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COMMENT

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Comment to the paper "A new approach to the determination of the statistical segment length of wormlike polymers" by A. Dondos and G. Staikos

A new and advanced method for determination of molecular parameters for wormlike polymer from the viscosity data has been recently developed [1]. The method is briefly described. First, the Mark–Kuhn–Houwink–Sakurada (MK) Eq. (1) is readily obtained from molecular weight (M) dependent data of intrinsic viscosity $[\eta]$:

$$[\eta] = KM^{a} . \tag{1}$$

Next, the statistical segment length, A, is determined from the unperturbed dimension parameter K_θ using the Burchard [2] plot of $[\eta]/M^{1/2}$ against $M^{1/2}$, or Dondos–Benoit [3] plot of $[\eta]^{-1}$ against $M^{-1/2}$:

$$[\eta]/M^{1/2} = K_\theta + 0.287\, B\, \Phi\, M^{1/2} \tag{2}$$

$$1/[\eta] = -A_2 + K_\theta^{-1}\, M^{-1/2} . \tag{3}$$

Here, B and A_2 are both the long-range interaction parameters, and Φ is the Flory viscosity parameter in:

$$[\eta] = \Phi \langle R^2 \rangle^{3/2}/M , \tag{4}$$

where $\langle R^2 \rangle$ is the mean-square end-to-end distance of a wormlike macromolecule. Parameter K_θ in Eqs. (2, 3) is equal to K in the MK equation for θ-system:

$$K_\theta = [\eta]_\theta/M^{1/2} = \Phi_\theta(\langle R^2 \rangle_0/M)^{3/2} = \Phi_\theta(A/M_L)^{3/2} . \tag{5}$$

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Here, M_L is the shift factor (the ratio of M to the contour length L of the macromolecule) and Φ_θ is the Φ value at $T = \theta$. Φ_θ is equal to 2.870×10^{23} mol^{-1} in the limit of non-draining random coil [4].

To apply Eq. (4) to data on draining chain it is necessary to know the Φ value which is very sensitive to the draining effect. Namely, the Φ value decreases strongly with decrease of both the number of segments L/A in the chain and the reduced diameter d/A (Fig. 1).

To choose the Φ value (with the known a one), Dondos and Staikos [1] have proposed (and this is the basis of the method) the relation between the Flory parameter Φ and the exponent a:

$$\Phi = 0.52 \times 10^{23}\, a^{-2.32} . \tag{6}$$

This relation was found to be a suitable approximation form for the viscosity data known for seven different polymer + solvent systems and treated in terms of the Yamakawa–Fujii theory [4, 5] either by the Yamakawa method [4], or by the Bushin plot [6] of $(M^2/[\eta])^{1/3}$ versus $M^{1/2}$. Equation (6) was claimed as the universal relation describing the influence of the draining effect on the Φ value for the wormlike macromolecules, the exponent a being the adequate characteristic quantity of the draining effect.

The important question is left open of how this proposal agrees with the theories developed for viscometric properties of the wormlike model chains [4, 5]. Let us use the wormlike sphere-cylinder model which is perfectly applicable to many experimental properties of the molecules discussed [7]. The Φ value for this model is shown in Fig. 1 at the different L/A and d/A values. The exponent a for wormlike chains with the same L/A and d/A values was calculated by Kolomiets et al. [8] and illustrated by Fig. 2 in Ref. [7]. The principal a and Φ values are listed in Table 1.

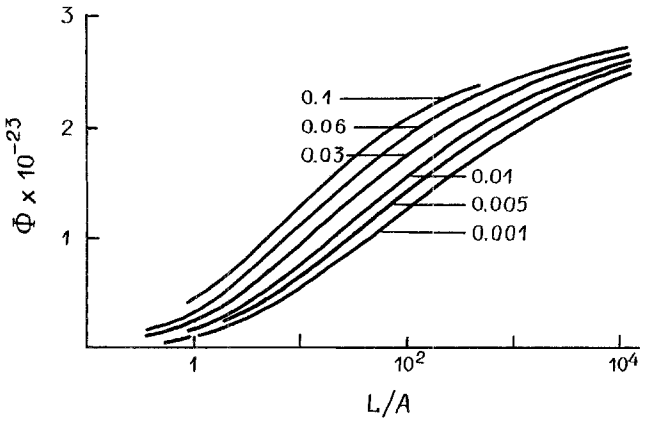

Fig. 1 Φ plotted against L/A for wormlike sphere-cylinders with the indicated d/A values according to [4, 5]; $\Phi_\infty = 2.780 \times 10^{23}$ mol^{-1}

