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Fractal aggregate model of sedimenting macromolecules

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Abstract

The dissolved macromolecules are represented by fractal aggregates of the same mass and hydrodynamic properties, composed of solid particles. The model presented gives the relation between sedimentation coefficient of an individual coil and that for the semidilute solution if the coil and blobs can be modeled by the same fractal aggregate. Using this model the sedimentation coefficient of an individual macromolecule is recalculated into the sedimentation coefficient of semidilute solution. The sedimentation coefficients are then compared by plotting them against the mass of object under consideration (macromolecule or blobs). The points for individual coils are situated lower. This incompatibility is analyzed in terms of the coil size reduction with concentration in the dilute region. The reduction of coil size corresponds to the increase of the size of non-porous particles forming the equivalent aggregate. In a good solvent such contraction can be also possible by reduction of the excluded volume exponent.

Keywords: Model aggregate; Blob mass; Chain concentration

1. Introduction

Sedimentation in an ultracentrifuge is a method used for characterizing macromolecules and bioparticles. The proper interpretation of measured values, however, requires the knowledge of the structure and hydrodynamic behavior of macromolecules in solution. The description of hydrodynamics of semidilute solutions has become possible thanks to the scaling concepts and the blob theory, introduced by de Gennes' group [1–3] and developed [4] with the use of the idea of Debye [5] and Brinkman [6,7], to describe macromolecules as permeable objects.

The power dependences appearing in the macromolecular mass–radius relation and blob theory are the same as for fractal aggregates [4]. Therefore, the Flory exponent can be identified with the reciprocal fractal dimension of equivalent solid particle fractal aggregate. This paper is devoted to find correlation between sedimentation coefficient of individual macromolecule and that of semidilute solution. This is done by assuming that the individual coil and the blob of the same mass existing in a semidilute solution can be modeled by fractal aggregates of non-porous primary particles.

2. Fractal model of coils and blobs and their sedimentation behavior

Assume that a polymer coil of molecular mass M can be represented by a fractal aggregate of the same mass and hydrodynamic properties, composed of i non-porous primary particles of radius a and mass M_a. This is illustrated by Fig. 1. The hydrodynamic radius r is the radius of an impermeable sphere of the same mass having the same dynamic properties.

The translational friction coefficient of a macromolecular coil or equivalent fractal aggregate of radius R, being the radius of the sphere circumscribed on aggregate, can be written in the following form

$$f_T = 6\pi\mu R \frac{r}{R} \tag{1}$$

where μ is the solvent viscosity. The hydrodynamic radius is introduced, to show the dependence of the translational

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Nomenclature

a	non-porous primary particle radius (m)
const	constant appearing in Eq. (10) (m^2)
D	fractal dimension (–)
i	number of non-porous primary particles in a coil or blob (–)
k	permeability coefficient (m^2)
M	mass of a macromolecule or blob (u)
M_a	mass of non-porous primary particle (u)
r	hydrodynamic radius of a coil or blob (m)
R	radius of a solid particle aggregate equivalent to a coil or blob (m)
s	sedimentation coefficient of a macromolecular solution (s)
s_0	sedimentation coefficient of an individual macromolecule (s)
$1-\varepsilon$	solute volume fraction (–)
$(1-\varepsilon)_R$	solute volume fraction in solid particle aggregates equivalent to blobs (–)
$(1-\varepsilon)_r$	solute volume fraction in impermeable spheres equivalent to coils or blobs (–)
ϕ	volume fraction of solid particle aggregates equivalent to blobs (–)
ϕ_0	volume fraction of swarm of impermeable spheres equivalent to an arrangement of coils or blobs (–)
μ	solvent viscosity (kg m^{-1} s^{-1})
ν	excluded volume (Flory) exponent (–)
ρ_f	solvent density (kg m^{-3})
ρ_s	solute density (kg m^{-3})

friction coefficient on the internal permeability of the aggregate. The dependence was obtained by Brinkman [7] in the form

$$\frac{r}{R} = \frac{1-(\tanh\sigma/\sigma)}{1+(3/2\sigma^2)(1-(\tanh\sigma/\sigma))} \tag{2}$$

where $\sigma = R/\sqrt{k_R}$ is the reciprocal square root of dimensionless internal permeability of an aggregate or polymer coil.

