Macromolecular Research, Vol. 17, No. 10, pp 807-812 (2009)

Tumbling Dynamics of Rod-like and Semi-flexible Polymers in Simple Shear and Mixed Flows

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Received March 23, 2009; Revised April 11, 2009; Accepted April 11, 2009

Abstract: In this work, we focus on the tumbling dynamics of rod-like and semi-flexible polymers in mixed flows, which vary from simple shear to pure rotation. By employing a bead-rod model, the tumbling pathways and periods are examined with a focus on the angular distribution of their orientation. Under the mixed flows, the tumbling dynamics agreed well with earlier studies and confirmed the predicted scaling laws. We found that the angular distribution deviates from that of shear flow as the flow type approaches pure rotation. Finally, we investigated the angular distribution of λ-DNA in a shear flow and found that the present numerical simulations were in quantitative agreement with the previous experimental data.

Keywords: brownian dynamics, mixed flows, rod-like polymers, semi-flexible polymers, tumbling.

Introduction

Recently, the dynamics of single polymer molecules has attracted much attention due to its importance in polymer physics and rheology. It is also an essential step in manipulating a single polymer in many lab-on-a-chip applications such as DNA separation[1,2] and stretching devices.[3] Understanding polymer dynamics is also essential in manufacturing processes involving complex fluids such as polymer solutions. The conformational change of polymer molecules is strongly concerned with the macroscopic flow characteristics, such as the normal stress difference. For the last decade, much progress has been made in theoretical, experimental and numerical schemes to elucidate the dynamics of a single polymer. Those readers who are interested in obtaining more details on this subject may refer to the two recent review papers by Larson[4] and Shaqfeh.[5]

Many characteristics of the dynamical behaviors of polymers have been revealed in various flow situations since the pioneering works of the Chu group.[6-9] They utilized video-microscopy techniques to observe a single dye-stained DNA molecule in various field gradients. A shear flow is composed of extension and rotation, which is of considerable practical importance, since shear flows are encountered in almost every flow system. Especially, shear flows are strongly developed near solid walls due to the no-slip boundary conditions. The Chu group showed that a single DNA molecule is stretched and tumbled in a shear flow. Later, it was shown that there is periodicity in the tumbling of polymer molecules in a shear flow, and this process was also theoretically analyzed.[8] Basically, due to the vorticity component in the rate of deformation tensor, the polymer molecules in all of the flows considered experience end-over-end tumbling, resulting in fluctuations in the fractional molecular extension and in the polymer orientation angle. Teixeira *et al.*[9] connected the conformation change of polymer molecules with the development of macroscopic normal stress differences using numerical simulations. The above-mentioned researches are mainly concerned with the analysis of the stretching behavior and rotation time in a simple shear flow.

Most experimental and theoretical investigations of the conformational change of DNA molecules have only been accomplished in planar extensional or simple shear flows. However, more general flow characteristics which are represented by the flow strength and the flow type are frequently encountered in a realistic microfluidic device. Moreover, rotation-dominant flow is also important in many kinds of complex geometries, such as bent, curved and grooved channels, however little research has been done on the DNA dynamics in rotational-dominant flows. A pure rotational flow, which is difficult to induce in microfluidic devices, can be realized with the recently devised microfluidic four-roll mill,[10] which makes it possible to explore the

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conformational change of flexible polymers in rotational flows.

On the other hand, the statistical angular distribution of a single polymer has attracted much attention in a shear flow with random velocity fluctuation which can be generated by the 'elastic turbulence' or thermal motion of solvents.[11-13] Recent experimental works showed that there are asymptotic behaviors in the angular distribution and tumbling time of polymers in a shear flow, which are consistent with the theoretical and numerical predictions. However, to the best of our knowledge, there have been few systematic studies on the angular dynamics in mixed flows. In this paper, we investigated the dynamics of rod-like and flexible polymers represented by angular predictions and the distribution of bead-rod chains in mixed flow.

