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Polymer 48 (2007) 4316–4321

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Polymer Communication

Fractal aggregate model of chain with mixed statistics

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Received 12 December 2006; received in revised form 17 May 2007; accepted 17 May 2007

Abstract

A fractal aggregate model is presented for chain molecules which are described by different statistics on different length scales. It describes the macromolecular chains as aggregates composed either of non-porous monomers or thermal blobs. The mass of non-porous monomer and the thermal blob mass are both dependent on the solvent quality. The blob mass can be calculated knowing the non-porous monomer mass in a solvent under consideration and that at the theta condition. Both the quantities can be deduced from the solution properties. The values of thermal blob mass normalized by that of monomer, deduced from intrinsic viscosity data for several polymers, form a dependence on Mark–Houvink–Sakurada exponent. This dependence is confirmed by the solvent quality dependence of the polymer mass at the onset of excluded volume behavior and some values obtained from sedimentation coefficients.

Keywords: Chain with mixed statistics; Thermal blob; Fractal aggregate model

1. Introduction

The hydrodynamic behavior of macromolecules in solution, which depends on the chain structure, is a basis for molecular characterization. The proper interpretation of measured values makes it possible to determine the structure of macromolecules in solution.

The structure of a linear macromolecule in a theta solvent is modeled by flexible chain by grouping a sufficient number of bonds into one effective segment [1,2] of length b, known as the Kuhn segment or monomer, such that the root-mean-square end-to-end distance R is described as

$$R \equiv \left\langle R^2 \right\rangle^{1/2} = bN^{1/2} \tag{1}$$

If the attraction between monomers becomes weaker than the repulsion, the chain swells, otherwise the chain collapses. The exponent in Eq. (1) is then replaced by a power ν (Flory exponent), 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. (1) for chains in good and poor solvents, by which the mixed statistics of the chain is manifested. On length scales smaller than the thermal blob size $\xi_T$the chain is ideal. On the scales larger than the thermal blob size the chain conformation in good solvents is a self-avoiding walk of thermal blobs while the conformation in a poor solvent is a collapsed globule of thermal blobs. For all the cases of the solvent thermodynamic quality considered, the root-mean-square end-to-end distance can be described by the formulae [3]

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

where g_T is the number of Kuhn monomers in thermal blob and ν is the excluded volume exponent, equal to the reciprocal fractal dimension. The strict relation takes place only for a macromolecule in a theta solvent and then is expressed by Eq. (1).

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doi:10.1016/j.polymer.2007.05.042

Nomenclature

a	Mark–Houvink–Sakurada exponent (–)
a_{m}	radius of non-porous monomer of fractal aggregate modeling a macromolecule (m)
a_{m_θ}	radius of non-porous monomer of fractal aggregates representing an individual macromolecule in a theta solvent and a thermal blob (m)
b	length of Kuhn segment (m)
c	mass concentration (kg m^{-3})
D	fractal dimension (–)
g_{T}	number of Kuhn monomers in thermal blob (–)
I	number of non-porous monomers in the fractal aggregate modeling a macromolecule (–)
i_{T}	number of non-porous monomers in the fractal aggregate modeling a thermal blob (–)
I	number of thermal blobs in macromolecule (–)
K_{s}	constant in power law dependence of sedimentation coefficient on the molar mass (s)
K_η	Mark–Houvink–Sakurada constant (m^3 kg^{-1})
K_θ	Mark–Houvink–Sakurada constant in theta solvent (m^3 kg^{-1})
M	mass of a macromolecule (u)
M_{m}	mass of non-porous monomer in aggregate representing an individual macromolecule (u)
M_{m_θ}	mass of non-porous monomer of fractal aggregates representing an individual macromolecule in a theta solvent and a thermal blob (u)
M_{K}	Kuhn segment mass (u)
M_{T}	thermal blob mass (u)
N	number of Kuhn segments in a chain (–)
r	hydrodynamic radius of a coil (m)
r_{T}	hydrodynamic radius of a thermal blob (m)
R	root-mean-square end-to-end distance (m)
$\langle R^2 \rangle$	mean-square end-to-end distance (m^2)
s_0	sedimentation coefficient of an individual macromolecule (s)
V	hydrodynamic volume of a chain (m^3)
V_0	hypothetical hydrodynamic volume of a chain in the absence of thermal blobs (m^3)
α_η	viscometric expansion factor (–)
η	solution viscosity (kg m^{-1} s^{-1})
η_0	solvent viscosity (kg m^{-1} s^{-1})
$[\eta]$	intrinsic viscosity (m^3 kg^{-1})
ν	excluded volume (Flory) exponent (–)
ξ_{T}	thermal blob size (m)
ρ_{f}	solvent density (kg m^{-3})
ρ_{s}	solute density (kg m^{-3})
ϕ	volume fraction of impermeable spheres equivalent to an arrangement of coils (–)