Dimensionless internal permeability of an aggregate k_R/R^2 depends on the fractal structure. For a homogeneous porous medium the permeability is proportional to the square of the characteristic pore size [8]. In the case of fractal aggregate the fluid flows mainly in the large pores, and hence their size determines the internal permeability of an aggregate. According to the self-similar structure of aggregates, the size of large pores scales as the size of the whole aggregate if the growth or breakage occurs under the condition of constant fractal dimension. So the internal permeability of an aggregate is expected to be proportional to the square of aggregate radius. Hence the ratio of the internal permeability and the square of aggregate radius is expected to be constant for aggregates of the same fractal dimension and to decrease with increasing fractal dimension due to the increment of the aggregate compactness [9,10].

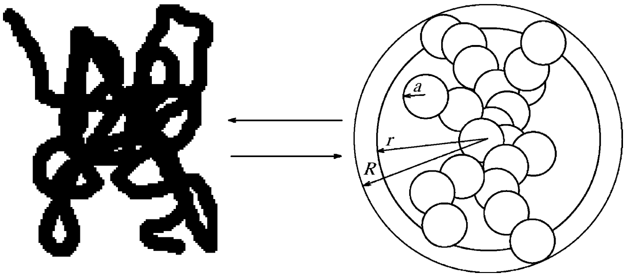

Fig. 1. A macromolecular coil or blob and equivalent solid particle aggregate, both of the same hydrodynamic radius.

The constancy of $k_R/R^2 = \sigma^{-2}$ for a given fractal dimension means that the normalized hydrodynamic radius does not depend on the aggregate radius, according to Eq. (2).

The sedimentation coefficient s_0 of an individual macromolecular coil, being the sedimentation velocity divided by the centrifugal acceleration, can be determined by equating the centrifugal force allowing for the buoyancy of the solvent with the opposing hydrodynamic force, as given by the Stokes law. After dividing by the centrifugal acceleration one gets

$$\frac{4}{3}\pi a^3 i(\rho_s - \rho_f) = 6\pi\mu r s_0 \tag{3}$$

where ρ_s and ρ_f are the solute density and solvent density, respectively. The number of non-porous primary particles in a coil is given either by its definition

$$i = \frac{M}{M_a} \tag{4}$$

or by the mass–radius relation describing the structure of fractal aggregates

$$i = \left(\frac{r}{a}\right)^D \tag{5}$$

The form of Eq. (5) expresses the fact, that the hydrodynamic radius of a fractal aggregate attains the primary particle radius at the aggregation number equal to one [11].

Rearranging Eq. (3) one gets

$$s_0 = \frac{2}{9\mu}(\rho_s - \rho_f)\frac{a^3 i}{r} \tag{6}$$

and using the mass–radius relation one obtains

$$s_0 = \frac{2}{9\mu}(\rho_s - \rho_f)a^2 i^{(D-1)/D} \tag{7}$$

The sedimentation coefficient can be also expressed in the following way

$$s_0 = \frac{2}{9}\frac{\rho_s - \rho_f}{\mu} a^2 \left(\frac{M}{M_a}\right)^{(D-1)/D} \tag{8}$$

when Eq. (4) is employed. The mass of non-porous primary particle is connected with its radius as follows

$$M_a = \frac{4}{3}\pi\rho_s N_A \times 10^3 a^3 \tag{9}$$

in which the coefficient $N_A \times 10^3$ connects the unit of molecular mass with the SI-unit.

According to Eq. (8), the sedimentation coefficient of a given macromolecule in a given solvent depends not only on the macromolecular mass but also on the mass of non-porous particles forming the equivalent aggregate. The size of the non-porous particle is thus the fitting parameter, which makes it possible to connect the sedimentation coefficient of an individual coil with the macromolecular mass. A macromolecular chain of a given mass and fractal dimension can be modeled by aggregates of different numbers of constituents and hence of different hydrodynamic radii. This is shown in Fig. 2.