Background Theory

When DNA molecules are subjected to hydrodynamic forces in a flow field, their conformational response depends on the flow strength and flow type, which are parametrized by the Weissenberg number (Wi) and the flow-type parameter (α), respectively.[14] In Figure 1, a schematic diagram for rod-like polymers is presented. We note that the angle (ϕ) is only considered for semi-flexible chains and that its definition is the same as that of Maier and Radler.[15] The length scale and time of the system are non-dimensionalized with rod length a and the bead diffusion time $\zeta a^2/k_BT$, respectively, and the force is non-dimensionalized with k_BT/a, where ζ denotes the friction coefficient of a bead, k_B is Boltzmann constant and T is absolute temperature. The Weissenberg number is defined as $Wi=\dot{\gamma}\tau$, where τ corresponds to the longest relaxation time and $\dot{\gamma}$ denotes the strain rate. For a rod-like polymer, the longest relaxation is equivalent to the rotational relaxation time ($=\zeta a^2/12k_BT$).[16] The longest relaxation of a multi bead-rod chain is defined as $0.0142N_b^2(\zeta a^2/k_BT)$, where N_b denotes the number of beads.[17] We note that the longest conformational and rotational relaxation times are equal for flexible polymer molecules.[18]

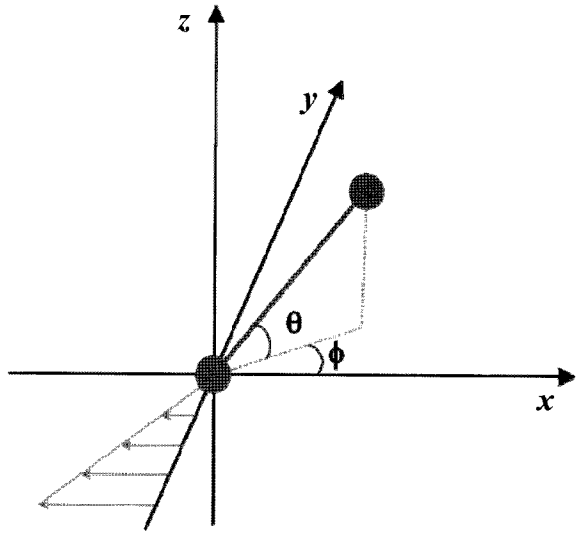

Figure 1. Schematic diagram of polymer chain and the applied flow field in this study.

Considering a planar mixed flow, the dimensionless velocity gradient is given by,

$$\frac{\partial u_i^{\infty}}{\partial x_j} = \dot{\gamma}\begin{bmatrix} 0 & 1 & 0 \\ \alpha & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{1}$$

We note that x_1, x_2 and x_3 correspond to the x, y and z coordinates, respectively. The flow type changes from pure shear to pure rotational flow as varies α from 0 to -1. In the above equation, $\dot{\gamma}$ denotes the strain rate.[14]

Recently, Gerashchenko and Steinberg[13] reported experimental results concerned with the statistical angular distribution of a λ-DNA molecule in a shear flow (α=0). Their experimental results clearly show that there are scaling behaviors in the rotational time (τ_R) and the angular probability distributions, $P(\theta)$ and $P(\phi)$, with $\Delta\theta$ and $\Delta\phi$, where $\Delta\theta$ and $\Delta\phi$ denote the widths of $P(\theta)$ and $P(\phi)$ at the half height of the maximum, respectively.

Their results are also consistent with previous theoretical predictions.[19] The tails of the probability distribution functions (PDFs) are $P(\phi) \propto (\sin\phi)^{-2}$ for $|\phi| >> \Delta\phi$ and $P(\theta) \propto |\theta|^{-2}$ for $1 >> \Delta\theta >> \Delta\phi$[19]. The predicted scaling laws[19] can be denoted as follows:[13]

For sufficiently small extensions,

$$\Delta\phi \propto Wi^{-1},\ \tau_R \propto \tau \tag{2}$$

For a stretched polymer which is equivalent to a rigid rod,

$$\Delta\phi \propto Wi^{-1/3},\ \tau_R \propto \tau Wi^{-2/3} \tag{3}$$

where τ_R denotes the rotational time.

We note that for a rod-like polymer, the analytical expression for the PDF in a shear flow was previously derived by Hinch and Leal.[20] Up to now, there have been rather extensive studies on the angular distribution of rod-like or flexible polymers in a shear flow. However, there have been few studies conducted in mixed flows. In this work, we systematically investigate the change in the angular distribution of a rod-like polymer according to the variation of the flow type. A short DNA molecule whose length is less than one persistence length (~50 nm) can be considered to be a rod-like polymer.

In this study, we also show some results for the angular distribution of λ-DNA in a shear flow with a multi bead-rod chain model, which can be considered to be a flexible polymer. Celanti *et al.*[11] previously reported some numerical results which are qualitatively consistent with experimental results. We visit this problem with a more sophisticated model.

