Viscosity and longest relaxation time of semi-dilute polymer solutions: II. Theta solvent

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Viscosity and longest relaxation time of semi-dilute polymer solutions: II. Theta solvent

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Résumé. — Nous présentons des mesures de viscosité à taux de cisaillement nul et de temps de relaxation de solutions semi-diluées au voisinage de la température θ. Le comportement viscoélastique de ces solutions ne peut pas être décrit par des lois d'échelles en concentration et en température. Nous montrons que deux longueurs influencent les propriétés viscoélastiques.

Abstract. — We present zero shear viscosity and longest relaxation time measurements on semi-dilute solutions in the θ region, as a function of concentration and temperature. Our results cannot be described using scaling laws. We show that viscoelastic properties are governed by two differents lengths.

In a previous paper [1] devoted to semi-dilute solutions of polystyrene-benzene (good solvent), we obtained the following results, for the reduced viscosity η_r, the longest relaxation time T_R and the shear elastic modulus G :

1) the reduced viscosity

$$\eta_r \simeq \left(\frac{C}{C^*}\right)^{x_c} \tag{1}$$

where C^* and C are the overlap concentration and the concentration, respectively.

2) The longest relaxation time

$$\frac{T_R}{T_1} \simeq \left(\frac{C}{C^*}\right)^{y_c}, \tag{2}$$

where T_1 is the first Zimm mode of a single chain.

The molecular weight (M_w) dependence of both quantities is :

$$\eta_r \sim T_R \sim M_w^{x_M}. \tag{3}$$

3) The elastic shear modulus is independent of molecular weight :

$$G \sim C^{2.36}. \tag{4}$$

Thus $\frac{C}{C^*}$, the reduced concentration, is the only variable on which η_r and $\frac{T_R}{T_1}$ depend, in agreement with the theoretical predictions [2].

However the effective exponents :

$$x_c = 4.07, \qquad y_c = 2.05$$

determined over the whole range of C/C^*

$$\left(4 < \frac{C}{C^*} < 70\right)$$

were in fact found to be a function of C/C^*. x_c and y_c were found to increased with C/C^* and for $C/C^* > 10$, x_c reached its well known constant value of 4.46 ± 0.05. The effective exponent x_M was an increasing function of the samples concentrations. Those facts could not be explained by the simple reptation model [1].

In this paper we will show that the viscoelastic properties of a semi-dilute θ solvent (polystyrene in cyclohexane) cannot be described using the reptation model and the resulting scaling laws : $\frac{C}{C_\theta^*}$ is not the reduced concentration variable of the quantities η_r and $\frac{T_R}{T_{1\theta}}$. Both the reduced viscosity and the relaxation time decrease as the temperature is increased away from the θ temperature whereas temperature scaling laws predict an increase of these quantities.

1. Experimental conditions.

A detailed description of our magnetorheometer has been presented elsewhere [1, 3].

The experimental precision is about 10 % and 4 % for the relaxation time and the viscosity, respectively. For the viscosity it is not possible to get the same accuracy as for the case of the polystyrene benzene solutions. The solvent used is cyclohexane of analytical grade (R.P.) the polymer used is polystyrene. We choose as the θ temperature, the temperature at which the second virial coefficient vanishes which is

35 °C in our case [4]. We define the overlap concentration as $C_\theta^* = \frac{M_w}{N_A R_g^3}$ where N_A is the Avogadro's number, R_g the radius of gyration of a chain and M_w the weight average molecular weight.

Inserting numerical values one obtains :

$$C_\theta^*(\text{g/cm}^3) = 40\, M_w^{-1/2}, \qquad (5)$$

C_θ^* corresponds to the concentration at which the osmotic compressibility [5] no longer depends on the molecular weight. This behaviour is characteristic of semi-dilute solutions.

Since for a given molecular weight the values of C_θ^* are much higher in a θ solvent than in a good solvent, we have to use high molecular weights in order to fullfil the condition $C_\theta^* < C < 10^{-1}$ g/cm^3 (see table for details about the polystyrene samples).

