Polymer Vol. 39 No. 23, pp. 5627–5631, 1998
0032-3861/98/$ – see front matter

PII: S0032-3861(98)00028-7

Static and quasielastic light scattering from solutions of poly(ethylene oxide) in methanol

C. Vandermiers, P. Damman and M. Dosière*
Université de Mons-Hainaut, Laboratoire de Physicochimie des Polymères, Place du Parc, 20, B-7000 Mons, Belgium
(Received 16 July 1997; accepted 5 December 1997)

Static and quasielastic light scattering measurements on dilute and semi-dilute solutions of monodisperse poly(ethylene oxide) in methanol have been carried out at 25°C. Four PEO fractions having weight average molecular weights equal to 31 500, 90 000, 230 000 and 904 000 and degrees of polydispersity lower than 1.1 were used. The angular dependence of Zimm plots shows no downturn at low angles. In addition, monomodal distribution curves were computed from the quasielastic measurements, confirming that PEO are molecularly dispersed in methanol at 25°C. Experimental scaling laws for the radius of gyration R_G, the second virial coefficient A_2 and the hydrodynamic radius R_H have been determined. The exponents characterizing these scaling laws confirm that methanol is a good solvent for this polymer. Finally, the overlap concentrations corresponding to the transition between the dilute and semi-dilute regimes were determined for the different PEO samples. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ethylene oxide); light scattering dilute-semidilute transition)

INTRODUCTION

The aggregative behaviour of poly(ethylene oxide) (PEO) in various solvents has been studied by many authors[1–6]. First of all, Strazielle has evidenced, using static light scattering, the aggregation of PEO in methanol[1]. These aggregates were assumed to be constituted of PEO single crystals which completely disappeared when the solutions were heated at 40°C. After the thermal treatment, the excess Rayleigh ratio did not exhibit the downturn at low angles, typical of the aggregates. On the basis of the previous work by Strazielle, Kinugasa *et al.* determined the scaling laws of R_G and A_2 which demonstrate that methanol is a good solvent of PEO[5,6].

As concerns the dynamic light scattering, Zhou and Brown[4] observed two relaxation modes in the autocorrelation functions of untreated PEO solutions. The slow and fast modes correspond to the aggregates and the molecularly dispersed macromolecules, respectively.

This paper reports static and dynamic light scattering study of dilute and semi-dilute solutions of PEO in methanol at 25°C. The molecular weight dependences of the radius of gyration R_G, the second virial coefficient A_2 and the hydrodynamic radius R_H are discussed. Finally, the transition between the dilute and semi-dilute regimes is investigated by dynamic light scattering.

EXPERIMENTAL SECTION

Sample preparation

Four PEO fractions with a very low degree of polydispersity were used. Their characteristics are listed in *Table 1*. Spectral grade methanol purchased from Aldrich was distilled before preparing the solutions. As pointed out by several authors, special care must be taken in preparing the PEO solutions[1,5,6]. Indeed, the formation of the aggregates is assumed to be an intrinsic property of PEO in solution, i.e. a decrease of $\frac{1}{\Delta I \sin\theta}$ at small angles is observed for intensity measurements carried out after a simple filtration of the solutions. These downturns, illustrating the presence of aggregates, disappear, however, after heating at 50°C of PEO solutions while stirring. In addition, when heated up to 50°C, the PEO–methanol solutions present a good stability over time: no evidence of aggregate formation is observed in static light scattering intensity measurements even after several months of aging. For optical clarification, the solutions were slowly filtered directly into light scattering cells through 0.2 μm PTFE filters.

Characterization

The static light scattering (SLS) measurements were carried out with a Brookhaven BI200SM goniometer. Light from a Lexel 1W Ar laser ($\lambda = 488$ nm) was used as the incident beam. The intensities of scattered light were measured at scattering angles θ ranging from 35° to 130°. All experiments were performed at 25°C.