Numerical Schemes and Parameters

The bead-rod chain model is employed to simulate a flexible polymer molecule and a rod-like polymer is modeled as a rigid dumbbell consisting of two beads connected by a rigid rod. The present numerical model is well described in the open literature.[21] We consider a bead-rod chain with N_b beads connected by N_r rigid rods (=N_b-1) with a constant length, a. The evolution equation of bead i is:

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{u}_i^{\infty}(\mathbf{r}_i) + \frac{1}{\zeta}(\mathbf{f}_i^B(t) + \mathbf{f}_i^C(t)) \tag{4}$$

where $\boldsymbol{r}_i$ is the position vector of bead i at time t, $\mathbf{u}_i^{\infty}(\mathbf{r}_i)$ the fluid velocity at bead i, $\mathbf{f}_i^B(t)$ the Brownian force and $\mathbf{f}_i^C(t)$ the constraint force keeping two neighboring beads at a constant distance of a. The Brownian force $\mathbf{f}_i^B(t)$ models the random kicking by solvent molecules. The expectation values of $\mathbf{f}_i^B(t)$ can be denoted as follows:

$$\langle \mathbf{f}_i^B(t) \rangle = 0 \tag{5a}$$

$$\langle \mathbf{f}_i^B(t_1)\mathbf{f}_j^B(t_2) \rangle = 2k_BT\zeta\delta_{ij}\delta(t_1-t_2)\boldsymbol{I} \tag{5b}$$

where $\boldsymbol{I}$ is the unit tensor, δ_{ij} the Kronecker delta, and $\delta(t_1-t_2)$ is the Dirac delta function.

The constraint force $\mathbf{f}_i^C(t)$ can be expressed in terms of the tension t_i in the rods, as follows:

$$\mathbf{f}_i^C(t) = t_i\mathbf{u}_i - t_{i-1}\mathbf{u}_{i-1} \tag{6}$$

where $\mathbf{u}_i = (\mathbf{r}_{i+1}-\mathbf{r}_i)/a$ is the orientation vector of rod i. Eq. (6) is solved by the iterative solution scheme devised by Liu[22] with the following constraint.

$$(\mathbf{r}_{i+1}-\mathbf{r}_i)\,(\mathbf{r}_{i+1}-\mathbf{r}_i)/a^2 - 1 = \varepsilon_{tol}^2 \tag{7}$$

where ε_{tol}^2 is a tolerance and we set ε_{tol}^2 to 10^{-4}. We validated our computer code by directly comparing the recent results obtained by Hsieh *et al.*[23] with our results.

Results and Discussion

Rod-like Polymer. For the rod-like polymer, we observed that the results of the tumbling pathway and period are quite similar to those of the worm-like chain, which is one of the semi-flexible polymers.[14] The transition of the tumbling dynamics from the shear-like to the rotational regime was also substantiated by showing the change of the rotational time (τ_R) according to the flow type (α), as shown in Figure 2(a). Lee *et al.*[14] observed that the rotational times are classified into three modes (i.e., constant rotational time due to weak flows, shear-like regime scaled by $Wi^{-2/3}$, and rotation-like regime scaled by Wi^{-1}) in the case of a semi-flexible polymer, which can be applied to rod-like polymers, as shown in Figure 2(a). We observed that the rotational time (τ_R) is nearly constant up to Wi~1 and starts to decrease at around Wi~1. It is observed that the rotational time decreases more quickly with decreasing α, as shown in Figure 2(a). To elucidate the change of the tumbling period with the flow strength and flow type of rod-like polymers, the effective Weissenberg number ($Wi_{eff}=Wi\sqrt{-\alpha}$) is introduced and is used in a similar way to that in the bead-spring model.[14] As shown in Figure 2(b), these rotational times over a very broad range of α and Wi obey a universal scaling law when Wi is rescaled to Wi_{eff} without any fitting parameter, except in the weak flow regime when Wi_{eff} is less than unity. Thus, we can conclude that this scaling law is valid, irrespective of whether the model is the bead-spring or bead-rod one, that is, the scaling law can be applied to both rod-like and rigid polymers.