Sedimentation coefficient decreases considerably when the concentration increases. In semidilute polymer solutions the macromolecular coil overlap. The structure of overlapping coils is observed only on the length scales up to a characteristic length, the correlation length [1,12]. The correlation length is a function of the solute volume fraction in the solution irrespective of the macromolecular mass and polydispersity in coil size. Hence given the solute volume fraction in the system and the fractal dimension of coils, the same value of the correlation length is expected for monodisperse and polydisperse systems. A semidilute solution may be considered as composed of fractal blobs of size equal to the correlation length. The correlation length diminishes as the system concentration increases. In the semidilute region the power dependence is observed of the permeability on the concentration [4]

$$k = \mathrm{const}(1-\varepsilon)^{2/(D-3)} \tag{10}$$

where ε is the solution porosity. The permeability is connected with the sedimentation coefficient as follows [13]

$$k = \frac{\mu}{\rho_s - \rho_f}\frac{s}{1-\varepsilon} \tag{11}$$

which is valid in full range of concentrations of monodisperse macromolecules dissolved [14], where the measurement of sedimentation coefficient is possible, and for overlapping macromolecules irrespective of the mass distribution. From Eqs. (10) and (11) one gets the following formula

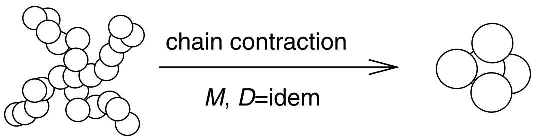

Fig. 2. Fractal aggregate model of chain contraction.

$$s = \frac{\rho_s - \rho_f}{\mu}\mathrm{const}(1-\varepsilon)^{(D-1)/(D-3)} \tag{12}$$

For a semidilute solution the concentration is proportional to the solute concentration in aggregates equivalent to blobs [4,14]

$$1-\varepsilon = \phi(1-\varepsilon)_R = \phi\frac{ia^3}{R^3} \tag{13}$$

Employing the mass–radius relation (Eq. (5)) one gets

$$1-\varepsilon = \phi\left(\frac{r}{R}\right)^3 i^{(D-3)/D} = \phi_0 i^{(D-3)/D} \tag{14}$$

Volume fraction of swarm of impermeable spheres equivalent to a dense arrangement of blobs, $\phi_0 = \phi(r/R)^3$, is a determined [14] function of the fractal dimension. Therefore,

$$1-\varepsilon = \frac{D-1}{2(4-D)} i^{(D-3)/D} \tag{15}$$

Employing Eq. (4) one gets the following relation between the concentration of semidilute polymer solution and the molecular mass of the blobs:

$$1-\varepsilon = \frac{D-1}{2(4-D)}\left(\frac{M}{M_a}\right)^{(D-3)/D} \Rightarrow M = M_a\left[\frac{2(4-D)}{D-1}\right]^{D/(D-3)}(1-\varepsilon)^{D/(D-3)} \tag{16}$$

Sedimentation velocity is given by Eqs. (12) and (16) as follows

$$s = \frac{\rho_s - \rho_f}{\mu}\mathrm{const}\left[\frac{D-1}{2(4-D)}\right]^{(D-1)/(D-3)}\left(\frac{M}{M_a}\right)^{(D-1)/D} \tag{17}$$

