^2$ , the slope becomes

$$\frac{dh}{d\omega^2} = \frac{2\pi^2 a}{\sigma\sqrt{S}} \left( \frac{4\beta}{4 + \kappa} - \frac{\rho a^2}{2 + \kappa} \right) \quad (4)$$

Then,  $\beta$  is calculated in terms of  $\sigma$  and  $(dh/d\omega^2)_{\omega \rightarrow 0}$  as follows:

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

For many polymeric systems,  $\Psi_2$  is negative and is much smaller than  $\Psi_1$ . Therefore, in our study, the approximation  $\Psi_2/\Psi_1 \cong -0.1$  was used, and eq. (3) becomes

$$\beta \cong 0.3\Psi_1 \quad (6)$$

With this relation, the theoretical value of the  $N_1$  is obtained as

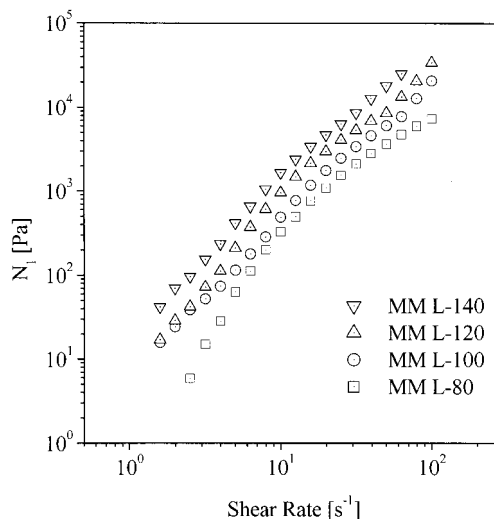
$$N_1 = \Psi_1 \dot{\gamma}^2 = \frac{10}{3} \beta \dot{\gamma}^2 \quad (7)$$

Furthermore, note that the relationship between the rheological parameters in the zero frequency and shear rate limit, based on the Cox–Merz rule,<sup>21</sup> is expressed as

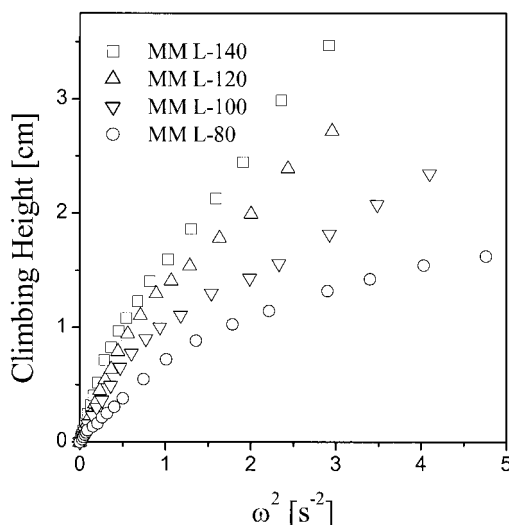
$$\lim_{\dot{\gamma} \rightarrow 0} \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2} = \lim_{\omega \rightarrow 0} \frac{2G'(\omega)}{\omega} = \frac{10}{3} \beta \cong \Psi_{1,0} \quad (8)$$

The shear viscosity and first normal stress difference, as a function of shear rate for suspended particles in PIB/PB solutions with different polymer concentrations and molecular weights measured using rotational rheometers (Physica MC-120 and ARES), exhibited typical Boger fluid characteristics; constant viscosity and a quadratic dependency of  $N_1$  on shear stresses (Figs. 2 and 3). Although a slight shear thinning behavior appears at a high shear rate region for a 0.75 wt % PIB concentration (Fig. 2), the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles suspended in PIB/PB solutions show typical Boger fluidlike time-independent high shear viscosity. It also indicates that the shear viscosity increases with polymer concentration, which is similar to a typical particle-suspended polymer solution.<sup>22</sup> However, in contrast to typical particle-suspended polymer solutions or melts,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> suspended-particle systems show that the  $N_1$  increases with particle concentration (not shown here). In general, it is known that the addition of inert solid particles to a polymer decreases the melt elasticity; that is, the  $N_1$  decreases as the filler concentration increases.<sup>23,24</sup> The observation that polymers with high filler concentrations have smaller  $N_1$  than those with low concentrations can be explained by the fact that the filler itself can increase the rigidity of the polymer.<sup>25</sup>

For both polymer solutions with and without particles, the rod-climbing heights are found to increase as the polymer concentration increases. Higher polymer concentrations (producing higher elasticity) exhibit higher rod-climbing heights. This phenomenon



**Figure 3** First normal stress difference ( $N_1$ ) versus shear stress for four different polymer molecular weights (PIB L-80, -100, -120, and -140) in PB (99.75% w/w)/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (0.03 v/v) at 30°C.