Table I. — *Molecular weight, polydispersity index and overlap concentration of the polystyrene samples (Toyo-Soda) studied.*

M_w	M_w/M_n	C_θ^* (g/cm^3)
—	—	—
2.06×10^7	—	8.81×10^{-3}
6.77×10^6	1.14	1.54×10^{-2}
3.84×10^6	1.05	2.04×10^{-2}
2.89×10^6	1.09	2.35×10^{-2}

Thus the range of molecular weights studied here is more restricted than in reference [1], and the experiments are performed at lower values of $\frac{C}{C_\theta^*}$

$$\left(1 < \frac{C}{C_\theta^*} < 10\right).$$

The samples are prepared in the measuring cell a long time in advance ($\approx$ 9 months). If any accidental demixion occurs it is necessary to wait at 60 °C several weeks in order to reobtain a homogeneous semi-dilute solution. The homogeneity is checked by measuring the viscosity at various locations of the cell. The same samples were used for intensity light scattering experiments :

— the intensity scattered at zero transfer vector for a given concentration was independent of the molecular weight,

— the correlation length of the density-density correlation function agrees with neutron scattering experiments.

These allows us to be confident in the homogeneity of the samples.

The monomer weight fraction w(g/g) is measured just after the viscoelastic experiments are performed. The concentration C(g/cm^3) and the weight fraction w are linked by the density $\rho(w)$ of the polymer solutions : $C = w\rho(w)$. Following reference [6] at 35 °C we have : $\rho(w)/\rho = 1 + 0.290\, w + 3.01 \times 10^{-2}\, w^2$, where $\rho(= 0.764$ g/cm$^3)$ is the density of cyclohexane. In the weight fraction range investigated $10^{-2} < w \leqslant 10^{-1}$, the density $\rho(w)$ can be approximated ($\rho(w)/\rho - 1 \leqslant 3\,\%$) by the density of the cyclohexane. So it follows that in a first approximation : C is proportional to w and C/C_θ^* is equal to w/w_θ^* ($w_\theta^* = 52.3/\sqrt{M_w}$).

2. Experimental results at 35 °C (θ-point).

2.1 Concentration dependence.

2.1.1 *Relative viscosity.* — By measuring the zero shear viscosity, η, we deduce the relative viscosity : $\eta_r = \eta/\eta_0$ where η_0 is the viscosity of cyclohexane [7] :

$$\eta_0 = 6.173\,9 \times 10^{-5} \exp \frac{1\,481.6}{t} \qquad (6)$$

t being the absolute temperature.

The relative viscosity $\eta_{r\theta}$, is plotted on a log log scale (Fig. 1) as a function of the ratio $\frac{C}{C_\theta^*}$ which is indeed the reduced concentration variable for static properties [5] but also for dynamical properties such as for example the sedimentation coefficient [8] and the gradient concentration measurements of the diffusion coefficient [9]. The experimental results and figure 1 lead to the following conclusions :

1) $\frac{C}{C_\theta^*}$ is not the reduced variable of $\eta_{r\theta}$, because $\eta_{r\theta}$ depend on the molecular weight in this representation (Fig. 1).

2) The following relations are obtained :

$$M_w = 20.6 \times 10^6 : \quad \eta_{r\theta} = 5.8 \times 10^2 \left(\frac{C}{C_\theta^*}\right)^{5.04 \mp 0.1},$$

$$M_w = 6.77 \times 10^6 : \quad \eta_{r\theta} = 1.4 \times 10^2 \left(\frac{C}{C_\theta^*}\right)^{5.3 \mp 0.2},$$

$$M_w = 3.84 \times 10^6 : \quad \eta_{r\theta} = 94 \left(\frac{C}{C_\theta^*}\right)^{5.08 \mp 0.1} \qquad (7)$$

