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Chain contraction at the critical overlap concentration

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Abstract

The sedimentation of dissolved macromolecules is analyzed in both the regions of very dilute solution and in semidilute regime employing the fractal aggregate model of macromolecular coils and blobs. The macromolecules entering the overlapping region are represented by more compact aggregates than that modeling the individual macromolecule of the same mass and fractal dimension. This regularity is confirmed by analyzing the hydrodynamic behavior of several polymer–solvent systems in a wide interval of fractal dimension including the polymers dissolved in both the theta and real solvents. The reduced hydrodynamic volume of macromolecules is about 0.3–0.5 of that of the individual macromolecule. This well corresponds with the literature data obtained by measurement of the reduction of the static correlation length with concentration and those determined by dielectric study of the end-to-end distance.

Keywords: Chain contraction; Critical overlap concentration; Fractal aggregate model

1. Introduction

Sedimentation of macromolecules and bioparticles in an ultracentrifuge is a method used for their characterization. Since the hydrodynamic behavior is determined by the structure, the proper interpretation of measured values makes it possible to determine the structure of macromolecules in solution.

The structure of flexible linear macromolecule is modeled by the freely joined chain. The mean-square end-to-end distance for long chains consisting of n bonds of length l is given [1] as

$$\langle R^2 \rangle = C_\infty n l^2 \quad (1)$$

where C_∞ is the Flory characteristic ratio representing the stiffness of the polymer chain with typical numbers of 5–10. The chain, however, can be treated as though it was flexible by grouping a sufficient number of bonds into one effective segment [2] of length b, known as the Kuhn segment or monomer, such that

$$\langle R^2 \rangle = N b^2 \quad (2)$$

$$R_{\max} = N b \quad (3)$$

where N is the number of Kuhn segments in the chain and $R_{\max}$ is the maximum length of the end-to-end vector.

This is a good model for macromolecular coils in theta solvents, where the attractive and repulsive parts of monomer–monomer interactions cancel each other. It defines the root-mean-square end-to-end distance for flexible polymers in the ideal state

$$R \equiv \langle R^2 \rangle^{1/2} = b N^{1/2} \quad (4)$$

If the attraction between monomers becomes weaker than the repulsion, the chain swells, otherwise the chain collapses. The chain swelling is observed in good and athermal solvents, whereas the polymer is in collapsed conformation in poor

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Nomenclature

a	radius of monomer of fractal aggregate (m)
a_0	radius of non-porous primary particle in aggregate representing an individual macromolecule (m)
a^*	non-porous primary particle radius in overlapping range of concentration (m)
b	length of Kuhn segment (m)
C_∞	Flory characteristic ratio (–)
d	diameter of cylindrical Kuhn monomer (m)
D	fractal dimension (–)
g_T	number of Kuhn monomers in thermal blob (–)
i	number of non-porous primary particles in the fractal aggregate modeling a macromolecule (–)
k	permeability coefficient (m^2)
l	bond length (m)
M	mass of a macromolecule or blob (u)
M_{a_0}	mass of non-porous primary particle in aggregate representing an individual macromolecule (u)
M_{a^*}	mass of non-porous primary particle in overlapping range of concentration (u)
M_K	Kuhn segment mass (u)
n	number of bonds (–)
N	number of Kuhn segments in a chain (–)
r	hydrodynamic radius of a coil (m)
R	root-mean-square end-to-end distance (m)
$\langle R^2 \rangle$	mean-square end-to-end distance (m^2)
$R_{\max}$	maximum length of the end-to-end vector (m)
s	sedimentation coefficient of a macromolecular solution (s)
s_0	sedimentation coefficient of an individual macromolecule (s)
v	excluded volume (m^3)
V_0	hydrodynamic volume of an individual macromolecule (m^3)
V^*	hydrodynamic volume of a macromolecule at critical overlap concentration (m^3)
$1-\varepsilon$	solute volume fraction (–)
$1-\varepsilon^*$	solute volume fraction at critical overlap concentration (–)
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})
ξ_T	thermal blob size (m)