**Figure 4** Effect of polymer molecular weights (0.25 wt % in PB) on the climbing height with 1.0 cm diameter rod at 30°C ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, 3% v/v).

can be explained from the result of  $N_1$  (Fig. 3); that is, higher molecular weight polymer solutions can produce the same effect as that of different polymer concentrations. The relationship between  $\beta$  and PIB concentration ( $C$ ) can be investigated from the theory developed by Brunn,<sup>26</sup> who adopted Brinkman's analysis for the dumbbell (polymer) to describe a second-order fluid. Using the material functions ( $\eta$ ,  $\Psi_1$ , and  $\Psi_2$ ) obtained by Brunn<sup>26</sup> and eq. (3), we can derive results in the following equation:

$$\beta = \frac{M\eta_s^2[\eta]^2C(1 + 0.75C[\eta])}{RT} \quad (9)$$

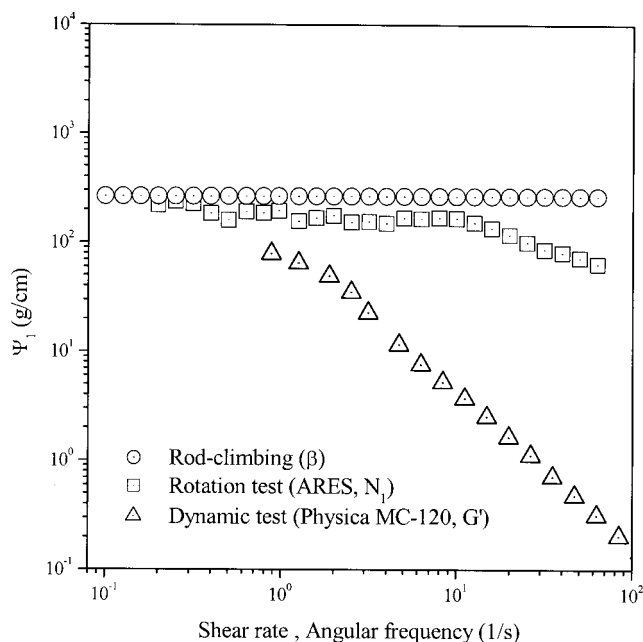
Equation (9) implies that the rod-climbing height increases with both polymer concentration and solvent viscosity ( $\eta_s$ ). Here,  $[\eta]$  is the intrinsic viscosity,  $M$  is the molecular weight,  $R$  is the gas constant, and  $T$  is the absolute temperature. These trends are identified by the fact that the  $N_1$ , which possesses the restoring force induced by the anisotropic structure of polymeric fluid exposed to flow, increases with increasing concentration. Experimentally, the rod-climbing height was observed to increase with the square of the solvent viscosity, which is in agreement with eq. (8). Rearranging eq. (9) yields

$$\frac{\beta}{\eta_s^2C} = B(1 + 0.75C[\eta]) \quad (10)$$

where  $B = M[\eta]^2/RT$ . Equation (10) predicts a linear correlation between  $\beta/\eta_s^2C$  and  $C$ . This correlation was confirmed in the particle-suspended systems.

The rod-climbing heights were obtained for different PIB molecular weight solutions as presented in Figure 4. The climbing constants increase as the PIB molecular weight increases. Equation (10) also indicates that  $\beta$  is proportional to the molecular weight of the polymer, which corresponds to the fact that the elasticity of polymer solution increases with PIB molecular weight. Therefore, we can see that the elasticity of the polymer solution increases with PIB molecular weight. This result is the same as Figure 3.

The  $N_1$  values computed from the rod-climbing rheometer were found to agree well with those measured with the rotational rheometers for PIB/PB systems.<sup>10</sup> To apply this concept to the particle-suspended Boger fluid system, the  $N_1$  of the system was measured with rotational rheometers (Physica MC-120 and ARES) at 30°C and then compared with the  $N_1$  obtained from the rod-climbing rheometer (Fig. 5). The results show typical Boger fluid characteristics, exhibiting quadratic dependency on  $\dot{\gamma}$  over a broad range of  $\dot{\gamma}$  values, both from the rod-climbing experiment and the rotational rheometers. Notice that  $\beta$  is related to the rheological properties of the fluid by eq. (8). The comparison between the climbing constants and the values from rheometers (simple shear and dynamic modes) was also conducted. The results showed that the theoretical predictions obtained from  $\beta$  are well correlated with each other, especially at low shear rates and low-frequency regions (Fig. 5). This was previously reported using a rod-climbing rheometer for various fluids, such as heavy crude oils,<sup>2</sup> poly(methyl methacrylate), and poly(acrylic acid).<sup>19</sup>



**Figure 5** Comparison of the first normal stress difference coefficients ( $\Psi_1$ ) obtained from the three different methods for 0.25 wt % PIB L-140 in PB- $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (0.03 v/v).



