solution. This finding can again be attributed to a higher value of s in case of a polyacrylamide solution[10]. Recently, in contradiction to the findings of Virk *et al.*[12], Hansen and Little[13] have reported that for Polyox solution of different concentrations, the wall shear stress at the onset of drag reduction, $(\tau_w)_{\mathrm{onset}}$, decreases with increasing concentration. This result can be explained qualitatively by considering the fact that the value of s for any given polymeric solution increases with increasing concentration and hence should result in lowering of $\mathrm{Re}_{\mathrm{onset}}$.

The assumption of similar velocity profiles for different diameter pipes leads to the result that the critical Reynolds number is a single parametric function of pipe diameter with an exponent of 8/7. Experimental results of Elata and Tirosh[14], White[1], and Hershey and Zakin[9] confirm this conclusion. The experimental data obtained by Sharma[15] with solutions of various concentrations (up to 2000 ppm weight) of hydroxylpropylmethyl cellulose (Trade Name: Methofas, manufactured by ICI, UK) in different diameter pipes indicate similar diameter and concentration effects at the threshold of drag reduction.

Equation (7) indicates a possibility of controlling the onset of drag reduction by suitably adjusting the governing parameters. For a given type of polymer and its concentration in the solution, the drag reduction will occur earlier as the size of the pipe decreases. For given D and s, the threshold of drag reduction can be made to occur earlier by decreasing the velocity gradient in the region of maximum dissipation of small-scale eddies. Thus the inception of drag reduction occurs earlier as the velocity profile in the wall region becomes flatter. One possible method to achieve this may be by injecting the concentrated solution of drag-reducing polymer next to the wall. In this connection it may be noted that addition of drag-reducing polymers results in thickening of the viscous sublayer which in turn tends to reduce the velocity gradient in the wall region.

REFERENCES

1 White, A. *J. Mech. Eng. Sci.* 1966, **8**, 452

2 Vleggaar, J., Dammers, W. R. and Tels, M. *Chem. Eng. Sci.* 1968, **23**, 1159

3 Whitshitt, N. F., Horrington, L. J. and Crawford, H. R. 'Effect of Wall Shear Stress on Drag Reduction of Viscoelastic Solutions', in Viscous Drag Reduction, (Ed. C. S. Wells) Plenum Press, New York, 1969, p 256

4 Virk, P. S. and Merrill, E. W., 'The Onset of Dilute Polymer Solution Phenomenon', in Viscous Drag Reduction, (Ed. C. S. Wells), Plenum Press, New York, 1969, p 107

5 Hasegawa, T. and Tomita, Y. *Bull. Jpn Soc. Mech. Engrs.*, 1974, **17**, 73

6 Ferry, J. D., 'Experimental Techniques for Visoelastic Bodies', in Rheology, (Ed. F. R. Eirich), Academic Press, 1958

7 Patterson, G. K. and Zakin, J. L. AIChE J., 1968, **14**, 434

8 Landau, L. D. and Lifshitz, E. M. 'Fluid Mechanics', Pergamon Press, 1963

9 Hershey, H. C. and Zakin, J. L. *Chem. Eng. Sci.* 1967, **22**, 1847

10 Oliver, D. R. *Can. J. Chem. Eng.*, 1966, **14**, 100

11 Virk, P. S. and Baher, H. *Chem. Eng. Sci.* 1970, **25**, 1183

12 Virk, P. S., Merrill, E. W., Mickley, H. S., Smith, K. A. and Mollo-Christensen, E. L. *J. Fluid Mech.* 1967, **30**, 305

13 Little, R. C., Hansen, R. J., Hunston, D. L., Kim, oh-Kil, Patterson, R. L. and Ting, R. Y., *Ind. Eng. Chem. Fund.* 1975, **21**, 625

14 Elata, C. and Tirosh, J. *Israel J. Tech.* 1966, **4**, 87

15 Sharma, R. S., Ph. D. Thesis, Indian Institute of Technology, New Delhi, 1977

Concentration dependence of the diffusion coefficient of polystyrene at theta-condition