Eq. (2) gives either the power-law dependence of the ratio of chain size to that of thermal blob on the number of thermal blobs or the corresponding dependence of the chain size normalized by the Kuhn segment length on the number of the Kuhn monomers. The second formula contains a prefactor, the form of which indicates the existence of two-level structure.

This is the standard picture due to de Gennes [4], according to which inside the thermal blob the chain is a random walk ($D = 2$) and on larger scales the chain must be either collapsed ($D = 3$) or self-avoiding ($D = 5/3$). No other fractal dimensions are understood when calculated by the renormalization group method as described by Freed [5] and by des Cloizeaux and Jannink [6]. The crossover from poor solvent to good solvent is treated by the thermal blob first growing up to the theta temperature and then shrinking again. There are, however, some problems with the crossover description by the blob model [5].

The self-similar nature of polymer chains can be easily demonstrated. Rubinstein and Colby [3] analyze the number of cubes containing monomers in their box-counting model of polymer chain to show the fractal nature of ideal chain. Witten and Pincus [7] demonstrate the transition from random walk to self-avoiding chain by progressive chain swelling. They show that the self-avoidance alters the scaling relationship between chain length and size. The corresponding exponent, called the Flory swelling exponent, is a continuous function of the swelling factor.

The continuous scaling exponent is a theoretical support for many power-law experimental data of solution properties changing over a range of molecular mass and hence makes it possible to model the macromolecular chains as fractal aggregates of fractal dimension dependent on thermodynamic quality of the solvent. It is shown in this paper that using the fractal aggregate model, it is possible to deduce the chain structure from the hydrodynamic behavior of macromolecules.

To analyze hydrodynamic behavior of dissolved macromolecules it is more convenient to use the hydrodynamic radius r instead of the root-mean-square end-to-end distance. Then the size of effective monomer is such that the hydrodynamic radius normalized by the monomer radius is strictly a power of number of monomers in the model aggregate for any fractal dimension [8–10]. Previously [8,9] some investigations were performed on hydrodynamic behavior of dissolved macromolecules by modeling them as fractal aggregates of non-porous particles.

This paper is an extension of the fractal aggregate model of dissolved polymers describing the polymer chains such that they have different fractal dimensions on different length scales. Such macromolecular chains are termed as the chains with mixed statistics.

2. Model

The number i of non-porous monomers of radius a_{m} in an aggregate of fractal dimension D is described by the mass–radius relation in the following form [8]

$$i = \left(\frac{r}{a_{\mathrm{m}}}\right)^D \tag{3}$$

where the hydrodynamic radius of aggregate r is the radius of an impermeable sphere of the same mass having the same dynamic properties. Eq. (3) has no prefactor independent of the value of fractal dimension, since the hydrodynamic radius tends to the monomer radius for the aggregation number tending to one [10]. The dynamic properties of fractal aggregate will be saved when non-porous monomers are replaced by fractal aggregates of finer primary particles of the hydrodynamic radii equal to that of non-porous monomers.

Assume that a polymer chain of molecular mass M can be represented by a fractal aggregate of the same mass and hydrodynamic properties, composed either of i non-porous monomers of radius a_{m} and mass M_{m}, as considered previously [8,9], or of I thermal blobs of hydrodynamic radius r_{T} and mass M_{T}, containing i_{T} non-porous monomers of radius a_{m_θ} and mass M_{m_θ} each. The model of aggregate with mixed statistics is represented by Fig. 1.