## CONCLUSIONS

The rod-climbing experiment and its relationship to the first normal stress difference of particle-suspended PIB/PB systems possessing Boger fluid characteristics (no shear-thinning and highly elastic) were investigated. Based on the second-order fluid model, we systematically examined the climbing phenomenon of the particle-suspended Boger fluid. The rod-climbing constants of the fluids were found to increase with polymer concentration and molecular weight. In addition, in contrast to polymer melts,  $\beta$  for suspended-particle systems increased with particle concentration because of the screening effect of solvent on particles.<sup>25</sup>

The measured values of both  $N_1$  and  $\eta$  in our study imply that the suspended particles in PIB solutions exhibited Boger fluid behavior. The amount of suspended particles and the solvent viscosity increased. This increase is related to the rigidity of the polymer, which induces the increases in the overall elasticity of the system. The first normal stress differences calculated from the second-order fluid model were well correlated with the measured values. Therefore, from the climbing height of the free surface near the rod, we can obtain precise measurements, in a simple manner, of the elastic nature of the fluid in a low deformation rate region.

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## References

1. Weissenberg, K. *Nature* 1947, 159, 310.
2. Nuñez, G. A.; Ribeiro, G. S.; Arney, M. S.; Feng, J.; Joseph, D. D. *J Rheol* 1994, 38, 1251.
3. Zarraga, I. E.; Hill, D. A.; Leighton, D. T. *J Rheol* 2001, 45, 1065.
4. Melzner, K.; Odenbach, S. *J Magn Magn Mater* 2002, 252, 250.
5. Chiruvolu, S.; Warriner, H. E.; Naranjo, E.; Idziak, S. H. J.; Radler, J. O.; Plano, R. J.; Zasadzinski, J. A.; Safinya, C. R. *Science* 1994, 266, 1222.
6. Joseph, D. D.; Beavers, G. S. *Rheol Acta* 1977, 16, 169.
7. Beavers, G. S.; Joseph, D. D. *J Fluid Mech* 1975, 69, 475.
8. Joseph, D. D.; Beavers, G. S. *Arch Rat Mech Anal* 1997, 62, 323.
9. Choi, H. J.; Prieve, D. C.; Jhon, M. S. *J Rheol* 1987, 31, 317.
10. Choi, H. J.; Shon, H. S.; Lee, H. J.; Jhon, M. S. *Int J Polym Anal Char* 1996, 3, 75.
11. Quinzani, L. M.; McKinley, D. H.; Brown, R. A.; Armstrong, R. C. *J Rheol* 1990, 34, 705.
12. Choi, H. J. *Korean J Chem Eng* 1991, 8, 18.
13. Choi, H. J.; Kim, C. A.; Jhon, M. S. *Polymer* 1999, 40, 4527.
14. Kim, C. A.; Jo, D. S.; Choi, H. J.; Kim, C. B.; Jhon, M. S. *Polym Test* 2001, 20, 43.
15. Choi, H. J.; Jhon, M. S. *Ind Eng Chem Res* 1996, 35, 2993.
16. Lee, K.; Kim, C. A.; Lim, S. T.; Kwon, D. H.; Choi, H. J.; Jhon, M. S. *Colloid Polym Sci* 2002, 280, 779.
17. Choi, H. J.; Lim, S. T.; Lai, P. Y.; Chan, C. K. *Phys Rev Lett* 2002, 89, 088302.
18. Kaye, A. *Rheol Acta* 1972, 12, 207.
19. Joseph, D. D.; Beavers, G. S.; Cers, A.; Dewald, C.; Hoger, A.; Than, P. T. *J Rheol* 1984, 28, 325.
20. Choi, H. J.; Sim, I. S.; Lim, S. T.; Jhon, M. S. *J Appl Polym Sci* 2000, 75, 572.
21. Cox, W. P.; Merz, E. H. *J Polym Sci* 1958, 28, 619.
22. White, J. L.; Crowder, J. W. *J Appl Polym Sci* 1974, 18, 1013.
23. Chan, Y.; White, J. L.; Oyanagi, Y. *J Rheol* 1978, 22, 507.
24. Tanaka, H.; White, J. L. *Polym Eng Sci* 1980, 20, 949.
25. Choi, H. J.; Vinay, S. J.; Jhon, M. S. *Polymer* 1999, 40, 2869.
26. Brunn, P. *J Rheol* 1980, 24, 263.