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Short Communication

Non universality of scaling laws in semi-dilute and good solvent solutions

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Résumé . — Cet article présente une évidence expérimentale de la non universalité du comportement de la viscosité réduite en fonction de la concentration réduite C/C^*, en solutions semi-diluées et bon solvant de polymères linéaires. Les résultats montrent deux régimes semi-dilués : non-enchevêtré et enchevêtré, et soulignent le rôle du nombre N_e de blobs entre enchevêtrements. Ce nombre est une constante qui dépend du type de polymère considéré et cause le manque d'universalité.

Abstract . — This paper reports experimental evidence of non universal behavior of the reduced viscosity *versus* the reduced concentration C/C^* in semi-dilute good solvent solutions of linear polymers. Results manifest two semi-dilute regimes: non-entangled and entangled, and outline the role of the number N_e of blobs between entanglements. This number is a constant which depends on the polymer species and causes the universality failure.

Introduction.

Static properties of linear polymers in good solvent are well understood and experimental evidence for the validity of the scaling concept are reported in the literature. For example, in the concentration range at which solvent prevails ($C \ll 1$) but polymers do overlap, i.e. in semi-dilute solution, a universal behavior is theoretically expected for the reduced gradient of the osmotic pressure [1]:

$$(d\pi/dC)/(d\pi_o.dC) = (C/C^*)^{D/(3-D)} \qquad (1)$$

where $(d\pi/dC)$ and $(d\pi_o/dC)$ are the concentration gradient of the osmotic pressure and its $C = 0$ limit respectively, C^* the overlap concentration and D the fractal dimension of polymers. All the parameters specific to the kind of polymer, such as the size a of monomers or the degree

of polymerization N, vanish in such a scaling law. Experimentalists using relevant reduced variables are able to superimpose data obtained on different polymer systems. This scaling behavior was experimentally checked in previous works [2, 3] by light scattering measurements on polyisoprene and poly($\alpha-$ methylstyrene) samples and results are recalled in figure 1. The exponent value $D/(3 - D)$ was found to be equal to 1.30 ± 0.02 in good agreement with the theoretical prediction of the self avoiding walk fractal dimension, $D = 1.70$ [4].
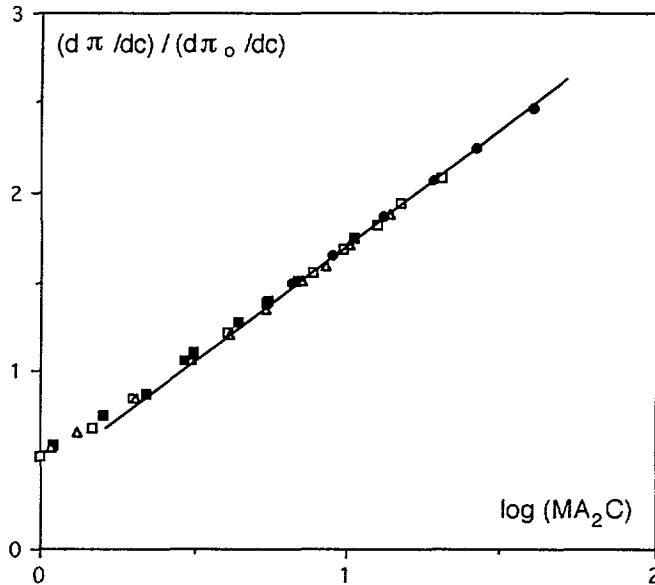

Fig. 1. — Log-Log plot of the reduced gradient of osmotic pressure $(d\pi/dC)/(d\pi_0/dC)$ versus $M_W A_2 C$ for polyisoprene and poly($\alpha-$ methylstyrene) samples. Straight line corresponds to the best fits of high concentration part of data $(M_W A_2 C > 3)$ and has a slope equal to 1.30 ± 0.02.

In this paper, we report experimental evidence that dynamical behavior is not as easy to understand and scaling law to apply.

Theory.

