

SHORT COMMUNICATIONS

Correlation Length Calculated from Sedimentation Data

Lech GMACHOWSKI†

Institute of Physical Chemistry, Polish Academy of Sciences, 01–224 Warsaw, Poland

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In a previous paper¹ the extended Brinkman model for the fluid flow through an arrangement of permeable spheres proved to give a good description of the dependence of the sedimentation coefficient s on the polymer solution concentration c

$$s = \frac{1 - \rho_1/\rho_s}{\mu} \cdot \frac{c}{\lambda^2} \quad (1)$$

where ρ_1 and ρ_s are the solvent density and solute density, respectively, μ is the solvent viscosity, and λ is the reciprocal square root of solution permeability. The model, which is valid in both dilute and semidilute regimes and for different polymer–solvent systems, predicts a constant value of dimensionless parameter λR in the semidilute range, where R is the blob radius, which is in qualitative agreement with previous considerations reported by Brochard and de Gennes.² This value corresponds to the slope of the concentration dependence of the sedimentation coefficient. The semidilute range, in which a reduction of correlation length with concentration occurs, is regarded such that each point of the dependence may be described by the parameters at the inflection point of the theoretical Brinkman curve of $\ln s$ vs. $\ln c$, generated¹ for a corresponding blob weight by choosing a value of dimensionless internal blob permeability such to obtain the same slope. According to the Brinkman model, the λR -value changes with the slope at the inflection point as follows

$$\lambda R \cong 1.39 \cdot \left(1 - \frac{d \ln s}{d \ln c}\right)^{1.47} \quad (2)$$

In the range of moderate solute volume fraction, the slope is constant and this fact has been utilized previously¹ to determine the molecular weight of polymers dissolved. When the concentration increases, however, the straight line curves to be steeper and steeper. This is found at concentrations sufficiently high but lower than that corresponding to a critical value of the correlation length ($\xi \sim 2$ nm for polystyrene), above which the changes in blob structure are observed,^{3,4} and seems to be caused by the increasing reduction in size of channels by which the solvent could flow. As a result, the value of the dimensionless internal blob permeability becomes higher, without changing the blob structure, but only because of the increasing importance of the size of solvent molecules. The actual λR -value is determined by the

local slope of the sedimentation curve. Then, taking into account the relation between radius R and radius of gyration ξ of the blob fractal structure⁵ and the dependence of the permeability on the sedimentation coefficient, one calculates the correlation length as follows

$$\xi = 1.39 \sqrt{\frac{D}{2+D}} \cdot \left(1 - \frac{d \ln s}{d \ln c}\right)^{1.47} \sqrt{\frac{\mu}{1 - \rho_1/\rho_s} \cdot \frac{s}{c}} \quad (3)$$

where the blob fractal dimension D was taken equal 5/3 in a good solvent and 2 in a theta solvent, as deduced from the correlation length dependence of the number of monomeric units involved with this range, determined for semidilute solution of polystyrene in toluene and cyclohexane.^{3,4}

The data of sedimentation coefficient⁶ were utilized, measured for polystyrene solutions in toluene (a good solvent) and in cyclopentane (a theta solvent). The obtained lines are presented in Figure 1, where they are compared with the data of static correlation length, measured by small angle X-ray scattering from polystyrene solution in toluene, a good solvent,³ and by neutron scattering from polystyrene solution in cyclohexane at the theta point.⁷

The results calculated for good solvent are close to that of the correlation length measured by dynamic light scattering, exceeding near twice the values of static

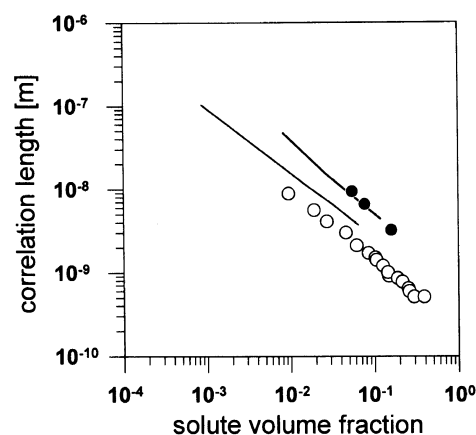


Figure 1. The solute volume fraction dependences of the correlation length in semidilute solutions of polystyrene. The lines represent the values calculated by eq 3 for solution in toluene (thin line) and cyclopentane (thick line). The points represent experimental data measured by small angle X-ray scattering from polystyrene solution in toluene (○) and by neutron scattering from polystyrene solution in cyclohexane at the theta point (●).

† E-mail: gmach@ichf.edu.pl

correlation length, as deduced⁸ on the basis of many experimental data. This strongly suggests the effectiveness of the reported method of the correlation length calculation from the sedimentation data. The values calculated for polystyrene in a theta solvent are close to that of the static correlation length. However the values of dynamic correlation length are also expected to slightly exceed the static ones. To achieve this, at least partly, one may convert the calculated values of radius of gyration into the corresponding values of hydrodynamic radius, which in the vicinity of the fractal dimension of 2 is higher of about 10%,⁹ whereas such effect is negligible for a polymer-good solvent system.

The concept of the reduction of the flow channels and the increasing importance of the size of solvent molecules seems to be useful to rough explanation of the observed dependences. As a result of molecular interactions, the good solvent molecules are partly immobilized inside the polymer coils and blobs, more than the theta solvent molecules having a greater possibility to flow through the interior of blobs. Hence the blobs in good solvents are generally less permeable than those in the theta solvents² for the same concentration, which is an experimental evidence that the phenomenon of hampering the solvent flow through the blobs are of greater significance for polymer-good solvents systems. In a dense system of blobs a slight reduction of the internal permeability of blobs causes a significant increase in the blob radius, according to the flow model employed. Therefore the calculated dynamic correlation length is greater than the static correlation length, and the divergence observed is more pronounced for polymer-good solvent systems.

Nevertheless, the obtained results are difficult to

quantitative interpretation, since the problem of mutual relation of both correlation lengths seems to be still unsolved.⁸ Some minor discrepancies in the calculated correlation lengths may be also caused by the lack of the possibility to properly convert the sedimentation data to the permeability, since the sedimentation data, although corrected for pressure effects, do not fully correspond to the physical properties used to calculate the permeability. The calculated values of permeability are thus only proportional to the real ones, and hence the calculated correlation length behaves in the same way giving a line parallel to that representing the experimental data. This fact as well as the nearness of the measured and calculated values of correlation length confirm however the agreement between the structure and dynamics of semidilute polymer solutions up to a very high concentration.

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