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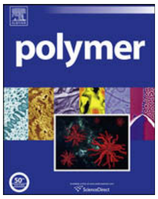

Polymer Communication

Thermal blob size as determined by the intrinsic viscosity

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ABSTRACT

It is shown that the mass of the thermal blob, normalized by the mass of its effective monomer, is a unique function of the solvent quality represented by the Mark–Houwink–Sakurada exponent. This function specifies the relation between intrinsic viscosity and that measured in a theta solvent. As a result, the Mark–Houwink–Sakurada exponent can be determined from intrinsic viscosities measured for a single molecular mass. The form of the derived function is also confirmed by the constancy of calculated thermal blob mass for a given polymer of different molecular masses, dissolved in a solvent of a given quality.

1. Introduction

The intrinsic viscosity is a quantity which characterizes the hydrodynamic behavior of macromolecules in solution. It is a basis for molecular characterization. The proper interpretation of measured values makes it possible to determine the structure of macromolecules in solution. Intrinsic viscosity for a given dissolved polymer strongly depends on the solvent quality.

According to standard view the scaling behavior is observed only for the self-avoiding, random walk and collapsed chains [1]. The crossover domain in-between is described by the thermal blob model, in which the chain is viewed as a sequence of blobs.

The blob model was introduced to illustrate the results of first calculations of the renormalization group [2]. An excluded volume dependent cutoff distance has been postulated to exist in a polymer coil, within which the chain is Gaussian and beyond which is swollen. The size of the thermal blob depends thus on the solvent quality. The theta chain is a random walk, whereas a macromolecule in a very good (athermal) solvent is maximally uncoiled, so the blob has a size of the order of the Kuhn monomer.

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. The number of thermal blobs in a chain, changing with temperature, is connected with the chain expansion factor, calculated [3] for both the static and dynamic properties of the chain.

The intrinsic viscosities can be represented by the Mark–Houwink–Sakurada equation, which can be written for the theta solvent as

$$[\eta]_\theta = K_\theta M^{1/2} \tag{1}$$

and for any solvent quality in the form

$$[\eta] = K_\eta M^a \tag{2}$$

The intrinsic viscosity of a given polymer in a solvent crosses over to the theta result at a molecular mass, which is the thermal blob mass [1].

Viscometric expansion factor α_η can be expressed as follows

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

Putting $\alpha_\eta^3 = 1$ one gets the thermal blob mass

$$M_T = \left(\frac{K_\theta}{K_\eta}\right)^{1/(a-1/2)} \tag{4}$$

The Mark–Houwink–Sakurada relations are empirical equations that have intermediate effective exponents, usually in the range 0.5–0.8, which correspond to the crossover between Gaussian and self-avoiding chains. The effective exponent varies with excluded volume. The chain structure in this nonscaling region, however, can be analyzed in more detail.

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Nomenclature

a	Mark–Houwink–Sakurada exponent (–)
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 (–)
i	number of non-porous monomers in the fractal aggregate modeling a macromolecule (–)
K_η	Mark–Houwink–Sakurada constant (m^3 kg^{-1})
K_θ	Mark–Houwink–Sakurada constant in theta solvent (m^3 kg^{-1})
M	mass of a 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_T	thermal blob mass (u)
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)
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 (–)
ρ_s	solute density (kg m^{-3})
ϕ	volume fraction of impermeable spheres equivalent to an arrangement of coils (–)

Witten [4] and Witten and Pincus [5] demonstrate the transition from random walk to self-avoiding chain by chain swelling, modeled by progressive grouping monomers and discarding all configurations with intersections. They show that the scaling between chain length and size is possible and the self-avoidance alters the scaling relationship. The corresponding exponent, called the Flory swelling exponent, is a function of the swelling factor. The scaling is thus permitted and the Mark–Houwink–Sakurada relations have a theoretical support.

The continuous scaling exponent demonstrated by Witten [4] and Witten and Pincus [5] can be regarded as 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.

The last two equations give the relation between viscometric expansion factor and the number of thermal blobs in a chain

$$\alpha_\eta^3 = \left(\frac{M}{M_T}\right)^{a-1/2} \tag{5}$$

or

$$\alpha_\eta^3 = \left(\frac{M}{M_T}\right)^{3\nu-1.5} \tag{6}$$

where

$$\nu = \frac{a+1}{3} \tag{7}$$

This equation can be confronted to the Han equation [3], describing the crossover between Gaussian and self-avoiding chains by the blob model,

$$\alpha_\eta^3 = \frac{4(1-\nu)(2-\nu)}{(2\nu+1)(\nu+1)}\left(\frac{M}{M_T}\right)^{3\nu-1.5} \tag{8}$$

to conclude that the viscometric expansion factor is underestimated for good solvents ($\nu = 3/5$) by a factor of 0.636 if determined by the Han equation. Calculating the thermal blob mass by Eq. (8) one should expect an underestimation by a factor of 0.222.