According to theoretical analysis of aggregate size reduction with increasing solid concentration, performed in Ref. [4] with the use of Brinkman model, const is connected with the radius of non-porous primary particle and the fractal dimension

$$a = \frac{11.6}{(3-D)^{1.82}}\sqrt{\mathrm{const}} \tag{18}$$

hence

$$s = \frac{\rho_s - \rho_f}{\mu} a^2 \frac{(3-D)^{3.64}}{135}\left[\frac{D-1}{2(4-D)}\right]^{(D-1)/(D-3)}\left(\frac{M}{M_a}\right)^{(D-1)/D} \tag{19}$$

and with the use of Eq. (12) one gets the concentration dependence of the sedimentation coefficient in semidilute region in the form which takes into account the radius of non-porous primary particle

$$s = \frac{\rho_s - \rho_f}{\mu} a^2 \frac{(3-D)^{3.64}}{135}(1-\varepsilon)^{(D-1)/(D-3)} \tag{20}$$

Dividing sedimentation coefficient of semidilute solution, expressed by Eq. (19), by sedimentation coefficient for individual coil (Eq. (8)) one gets

$$\frac{s}{s_0} = \frac{9}{2}\frac{(3-D)^{3.64}}{135}\left[\frac{2(4-D)}{D-1}\right]^{(D-1)/(3-D)} \tag{21}$$

which expresses the reduction of sedimentation coefficient caused by the concentration increase from zero to that characteristic for a molecular mass of blobs present in semidilute solution equal to the molecular mass of the coil under consideration. Eq. (21) is valid for the same mass of non-porous primary particle. The ratio of sedimentation coefficients depends only on the fractal dimension.

The sedimentation coefficient s_0 of an individual macromolecular coil can be also determined by taking into consideration the hydrodynamic equivalent sphere. By analogy to Eq. (3), the sedimentation coefficient can be determined from the following formula, expressing the Stokes law

$$\frac{4}{3}\pi r^3 (1-\varepsilon)_r(\rho_s - \rho_f) = 6\pi\mu r s_0 \tag{22}$$

where $(1-\varepsilon)_r$ is the solute volume fraction inside the hydrodynamic equivalent sphere (impermeable coil) equal according to Eqs. (4) and (5)

$$(1-\varepsilon)_r = \frac{(4/3)\pi a^3 i}{(4/3)\pi r^3} = i^{(D-3)/D} = \left(\frac{M}{M_a}\right)^{(D-3)/D} \tag{23}$$

Hence with the use of Eqs. (4), (5) and (22) one gets the following equation

$$\begin{aligned} s_0 &= \frac{2}{9\mu}(\rho_s - \rho_f)(1-\varepsilon)_r r^2 \\ &= \frac{2}{9\mu}(\rho_s - \rho_f)a^2\left(\frac{M}{M_a}\right)^{(D-1)/D} \end{aligned} \tag{24}$$

which is in agreement with Eq. (8). From Eqs. (11) and (24) one gets

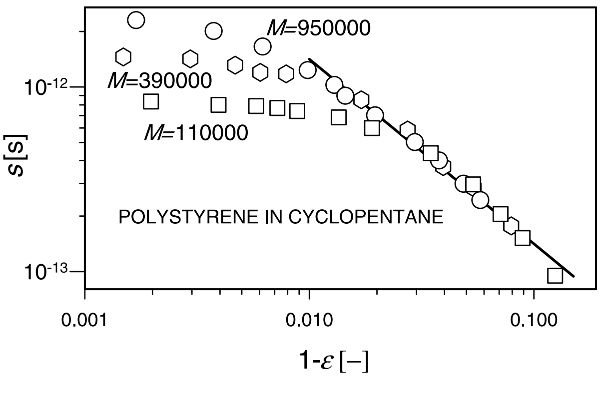

Fig. 3. Sedimentation coefficient as dependent on solute volume fraction depicted for polystyrene of different molecular masses dissolved in cyclopentane [15]. Solid line is described by Eq. (31).

$$\frac{s}{s_0} = \frac{9}{2}\frac{1-\varepsilon}{(1-\varepsilon)_r}\frac{k}{r^2} \tag{25}$$

Using Eq. (23) one can calculate the volume fraction of impermeable spheres equivalent to an arrangement of coils

$$\frac{1-\varepsilon}{(1-\varepsilon)_r} = (1-\varepsilon)\left(\frac{M}{M_a}\right)^{(3-D)/D} = \phi_0 \tag{26}$$