Mass radius relation for the model aggregate is described by Eq. (3) and

$$I = \left(\frac{r}{r_{\mathrm{T}}}\right)^{D} \tag{4}$$

whereas the corresponding relation for the thermal blob reads

$$i_{\mathrm{T}} = \left(\frac{r_{\mathrm{T}}}{a_{\mathrm{m}_\theta}}\right)^{2} \tag{5}$$

The mass of the model aggregate can be expressed in two ways. Hence

$$i a_{\mathrm{m}}^3 = I i_{\mathrm{T}} a_{\mathrm{m}_\theta}^3 \tag{6}$$

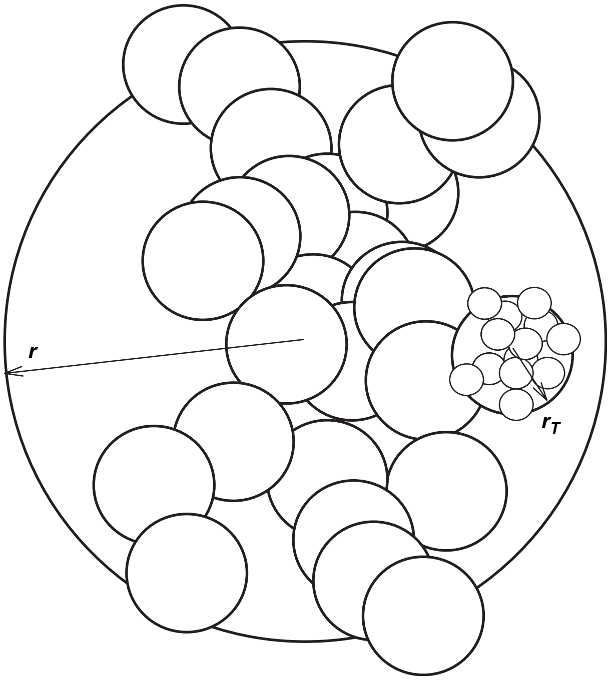

Fig. 1. Graphical representation of the fractal aggregate model of chain with mixed statistics. Inside the blob random walk statistics apply. Any fractal dimension is assumed to be possible on larger scales.

The aggregation number of the fractal blob model is deduced from Eqs. (3–6) to get

$$i_{\mathrm{T}} = \left(\frac{a_{\mathrm{m}}}{a_{\mathrm{m}_\theta}}\right)^{2(3-D)/(2-D)} \tag{7}$$

from which

$$\frac{M_{\mathrm{T}}}{M_{\mathrm{m}_\theta}} = \left(\frac{M_{\mathrm{m}}}{M_{\mathrm{m}_\theta}}\right)^{(2/3)(3-D)/(2-D)} \tag{8}$$

The last formula makes it possible to calculate the mass of thermal blob provided the non-porous monomer mass in a solvent under consideration and that in a theta solvent are known. These values can be deduced from the solution properties.

The viscosity of a polymer solution can be calculated using the Einstein formula [11] for the viscosity of a suspension

$$\eta = \eta_0\left(1 + \frac{5}{2}\phi\right) \tag{9}$$

being dependent on the volume fraction ϕ of suspended impermeable particles, which can be hydrodynamic spheres equivalent to coils [12]. Assuming that the particles are aggregates represented by their hydrodynamic size according to mass–radius relation given by Eq. (3), the mass concentration of suspension can be expressed as

$$c = \phi\rho_{\mathrm{s}}\frac{i a_{\mathrm{m}}^3}{r^3} = \phi\rho_{\mathrm{s}} i^{1-3/D} = \phi\rho_{\mathrm{s}}\left(\frac{M}{M_{\mathrm{m}}}\right)^{-a} \tag{10}$$

where a is the Mark–Houvink–Sakurada exponent.