Besides these rotational times for various flow strengths and flow types, the angular distributions of rod-like polymers were also investigated. As previously mentioned, there are two definitions of the orientation angle of a rod-like

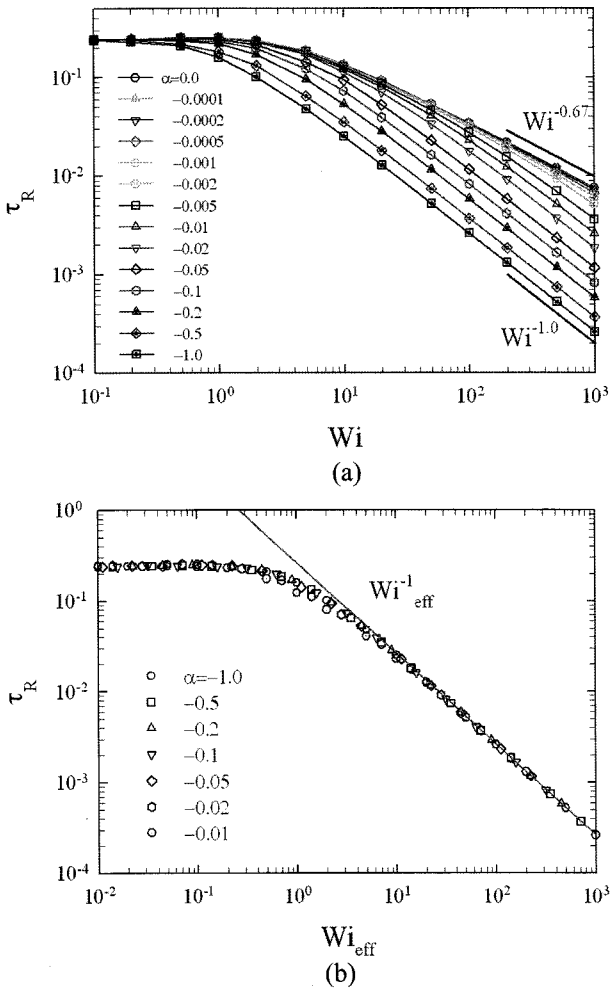

Figure 2. The rotational time (τ_R) of the bead-rod chain in the mixed flow (a) for different flow strengths (Wi) and (b) the master curve using the effective Weissenberg number (Wi_{eff}).

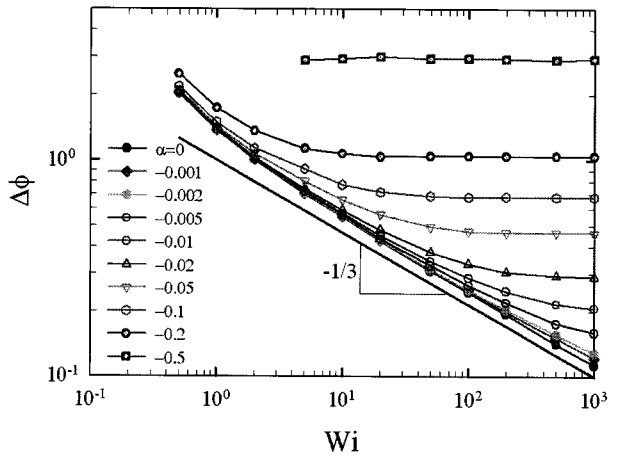

Figure 3. Flow strength dependence on $\Delta\phi$ distribution in mixed flows varying from simple shear flow to rotation-dominant regime.

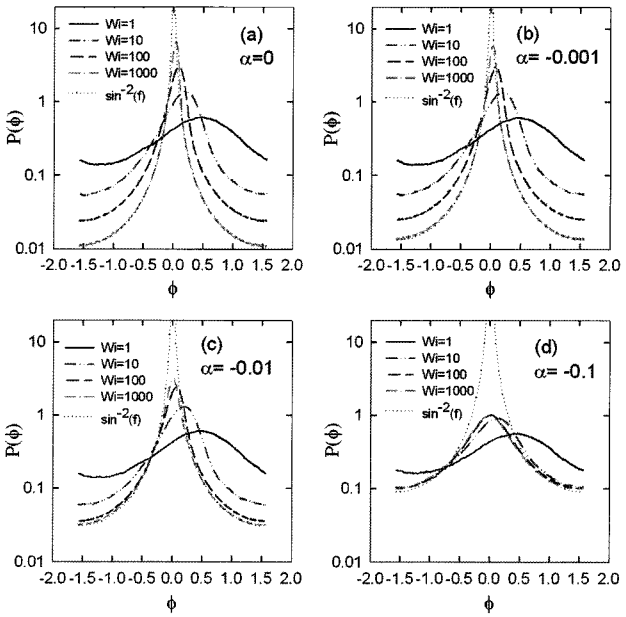

Figure 4. Probability distribution function (PDF) of the molecular angle with respect to the flow field (ϕ) for different flow strength (Wi) and flow type parameters (α).