Hence

$$\frac{s}{s_0} = \frac{9}{2}\phi_0\frac{k}{r^2} \tag{27}$$

In order to simplify the description, a polymer solution containing permeable macromolecular coils has been replaced by hydrodynamic equivalent arrangement of impermeable spheres, present at the same number concentration and having the same overall permeability. The constancy of the overall permeability is achieved by the reduction of the coil radius to the hydrodynamic radius at the cost of internal coil permeability, which results in the increase of the size of inter-coil spaces through which the fluid can flow. The permeability normalized by the square of the radius of impermeable particles depends only on the packing density [4]

$$\frac{k}{r^2} = f(\phi_0) \tag{28}$$

The normalized permeability coefficient, expressed by sedimentation coefficient, can be derived using Eqs. (8), (26) and (27) to get

$$\frac{k}{r^2} = \frac{\mu}{\rho_s - \rho_f}\frac{s}{1-\varepsilon}\left(\frac{M}{M_a}\right)^{-2/D} a^{-2} \tag{29}$$

According to the modified Brinkman model [7,11], verified by the data of many aggregated solid–liquid systems in a wide interval of volume fraction of aggregates, as well as those for ultracentrifugal sedimentation of polymer solutions, the normalized permeability coefficient for an arrangement of impermeable spheres is described as follows

$$\frac{k}{r^2} = \frac{2}{9\phi_0}U \tag{30}$$

where

$$U = \frac{5(b+h)^2 + (2b+j)(2b+l)}{20b(b+h)/\phi_0 + 2b(2b+j)},$$

$$b = 3\sqrt[6]{\phi_0}\frac{}{\sqrt{2U}} + 1, \quad h = -\frac{3}{\sqrt{2U\phi_0}} - \frac{3}{\sqrt[3]{\phi_0}}$$

$$j = -\frac{4U}{9\phi_0}\left(\frac{27\sqrt{2\phi_0}}{4U\sqrt{U}} + 27\sqrt[3]{\phi_0}\frac{}{U} + 135\sqrt[6]{\phi_0}\frac{}{\sqrt{2U}} + 45\right),$$

$$l = -\frac{3\sqrt{2\phi_0}}{\sqrt{U}}$$

3. Experimental data analysis

The values of sedimentation coefficient as dependent on molecular mass and volume fraction of polystyrene dissolved in cyclopentane at the θ-temperature and toluene (a good solvent) were recalculated from the experimental data [15,16]. They are depicted in Figs. 3 and 4 as log–log plots. For higher solute volume fractions the dependences become close to linear and common for all molecular masses analyzed. They were approximated by the following formulae:

for cyclopentane

$$s = 1.415 \times 10^{-14}(1-\varepsilon)^{(D-1)/(D-3)}\text{s}, \quad D = 2 \tag{31}$$

for toluene

$$s = 9.891 \times 10^{-15}(1-\varepsilon)^{(D-1)/(D-3)}\text{s}, \quad D = 1.8 \tag{32}$$

The location of the points for highest concentrations in Figs. 3 and 4 under corresponding straight lines is probably caused by the vicinity of the onset of the concentrated regime, in which each segment of the polymer chain does not have a sufficient space available and the dependences become steeper and steeper with the concentration increase. Typically, the volume fraction of the polymer at the crossover is between 0.2 and 0.3 [17].

The values of fractal dimension determined correspond, respectively, to the Flory exponent $\nu = 0.5$ for the theta-solvent, and $\nu = 5/9$ calculated for the good solvent. The last value lies in the range observed for real solvents (0.553–3/5) [17].

The radius of non-porous primary particle was determined by comparing the form of fit equations with that of Eq. (20). The corresponding mass was calculated by Eq. (9). The results were:

for cyclopentane

$$a = 1.638 \times 10^{-9}\text{m}, \quad M_a = 11750\ \text{u} \tag{33}$$

for toluene

$$a = 1.388 \times 10^{-9}\text{m}, \quad M_a = 7140\ \text{u} \tag{34}$$

The obtained values of non-porous primary particle radius are close to that determined [13] for the solutions of poly-α-methylstyrene in cyclohexane and toluene using a simple Brinkman model.