The Rayleigh ratio $R_0 = 4 \times 10^{-5}\ \mathrm{cm}^{-1}$ of toluene at $\lambda = 488$ nm was used to calculate the Rayleigh ratio of the scattered light. Scattered intensity data were analyzed with the Zimm method[7]: $\frac{KC}{\Delta R_\theta}$ was plotted against $\sin^2\left(\frac{\theta}{2}\right) + kC$ according to the following relation:

$$\frac{KC}{\Delta R_\theta} = \frac{1}{\bar{M}_W}\left(1 + q^2\frac{R_G^2}{3}\right) + 2A_2C$$

where q is the modulus of the wave vector equal to $q = \frac{4\pi}{\lambda} n \sin\left(\frac{\theta}{2}\right)$, $\bar{M}_W$, R_G and A_2 are the weight average molecular weight, the radius of gyration and the second virial coefficient, respectively. K is an optical constant defined as $K = 4\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}C)^2/N_a\lambda^4$ where N_a is the Avogadro number.

---

* To whom correspondence should be addressed

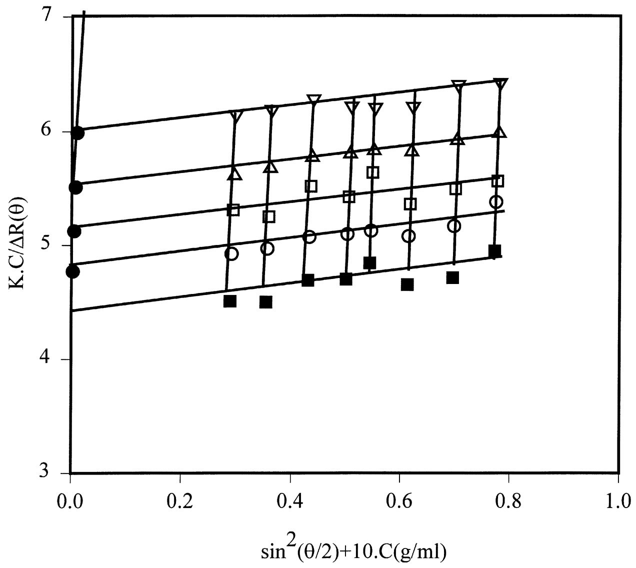

Figure 1 Zimm-plot for PEO ($\bar{M}_W = 230\,000$) in methanol at 25°C

Table 1 Molecular characteristics of PEO fractions

$\langle M_W \rangle$	$\langle M_W \rangle / \langle M_n \rangle$	Supplier
31 500	1.1	Hoechst
90 000	1.02	Polymer laboratories
230 000	1.06	Polymer laboratories
904 000	1.1	Polymer laboratories

The dynamic light scattering (DLS) measurements were also performed at 25°C. The analysis of the scattered light intensity fluctuations was carried out using a BI 9000 AT correlator. Dynamic properties of the studied system, such as the hydrodynamic radius R_H, were deduced from the correlation function. The autocorrelation function of the scattered intensity $g_2(\tau)$ was measured on the PEO solutions at different scattering angles and different concentrations. The autocorrelation function $g_2(\tau)$ is given by[8]:

$$g_2(\tau) = 1 + \beta |g_1(\tau)|^2$$

where $g_1(\tau)$ is the first-order correlation function depending only on time and wave vector. So, we can make it equal to $S(q,t)$ and for a monodisperse system, $g_1(\tau)$ is expressed as:

$$g_1(\tau) = S(q,t) = S(q,0) \cdot e^{-\Gamma t} d\Gamma$$

if the condition $qR \ll 1$ is respected, R being the radius of the diffusive particles, the first cumulant Γ is defined as $\Gamma = q^2 D$, where D is the diffusion coefficient.

The hydrodynamic radius R_H is thus obtained from the diffusion coefficient according to the Stokes–Einstein relation:

$$R_H = \frac{k_B T}{6\pi\eta_0 D}$$

where k_B, T, η_0 and D_0 are the Boltzmann's constant, the absolute temperature, the solvent viscosity and the diffusion coefficient extrapolated at infinite dilution, respectively.