In the melt, the classical al theory of elasticity [5] and the reptation theory [1, 6] predict the expression for the elastic modulus G and the longest relaxation time τ respectively:

$$G = kT\nu = kT \left[1/ \left(N_e a^3 \right) \right] \tag{2}$$

$$\tau = \tau_o N^3 / N_e \tag{3}$$

where the subscript "o" refers to local properties, ν is the number of entanglements per unit volume and N_e the number of monomers between entanglements. These equations lead to an expression for the viscosity η which is equal to the product $G\tau$:

$$\eta = \eta_o N^3 / N_e^2 \tag{4}$$

The main question is the relevance of N_e in the semi-dilute concentration regime. Following de Gennes, a semi-dilute solution may be considered as a melt of blob chains, scaling laws concerning static properties can be established starting from this picture [1, 7]. In the same way, dynamic scaling laws may also be established replacing monomers by blobs, which are the constitutive units of chains in the melt and semi-dilute solutions, respectively. In this description of semi-dilute solutions, the polymer preserves a swollen fractal conformation at a length scale smaller than the size of blobs ξ and a Gaussian one at length scales larger than ξ. So, calling g the number of monomers per blob, we have $g = C\xi^3$ and $\xi \sim C^{1/(D-3)}$ because of the compact filling of space by blobs [8]. One obtains for the concentration dependence of the number g:

$$g \sim C^{D:(D-3)} \tag{5}$$

In this picture, the concentration dependence of dynamic properties comes from those of g and ξ. In equation (2), the number of entanglements per unit volume $\nu = 1/\left(N_e a^3\right)$ becomes:

$$\nu = 1/\left(N_e \xi^3\right) \tag{6}$$

and

$$G = kT/\left(N_e \xi^3\right) \tag{7}$$

In equation (3), the number N of entities per chain becomes N/g the number of blobs per chain and the local time τ_o becomes $\tau_s \xi^3$ assuming a Zimm behavior inside a blob [7]. The subscript "s" refers to the solvent which prevails in semi-dilute regime [9]. We obtain for the longest relaxation time:

$$\tau \approx \tau_s \xi^3 (N/g)^3/N_e \tag{8}$$

So, the viscosity in semi-dilute regime is expected to obey the equation:

$$\eta = \eta_s (N/g)^3/N_e^2 \tag{9}$$

It was previously shown, by comparison of elastic and osmotic moduli, that the number N_e of blobs between entanglements does not depend on the concentration in good solvent solutions [10]. Therefore in equation (9) the only concentration dependence comes from the ratio N/g. Recalling that the overlap concentration C^* scales as $N/R^3 \sim N^{1-3/D}$ and using equations (5) and (9), we obtain:

$$N/g = (C/C^*)^{D/(3-D)} \tag{10}$$

and then:

$$\eta/\eta_s = (C/C^*)^{3D/(3-D)}/N_e^2 \tag{11}$$

By increasing the ratio C/C^* the size of blobs decreases, their number per chain increases and so the viscosity increases. Such a viscosity behavior is the analogue of the N dependence in the melt. Consequently, if N_e plays a role in semi-dilute solution, we expect a non-entangled semi-dilute regime corresponding to $N/g < N_e$ and an entangled semi-dilute regime for $N/g > N_e$. In the former case, the reduced viscosity is expected to be Rouse like and proportional to (N/g), while in the latter case the viscosity obeys equation (11) and scales as $(N/g)^3$. These possible two concentration regimes in semi-dilute solutions were previously discussed in reference [11] but denied in reference [12].

Experimental conditions.

Experiments were performed on two kinds of polymers having quite a different number N_e: polyisoprene ($N_{ePI} = 74$ [13]) and polystyrene ($N_{ePS} = 166$ [5]). In both cases, two different samples having different weight average molecular weights and low polydispersity ($M_w/M_n < 1.10$) were examined. Polystyrene samples were purchased from TOYOSODA and polyisoprene samples were provided by Fetters (Exxon Research & Engineering Co.). Solutions were prepared in good solvent: cyclohexane for polyisoprene and benzene for polystyrene samples. Maximum polymer concentration was fixed at 0.1 g/cm^3.