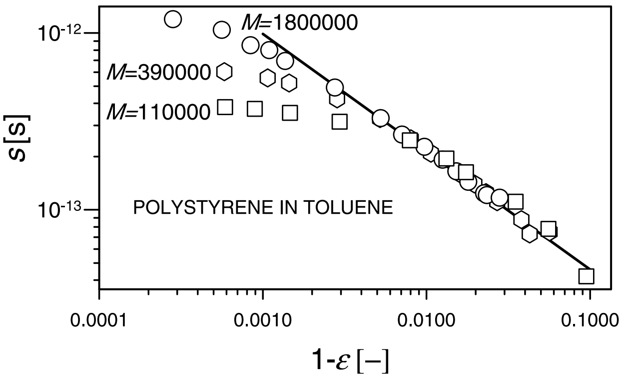

Fig. 4. Sedimentation coefficient as dependent on solute volume fraction depicted for polystyrene of different molecular masses dissolved in toluene [16]. Solid line is described by Eq. (32).

Then the experimental dependences of sedimentation coefficient in dilute region are recalculated to generalized coordinates with Eqs. (26) and (29) to represent the normalized permeability coefficient as a function of volume fraction of impermeable coils. Fig. 5 shows that all the experimental data analyzed are situated on one curve and this is the Brinkman curve described by Eq. (30). All this verifies a posterior the method of treating the polymer coils as permeable objects, employed in this paper.

Then the concentration dependence of blob mass in semidilute region was calculated using Eq. (16) and the blob mass dependence of the sedimentation coefficient by Eq. (19) to get:

for cyclopentane

$$M = 734.4(1-\varepsilon)^{-2}, \quad s = 5.220 \times 10^{-16} M^{1/2}\text{s} \tag{35}$$

for toluene

$$M = 553.8(1-\varepsilon)^{-3/2}, \quad s = 5.970 \times 10^{-16} M^{4/9}\text{s} \tag{36}$$

Sedimentation coefficients for individual macromolecules were recalculated by Eq. (21) into the corresponding values for semidilute solution containing blobs, which can be modeled by the same fractal aggregates as the individual coil. The recalculated sedimentation coefficients are compared in Figs. 6 and 7 with that measured for semidilute solutions.

The points for individual coils well follow the slope of the sequence of points measured in the semidilute regime but are situated lower. Such an incompatibility was not observed previously [18] for fractal aggregates of solid particles, for which even small difference in fractal dimension of individual aggregates and that existing in overlapping region did not cause such a difference in sedimentation velocities. The different location of the points is caused by different sizes of model primary particles. According to Eq. (8), the larger size of primary particles,

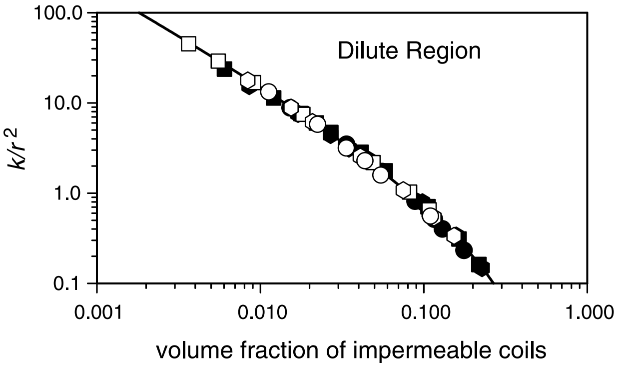

Fig. 5. Concentration dependence of permeability coefficient for dilute solutions of polystyrene of different molecular masses in cyclopentane [15] (filled symbols) and toluene [16] drawn in generalized coordinates (Eqs. (26) and (29)) and compared with graphical representation of the Brinkman curve (Eq. (30)).