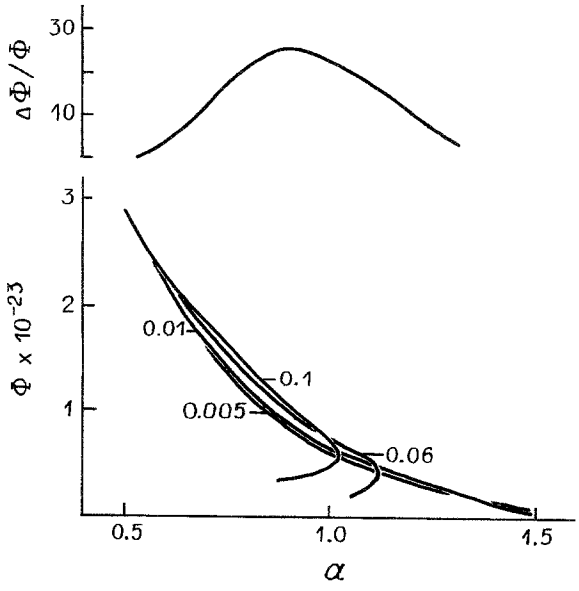

Fig. 2 Φ plotted against a for wormlike sphere-cylinders with the indicated d/A values according to [4, 5]; upper curve – relative dispersion $\Delta\Phi/\Phi$ (in %) of different $\Phi(a)$ dependences shown below

The $\Phi(a)$ functions obtained at different d/A are shown in Fig. 2. In contrast to Eq. (6), Φ is not a monotonous function of a over a wide M range. Nevertheless, for the model chains with $d/A = 0.1$ and 0.005, the monotonous part of the $\Phi(a)$ function may be well approximated by relations:

$$\lg(\Phi/\Phi_\infty) = -0.517\,a \quad (d/A = 0.1;\ L/A \geq 5) \tag{7}$$

$$\lg(\Phi/\Phi_\infty) = -0.654\,a \quad (d/A = 0.005;\ L/A \geq 2) \tag{8}$$

where $\Phi_\infty = \lim \Phi(L/A \to \infty) = 2.870 \times 10^{23}$ mol^{-1} [4].

The following conclusions may be made from the analysis of Fig. 2. The theory predicts, firstly, that the $\Phi(a)$ dependences obtained for different d/A, differ one from another not so significantly as the $\Phi(L/A)$ functions (Fig. 1). This means that the a exponent may be considered as a more universal parameter describing the draining effect than L/A. Hence, the proposal discussed has an important theoretical support.

On the other hand, replacement of different curves $\Phi(a)$ in Fig. 2 by single average curve (for instance, described by Eq. (6)) leads to error in the Φ value used later for the A determination. The upper limit of the error is shown by the upper curve in Fig. 2. Notice, however, that the inaccuracy in the A values is smaller than in the Φ ones since $A \sim \Phi^{-2/3}$ (see Eq. (5)).

Finally, such approximation (similar to Eq. (6)) is applicable if only $L/A \geq 2$ (monotonous part of the $\Phi(a)$ dependence). This means that the L/A parameter may be taken as the reasonable criterion of the method applicability to the wormlike macromolecules with the significant draining effect.

Table 1 a exponent and ratio Φ/Φ_∞ for wormlike sphere-cylinder chains with different d/A values according to [4, 5]; $\Phi_\infty = 2.870 \times 10^{23}$ mol^{-1}

$d/A = 0.10$							
a	0.894	0.990	1.021	0.908	0.830	0.630	0.515
Φ/Φ_∞	0.1185	0.1620	0.2334	0.3537	0.4568	0.7533	0.9693
$d/A = 0.06$							
a	1.068	1.119	1.111	0.962	0.856	0.656	0.523
Φ/Φ_∞	0.0784	0.1181	0.1833	0.2962	0.3930	0.6836	0.9547
$d/A = 0.010$							
a	1.442	1.379	1.295	1.088	0.951	0.716	0.541
Φ/Φ_∞	0.0293	0.0533	0.0962	0.1868	0.2672	0.5453	0.9178
$d/A = 0.005$							
a	1.517	1.432	1.334	1.108	0.972	0.736	0.546
Φ/Φ_∞	0.0223	0.0443	0.0822	0.1631	0.2369	0.5087	0.9066

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