As the distribution of the studied system can be polymodal or monomodal, $g_1(\tau)$ is defined as:

$$g_1(\tau) = \int w(\Gamma) e^{-\Gamma t} d\Gamma$$

Two numerical methods were used to analyze the correlation functions: the cumulant method for polydisperse systems and CONTIN that computes $w(\Gamma)$ from experimental measurements.

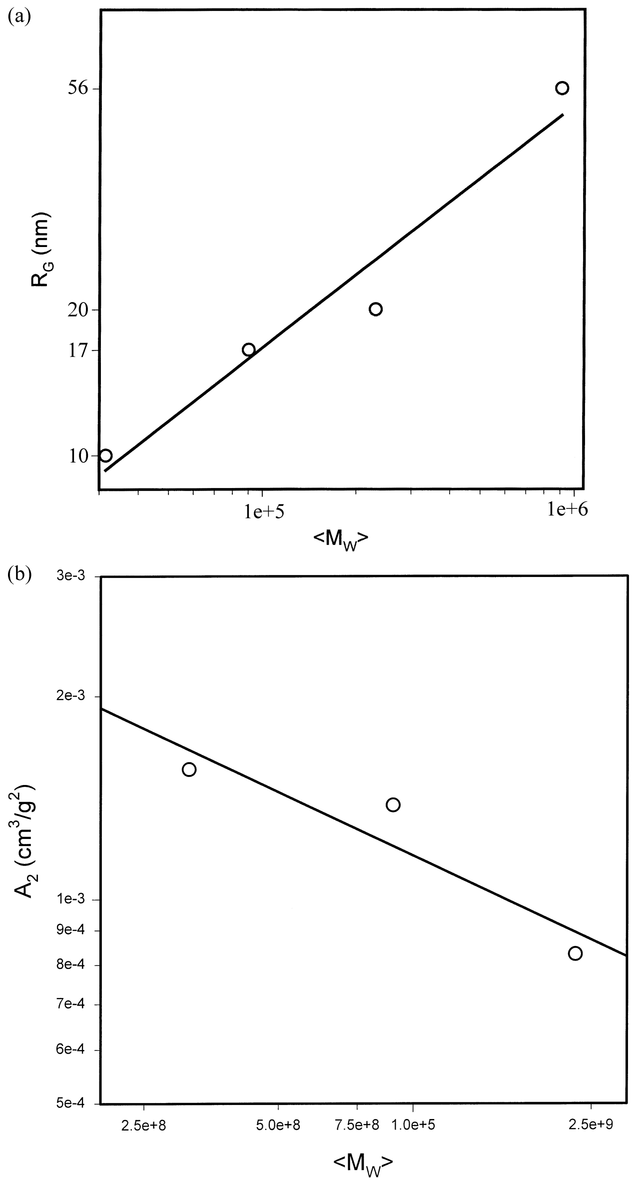

Figure 2 (a) Radius of gyration R_G of PEO *versus* the weight average molecular weight $\bar{M}_W$. (b) Second virial coefficient A_2 *versus* the weight average molecular weight $\bar{M}_W$

RESULTS AND DISCUSSION

Static light scattering measurements

The angular dependence of the excess scattered light from the different PEO solutions in methanol was experimentally determined. The radius of gyration R_G and the second virial coefficient A_2 were obtained from the average slopes of $KC/\Delta R_\theta$ *versus* $[\sin^2(\theta/2) + kC]$. As shown in *Figure 1* for the PEO fraction with $\bar{M}_W = 230\,000$, the experimental data are distributed onto straight lines in the Zimm plot without downturn of $KC/\Delta R_\theta$ at small scattering angles. The solutions are thus aggregate free and the PEO chains are molecularly dispersed. As described in the experimental section, the solutions were heated up to 50°C before filtration to dissolve the PEO crystals and aggregates