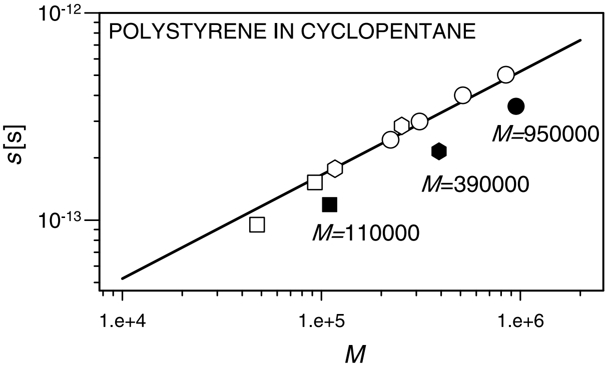

Fig. 6. Comparison of the sedimentation coefficients for individual macromolecules (filled symbols) and for semidilute solution of polystyrene in cyclopentane. Solid line is described by Eq. (35).

the lower is situated the point representing the sedimentation coefficient. A fractal aggregate of given mass and fractal dimension composed of bigger primary particles has a smaller hydrodynamic radius, as can be deduced from Eq. (5)

$$ia^3 = \text{const} = r^D a^{3-D} \Rightarrow r \propto a^{(D-3)/D} \tag{37}$$

This tendency is shown by Fig. 2.

The incompatibility observed for sedimentation of macromolecules is analyzed in terms of the coil size reduction with concentration in the dilute region. The chain contraction can be predicted theoretically [19]. It was also observed experimentally for polymers dissolved in good and marginal solvents [20], by measuring the reduction of the static correlation length with concentration. In the dilute range the correlation length can be identified with the chain size.

The method presented in this paper makes it possible to describe this phenomenon by comparing the sedimentation coefficients for individual coils and that for semidilute solution. According to Eq. (6) the sedimentation coefficient of an individual macromolecule of a given mass is inversely proportional to its hydrodynamic radius. Comparing s_0 with the corresponding value recalculated from semidilute region for the blob mass equal to that of individual macromolecule, one can estimate the chain contraction at the critical concentration beginning the range of semidilute solution, according to the formula

$$\frac{r}{r_0} = \frac{s_0}{s} \tag{38}$$

The calculated values are presented in Fig. 8. They are in agreement with that observed in light scattering experiments [20].

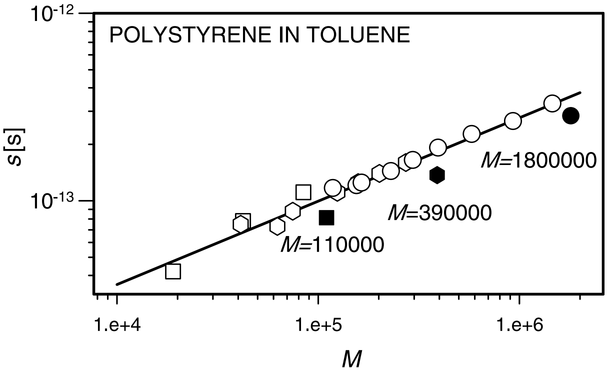

Fig. 7. Comparison of the sedimentation coefficients for individual macromolecules (filled symbols) and for semidilute solution of polystyrene in toluene. Solid line is described by Eq. (36).

4. Discussion and conclusions

The sedimentation behaviors of polystyrene dissolved in two solvents of different quality were analyzed to show that that the individual coil and the blob of the same mass existing in a semidilute solution can be modeled by fractal aggregate of non-porous particles, but the blobs existing at the critical concentration, which are of the mass of polymer chain, have smaller hydrodynamic radius as compared to that of individual coil. The sedimentation data reflects thus the chain contraction under concentration of the polymer solution.