In this paper the thermal blob mass is investigated as dependent of the solvent quality and the relation between intrinsic viscosity and that measured in a theta solvent is derived.

2. Model

The viscosity of a polymer solution can be calculated using the Einstein formula [6] 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. To determine ϕ for a polymer solution, it is necessary the polymer coils be represented by spheres which are impermeable to solvent [7]. The hydrodynamic spheres equivalent to coils can have, however, an internal structure characteristic for aggregates. The knowledge of this structure makes it possible to connect the volume fraction of equivalent spheres to the solution mass concentration.

Assuming that the polymer is dissolved in a theta solvent and can be represented by an aggregate of fractal dimension $D = 2$, composed of non-porous spheres of radius a_{m_θ} and mass M_{m_θ}, the mass-radius relation can be expressed according to [8]

$$i = \frac{M}{M_{m_\theta}} = \left(\frac{r}{a_{m_\theta}}\right)^2 \tag{10}$$

where the hydrodynamic radius of aggregate r is the radius of an impermeable sphere of the same mass having the same dynamic properties.

The mass concentration of the solution can be expressed as

$$c = \phi\rho_s\frac{i a_{m_\theta}^3}{r^3} = \phi\rho_s i^{-1/2} = \phi\rho_s\left(\frac{M}{M_{m_\theta}}\right)^{-1/2} \tag{11}$$

The intrinsic viscosity is

$$[\eta]_\theta \equiv \lim_{c\to 0}\frac{\eta-\eta_0}{\eta_0 c} = \lim_{c\to 0}\frac{\frac{5}{2}\frac{c}{\rho_s}\left(\frac{M}{M_{m_\theta}}\right)^{1/2}}{c} = \frac{5}{2\rho_s}\left(\frac{M}{M_{m_\theta}}\right)^{1/2} \tag{12}$$

Comparing with the Mark–Houwink–Sakurada equation one gets

$$[\eta]_\theta = \frac{5}{2\rho_s}\left(\frac{M}{M_{m_\theta}}\right)^{1/2} = K_\theta M^{1/2} \tag{13}$$

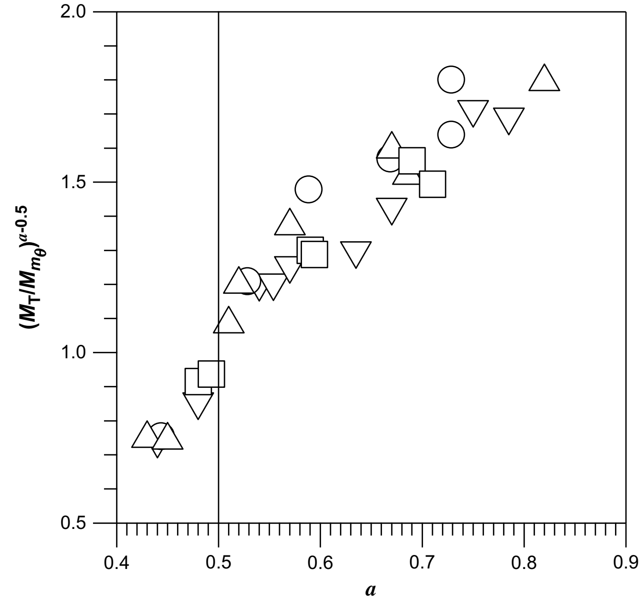

Fig. 1. Dependence of normalized mass of thermal blob in aggregate representing an individual macromolecule on Mark–Houwink–Sakurada exponent, depicted for intrinsic viscosity data [11] for several polymers: Δ – poly(oxyethylene); ○ – poly(2-vinylpyridyne); ▽ – poly(styrene); □ – poly(α-methylstyrene).

From Eq. (13) one derives

$$M_{m_\theta} = \left(\frac{2.5}{\rho_s K_\theta}\right)^2 \tag{14}$$

The obtained formula 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.