solvents and non-solvents. The exponent in Eq. (4) is then replaced by a power ν, which is about 3/5 for good and athermal solvents and 1/3 for poor solvents and non-solvents instead of 1/2. Besides the prefactor appears in Eq. (4) by which the mixed statistics of the chain is manifested. On length scales smaller than the thermal blob size ξ_T the chain is ideal. On the scales larger than the thermal blob size the chain conformation in athermal and good solvents is a self-avoiding walk of thermal blobs while the conformation in a poor solvent and non-solvent is a collapsed globule of thermal blobs. For any thermodynamic quality of the solvent the root-mean-square end-to-end distance can be described by the formula [3]

$$R \approx \xi_T \left(\frac{N}{g_T}\right)^{\nu} \approx b\left(\frac{|v|}{b^3}\right)^{2\nu-1} N^{\nu} \tag{5}$$

where g_T is the number of Kuhn monomers in thermal blob, v is the excluded volume and ν is the excluded volume (Flory) exponent, equal to the reciprocal fractal dimension.

The dimension of a macromolecule dissolved depends on polymer concentration. It is smaller than that for an isolated chain. The theoretical models [4,5] make it possible to estimate progress in the chain contraction with increasing concentration, but the results differ considerably and are not in agreement with the experimental data [6]. To analyze the problem, some investigations of hydrodynamic behavior of dissolved macromolecules can be performed by modeling them by fractal aggregates of non-porous particles [7].

The number i of monomers of radius a in an aggregate of fractal dimension D is described by the mass–radius relation in the following form

$$i = \left(\frac{r}{a}\right)^{D} \tag{6}$$

where the hydrodynamic radius of aggregate r is the radius of an impermeable sphere of the same mass having the same dynamic properties. Eq. (6) has no prefactor independently of the value of fractal dimension, since the hydrodynamic radius tends to the monomer radius for the aggregation number tending to one [8]. The form of this formula makes it possible to realize that the reduction of the radius of fractal aggregate of given mass and the fractal dimension is possible by the increase of the monomer size, according to the proportionality [7]

$$r \propto a^{(D-3)/D} \tag{7}$$

Polymer hydrodynamics in semidilute solutions is described by a power-law concentration dependence of the system permeability [9]

$$k = \mathrm{const}(1-\varepsilon)^{2/(D-3)} \tag{8}$$

where ε is the solution porosity, which can be transformed [10] to the concentration dependence of the sedimentation coefficient

$$s = \frac{\rho_s - \rho_f}{\mu}\,\mathrm{const}(1-\varepsilon)^{(D-1)/(D-3)} \tag{9}$$

where ρ_f and ρ_s are the solvent density and solute density, respectively, and μ is the solvent viscosity.

According to theoretical analysis of blob mass reduction with increasing concentration, performed [11] for the fractal dimension range of 1.57–3, const is connected with the radius of non-porous primary particle of model aggregate and the fractal dimension

$$a = \frac{11.6}{(3-D)^{1.82}}\sqrt{\mathrm{const}} \tag{10}$$

The same dependences describe hydrodynamics of dense aggregated systems. The sedimentation coefficient of a dense arrangement of aggregates is thus described by a power-law concentration dependence, represented in Eqs. (9) and (10), along which the aggregate mass diminishes due to progress in volume constrains with the system concentration and the fractal structure. Interpretation of the sedimentation data of both individual aggregates and dense aggregated systems provides the values of monomer size. It was checked up that for aggregates of solid particles both values are the same [12]. The method makes it possible, however, to detect any potential difference in monomer size and hence to estimate the change in aggregate size according to proportionality in Eq. (7).

Using Eqs. (4) and (6) with $D = 2$ for a macromolecule and a fractal aggregate of the same mass and hydrodynamic properties, it is possible to derive the mass ratio of non-porous aggregate monomer of radius a to that of the Kuhn cylindrical segment of length b and diameter d

$$\frac{M_a}{M_{\mathrm{K}}} = \frac{9}{256}\frac{(R/r)^6}{(b/d)^4} \tag{11}$$

Flexible polymers have aspect ratio $b/d = 2$–3 [3] and the ratio of radii in theta solvent is 3.69 [13], hence the aggregate monomer has a greater mass that the Kuhn segment. Eq. (11) also shows that the mass of aggregate monomer grows fast with the chain contraction.