In Fig. 5 one can observe a very good agreement of the Brinkman curve with sedimentation data despite they were recalculated using the mass of non-porous primary particle valid in semidilute region. This requires more explanation. Let us allow to analyze the effect of the size of model primary particle on the values of generalized coordinates described by Eqs. (26) and (29). This can be calculated as follows

$$\frac{k}{r^2} = \frac{\mu}{\rho_s - \rho_f}\frac{s}{1-\varepsilon}\left(\frac{M}{M_a}\right)^{-2/D} a^{-2} \propto a^{(2(3-D))/D} \tag{39}$$

$$\phi_0 = (1-\varepsilon)\left(\frac{M}{M_a}\right)^{(3-D)/D} \propto a^{(3(D-3))/D} \tag{40}$$

Hence

$$\frac{k}{r^2} \propto \phi_0^{-2/3} \tag{41}$$

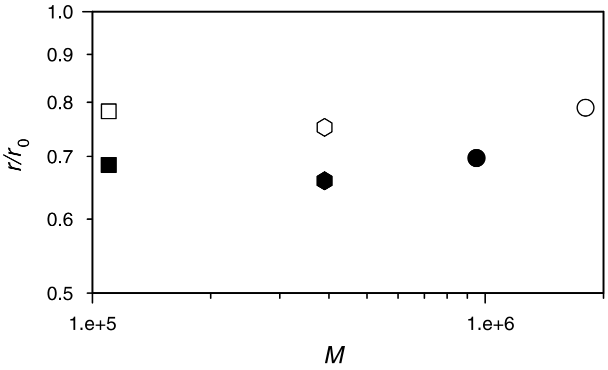

Fig. 8. Chain contraction as dependent on macromolecular mass deduced from sedimentation data for individual coil and the semidilute region of polystyrene in cyclopentane [15] (filled symbols) and toluene [16].

The slope of this dependence in a log–log plot is −2/3. A change in the size of model primary particles will cause o shift of an experimental point under consideration along such a line. Since the Brinkman curve has a similar slope in dilute concentration range such changes have little effect on the visual agreement of experimental data with the theoretical Brinkman curve.

The quantitative determination of the primary particle size from the equating of the experimental and theoretical generalized coordinates for a given experimental point would be questionable because of experimental errors. Otherwise, the values of sedimentation coefficient of individual coil as well as the form of equation describing the concentration dependence of the sedimentation coefficient in the semidilute region are determined based on many experimental points and, therefore, can be considered as reliable. They can by utilized to estimate the chain contraction at the critical concentration beginning the semidilute region.

Macromolecular coils consist of thermal blobs. Inside a thermal blob the chain is ideal, while on larger length scales the chain interact with itself via excluded volume effects. The concentration blobs, present in semidilute solution, do not feel the excluded volume by other blobs. Therefore, a chain in semidilute solution takes a conformation of an ideal chain consisting of blobs. The mass of thermal blobs decreases with the increase of solvent quality. The corresponding model is presented by Dondos [21,22].

The points depicted in Fig. 7 for semidilute solutions are situated along a straight line over a wide concentration interval. Therefore, it seems not to be possible to analyze the changes in slope with the blob mass as given by Daoud and Jannink [23]. The points for individual macromolecules well follows the slope of the line valid in semidilute regime. This, however, could be apparent. As discussed by Weil and des Cloizeaux [24], small changes in the slope can be caused by the mixed statistics of the chain and reaching the asymptotic behavior. It is now assumed that the structure of individual macromolecules is more close to that characterized by $\nu=3/5$ ($D=1.67$). The sedimentation coefficients recalculated by Eq. (21) become much more close to the straight line. Moreover, the investigated macromolecules with such excluded volume exponent consist of some scores till a thousand of thermal blobs [22], for which the exponent is indeed close to the asymptotic value [24]. The incompatibility observed for sedimentation of macromolecules in a good solvent can be thus analyzed in terms of the change in coil structure with concentration in the dilute region.

The difference in the structure of individual sedimenting macromolecules and blobs of the corresponding masses has been analyzed in this paper. It is interpreted as caused by a chain contraction with concentration in the dilute region, occurring with constant fractal dimension. In a good solvent such contraction can be also possible by reduction of the excluded volume exponent.

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