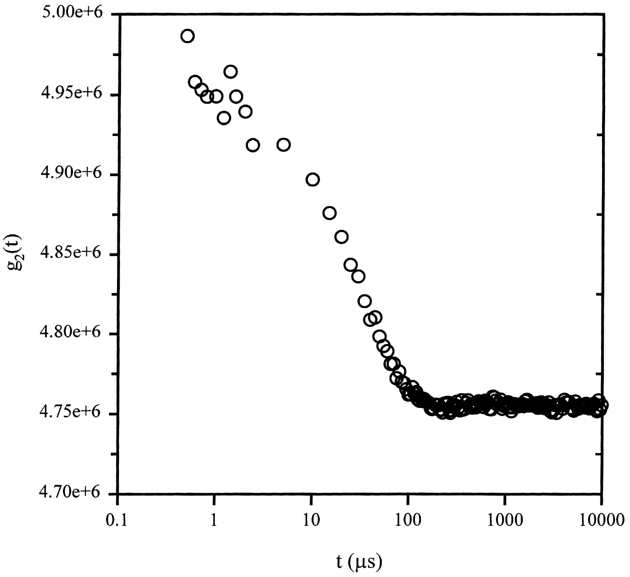

Figure 3 Correlation function measured at $\theta = 90°$ for PEO ($\bar{M}_W = 230\,000$)

present at room temperature. The radius of gyration R_G is plotted as a function of the molecular weight $\bar{M}_W$ (*Figure 2a*). The linear variation observed in the log–log curve corresponds to the following expression:

$$R_G = 0.063\cdot\bar{M}_W^{0.5\pm0.1}$$

The 0.5 power law is in good agreement with theory[10]. Indeed, the positive A_2 values derived from the Zimm plots show that methanol is very likely a good solvent for PEO: an exponent equal to 0.6 is then predicted from the theory of Flory[9]. However, we note that the exponent experimentally determined for different polymer–good solvent systems actually vary between two limiting values of 0.5 for a θ solvent and 0.6 for a good solvent, depending upon the swelling of the polymer coils[10].

In a similar way, a linear relationship between $\log(A_2)$ and $\log(\bar{M}_W)$ is observed in *Figure 2b* and corresponds to the power law:

$$A_2 = 0.043\cdot\bar{M}_W^{-0.31\pm0.1}$$

Obviously, the negative exponent illustrates the decrease of the polymer solubility with increasing molecular weights. The experimental value of the exponent − 0.31 is in agreement with the value previously reported by Kinugasa *et al.*[6] (−0.28±0.06).

Dynamic light scattering (DLS) measurements

Dilute solutions. The correlation functions $g_2(\tau)$ for the different PEO samples were recorded at different angles and different concentrations. The g_2 function of the PEO fraction with $\bar{M}_W = 230\,000$ measured at $\theta = 90°$ is shown in *Figure 3*, the related distribution function computed according to the CONTIN method being given in *Figure 4*.

For all studied PEO samples and scattering angles, only monomodal distribution curves have been observed for thermally treated methanol solutions. These observations confirm that aggregate-free methanol solutions of PEO can be obtained with adequate thermal treatment. The occurrence of a single distribution allows us to use the cumulant method which makes it possible to estimate the mean value of Γ.

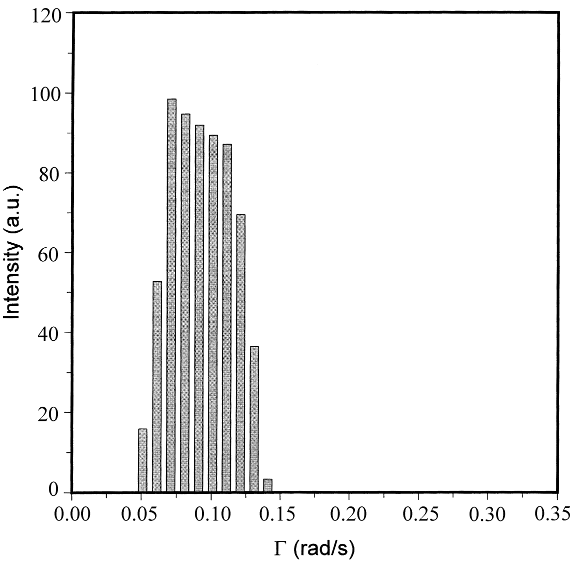

Figure 4 Distribution function recorded at 90° for PEO ($\bar{M}_W = 230\,000$)