polymer. One is the angle between the bead-rod polymer and the flow direction (ϕ), while the other is the angle between the bead-rod polymer and the out-of-plane direction (θ). The probability density functions of these molecular angles strongly depend on the flow strength (Wi) and flow type (α). We observe that the half width of $P(\phi)$ at the half height of the maximum decreases are strongly dependent upon Wi and α, as shown in Figure 3. For the shear-like regime, $\Delta\phi$ can be scaled by $Wi^{-1/3}$ which is consistent with the previous theoretical prediction,[19] however, it dramatically departs from that of the shear flow case with decreasing α. Especially, $\Delta\phi$ is independent of the flow strength in the case where α<-0.5. In the rotation-dominant regime, the polymer chains cannot be aligned along with the flow direction, because of the relatively weak extensional component in the rate of the deformation tensor and, hence, they just tumble according to the rotational component without further deformation. Moreover, the PDFs ϕ of in logarithmic coordinates are plotted on Figure 4 for various Wi and α values. In the low Wi regime, the peak point of $P(\phi)$ is skewed towards (+) ϕ values and the peak point approaches (0) with increasing Wi. During a tumbling cycle in the simple shear flow regime, the polymer chains undergo stretch, align, flip, and collapse phases,[8] so that they exist in configurations with a certain angle during the stretch and align phases. Moreover, the peaks become narrower with increasing flow strength, because the molecules tend to align closer to the flow axis, However, the PDF of ϕ is almost the same, due to the vane-like tumbling in the case of the rotation-dominant flows, i.e., $\alpha\rightarrow$-1. In the case of the vane-like motion, the chains do not allocate any time to stretching or alignment anymore, so the molecular angle with respect to the flow direction loses its dependency on Wi.

The angle of the rod-like polymer with respect to the out-of-plane direction (θ) was also examined. In the small Wi regime, $\Delta\theta$ is almost constant and the statistics do not differ much according to Wi, as shown in Figure 5. In the large Wi regime, $\Delta\theta$ is decreased and is scaled by $Wi^{-1/3}$ for the shear-like regime, which was observed for a flexible polymer.[11] However, this scaling law does not apply, when the flow type changes to the rotational-like regime. As regards $\Delta\phi$, it is shown to be almost constant independent of the flow strength (Wi) in the rotation-dominant flow, because of the vane-like motion. However, $\Delta\theta$ is drastically decreased after critical Wi scaling as Wi^{-1}. While the Brownian motion can kick out the polymer chains toward the out-of-plane in the low Wi regime, this is impossible when Wi is very large and, hence, the polymer chains are trapped on the in-plane.

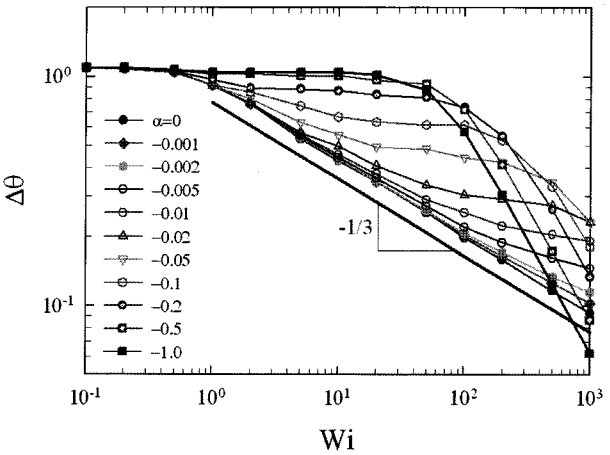

Figure 5. Flow strength dependence on $\Delta\theta$ distribution in mixed flows varying from simple shear flow to pure rotational flow.