2. Model

In a previous paper [7] a fractal aggregate model was presented, in which sedimenting macromolecules are described as fractal aggregates of the same mass M and hydrodynamic properties, consisting of non-porous spheres. Analyzing the sedimentation data there, it was concluded that the structure of macromolecule at the critical overlap concentration is more compact than that of individual coil. Employing the fractal aggregate model, the individual coil was interpreted as consisting of smaller non-porous particles resulting in bigger hydrodynamic volume of macromolecule. As a result the individual coil can be regarded as an aggregate of solid particles of radius a_0 and the mass M_{a_0}, whereas the macromolecule entering the semidilute region consists of bigger particles of a^* and M_{a^*}, respectively. The growth of the non-porous primary particles, occurring in the dilute region, is finished at the overlap concentration, according to the model represented in Eqs. (9) and (10).

Increasing the solution concentration above that of overlap for given macromolecules, a semidilute solution may be considered as composed of fractal aggregates equivalent to blobs. The fractal aggregates, the aggregation number of which decreases with concentration, consist of non-porous particles of constant mass M_{a^*}.

According to the model, sedimentation coefficient of an individual macromolecule can be calculated as follows:

$$s_0 = \frac{2}{9}\frac{\rho_{\mathrm{s}}-\rho_{\mathrm{f}}}{\mu}a_0^2\left(\frac{M}{M_{a_0}}\right)^{(D-1)/D} \tag{12}$$

The mass of non-porous particle is given by

$$M_{a_0} = \frac{4}{3}\pi\rho_{\mathrm{s}}N_{\mathrm{A}}10^3 a_0^3 \tag{13}$$

in which the coefficient $N_{\mathrm{A}}10^3$ connects the unit of molecular mass with the SI-unit. Hence,

$$s_0 = \frac{2}{9}\frac{\rho_{\mathrm{s}}-\rho_{\mathrm{f}}}{\mu}\left(\frac{4}{3}\pi\rho_{\mathrm{s}}N_{\mathrm{A}}10^3\right)^{-2/3}M^{(D-1)/D}M_{a_0}^{(3-D)/3D} \tag{14}$$

The sedimentation coefficient decreases with increasing concentration. The critical overlap concentration is reached when the volume fraction of impermeable spheres equivalent to macromolecules rises to the value characteristic for semidilute range, which is equal to $(D-1)/2/(4-D)$ [11,12]. The solid volume fraction in equivalent impermeable sphere ia^3/r^3 is $i^{(D-3)/D}$ according to Eq. (6). Hence, the critical overlap concentration for macromolecules of mass M is given [7] as

$$1-\varepsilon^* = \frac{D-1}{2(4-D)}\left(\frac{M}{M_{a^*}}\right)^{(D-3)/D} \tag{15}$$

With Eqs. (9) and (10) one gets [7] the sedimentation coefficient of a macromolecular semidilute solution, containing either macromolecules at critical overlap concentration or blobs of mass M diminishing with further concentration, which is described by the formulae

$$s = \frac{\rho_{\mathrm{s}}-\rho_{\mathrm{f}}}{\mu}a^{*2}\frac{(3-D)^{3.64}}{135}\left[\frac{D-1}{2(4-D)}\right]^{(D-1)/(D-3)}\left(\frac{M}{M_{a^*}}\right)^{(D-1)/D} \tag{16}$$

or

$$s = \frac{\rho_{\mathrm{s}}-\rho_{\mathrm{f}}}{\mu}\left(\frac{4}{3}\pi\rho_{\mathrm{s}}N_{\mathrm{A}}10^3\right)^{-2/3}\frac{(3-D)^{3.64}}{135} \times\left[\frac{D-1}{2(4-D)}\right]^{(D-1)/(D-3)}M^{(D-1)/D}M_{a^*}^{(3-D)/3D} \tag{17}$$

which are valid at and above the critical overlap concentration till the onset of the concentrated region, in which the segments of the polymer chain do not have sufficient space available and the concentration dependence of the sedimentation coefficient becomes more and more steeper. Usually, the volume fraction of the polymer at the crossover is in the range 0.2–0.3 [13].