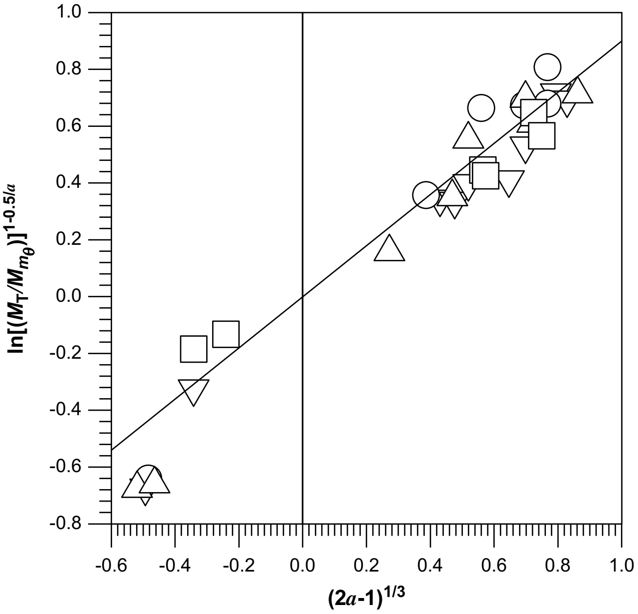

Fig. 2. Linearized dependence of normalized mass of thermal blob in aggregate representing an individual macromolecule on Mark–Houwink–Sakurada exponent, supported by intrinsic viscosity data [11] for several polymers: Δ – poly(oxyethylene); ○ – poly(2-vinylpyridyne); ▽ – poly(styrene); □ – poly(α-methylstyrene). The solid line represents Eq. (18).

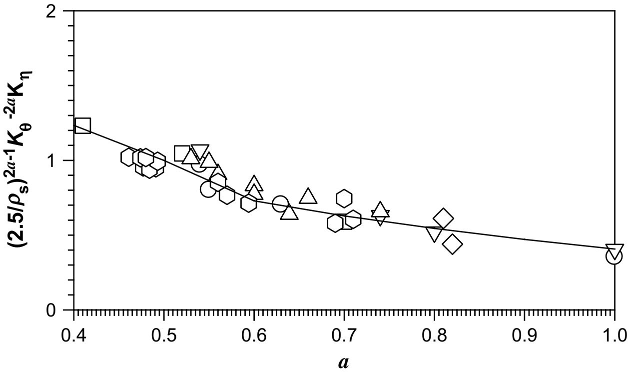

Fig. 3. Confirmation of Eq. (16) with the generalized Mark–Houwink–Sakurada exponent dependence of the normalized thermal blob mass (Eq. (18)) by viscosity data [11] of several polymers: Δ – poly(isobutene);○ – poly(vinyl chloride); ▽ – poly (propylene), isotactic; □ – poly(methyl methacrylate), atactic; ◇ – poly(butyl methacrylate); – ⬡poly(α-methylstyrene).

The above approach differs from the standard picture, in which 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 [9,10] of length *b*, known as the Kuhn segment or monomer, such that the root-mean-square end-to-end distance *R* is described as

$$R \equiv \left\langle R^2 \right\rangle^{1/2} = bN^{1/2} \tag{15}$$

The Kuhn segment is not similar geometrically to equivalent sphere, taken here as a model of macromolecular coil, which becomes more pronounced with growing stiffness of the chain.

The thermal blob mass M_T depends on the solvent quality [8]. The form of this dependence is strongly influenced by the mass of non-porous monomer M_{m_θ} of fractal aggregates, which is different for different polymers. The thermal blob mass normalized by the mass of non-porous monomer, however, is the number of non-porous monomers in one thermal blob and therefore it is expected to be a unique function of the solvent quality. Using Eqs. (4) and (14) one gets

$$\frac{M_T}{M_{m_\theta}} = \left(\frac{2.5}{\rho_s}\right)^{-2}\left(K_\theta^{-2a}K_\eta\right)^{1/(1/2-a)} \tag{16}$$

It is also possible to derive from Eqs. (1), (2), (16)

$$[\eta]_\theta = \left(\frac{2.5}{\rho_s}\right)^{1-1/(2a)}\left(\frac{M_T}{M_{m_\theta}}\right)^{(a-0.5)/(2a)}[\eta]^{1/(2a)} \tag{17}$$