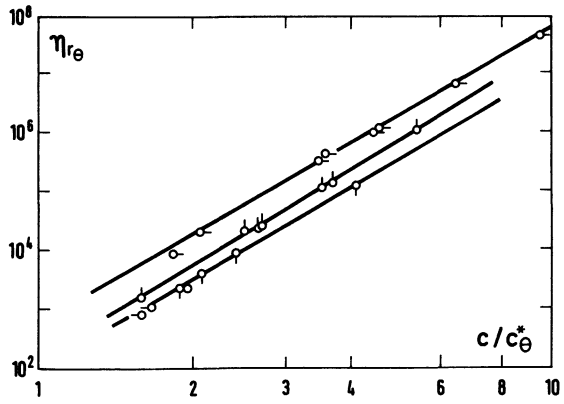

Fig. 1. — Relative viscosity as a function of the reduced concentration C/C_θ^* (log log scale). Straight lines correspond to equation (7). The following symbols are used for different molecular weights M_w : O— : 2.06×10^7; ♁ : 6.77×10^6, ♀ : 3.84×10^6, —O : 2.89×10^6. Raw results are given in the appendix.

We see that the prefactor is strongly molecular weight dependent.

3) The concentration exponent x_c (see Eq. (1))

$$x_c = 5.14 \mp 0.16 \qquad (8)$$

is both independent of the molecular weight, and of the concentration when $C/C_\theta^* > 1$. The domain between the dilute and the semi-dilute regime is much smaller for a θ solvent (polystyrene cyclohexane) than for a good solvent (polystyrene benzene).

4) We have also considered the variation of the viscosity as a function of the product $M_w C$ and find that, contrary to the common belief [10], this quantity is not a reduced variable of η_r.

5) If $\frac{C}{C^*} = 5$, the relative viscosity is 10^4 higher for the polystyrene of molecular weight 20.6×10^6 in cyclohexane than in benzene. However if we compare the relative viscosity for a molecular weight of 20.6×10^6, as a function of concentration we find that, at low weight fraction (2 %), the relative viscosity is smaller by a factor of 4 in the case of cyclohexane (35 °C) compared to the case of benzene. The viscosities in a θ and a good solvent become equal at a weight fraction w_{cross} of about 10 %. w_{cross} seems to be molecular weight dependent and increases as the molecular weight decreases. This is in agreement with the results of reference [11], the authors find, for polyαmethylstyrene in transdecalin (30 °C) and in toluene, a w_{cross} of the same order of magnitude ($\approx$ 10 %) as ours, although their range of molecular weight is lower ($10^5 < M_w < 10^6$) than our range ($10^6 < M_w < 2 \times 10^7$). We do not consider this w_{cross} as a significant quantity because we think that it depends on the particular choice of the two solvents that are compared.

2.1.2 *Longest relaxation time.* — We measure the longest viscoelastic relaxation time T_R of the polymeric system [3]. In figure 2 we plot, as a function of the ratio $\frac{C}{C_\theta^*}$, the longest relaxation time $T_{R\theta}$ divided by the first Zimm mode of the single chain $T_{1\theta}$.

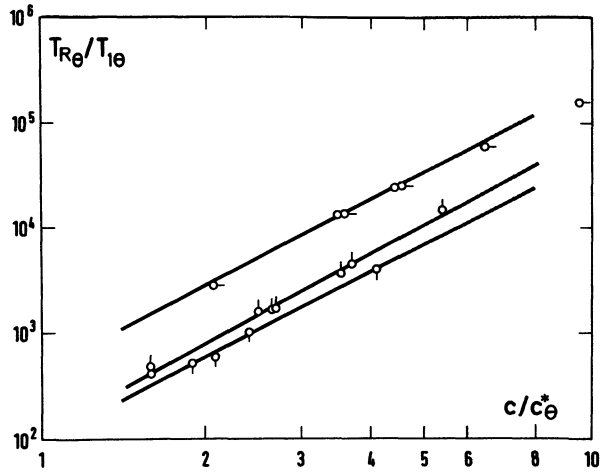

Fig. 2. — Longest relaxation time $T_{R\theta}$ divided by the characteristic time of the first Zimm mode of a single chain as a function of the reduced concentration $\frac{C}{C_\theta^*}$ (log-log scale). Straight lines correspond to equation (11). The symbols have the same meaning as in figure 1 and the raw results are given in the appendix.