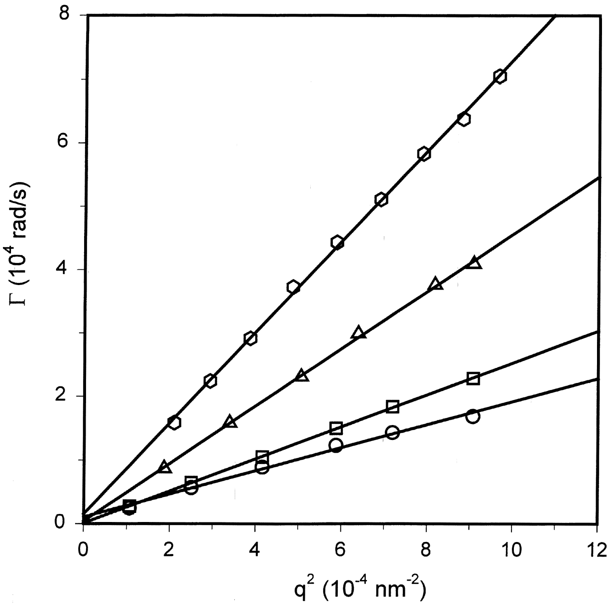

Figure 5 First cumulant Γ *versus* the square of the wave vector q^2 for various weight average molecular weights $\bar{M}_W$: (a) $\bar{M}_W = 904\,000$ (○); (b) $\bar{M}_W = 230\,000$ (□); (c) $\bar{M}_W = 90\,000$ (△); (d) $\bar{M}_W = 31\,500$ (⬡)

As previously reported by Zhou and Brown[4], bimodal correlation functions are observed for untreated PEO solutions. Based on the concentration dependences of the two modes, these authors concluded that the slow mode probably arises from the presence of molecular clusters and the fast mode represents the collective motions of individual chains. These two diffusive modes were observable in the dynamic light scattering experiments as a consequence of the size polydispersity in the system.

The linear dependence of Γ with q^2 shown in *Figure 5* confirms that the condition $qR \ll 1$ is fulfilled. Accordingly, the diffusion coefficient D can be calculated using the relation

$$D = \frac{\Gamma}{q^2}$$

where q is the scattering vector.

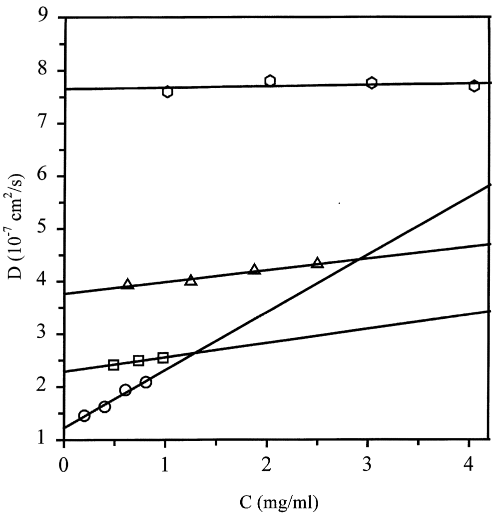

Figure 6 Diffusion coefficient *D versus* the concentration *C* for various weight average molecular weights $\bar{M}_W$: (a) $\bar{M}_W = 904\,000$ (○); (b) $\bar{M}_W = 230\,000$ (□); (c) $\bar{M}_W = 90\,000$ (△); (d) $\bar{M}_W = 31\,500$ (⬡)