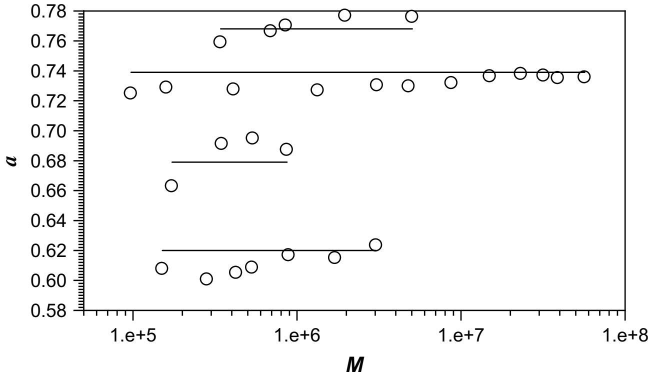

Fig. 4. Comparison of the Mark–Houwink–Sakurada exponent with these calculated by Eqs. (17) and (18) for different molecular mass of the systems at 25 °C: poly (chloroprene) – *n*-butyl acetate, $a = 0.620$ [15]; poly(ethylene oxide) – water $a = 0.679$ [16]; poly(styrene)-benzene, $a = 0.739$ [17]; poly(ethylene oxide) – methanol, $a = 0.768$ [18].

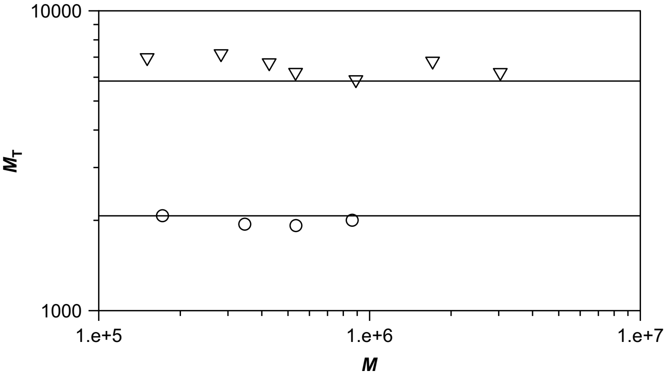

Fig. 5. The thermal blob mass over a range of macromolecular mass depicted for comparison the values determined either from Eq. (19) by the Mark–Houwink–Sakurada exponent or these calculated by Eq. (20) for different molecular masses of the systems at 25 °C: ▽ – poly(chloroprene) – *n*-butyl acetate, $a = 0.620$ [15]; ○ – poly (ethylene oxide) – water $a = 0.679$ [16].

which is the relation between intrinsic viscosity and that measured in a theta solvent, in which the normalized thermal blob mass is involved.

To determine the solvent quality dependence of the normalized thermal blob mass, there were analyzed the viscosity data collected in Ref. [11]. The values of the Mark–Houwink–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 normalized thermal blob mass were calculated by Eq. (16) for available values of the Mark–Houwink–Sakurada constants. They are presented in Fig. 1. Depicted in an accurately selected coordinate system, the dependences can be approximated by a straight line, common for all data. The generalized Mark–Houwink–Sakurada exponent dependence of the normalized thermal blob mass, as deduced from Fig. 2, has the following form

$$\frac{M_T}{M_{m_\theta}} = \left\{\exp[0.9\cdot(2a-1)^{1/3}]\right\}^{a/(a-0.5)} = \exp\left[1.13a(a-0.5)^{-2/3}\right] \qquad (18)$$

According to the formula obtained, the thermal blob mass is infinite in a theta solvent. This is expected since the thermal blob size is reversely proportional to the excluded volume which vanishes at the theta condition [1]. In this case the macromolecular mass is smaller than the thermal blob mass.

The thermal blob mass can be calculated by Eqs. (14) and (18) as follows

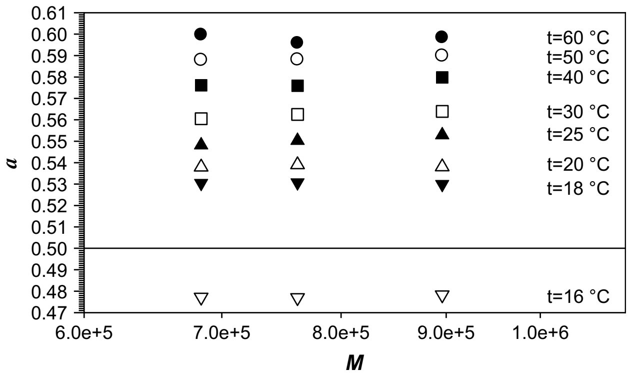

Fig. 6. Mark–Houwink–Sakurada exponent calculated by Eqs. (17) and (18) for different values of molecular mass of the system poly(*p*-methylstyrene) – diethyl succinate [19] above and below the theta-temperature (16.4 °C).