$T_{1\theta}$ is calculated using the relation :

$$T_{1\theta} = A \frac{M[\eta] \times \eta_0}{k_B t N_A}, \qquad (9)$$

where k_B and t are the Boltzmann constant, and the absolute temperature respectively ; A is a numerical constant equal to 0.42 for a Gaussian chain with hydrodynamics interactions [12]; $[\eta]$ is the intrinsic viscosity which, in the case of polystyrene cyclohexane at 34.5 °C, is [13] :

$$[\eta] = 8.8 \times 10^{-2} M_w^{0.5} \text{ cm}^3/\text{g}. \qquad (10)$$

From the experimental results shown in figure 2 we draw the following conclusions.

1) $\frac{C}{C_\theta^*}$ is not the reduced variable of $\frac{T_{R\theta}}{T_{1\theta}}$, and the following laws are obtained :

$$\frac{T_{R\theta}}{T_{1\theta}} = 4.25 \times 10^2 \left(\frac{C}{C_\theta^*}\right)^{2.75 \mp 0.2} \quad \text{for} \quad M_w = 20.6 \times 10^6,$$

$$\frac{T_{R\theta}}{T_{1\theta}} = 1.13 \times 10^2 \left(\frac{C}{C_\theta^*}\right)^{2.85 \mp 0.1} \quad \text{for} \quad M_w = 6.77 \times 10^6, \qquad (11)$$

$$\frac{T_{R\theta}}{T_{1\theta}} = 86 \left(\frac{C}{C_\theta^*}\right)^{2.76 \mp 0.2} \quad \text{for} \quad M_w = 3.84 \times 10^6,$$

the prefactor is molecular weight dependent.

2) The exponent y_c (see Eq. (2)) is, within experimental precision, independent of the molecular weight :

$$y_c = 2.8 \mp 0.05. \qquad (12)$$

The comparison of $\frac{T_{R\theta}}{T_{1\theta}} = f\left(\frac{C}{C^*}\right)$ and of $\frac{T_{R\theta}}{\eta_0} = f'(w)$ between cyclohexane at 35 °C (θ solvent) and benzene (good solvent) leads to the same observations as those described above for the viscosity.

2.1.3 *Elastic shear modulus.* — We calculate the modulus G_θ with the relation $\frac{\eta_\theta}{T_{R\theta}}$ (13) from the measured values of the viscosity η_θ and the longest relaxation time $T_{R\theta}$.

On figure 3 we represent on a log-log scale the elastic shear modulus as a function of the concentration for 3 different molecular weights. At a given concentration, the experimental values of $G(M_w)$ obtained for molecular weight $M_w = 3.84 \times 10^6$ are between the values obtained for $M_w = 20.6 \times 10^6$ and $M_w = 6.77 \times 10^6$:

$$G(20.6) < G(3.84) < G(6.77), \qquad (13)$$

thus there is no relation between G and the molecular weight and to a first approximation we can consider both quantities as being independent of each other.

The relation obtained using all the experimental results of figure 3 is :

$$G_\theta\,(\text{dynes/cm}^2) = 1.34 \times 10^6\, C^{z_c} \quad \text{with } z_c = 2.5 \mp 0.2, \qquad (14)$$

where C is expressed in g/cm^3. We note that if we calculate :

$$\tilde{z}_c = x_c - y_c$$

using the values of x_c (Eq. (8)) and y_c (Eq. (12)) averaged over different molecular weights we obtain :

$$\tilde{z}_c = 2.34 \mp 0.2. \qquad (15)$$

This value is in agreement with the concentration exponent z_c determined directly (Eq. (14)).