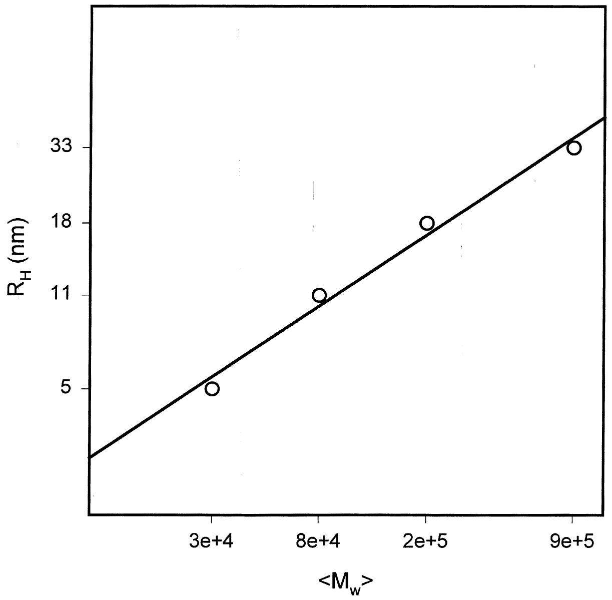

Figure 7 Hydrodynamic radius R_H of PEO in methanol solution *versus* its weight average molecular weight $\bar{M}_W$

In *Figure 6*, the *D* values are plotted *versus* the concentration for the different PEO molecular weights. Afterwards, the D_0 values are extrapolated at infinite dilution and the hydrodynamic radius R_H values are computed from the Stokes–Einstein equation. The log–log plot illustrating the scaling law between R_H and $\bar{M}_W$ is shown in *Figure 7*. The data are fitted according to the following expression:

$$R_H = 0.021\cdot\bar{M}_W^{0.54\pm0.05}$$

As shown above for the SLS study, the exponent of $\bar{M}_W$ (0.54) is in good agreement with the theory[9]. Again, the experimental exponents reported by Schaefer[10] for various systems range between 0.49 and 0.57 depending on the polymer and the solvent. As deduced from the SLS study, a value of the exponent close to 0.5 indicates the existence of weak excluded volume interactions. We note that the precision of the dynamic light scattering technique is slightly better than that of its static counterpart.

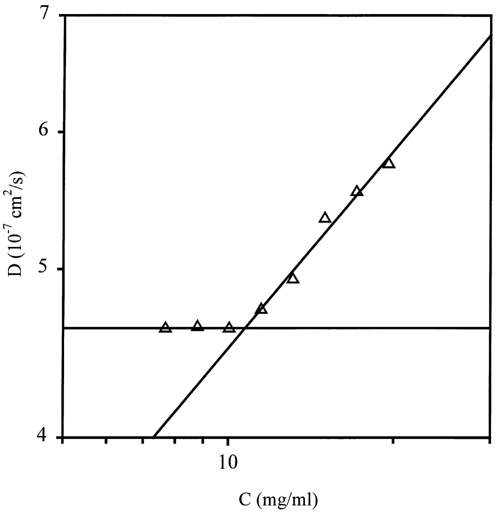

Figure 8 Diffusion coefficient *D versus* the concentration for a PEO with $\bar{M}_W = 90\,000$

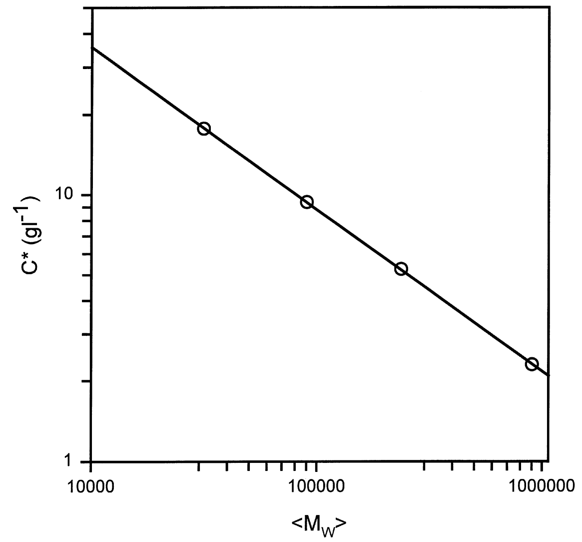

Figure 9 Overlap concentration *C** against the weight average molecular weight $\bar{M}_W$

Semi-dilute solutions. The transition between dilute and semi-dilute regimes is studied by DLS. In fact, the overlap concentration, *C**, at the transition between the two regimes can be determined experimentally from the concentration dependence of *D*.