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INTRODUCTION

Despite many experimental and theoretical studies, the concentration dependence of diffusion coefficient, k_D, of polymers at their theta-conditions still remain an unsettled problem. Many investigators found experimentally that k_D has a negative value[1–7]; furthermore, Cantow[8] found that the diffusion coefficient D is independent of the concentration at theta temperature. Meanwhile, theoretical investigations have been carried out by Yamakawa[9,10] and Imai[11] and also by Pyun and Fixman[12]. The Pyun and Fixman (P–F) approach uses a spherical model instead of the more realistic beads and spring model which was employed by Yamakawa and Imai (Y–I). But it has been pointed out by Pyun and Fixman that Yamakawa's earlier approach is incorrect due to the approximation made by assuming independent inter- and intramolecular distributions and consequently resulting in the neglect of correlations due to the intermolecular interactions. In the later work of Yamakawa[10], a negative concentration dependence of D was introduced through the change of coordinate system from actual polymer velocity to the drift velocity. Even though this model leads to a different magnitude for the k_D than the one obtained from P–F model, nonetheless both theories predict a negative and molecular weight independent k_D at the theta condition.

On the other hand, Kotaka *et al.*[13] has found that in the

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ultracentrifugation study, k_D depends on the centrifugation speed. So far, the only systematic investigation of a polymer-solvent binary system at its θ-condition by using a technique other than centrifugation is the quasielastic light scattering work by King *et al.*[1]. Unfortunately, due to the large experimental uncertainty, the results are not conclusive enough to distinguish between Y–I and P–F models and to demonstrate the molecular weight independence of k_D.

Due to the improved instrumental and experimental techniques, more precise study than hitherto has become possible. In this study we will present some carefully obtained results on a set of four monodisperse polystyrene samples at their theta-conditions by a newly constructed full-photon counting instrument[14]. The experimental procedures and sample preparation will be discussed, followed by the concentration dependence results and model comparisons.

EXPERIMENTAL

The quasielastic light scattering experiment is carried out with a full-photon counting Rayleigh spectrometer[14]. The 4880 Å line from a Ar-ion laser was used as the light source. Scattered light at any desired angle is detected by a thermoelectrically cooled photomultiplier. The photon pulses are shaped and counted for desired time intervals and then transferred to a minicomputer through direct memory access channel. The exact correlation function (unclipped) is calculated in real time. The correlation results are subsequently transferred to a larger computer for further analysis.

Four polystyrene samples of molecular weight ranging from 1.1×10^5 to 4.1×10^6 were used in this study. The molecular weights and M_w/M_n ratios of the samples are collected in *Table 1*. Four to five concentrations from each sample in cyclohexane were used and each concentration was studied at four different scattering angles ranging from 20 to 60 degrees. Temperature was controlled at 35 ±0.2°C throughout the experiment by a thermostatted oil bath of matching refractive index. All the solutions except those of the highest molecular weight were kept in a 40°C bath overnight with gentle stirring and then filtered into scattering cells through 0.45 μm filters. Solutions of the 4.1×10^6 molecular weight sample were prepared by filtering solvent into volumetric flasks containing the polymer and heating to 40°C for one day with occasional gentle shaking. The procedure used for preparing the three smaller molecular weight samples caused detectable degradation in the large molecular weight sample.

RESULTS AND DISCUSSION

The diffusion coefficient, D, can be written as[10] a function of concentration:

$$D = \frac{kT}{f}\left(1 - \frac{N\nu_1}{M}c\right)(1 + 2A_2Mc + 3A_3Mc^2 + \ldots) \quad (1)$$

where N is Avogadro's number, ν_1 is the partial specific volume of the polymer, with molecular weight M, concentration c, second virial coefficient A_2, third virial coefficient A_3, and frictional coefficient f. The frictional coefficient can also be expanded as a polynomial in c as[9,12]

$$f = f_0(1 + k_f c + \ldots) \quad (2)$$

By combining equation (2) with equation (1), we obtain

$$D = D_0\left[1 + \left(2A_2M - k_f - \frac{N\nu_1}{M}\right)c + \ldots\right] \quad (3)$$

where D_0 is the diffusion coefficient at infinite dilution and can be represented by AM^{-b}[10]. At theta condition, $D_0 = AM^{-1/2}$ and $A_2 = 0$. Equation (3) reduces to

$$D = D_0(1 + k_D c)$$

$$= AM^{-1/2}\left[1 - \left(k_f + \frac{N\nu_1}{M}\right)c + \ldots\right] \quad (4)$$