At the θ point the variation of the shear modulus with concentration ($G_\theta \sim C^{2.5}$) is different from the variation of the bulk modulus with concentration $\left(K_\theta = C\frac{\partial \pi}{\partial C} \sim C^3\ [5]\right)$. But the absolute values of those two quantities do not differ by two orders of magnitude as in a good solvent [1]. For example :

$$\frac{G_\theta}{K_\theta} = 0.34 \text{ at } C = 2 \times 10^{-2} \text{ g/cm}^3,$$

$$\frac{G_\theta}{K_\theta} = 0.17 \text{ at } C = 0.1 \text{ g/cm}^3.$$

Thus in a θ solvent G_θ is smaller but of the same order as K_θ.

The absolute values of the shear modulus in benzene, G_{BS} and in cyclohexane at 35 °C, G_θ, do not differ substantially. For example :

$$\frac{G_{BS}}{G_S} = 1.07 \text{ at } C = 2 \times 10^{-2} \text{ g/cm}^3,$$

$$\frac{G_{BS}}{G_\theta} = 0.86 \text{ at } C = 0.1 \text{ g/cm}^3.$$

This is in agreement with reference [14].

2.2 Molecular weight dependence. — In order to test the influence of the quality of the solvent on the molecular weight exponent x_M (see Eq. (3)) we prepared samples at a given weight fraction (5 %) using the 4 different molecular weights. Figure 4 gives a log-log representation of the relative viscosity $\eta_{r\theta}$ and of the longest relaxation time $T_{R\theta}$ as a function of the weight average molecular weight. We obtain :

$$T_{R\theta} = 3.8 \times 10^{-27} M_w^{3.8 \mp 0.1} \text{ (s)}$$

and

$$\eta_{r\theta} = 8.4 \times 10^{-22} M_w^{3.71 \mp 0.06} \qquad (16)$$

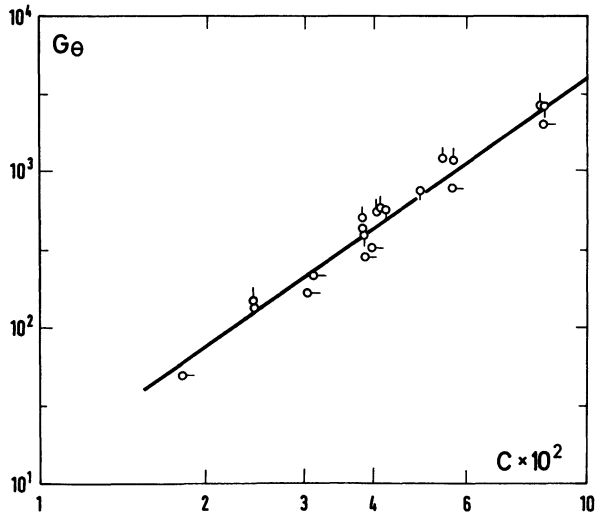

Fig. 3. — Elastic shear modulus G (dynes/cm^2) as a function of concentration (g/cm^3). The straight line corresponds to equation (14). Same symbols are used as in figure 1.

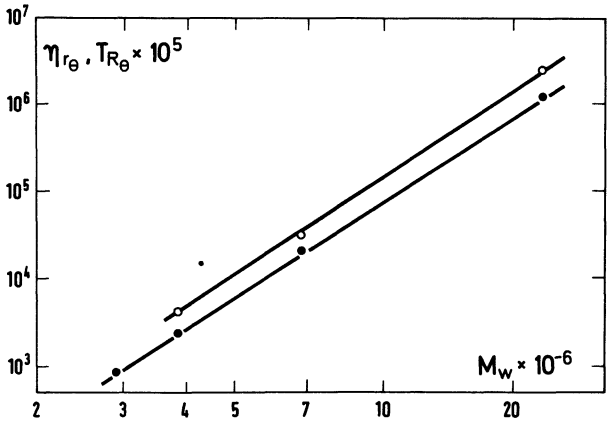

Fig. 4. — Relative viscosity (●) and longest relaxation time (in s. ○) as a function of molecular weight (log-log scale). Straight lines correspond to equation (16). The weight fraction is 5 %.