The intrinsic viscosity is

$$[\eta] \equiv \lim_{c\to 0}\frac{\eta-\eta_0}{\eta_0 c} = \lim_{c\to 0}\frac{\frac{5}{2}\frac{c}{\rho_{\mathrm{s}}}\left(\frac{M}{M_{\mathrm{m}}}\right)^{a}}{c} = \frac{5}{2\rho_{\mathrm{s}}}\left(\frac{M}{M_{\mathrm{m}}}\right)^{a} \tag{11}$$

Comparing with the Mark–Houvink–Sakurada equation one gets

$$[\eta] = \frac{5}{2\rho_{\mathrm{s}}}\left(\frac{M}{M_{\mathrm{m}}}\right)^{a} = K_\eta M^a \tag{12}$$

where K_η is the Mark–Houvink–Sakurada constant. From Eq. (12) one derives

$$M_{\mathrm{m}} = \left(\frac{2.5}{\rho_{\mathrm{s}} K_\eta}\right)^{1/a} \tag{13}$$

This formula makes it possible to calculate the mass of non-porous monomer in aggregate representing an individual macromolecule. The corresponding equation

$$M_{\mathrm{m}_\theta} = \left(\frac{2.5}{\rho_{\mathrm{s}} K_\theta}\right)^{2} \tag{14}$$

obtained from Eq. (12) written for a theta solvent

$$[\eta]_\theta = \frac{5}{2\rho_s}\left(\frac{M}{M_{m_\theta}}\right)^{1/2} = K_\theta M^{1/2} \tag{15}$$

can be utilized to determine the mass of non-porous monomer of fractal aggregates representing an individual macromolecule in a theta solvent and a thermal blob.

3. Determination of masses of non-porous fractal aggregate monomer and thermal blob

The viscosity data collected in Ref. [13] were analyzed. The values of the Mark–Houvink–Sakurada constant for polymers were utilized only if given in sufficient wide spectrum of the solvent quality covering the range from poor to good solvents. The values of non-porous monomer in aggregate representing an individual macromolecule were calculated by Eq. (13) for available values of the Mark–Houvink–Sakurada exponent. The obtained dependences are represented by Fig. 2.

After normalization by the mass of non-porous monomer of fractal aggregates representing an individual macromolecule in a theta solvent and a thermal blob, calculated by Eq. (14), the dependences form a common curve shown in Fig. 3. This suggests that a unique normalized thermal blob mass dependence on the solvent quality is expected according to the form of Eq. (8).

The solvent quality dependence of the normalized thermal blob mass is presented in Fig. 4. The points depicted are much more scattered, however, than those in Fig. 3. This is because of relatively high power $(2/3)(3-D)/(2-D) = a/(a-0.5)$ appearing in Eq. (8). The dependence is completed by some data obtained from recalculation of the solvent quality dependence of the polymer mass at the onset of excluded volume behavior.

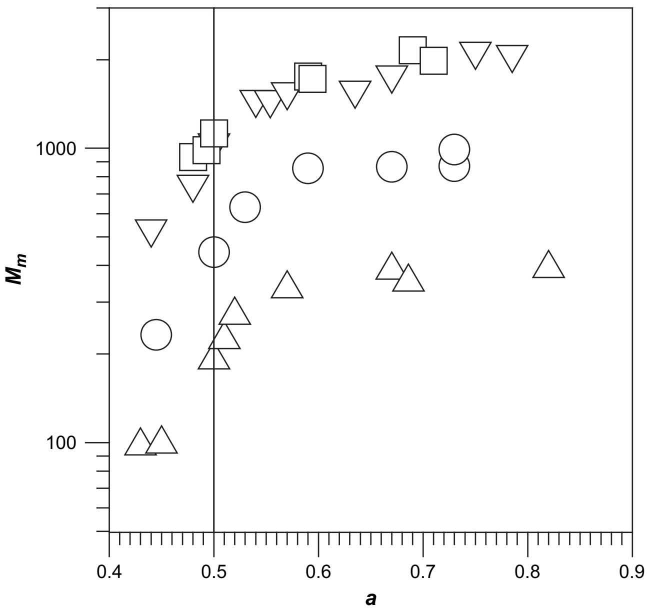

Fig. 2. Mark–Houvink–Sakurada exponent dependences of mass of non-porous monomer in aggregate representing an individual macromolecule depicted for several polymers: △ – poly(oxyethylene); ○ – poly(2-vinylpyridyne); ▽ – poly(styrene); □ – poly(α-methylstyrene).