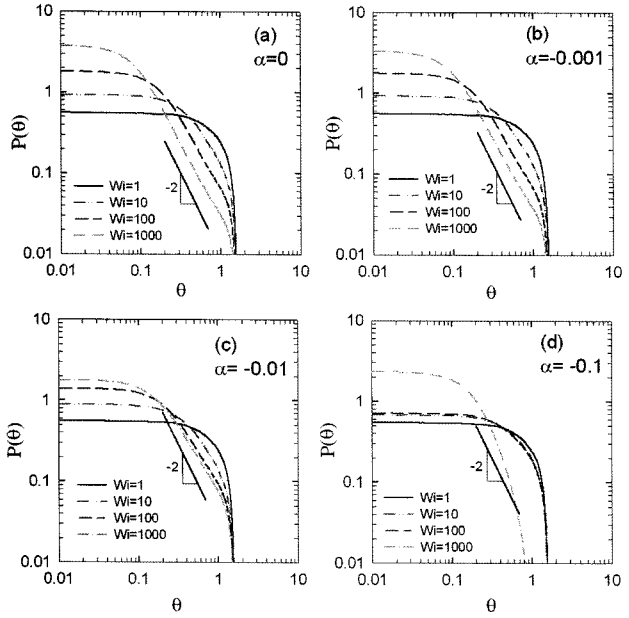

Figure 6. Probability distribution function (PDF) of the molecular angle with respect to the out-of-plane (θ) for different flow strength (Wi) and flow type parameters (α).

The PDFs of the angle θ are presented in Figure 6. In the shear-like regime, the tails decay as θ^{-2} when a sufficient strength flow is applied and approach $\pi/2$ independently of the flow strength, even at Wi=1,000. As the rotational component increases, the polymer chain does not obey this scaling and shows a gentler slope in the moderate θ regime, eventually converging drastically to the $\pi/2$ point. In the case where Wi=1,000 and α = -0.1 (Figure 6(d)), $P(\theta)$ does not show a gentler slope and the tail suddenly decays. That is, less polymer chains are kicked out to the out-of-plane than in the shear-like regime. This is due to the vane-like tumbling motion in the rotational-like regime.

Semi-flexible Polymer. We also examined the dynamic behavior of semi-flexible polymer chains using the multi bead-rod model. Like the rod-like chain in the previous chapter, the angular distribution was calculated in the shear flow regime. To compare the theoretical angular distribution with the experiments, we extracted the experimental data from the literature.[13] The PDF of ϕ at Wi=25 was calculated using a bead-rod chain with 150 Kuhn segments,[24] and it shows good agreement with the experimental data, as shown in Figure 7. The half-height width of the PDFs ($\Delta\phi$) as a function of Wi was also examined. To illustrate this point, $\Delta\phi$ is scaled by Wi, as shown in the inset in Figure 7 together with the fitting and the results of the numerical simulations based on the FENE[11] and bead-rod models. The experimental data are scaled by $Wi^{-0.51\pm0.04}$ and the bead-rod model shows qualitatively good agreement, while the FENE model overestimated the experimental data. The present study shows that numerical simulations with a sophisticated

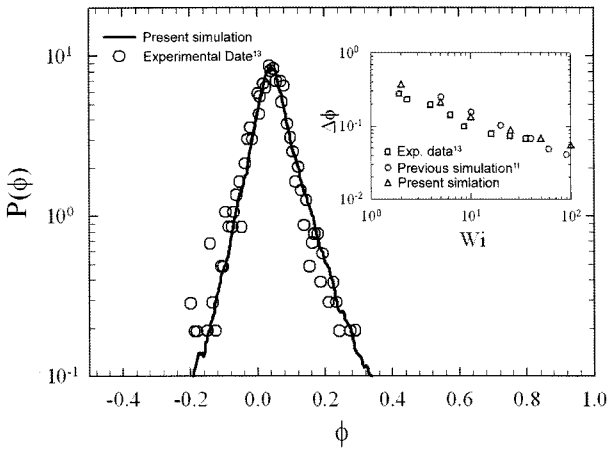

Figure 7. Direct comparison of previous experimental[13] and simulation[11] data with the Brownian dynamics simulation results obtained using the multi bead-rod chain in this study.

model such as the multi bead-rod chain allow the experimental data of the angular distribution to be accurately reproduced.

Conclusions

The tumbling dynamics for both rod-like and semi-flexible polymers was investigated via Brownian dynamics simulations using the bead-rod model in mixed flows that vary from simple shear to pure rotation. By conducting simulations in flows of varying flow strength (Wi) and type (α), the tumbling motion can be portrayed and the tumbling pathways and periods were found to similar to the results of previous simulation studies employing bead-spring chains and the experimental observations. The vane-like motion under the rotation-dominant flows can be confirmed not only by the molecular length ratio,[8,9,14] but also by the angular distributions of the polymer chains. Due to the rotational component in the rate of deformation tensor, the polymer chains skip the alignment phases in the tumbling pathway under shear flow, so that $\Delta\phi$ is almost constant with respect with Wi while $\Delta\theta$ is drastically decreased after a critical Wi.

Acknowledgements. This work was supported by a Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2008-331-D00116).

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