Thus the exponents x_M determined either through $T_{R\theta}$ or through $\eta_{r\theta}$ are identical (within experimental precision). This result corresponds to that already mentioned namely that the shear modulus is independent of the molecular weight.

— Although the lower value of the reduced concentration is 1.5, the log-log representation does not deviate, at low molecular weight from a straight line. Thus the regime between the dilute and the semi-dilute solution is much smaller for cyclohexane than for benzene.

— The value of x_M (3.75) is much larger than the value of x_M obtained in benzene (3.25) at the same weight fraction (5 %) for the same polystyrene samples.

— This large value of x_M is in agreement with the experimental evidence that $\frac{C}{C_\theta^*}$ is not the reduced variable of $\frac{T_{R\theta}}{T_{1\theta}}$ because

$$T_{R\theta} \simeq T_{1\theta}\left(\frac{C}{C_\theta^*}\right)^{2.8}$$

would lead to

$$T_{R\theta} \sim M_w^{2.9}.$$

— It is also in agreement with the fact that CM_w is not a reduced variable of $\eta_{r\theta}$ because $\eta_{r\theta} \sim (C.M_w)^{5.14}$ would lead to $\eta_{r\theta} \sim M_w^{5.14}$.

So the main results obtained in this section, besides the fact that $\frac{C}{C^*}$ is not a reduced variable, are :

$$\eta_{r\theta} \sim C^{5.14\mp0.16},$$
$$T_{R\theta} \sim C^{2.8\mp0.05},$$
$$G_\theta \sim C^{2.5\mp0.2}$$

and

$$\eta_\theta \sim T_{R\theta} \sim M_w^{3.75\mp0.05}.$$

We will discuss those results in section 4.

3. Temperature dependence.

The reduced temperature variable for static properties (correlation length [15] or osmotic bulk modulus [5]) was found to be $\frac{\tau}{\tau^{**}}$ where τ is the relative temperature $\frac{t-\theta}{\theta}$ and τ^{**} the crossover temperature between the θ and the good solvent regime, τ^{**} is proportional to concentration. We will see that the quantity $\frac{\tau}{C}$ is not the reduced variable for the viscoelastic properties.

3.1 VISCOSITY AND LONGEST RELAXATION TIME. — Taking into account the variation of the solvent viscosity (6) with temperature we observe that :

1) Usually both quantities η_r and $\frac{t}{\eta_0} T_R = \tilde{T}_R$ decrease (Fig. 5) when the temperature increases from θ, $\frac{\eta_r}{\eta_{r\theta}}$ and $\frac{\tilde{T}_R}{\tilde{T}_{R\theta}}$ are not universal function of the reduced temperature variable $\frac{\tau}{C}$.

2) At very low concentration the viscosity begins to decrease but then it increases (the longest relaxation times was not measurable on those samples). On figure 6 we represent the variation with temperature of the relative viscosity measured on samples chosen in order to have the same $\frac{C}{C_\theta^*}$ values (1.3) but different weight fractions (1.14×10^{-2} g/g and 2.63×10^{-2} g/g). The minimum of those curves occurs at the same temperature.

By measuring the viscosity as a function of temperature on samples at a given weight fraction (5 %) but of different molecular weights we determine the variation of the molecular weight exponent x_M (Eq. (3)) as a function of temperature. At temperature higher than θ we determine the exponent x_M only for three molecular weights (2.89×10^6, 3.84×10^6 and 6.77×10^6) instead of the four used precedently at the θ temperature. We observe (see Fig. 7) an x_M exponent which decreases as we increase the temperature from θ :

$$x_M = 3.7 \quad \text{for} \quad t = 35\ ^\circ\text{C},$$
$$x_M = 3.5 \quad \text{for} \quad t = 55\ ^\circ\text{C}.$$

This decrease is much larger than the experimental accuracy. It cannot be explained using the reptation model.