3. Hydrodynamic volume reduction

The ratio of the sedimentation coefficients of an individual macromolecule of a given mass to that of semidilute solution containing blobs of the same mass is obtained from Eqs. (14) and (17)

$$\frac{s_0}{s} = \frac{30}{(3-D)^{3.64}}\left[\frac{D-1}{2(4-D)}\right]^{(D-1)/(3-D)}\left(\frac{M_{a_0}}{M_{a^*}}\right)^{(3-D)/3D} \tag{18}$$

The number of non-porous particles in the fractal aggregate modeling a macromolecule is given by the mass–radius relation [7]

$$i = \left(\frac{r}{a}\right)^D = \left(\frac{M}{M_a}\right) \tag{19}$$

Hence, the hydrodynamic volume of a macromolecule is equal to

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi a^3\left(\frac{M}{M_a}\right)^{3/D} \tag{20}$$

For a given molecular mass the Eq. (20) reduces to the following proportionality

$$V \propto M_a^{(D-3)/D} \tag{21}$$

Eqs. (18) and (21) make it possible to calculate the reduction in hydrodynamic volume when a macromolecule changes its structure due to concentration of the solution from very dilute to that characteristic for the onset of overlap

$$\frac{V^*}{V_0} = \left[\frac{(3-D)^{3.64}}{30}\right]^3\left[\frac{D-1}{2(4-D)}\right]^{3(D-1)/(D-3)}\left(\frac{s_0}{s}\right)^3 \tag{22}$$

The corresponding increase in the mass of non-porous particles can be calculated by Eq. (21) to get

$$\frac{M_{a^*}}{M_{a_0}} = \left(\frac{V^*}{V_0}\right)^{D/(D-3)} \tag{23}$$

4. Determination of the mass of non-porous particle in semidilute region

The experimental points of sedimentation coefficients for higher concentrations form a straight line [7] in a log–log plot

$$s \propto (1-\varepsilon)^{(D-1)/(D-3)} \tag{24}$$

From the slope and location of the line, the fractal dimension and the proportionality coefficient can be deduced. The coefficient can be then compared to that in the formula describing quantitatively the sedimentation coefficient [7] in semidilute range, obtained from Eqs. (9) and (10)

$$s = \frac{\rho_s - \rho_f}{\mu}a^{*2}\frac{(3-D)^{3.64}}{135}(1-\varepsilon)^{(D-1)/(D-3)} \tag{25}$$

to calculate the radius of non-porous particle and then its mass. Then from Eq. (17) it is possible to calculate the sedimentation coefficient of macromolecules entering the overlap region.

5. Experimental data analysis

The values of sedimentation coefficient as dependent on the volume fraction of PMMA ($M = 1{,}400{,}000$) dissolved in toluene were recalculated from the experimental data [14]. They are depicted in Fig. 1 as a log–log plot. For higher solute volume fractions the dependence becomes close to linear. It was approximated by the following formula:

$$s = 1.436 \times 10^{-14}(1-\varepsilon)^{(D-1)/(D-3)}\ \mathrm{s},\ D = 1.85 \tag{26}$$

The radius of non-porous primary particle was determined by comparing the form of fit Eq. (26) with that of Eq. (25). The corresponding mass was calculated by the formula similar to Eq. (13). The results were

$$a^* = 1.404 \times 10^{-9}\ \mathrm{m}, \quad M_{a^*} = 8304\ \mathrm{u} \tag{27}$$

According to Eq. (16), the sedimentation coefficient of macromolecules entering the overlap region can be calculated as follows:

$$s = 7.528 \times 10^{-16} M^{0.460}\ \mathrm{s} \tag{28}$$

This sedimentation coefficient for the system analyzed was calculated for the molecular mass of sedimenting macromolecules to be 5.019×10^{-13} s. Comparing with the sedimentation coefficient of the individual macromolecule, $s_0 = 2.062 \times 10^{-12}$ s, it was possible to calculate the reduction in hydrodynamic volume by Eq. (22), equal to 0.430, and the corresponding increase in the mass of non-porous particles, equal to 3.88.

