

Title	Dynamics of Flexible High-Molecular-Weight Polymers in Dilute Solution under Circular Couette Flow (FUNDAMENTAL MATERIAL PROPERTIES-Molecular motion analysis)
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Citation	ICR annual report (1999), 5: 28-29
Issue Date	1999-03
URL	http://hdl.handle.net/2433/65194
Right	
Type	Article
Textversion	publisher

Dynamics of Flexible High-Molecular-Weight Polymers in Dilute Solution under Circular Couette Flow

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Chain dynamics of poly(α -methylstyrene) of high molecular weight in benzene, a good solvent, in dilute solution was investigated by dynamic light scattering under Couette flow. At the shear gradient above $2.8\text{--}4.5\text{s}^{-1}$, the internal modes of motions were exclusively suppressed and only the center-of-mass translational diffusion motion of the chain was detected. Whereas, in the intermediate shear region, the decay rate for the internal mode was constant, and that of the diffusion mode increased with increasing the shear rate. The obtained universal ratio Ω/D_0q^2 was located close to the theoretical curve predicted for the flexible chains with the *microscopic* description of chain dynamics in Θ state. This quantitative agreement between theory and experiments means that the coupled kinetic equations for chain segments and solvent in the same dynamic level is indispensable for describing rigorously chain dynamics in dilute solution.

Keywords: Dynamic light scattering/ Shear flow/ Diffusion/ Internal motions/ Dynamic coupling

In the quiescent, i.e., thermodynamically equilibrium state, dynamics of flexible linear polymers in dilute solution has not been understood fundamentally because the well-qualified experimental results disagreed quantitatively with the hydrodynamic descriptions of the polymer chain so far proposed theoretically. The reasons may be assigned to the following assumptions which have been made heretofore in the theoretical descriptions of chain dynamics in the quiescent state (the so-called *macroscopic* description of chain dynamics): (i) the polymer segments waggle in continuous viscous fluid (where the solvent motions are smeared and neglected) in accordance with a diffusion-type equation of the segment configurational distribution and (ii) the hydrodynamic disturbance of the fluid velocity caused by different polymer segments is described approximately by the Oseen tensor. This tensor was derived as a solution of the Stokes equation which neglects the nonlinear inertia term $(\mathbf{v} \cdot \nabla)\mathbf{v}$ of the Navier-Stokes (NS) general equation of motion,

$$\partial\mathbf{v}/\partial t + (\mathbf{v} \cdot \nabla)\mathbf{v} = \mathbf{K} - \nabla\mathbf{p}/\rho + \nu\Delta\mathbf{v}, \quad (1)$$

with \mathbf{v} the fluid velocity. However, the inertia term disappears essentially in the Couette flow. The Couette flow is thus a rigorous solution of the NS general equation of motion, as well as the Stokes equation. Therefore, if experiments were made under the Couette flow, not in the quiescent state, the results will give us new understanding to solve the disagreements between experimental facts and theoretical predictions. In this paper, we apply the dynamic light scattering (DLS) to the dilute solutions of high molecular-weight polymer sample in a good solvent in circular Couette flow and discuss the adequacy of the *microscopic* description¹ proposed for chain dynamics in dilute solution.

A monodispersed poly(α -methylstyrene) (PMS) fraction of $M_w = 6.85 \times 10^6$ was dissolved in benzene and the dilute solutions of different polymer mass concentration c ($c = 2.0 \sim 8.1 \times 10^{-4} \text{ g cm}^{-3}$) were prepared by filtering through a $0.2\mu\text{m}$ pore-size filter. The solution was set in

FUNDAMENTAL MATERIAL PROPERTIES — Molecular Dynamic Characteristics —

The Research activities in this subdivision cover structural studies and molecular motion analyses of polymers and related low molecular weight compounds in the crystalline, glassy, liquid crystalline, solution, and frozen solution states by high-resolution solid-state NMR, dynamic light scattering, electron microscopy, X-ray diffractometry, and so on, in order to obtain basic theories for the development of high-performance polymer materials. The processes of biosynthesis, crystallization, and higher-ordered structure formation are also studied for bacterial cellulose.



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the 2mm-gap between the concentrically rotating rotor and the stator (glass cylinders) which stood perpendicularly. In the gap, the one-dimensional shear flow with a constant low-shear gradient γ was induced by the eddy current.² The single-frequency Ar-ion laser light of 3W was plunged perpendicularly to the rotor and, at given γ of $\gamma=0\sim 4.5\text{s}^{-1}$, the intensity time correlation function $A(t)$ of the V_v component of the scattered light from the sample solution at the angle $\theta=75.6^\circ$ was measured at 27°C by homodyne method through a laboratory-made software correlator. The measured $A(t)$ was analyzed with the histogram method to obtain the decay rate Γ_i of the chain modes of motions i .