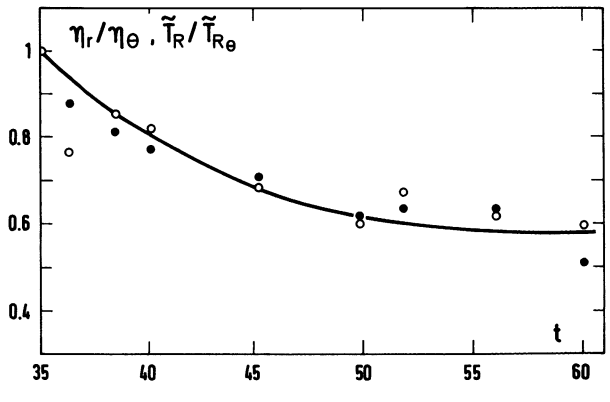

Fig. 5. — Variation with temperature (°C) of the relative viscosity (○) and of $\tilde{T}_R = \frac{t}{\eta_0} T_R$ (●), (η_0 being the cyclohexane viscosity at the given temperature t) reduced by their values at the θ temperature. Sample characteristics : $w = 5 \times 10^{-2}$ (g/g) and $M_w = 6.77 \times 10^6$. Solid line is a guide for the eye.

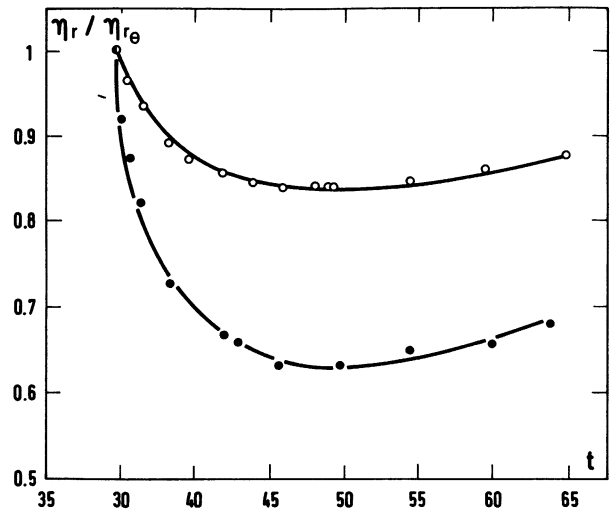

Fig. 6. — Relative viscosity reduced by its value at the θ temperature (35 °C) as a function of temperature (°C). Experiments were performed on samples at $\frac{C}{C_\theta^*} \approx 1$ for; ● $w = 1.14 \times 10^{-2}$ (g/g), $M_w = 20.6 \times 10^6$ and ○ $w = 2.63 \times 10^{-2}$ (g/g), $M_w = 3.84 \times 10^6$. Solid line is a guide for the eye.