(1) For dilute solutions, i.e. having a concentration $C < C^*$, the molecules are dispersed and the diffusion coefficient *D* strongly varies with molecular weight. *D* is defined by the Stokes–Einstein equation:

$$D = \frac{k_B T}{6\pi\eta_0 R_H}$$

Note that in the angular range of our experiments, only the diffusion of the whole chain is observed.

(2) In the semi-dilute regime, the solution can be considered as a network, since all chains overlap, the average cell dimension of the network corresponds to the ξ parameter[11]. The diffusion coefficient *D* becomes roughly independant of the average molecular weight but strongly varies with the polymer concentration. The

semi-dilute solutions can thus be assimilated to a packing of spheres with a radius ξ_H, the diffusion coefficient being expressed by the equation:

$$D = \frac{k_B T}{6\pi\eta_0\xi_H}$$

As expected, the variation of D with the polymer concentration exhibits a sharp transition (*Figure 8*) which can be assimilated to the transition between dilute and semi-dilute regimes, C^* corresponding to the concentration of the break. As R_G and R_H, a scaling law describes the dependence of C^* with $\bar{M}_W$. The log–log plot is shown in *Figure 9* and corresponds to the equation:

$$C^* = 9550 \cdot \bar{M}_W^{-0.607 \pm 0.003}$$

As reported above, the exponent varies between the limiting values of -0.5 for a θ solvent and -0.8 for a good solvent.

CONCLUSIONS

From static and dynamic light scattering studies of PEO–methanol solutions, it has been established that PEO does not aggregate in methanol at 25°C. The positive values of A_2 show that methanol is a good solvent of PEO at room temperature. The molecular weight dependences of R_G, A_2 and R_H have allowed scaling laws characterizing the behavior of PEO in solution to be established. The exponents appearing in the different power laws are in good agreement with usual theory describing polymer solutions. Finally, the overlap concentration, C^*, at the transition between the dilute and semi-dilute regimes and its molecular weight dependence were studied by DLS.

ACKNOWLEDGEMENTS

This work was supported by the FNRS (Belgium). The authors acknowledge Dr B. Lotz (Institut Charles Sadron, Strasbourg) and Dr R. Borsali (CERMAV, Grenoble) for fruitful discussions. P. Damman is a Research Asscociate of the Belgian National Funds for Scientific Research.

REFERENCES

1. Strazielle, C., *Makromol. Chem.*, 1968, **119**, 50.
2. Carpenter, D. K., Santiago, G. and Hunt, A. H., *J. Polym. Sci., Polym. Symp.*, 1974, **44**, 75.
3. Cuniberti, C., *Eur. Polym. J.*, 1974, **10**, 1175.
4. Zhou, P. and Brown, W., *Macromolecules*, 1990, **23**, 1131.
5. Kinugasa, S., Nakahara, H., Fudagawa, N. and Koga, Y., *Macromolecules*, 1994, **27**, 6889.
6. Kinugasa, S., Nakahara, H., Kawahara, J.-I., Koga, Y. and Takaya, H., *J. Polym. Sci. Part B, Polymer Physics*, 1996, **34**, 583.
7. Champetier, G., *Chimie Macromoléculaire II.* Hermann, Paris, 1972.
8. Brown, W. and Nicolai, T., *Dynamic Light Scattering: the Method and Some Applications*, ed. W. Brown. Oxford Science Publications, Oxford, 1993.
9. Flory, P.-J., *Principles of Polymer Chemistry*. Cornell University Press, New York, 1953.
10. Schaefer, D. W. and Han, C. C., *Dynamic Light Scattering: Application of Photons Correlation Spectroscopy*, ed. R. Pecora. Plenum Press, New York, 1985.
11. de Gennes, P.-G., *Scaling Concepts in Polymer Physics*. Cornell University Press, London, 1979.