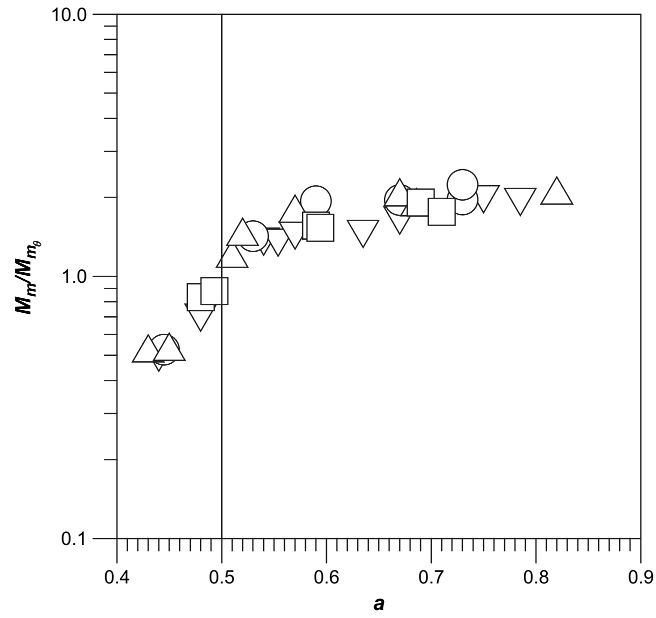

Fig. 3. Mark–Houvink–Sakurada exponent dependences presented in Fig. 2 after normalization of mass of non-porous monomer in aggregate representing an individual macromolecule.

Viscometric expansion factor α_η, using Eqs. (12,15), can be expressed as follows

$$\alpha_\eta^3 \equiv \frac{[\eta]}{[\eta]_\theta} = \frac{K_\eta}{K_\theta} M^{a-1/2} \tag{16}$$

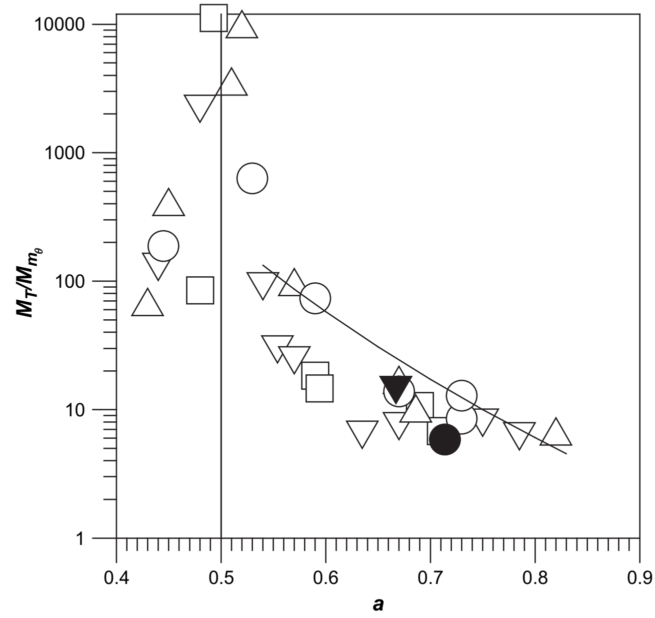

Fig. 4. Mark–Houvink–Sakurada exponent dependences of normalized mass of thermal blob calculated from viscosity data for several polymers: △ – poly(oxyethylene); ○ – poly(2-vinylpyridyne); ▽ – poly(styrene); □ – poly(α-methylstyrene). For comparison two points are depicted represented values obtained from sedimentation data for poly(α-methylstyrene) (●) [17] and poly(styrene) (▼) [18,19]. The line represents Eq. (20).