Using the same method, the sedimentation data of polystyrene in cyclohexane [15] were analyzed (Fig. 2), and those of PAMS in toluene and cyclohexane [10,16]. The results of the non-porous particle parameters are placed in Table 1, together with those earlier obtained [7] by analyzing the sedimentation data of polystyrene in toluene [17] and cyclopentane [18].

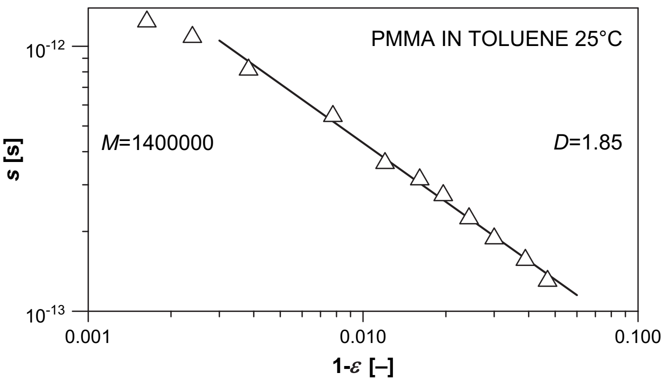

Fig. 1. Sedimentation coefficient as dependent on solute volume fraction depicted for PMMA dissolved in toluene [14]. Solid line is described in Eq. (26).

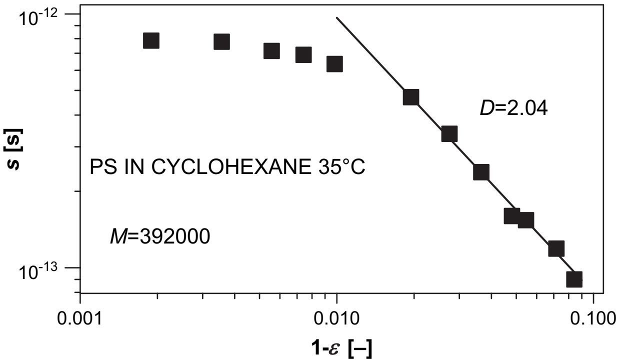

Fig. 2. Sedimentation coefficient as dependent on solute volume fraction depicted for polystyrene dissolved in cyclohexane [15].

Table 1
Characteristics of polymer–solvent systems analyzed

System	D	$a^* \times 10^{-9}$ (m)	M_{a^*} (u)	References	Symbol
PAMS-toluene	1.75	1.546	10,550	[10,16]	○
PS-toluene	1.80	1.388	7140	[7,17]	□
PMMA-toluene	1.85	1.403	8304	[14]	△
PAMS-cyclohexane	2.00	1.731	14,830	[10,16]	●
PS-cyclopentane	2.00	1.638	11,750	[7,18]	▼
PS-cyclohexane	2.04	1.672	12,500	[15]	■
PS-toluene	1.57			[6]	◇
PS-methyl ethyl ketone	1.79			[6]	◆
PI-benzene	1.72			[19–22]	▽
PI-hexadecane	1.85			[19–22]	▽

The reduction of static correlation length, evaluated in static light-scattering measurements [6] for solutions of polystyrene in toluene and methyl ethyl ketone, was also taken into account, as well as the chain contraction determined by dielectric study of the end-to-end distance of *cis*-polyisoprene in moderately good solvents [19–22].

Hydrodynamic volume reduction at the overlap concentration is presented in Fig. 3, whereas the corresponding increase in the mass of non-porous particles is depicted in Fig. 4.

6. Discussion and conclusions

The dimensions of isolated polymer chains in solution are determined by the solvent quality. The chains are expanded relative to their unperturbed size in good solvents owing to excluded volume interactions between monomers. At the theta condition the repulsive excluded volume interactions are compensated by attractive monomer–monomer interactions.

When the concentration increases the intermolecular interactions appear. The structure of macromolecular coils is now determined by the balance between intra- and intermolecular interactions. The compression of coils takes place which causes progressive chain contraction with concentration [4,13,23,24].