The theoretical result of Yamakawa and Imai gives $k_f = 1.2\,A_2M + N\nu_h/M$, or $k_f = N\nu_h/M$ at θ-condition, where ν_h is the hydrodynamic volume of the polymer chain. Pyun and Fixman's theory results in $k_f = [7.16 - K(A)]\ N\nu_h/M$, where

Table 1 Results for polystyrenes in cyclohexane at 35 ± 0.2°C

$M_w \times 10^{-5}$	M_w/M_n	c(g/ml) x 10^3	D(cm^2/sec) x 10^7	A(cm^{2}g$^{1/2}$/sec; mol$^{1/2}$) x 10^4	$-k_DM^{-1/2}$ x 10^2
1.1	1.06	2.56	3.97	1.38	6.12
		4.85	3.71		
		6.75	3.60		
		8.35	3.48		
1.8	1.06	1.26	3.13	1.37	6.00
		2.65	3.02		
		4.45	2.85		
		6.47	2.71		
6.7	1.15	1.14	1.75	1.44	5.60
		2.08	1.53		
		3.30	1.43		
		5.24	1.39		
41	1.1	0.320	0.627	1.36	5.26
		0.355	0.671		
		0.975	0.599		
		2.19	9,516		
		2.34	0.542		

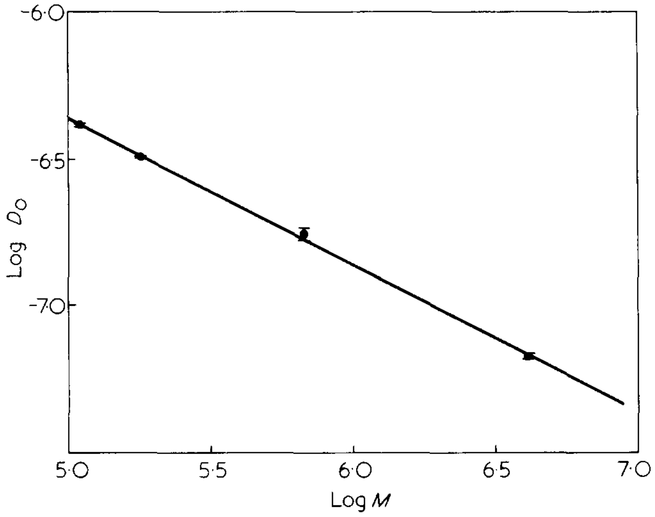

Figure 1 Log-log plot for polystyrene in cyclohexane at 35.0 ± 0.2°C of the diffusion coefficients of four different samples extrapolated to zero concentration vs. their corresponding molecular weights. The solid line of slope – ½ indicates the diffusion coefficient $D_0 = (1.38 \pm 0.04) \times 10^{-4}\ M^{-1/2}$

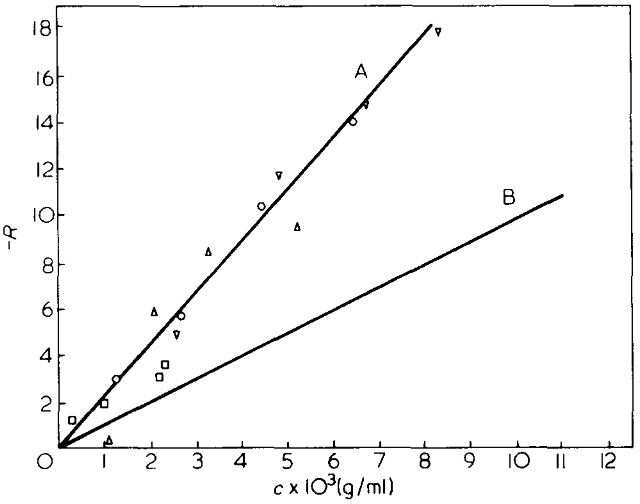

Figure 2 Plot of $-R$, which is $-(D/D_0 - 1 + c/\rho)/[(4/3)\pi NM^{1/2} \times (kT/6\pi\eta A)^3]$, vs. concentration c for the diffusion coefficients of four samples at various concentrations. The two solid lines represent the predictions from A. Pyun–Fixman and B. Yamakawa–Imai theories with slope 2.3 and 1 respectively. ▽, PC-4b; ○, PS-705; △, PC-13a; □, F-4

$K(A)$ is related to the segment–segment interaction in a polymer chain. At θ-condition, the soft sphere limit, $k_f = 2.23\,N\nu_h/M$, may be used. For the sake of convenience, we will define k_f as

$$k_f = B\frac{N\nu_h}{M} \tag{5}$$

with $B = 1$ for Y–I Model and $B = 2.23$ for P–F Model.