Samples were characterized in dilute solution by static light scattering, which allowed us to determine the radius of gyration (R_g), the weight average molecular weight (M_w) and second virial coefficient (A_2). Results are summarized in table I. Verification of the measurement quality was done by comparison of the values obtained for $C_1^* = M_w/R_g^3$ and $C_2^* = 1/M_w A_2$. Both quantities, corresponding to different definitions of C^*, have to be proportional [1]. For all the polymers we used, it is found:

$$\langle C_1^*/C_2^* \rangle = 6.63 \pm 0.33. \tag{12}$$

Table I. — *Static light scattering characteristization of samples: M_w is the weight average molecular weight, R_g is the radius of gyration, A_2 is the second virial coefficient. Concentrations C_1^* and C_2^* correspond to different definitions of C^*: $C_1^* = M_w/R_g^3$ and $C_2^* = 1/M_w A_2$.*

	M_w	R_g	$M_w A_2$	M_w/R_g^3	C_1^*/C_2^*
	(g/mol)	(nm)	(cm^3/g)	(g/cm^3)	
PS$_1$	1.24×10^6	54	520	1.29×10^{-2}	6.71
PS$_2$	4.00×10^6	110	1270	4.99×10^{-3}	6.32
PI$_1$	3.10×10^5	28	300	2.35×10^{-2}	7.06
PI$_2$	9.40×10^5	54	650	9.91×10^{-3}	6.44

In the following $1/M_w A_2$ will be taken for C^* instead of M_w/R_g^3 because of its more accurate determination, therefore the reduced variable for the concentration in equation (11) will be $M_w A_2 C$ instead of C/C^*.

Solvent viscosities were determined using a capillary viscometer and will be taken as the local viscosity η_s. Viscosity measurements on semi-dilute solutions were performed using a magnetorheometer which is described elsewhere [14]. This rheometer allows zero shear rate measurements on samples put in hermetically sealed cells avoiding solvent evaporation. Experiments were performed at 30 °C in the reduced concentration range: $4 < M_w A_2 C < 100$. Results are plotted in figure 2.
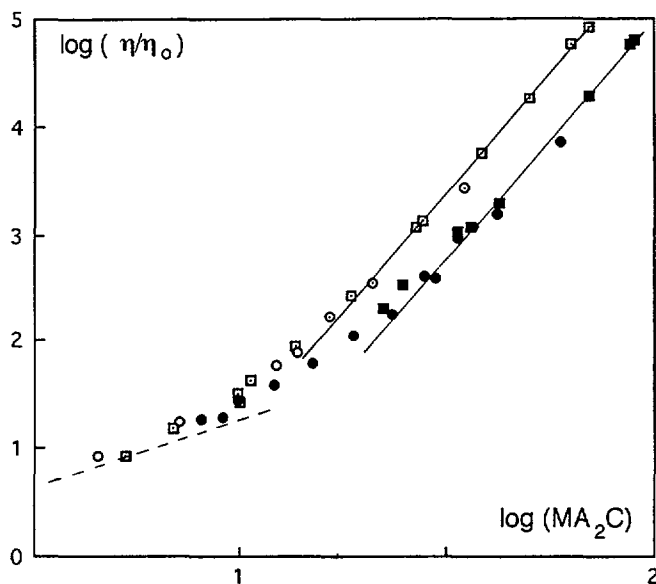
Fig. 2. — Log-Log of the reduced viscosity (η/η_s) versus $M_w A_2 C$ for polyisoprene and polystyrene samples. Straight lines correspond to the best fits in the high concentration part of the curve $(N/g > N_e)$ and dashed line is a guide for the eyes and corresponds to the expected behavior in the Rouse concentration regime $(N/g < N_e)$. PI1: (o), PI2: (□), PS1: (•), PS2: (■).

Results and discussion.

First of all, it is important to remember that all viscosity measurements were performed in a concentration range for which $M_w A_2 C$ is always greater than 4, that means that polymer samples are in semi-dilute solution. Previous work has shown that in the same concentration range the reduced osmotic pressure curve scales as a power law of $M_w A_2 C$ and is unique for polyisoprene and polystyrene samples (see Fig. 1 and Ref. [3]).