A plot drawn in $\log(\alpha_\eta^3)-\log M$ coordinates gives the value of the mass of thermal blob when extrapolated to $\alpha_\eta = 1$ [3]. Hence

$$M_\mathrm{T} = \alpha_\eta^{3/(1/2-a)} M \tag{17}$$

Dondos [14–16] analyzed the number of statistical segments of a polymer at the onset of excluded volume behavior as dependent on the solvent quality. The mass of a polymer at the onset of excluded volume behavior was calculated according to the formula

$$M_\mathrm{c} = \left[\frac{4(2-a)(5-a)}{(5+2a)(4+a)}\right]^{1/(a-1/2)} \alpha_\eta^{3/(1/2-a)} M \tag{18}$$

to get the final correlation

$$M_\mathrm{c}/M_\mathrm{K} = 0.3a^{-8} \tag{19}$$

This correlation can be modified to get the solvent quality dependence on the number of non-porous monomer in the thermal blob. Comparing the values of mass of non-porous monomer of fractal aggregates representing an individual macromolecule in a theta solvent and a thermal blob with those for the Kuhn segments estimated by Dondos, one concludes that the values of non-porous monomer mass is about 1/4 greater than the corresponding values for statistical segments. The modified correlation obtained from Eqs (17–19) has thus the form

$$\frac{M_\mathrm{T}}{M_{\mathrm{m}_\theta}} = 0.225\left[\frac{4(2-a)(5-a)}{(5+2a)(4+a)}\right]^{-1/(a-1/2)} a^{-8} \tag{20}$$

This dependence is represented in Fig. 4.

The sedimentation coefficient of an individual macromolecule can be correlated according to the following formula

$$s_0 = K_\mathrm{s} M^{(D-1)/D} \tag{21}$$

The mass of non-porous monomer in aggregate representing an individual macromolecule can be calculated [8,9] as follows

$$M_\mathrm{m} = \left(\frac{4}{3}\pi\rho_\mathrm{s} N_\mathrm{A} 10^3\right)^{2D/(3-D)} \left(\frac{9}{2}\frac{\eta_0}{\rho_\mathrm{s}-\rho_\mathrm{f}} s_0\right)^{3D/(3-D)} M^{3(1-D)/(3-D)} \tag{22}$$

From the last two formulae one gets

$$M_\mathrm{m} = \left(\frac{4}{3}\pi\rho_\mathrm{s} N_\mathrm{A} 10^3\right)^{2D/(3-D)} \left(\frac{9}{2}\frac{\eta_0}{\rho_\mathrm{s}-\rho_\mathrm{f}} K_\mathrm{s}\right)^{3D/(3-D)} \tag{23}$$

Writing the corresponding equation for the theta condition and dividing both equations one obtains

$$\frac{M_\mathrm{m}}{M_{\mathrm{m}_\theta}} = \left(\frac{4}{3}\pi\rho_\mathrm{s} N_\mathrm{A} 10^3\right)^{6(D-2)/(3-D)} \frac{\left(\frac{9}{2}\frac{\eta_0}{\rho_\mathrm{s}-\rho_\mathrm{f}} K_\mathrm{s}\right)^{3D/(3-D)}}{\left(\frac{9}{2}\frac{\eta_{0_\theta}}{\rho_\mathrm{s}-\rho_{\mathrm{f}_\theta}} K_{\mathrm{s}_\theta}\right)^{6}} \tag{24}$$

Two sets of sedimentation data were utilized measured in Refs. [17–19] for polymers of different molecular mass in different solvents. The systems investigated and the results calculated are given in Table 1. The obtained values of normalized thermal blob mass, calculated by Eqs. (8,24), are visualized in Fig. 4.

4. Discussion and conclusions

The fractal aggregate model presented in this paper makes it possible to analyze the power-law dependences describing the solution properties of macromolecules. As a result the thermodynamic quality of the solvent dependence of the normalized thermal blob mass has been deduced. This dependence is confirmed by experimental data interpreted [14–16] in a way to find the number of statistical segments of a polymer at the onset of excluded volume behavior as dependent on the solvent quality.