If we arrange equation (4) and equation (5), and use $\nu_1 \cong M/N\rho$, $\nu_h = 4\pi R_h^3/3$, and $D_0 = kT/6\pi\eta R_h = AM^{-1/2}$, we obtain

$$\frac{D}{D_0} - 1 + \frac{c}{\rho} = -B\,\frac{4}{3}\pi NM^{1/2}\left(\frac{kT}{6\pi\eta A}\right)^3 c$$

or

$$R = \left(\frac{D}{D_0} - 1 + \frac{c}{\rho}\right) \Big/ \left[\frac{4}{3}\pi NM^{1/2}\left(\frac{kT}{6\pi\eta A}\right)^3\right] = -Bc \tag{6}$$

Let us then look at the experimentally obtainable quantity which is the intensity correlation function of the quasi-elastically scattered light from the polymer solution. In the homodyne beating configuration this correlation function $C(\tau)$ can be expressed as[15]

$$C(\tau) = 1 + \beta e^{-2\Gamma\tau} \tag{7}$$

with $\Gamma = q^2D$

where q is the scattering wave vector with $|q| = (4\pi/\lambda)\sin\theta/2$, λ is the wavelength in the medium and θ is the scattering angle. The values of Γ obtained at different angles for a given polymer solution are fitted to q^2 according to equation (7) to obtain D. The diffusion coefficients thus obtained are collected in *Table 1*. The diffusion coefficients for each sample at different concentrations are then fitted to a linear dependence of c to obtain k_D and A according to equation (4). These values are also collected in *Table 1*. In *Figure 1*, a plot of log D_0 vs. log M is displayed to demonstrate the $M^{-1/2}$ dependence of D_0.

Using values of $\rho = 1.06$ g/ml and $\eta = 0.75 \times 10^{-2}$ poise, *Figure 2* shows the plot of

$$-\left(\frac{D}{D_0} - 1 + \frac{c}{\rho}\right) \Big/ \left[\frac{4}{3}\pi NM^{1/2}\left(\frac{kT}{6\pi\eta A}\right)^3\right] \text{ vs } c$$

together with the predictions of the Y–I and the P–F models. From this plot it is clear that the Pyun and Fixman's soft sphere model is a better representation than Yamakawa and Imai's model for polymers in solution at their θ-conditions. These results also demonstrate the molecular weight independence of B in equation (5) which is predicted by both the P–F and the Y–I theories.

REFERENCES

1 King. T. A., Knox, A., Lee, W. I., and McAdam, J. D. G. *Polymer* 1973, **14**, 151
2 Cowie, J. M. G. and Cussler, E. L. *J. Chem. Phys.* 1967, **46**, 4886
3 McIntyre, D., Wims, A., Williams, L. C., and Mandelkern, L. *J. Phys. Chem.* 1962, **66**, 1932
4 Homma, T., Kawahara, K., Fujita, H., and Ueda, M. *Makromol. Chem.* 1963, **67**, 132
5 Lacharojana, S. and Caroline, D. *Macromolecules* 1977, **10**, 365
6 Frost, R. A. and Caroline, D. *Macromolecules*, 1977, **10**, 616
7 Noda, I., Saito, S., Fujimoto, T., and Nagasawa, M. *J. Phys. Chem.* 1967, **71**, 4048
8 Cantow, H. J. *Makromol. Chem.* 1959, **30**, 169
9 Yamakawa, H. *J. Chem. Phys.* 1962, **36**, 2995
10 Yamakawa, H., 'Modern Theory of Polymer Solutions', Harper & Row, New York (1971)
11 Imai, S. *J. Chem. Phys.* 1969, **50**, 2116
12 Pyun, C. W., and Fixman, M. *J. Chem. Phys.* 1964, **41**, 937
13 Kotaka, T. and Donkai, N. *J. Polym. Sci. (A2)* 1968, **6**, 1457
14 Han, C. C. *Rev. Sci. Instrum.* 1978, **49**, 31
15 For example, see Chu, B. in 'Laser Light Scattering', Academic Press, New York (1974)