Present results show that $M_w A_2 C$ is a reduced variable of the reduced viscosity for each polymer species as expected with regard to previous work [10, 12]. This confirms that local friction is governed by solvent viscosity [9]. Nevertheless for the two polymers, the viscosity behavior reaches a power law concentration dependence at a value of $M_w A_2 C$ greater than the expected value from static properties. Moreover, the two kinds of polymers do not reach a power law behavior at the same reduced concentration and the two curves are distinct for $M_w A_2 C > 13$.

In the low concentration part of the curves, polyisoprene and polystyrene data join together with a decreasing slope as the concentration decreases. This concentration regime would correspond to the Rouse behavior because the number of blobs per chain is less than N_e for the two species. In this concentration range, the number N_e does not act in the expression of the viscosity, universal behavior is expected and the exponent value for η/η_s versus C/C^* is predicted to be $D/(3 - D) = 1.30$. Present experimental data, do not allow us to determine an exponent value because of the small concentration range corresponding to this regime. Nevertheless figure 2 shows that our results are not incompatible with theory.

Mean square fits of data were performed on the higher concentration parts: $M_w A_2 C > 15$ for polyisoprene and $M_w A_2 C > 28$ for polystyrene. It is found:

$$\text{polyisoprene} : (\eta/\eta_s)_{\text{PI}} = 6.60 \times 10^{-4} \, (M_w A_2 C)^{4.37 \pm 0.07} \tag{13}$$

$$\text{polystyrene} : (\eta/\eta_s)_{\text{PS}} = 1.55 \times 10^{-4} \, (M_w A_2 C)^{4.39 \pm 0.07} \tag{14}$$

Exponent values are identical for the two polymers but greater than the reptation prediction. This result is not surprising with regard to the experimental mass dependence of the viscosity in the melt: $\eta \sim N^\alpha$ The exponent α is found experimentally [15] closer to 3.4 rather than to the reptation value 3. The value $\alpha = 3.4$ and $D/(3 - D) = 1.30 \pm 0.02$ lead to $\eta/\eta_s \sim (C/C^*)^{4.42 \pm 0.07}$ in agreement with equations (13) and (14).

But, the main result is that the reduced viscosity as a function of C/C^* is not universal: polyisoprene and polystyrene data do not scale on a single curve. If the above scaling approach is relevant to describe viscosity behavior, equation (11) outlines that prefactors of the reduced viscosity *versus* C/C^* do not vanish and remains $1/N_e^2$. The ratio of reduced viscosities is expected to be equal to:

$$(\eta/\eta_s)_{\text{PI}} \, / \, (\eta/\eta_s)_{\text{PS}} = (N_{e\text{PS}}/N_{e\text{PI}})^2 \tag{15}$$

Using the N_e values mentioned above and determined in the melt, we obtain:

$$(N_{e\text{PS}}/N_{e\text{PI}})^2 = 5. \tag{16}$$

While expressions (13) and (14) lead to:

$$(\eta/\eta_s)_{\text{PI}} \, / \, (\eta/\eta_s)_{\text{PS}} = 4.26. \tag{17}$$

These two values are identical within the error bars. This preliminary result is an indication of the N_e role in semi-dilute solution.

Conclusion and prospect.

Static properties are universal and scaling laws are verified. This is because only one length scale, the size of blobs ξ, is relevant to describe the system from dilute to semi-dilute solutions and is defined in the whole concentration range. This is not the case for dynamic properties. The preliminary work presented in this paper shows the non universality of viscosity behavior. The reptation theory can be applied to semi-dilute solutions but the continuity from the melt to the semi-dilute regime introduces a second length: the mean distance between entanglements. Therefore in the entangled semi-dilute regime, the scaling of data, obtained on different polymer species, imposes to take into account the number N_e of blobs per entanglement. This number N_e being meaningless in the other concentration regimes (dilute and non-entangled semi-dilute), scaling vanishes. In other words, if we use the reduced variables which scale static properties, the curves corresponding to different polymers separate from each other at the concentration for which reptation and thus N_e act.

In order to confirm this result, experiments will be performed on other polymers having different N_e (polybutadiene for example). Measurements of osmotic and shear moduli will enable us to verify the independence of N_e with concentration whatever the polymer.

Acknowledgements.

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