According to the fractal aggregate model of macromolecules, the chain contraction is connected with the coarsening of non-porous primary particles. The size of the non-porous primary particle is an effective parameter which makes it possible to describe the hydrodynamic behavior of macromolecules modeled as fractal aggregates of solid particles. It is strongly connected, however, with the distribution of polymer material to form a structure permeable for the solvent. Coarser non-porous particles form a structure with larger pores. But the process of chain contraction occurs independently of the solvent flow [6,19–22].

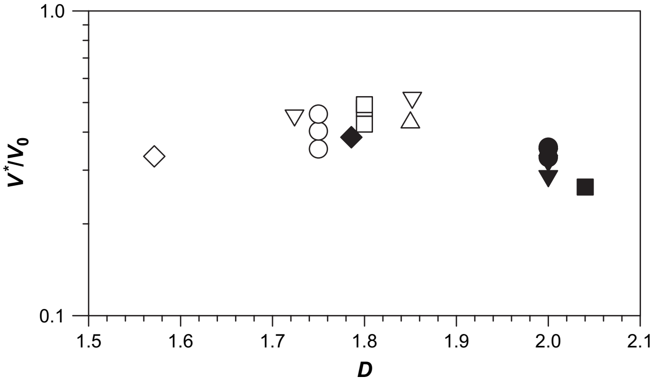

Fig. 3. Hydrodynamic volume reduced at the overlap concentration calculated for different polymer–solvent systems as dependent on the fractal dimension. Symbols are explained in Table 1.

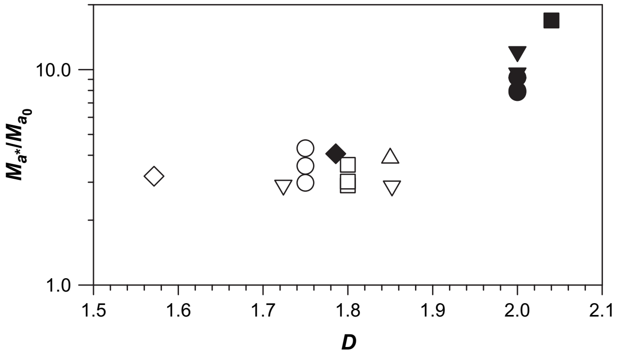

Fig. 4. Increase in the mass of non-porous particles at the overlap concentration calculated for different polymer–solvent systems as dependent on the fractal dimension. Symbols are explained in Table 1.

The reduced hydrodynamic volume of macromolecules is about 0.3–0.5 of that of the individual macromolecule, but it is possible to observe a slight maximum (Fig. 2). This means that the hydrodynamic volume is less reduced in the range between good and theta solvents. Beyond the maximum the chain contraction increases with decreasing solvent quality despite growing compactness of the isolated macromolecules. Because of that and the rapid increase of the absolute value of the exponent with the fractal dimension in Eq. (11), the increase in the mass of non-porous particles at the overlap concentration, which is nearly unchanged for lower fractal dimension, rises much for higher fractal dimensions, as can be observed in Fig. 4.

The difference in the structure of an isolated sedimenting macromolecule and that entering the semidilute region 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. The model utilized differs from those usually used to characterize the structure of individual macromolecules in the way of choice of effective monomer. The monomer in the model is neither the Kuhn segment nor the thermal blob. The Kuhn segment length and mass are characteristic for a polymer. The number of Kuhn monomers in thermal blob depends on the solvent quality [25]. The non-porous particle radius as a monomer of the model fractal aggregate is a dynamic quantity which is not only a function of solvent quality but also takes into account the degree of chain contraction.

The fractal dimension dependence of the reduction in hydrodynamic volume of macromolecule calculated from sedimentation data has been shown to be in agreement with those obtained by measurement of the reduction of the static correlation length with concentration and those determined by dielectric study of the end-to-end distance. This suggests a universal character of obtained dependence which can be considered as a basis for estimations of the structure of coil under contraction. This also confirms the reliability of the method of analysis of sedimentation data. The model, despite of a lower resolution in comparison with the Kuhn approach, is adequate to make the analysis of hydrodynamic behavior of macromolecules in solution.

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