Analyzing the viscosity data it has been shown (Fig. 2) that the mass of non-porous monomer in aggregate representing an individual macromolecule is not constant but increases with the solvent quality. Therefore the Mark–Houvink–Sakurada constant, which according to Eq. (13) can be described as

$$K_\eta = 10^{\log\frac{2.5}{\rho_\mathrm{s}} - a\log M_\mathrm{m}} \tag{25}$$

cannot be correlated in a wide range of solvent quality as it was done in Ref. [20]

$$K_\eta = 10^{\mathrm{const}_1 - a\,\mathrm{const}_2} \tag{26}$$

Regarding the mass of non-porous monomer in aggregate representing an individual macromolecule as independent of the solvent quality is unreasonable because according to Eq. (8), is equivalent to the assumption of the absence of thermal blobs in polymer chains.

The model makes it possible to calculate [9] the hydrodynamic volume of a chain related to the hypothetical value in the absence of thermal blobs

Table 1
Characteristics of polymer–solvent systems investigated by sedimentation

System	D	K_s (s)	K_{s_θ} (s)	M_m (u)	M_{m_θ} (u)	$M_\mathrm{T}/M_{\mathrm{m}_\theta}$	Reference
PAMS–toluene	1.75	3.65×10^{-15}		2995		5.83	[17]
PAMS–cyclohexane	2.00		1.78×10^{-15}		1765		[17]
PS–toluene	1.80	2.30×10^{-15}		2295		15.4	[18]
PS–cyclopentane	2.00		2.66×10^{-15}		1159		[19]

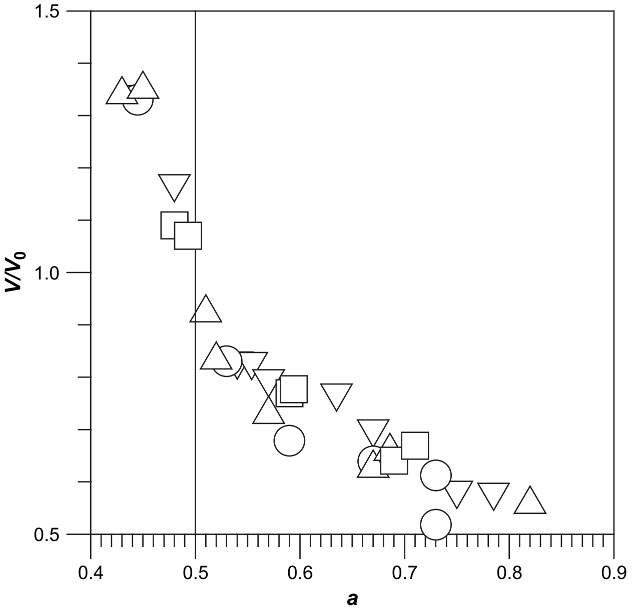

Fig. 5. Hydrodynamic volume of a chain related to hypothetical value in the absence of thermal blobs calculated by Eq. (27) for several polymers: △ – poly(oxyethylene); ○ – poly(2-vinylpyridyne); ▽ – poly(styrene); □ – poly(α-methylstyrene).

$$\frac{V}{V_0}=\left(\frac{M_\mathrm{m}}{M_{\mathrm{m}\theta}}\right)^{-a} \tag{27}$$

This relation is represented in Fig. 5. As the solvent quality turns better to the polymer from the theta condition the chain is less expanded than it would be after decomposition of thermal blobs. This is caused by the presence of thermal blobs which have more compact structure of the whole chain. More compact structure of the chain than that of the thermal blob, existing in a poor solvent, causes a reverse tendency.

Knowing the normalized non-porous monomer mass one can calculate the normalized thermal blob mass. The dependence has been obtained in a wide spectrum of the solvent quality covering the range from poor to good solvents (Fig. 4). In the range of $a = 0.54 - 0.83$ the dependence is confirmed by that resulting from recalculation of the solvent quality dependence of the polymer mass at the onset of excluded volume behavior [14–16]. The values calculated from sedimentation coefficient are also in agreement with the dependence obtained, confirming the general character of the model in describing the hydrodynamic behavior of macromolecules.

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