At all c examined, $A(t)$ curves were composed of two decay modes (slow and fast modes) at γ except the highest shear gradient γ_{max} of one slow mode. The slow mode with decay rate Γ_1 was the translational diffusion which represents the center-of-mass motion of the polymer chain, where the diffusion coefficient was $D_1 (= \Gamma_1 q^{-2})$ with q the scattering vector. The fast mode with decay rate Γ_2 was the intramolecular motions. The observation of slow mode alone at γ_{max} means that the intrachain motions are suppressed with the increase of the shear field. The γ and c dependence of D_1 below γ_{max} shows that, at fixed c , the D_1 increases with γ , as is the case for polystyrene-latex in aqueous solution² and for PMS of $M_w=2.71\times 10^6$ in benzene.³ However, with decreasing c , the D_1 changes from a descending to an ascending incline at higher γ . The double extrapolation to $\gamma, c\rightarrow 0$ gives the equilibrium value at infinite dilution $D_1(0,0)$. On the other hand, Γ_2/q^3 for internal motions at each c was constant independent of γ . Thus, the increasing decay rate with γ for translational mode and the γ -independent decay rate for internal modes indicate that, in shear field, the chain moves with a constant characteristic intramolecular frequency, though the translational motion is made faster by shear flow.

The first cumulant Ω , which represents all the motions the chain performs, was combined with the γ dependence of the translational motion and then the universal ratio $\Omega/D_0 q^2$ at the infinite extrapolations to $c\rightarrow 0$ and $\gamma\rightarrow \gamma_{\text{solvent}}$ was estimated to be 1.9 at $qR_G=3.03$. Here D_0 is the translational diffusion coefficient at infinite dilution and R_G is the radius of gyration of the chain. The obtained universal value is shown by a filled triangle () in Figure 1, where data for polystyrene and polyisoprene in Θ state () and the theoretical lines 1 and 2 calculated by the microscopic description of chain dynamics for Θ and good solvents¹ respectively are also given. The present data point is located near the line 1 and the feature is coincident with our recent one () obtained at low shear gradient for PMS of $M_w=2.71\times 10^6$ in benzene.⁴ It is very

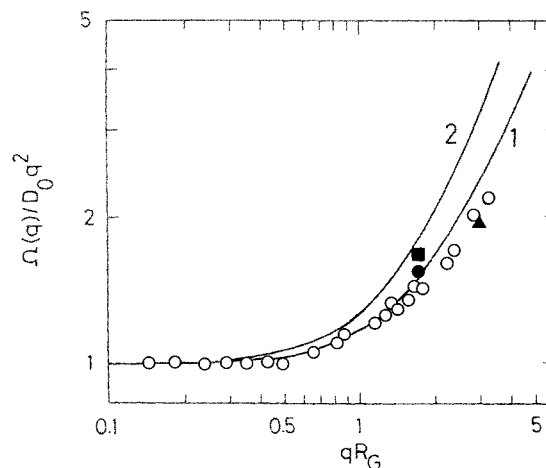


Figure 1. The $\Omega/D_0 q^2$ vs. qR_G plots for flexible polymers in dilute solution.

suggestive that data obtained in Couette flow in good solvent (,) are close to the data in Θ state () and are distinguished clearly from the data in good solvent in the quiescent state⁴ () which is located between lines 1 and 2. The microscopic description of polymer chain dynamics¹ is composed of the coupled kinetic model equations for polymer and solvent, where the segment velocity $\mathbf{c}(\tau, t)$ at the chain contour position τ and the solvent velocity $\mathbf{u}(\mathbf{r}, t)$ at the fluid position \mathbf{r} are expressed in the same dynamic level:

$$\frac{\partial \mathbf{c}(\tau, t)}{\partial t} = -\zeta_0^{-1} \delta \mathbf{H}\{\mathbf{c}\} / \delta \mathbf{c}(\tau, t) + \int d\mathbf{r} \mathbf{u}(\mathbf{r}, t) \delta(\mathbf{r} - \mathbf{c}(\tau, t)) + \mathbf{f}_c(\tau, t) \quad (\text{polymer}) \quad (2)$$

$$\frac{\partial \mathbf{u}(\mathbf{r}, t)}{\partial t} = \eta_c \nabla^2 \mathbf{u}(\mathbf{r}, t) - \int d\mathbf{r}' [\delta \mathbf{H}\{\mathbf{c}\} / \delta \mathbf{c}(\tau, t)] \times \delta(\mathbf{r} - \mathbf{c}(\tau, t)) + \mathbf{f}_u(\mathbf{r}, t) \quad (\text{solvent}) \quad (3)$$

with the incompressibility condition $\nabla \cdot \mathbf{u} = 0$. $\mathbf{H}\{\mathbf{c}\}$ is the chain potential and \mathbf{f} is the random force. In conclusion, the present result in Couette flow, which realizes an ideal fluid state in the hydrodynamic sense, can be explained by the microscopic view in Θ state, not in good solvents, and supports the necessity of the microscopic description in chain dynamics in dilute solution.⁵ The slight disagreement between data and the theoretical line 1 suggests further works in theoretical treatments in Θ state.

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