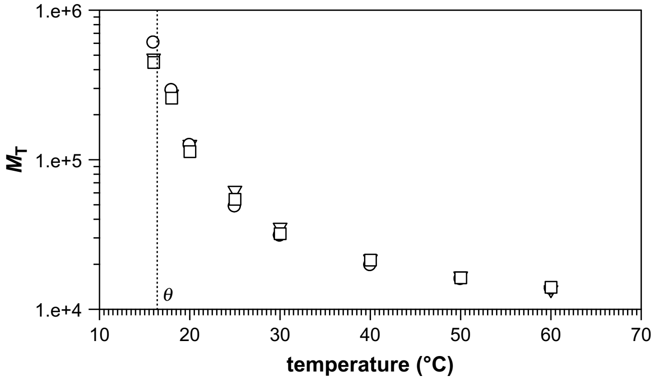

Fig. 7. Thermal blob mass calculated by Eq. (20) as dependent on temperature for the system poly(*p*-methylstyrene) – diethyl succinate [19] of different values of molecular mass: ▽ – 6.84×10^5; □ – 7.62×10^5; ○ – 8.96×10^5.

$$M_T = \left(\frac{2.5}{\rho_s K_\theta}\right)^2 \exp\left[1.13a(a-0.5)^{-2/3}\right] \qquad (19)$$

Eqs. (17) and (18) make it possible to determine the Mark–Houwink–Sakurada exponent solely on the basis of the value of intrinsic viscosity and that measured in a theta solvent for a single molecular mass.

The approach presented in this paper differs from that developed by Dondos [12–14], who analyzed the number of statistical segments of a polymer at the onset of excluded volume behavior as dependent on the solvent quality. The obtained results are also different because the mass of Kuhn segment is not strictly proportional to the mass of non-porous monomer [8].

3. Model confirmation

The intrinsic viscosity data [11], for other polymers than those used to construct the Figs. 1 and 2, were utilized to test the reliability of Eq. (18). The values of $(M_T/M_{m_\theta})^{1/2-a}$ were calculated from Eq. (16) and compared in Fig. 3 with the line being the graphical representation of Eq. (18). The obtained points are close to the line.

In Fig. 4 the values of Mark–Houwink–Sakurada exponent calculated by Eqs. (17) and (18) are compared with these calculated over a width interval of molecular mass [15–18]. The points are close to the corresponding values obtained by the Mark–Houwink–Sakurada relation.

For two of the systems analyzed [15,16], showing relatively considerable deviations from the horizontal lines, the values of thermal blob mass were calculated for several values of macromolecular mass by the following formula

$$M_T = \left(\frac{[\eta]_\theta}{[\eta]}\right)^{1/(a-0.5)} M \qquad (20)$$

obtained from Eqs. (1), (2), (4)

The calculated values are compared in Fig. 5 to a single value, determined from Eq. (19) for Mark–Houwink–Sakurada exponent valid in a range of molecular mass. As previously, the points are close to the corresponding lines.

The next system was the solution of poly(*p*-methylstyrene) of different molecular masses in diethyl succinate, investigated at different temperatures [19]. The constancy of the *a*-exponent at a given temperature is demonstrated in Fig. 6, both above and below the theta-temperature. The thermal blob at a given temperature was calculated by Eq. (20) for each molecular mass. The results are depicted in Fig. 7, in which the points form a common temperature dependence of the thermal blob mass.

4. Discussion and conclusions

A model of chain consisting of thermal blobs has been analyzed in this paper. Accordingly, the thermal blob mass can be determined either by the Mark–Houwink–Sakurada constants and exponent (Eq. (4)) or alternatively by the intrinsic viscosities and exponent (Eq. (20)).

The form of solvent quality dependence of the thermal blob mass normalized by the mass of non-porous monomer of fractal aggregates representing an individual macromolecule in a theta solvent and a thermal blob, has been also derived. It makes it possible to describe the relation between intrinsic viscosities measured for a polymer of single molecular mass.

The corresponding formulae make it possible to determine the Mark–Houwink–Sakurada exponent solely on the basis of the values of intrinsic viscosity and that measured in a theta solvent for a single molecular mass. This value changes negligibly with the molecular mass at a given temperature and is close to *a*-value determined by the Mark–Houwink–Sakurada relation over a width interval of molecular mass. It makes characterization of the structure of macromolecules easier.

The thermal blob mass calculated by Eq. (20) from intrinsic viscosities and the *a*-exponent, characteristic for a polymer of a single molecular mass, is close to that determined in a wider range of molecular mass.

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