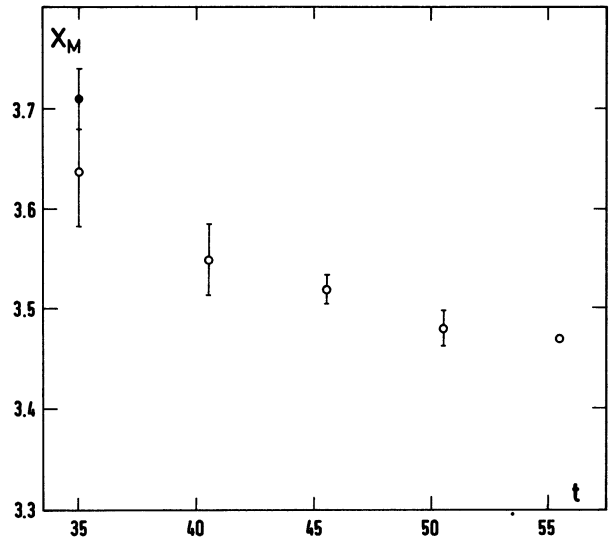

Fig. 7. — Variation of the viscosity molecular weight exponent x_M as a function of temperature (°C) measured on samples at $w = 5$ ‰, ○ points obtained from molecular weights : 2.89×10^6, 3.84×10^6, 6.77×10^6, ● points obtained from molecular weights : 2.89×10^6, 3.84×10^6, 6.77×10^6, 20.6×10^6.

3.2 ELASTIC SHEAR MODULUS. — The elastic shear modulus calculated from viscosity and longest relaxation time measurements decreases as the temperature increases (Fig. 8). However :

— We observe only a 20 % variation of the reduced shear modulus for a variation of temperature by 25 °C, furthermore we could not find any reduced temperature variable.

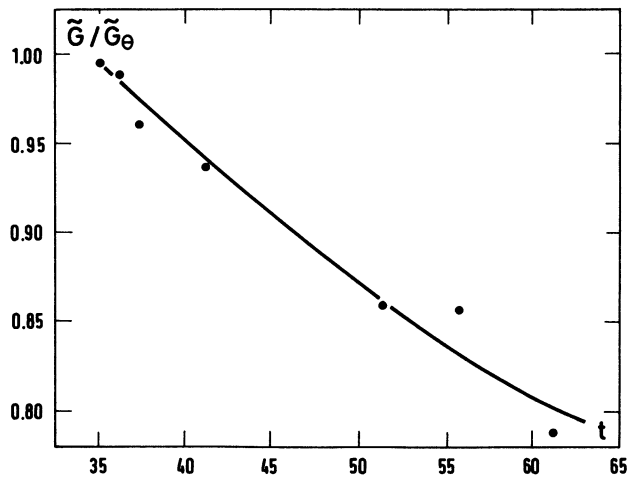

Fig. 8. — Variation with temperature (°C) of $\tilde{G} = \frac{G}{t}$ (G being the shear modulus measured at the temperature t) reduced by its value at θ. Sample characteristics : $w = 7$ % and $M_w = 6.77 \times 10^6$. Solid line is a guide for the eye.

— We also note that on the same sample, with the same variation of temperature we observe an increase of the osmotic bulk modulus $K = C \frac{\partial \pi}{\partial C}$ by more than a factor of 3 and $\frac{\tau}{C}$ is the reduced variable of K/K_θ [5].

Thus at and near the θ temperature G and K are not proportional to each other.

4. Discussion.

It is well known that in a semi-dilute good solvent solution static and dynamic properties are well described by one characteristic length, the correlation length ξ_{BS} of the density density correlation function [2] :

$$\xi_{BS} \simeq R_{BS}\left(\frac{C}{C^*}\right)^{-0.72} \quad \text{if} \quad \nu = 0.588 . \qquad (17)$$

where ν is the excluded volume exponent relating size to molecular weight.

In semi-dilute θ solutions, it has been pointed out [16, 17] that two lengths influence the physical properties. One the mean distance between two adjacent entanglements (binary contacts) ξ_2 ($\sim C^{-1/2}$). Since at the θ temperature the chain is Gaussian at all scales, ξ_2 depends on the number of monomer p between the entanglements following : $\xi_2 \sim p^{1/2}$. ξ_2 does not obey scaling law with respect to C. The other characteristic length in the θ region is the correlation length of the density correlation fonction ξ_θ ($\sim C^{-1}$) which corresponds to the mean distance between two consecutive ternary contact points. $\xi_\theta \sim g^{1/2}$, where g is the number of monomers in ξ_θ. ξ_θ obeys

scaling law with respect to C [2] :

$$\xi_\theta \simeq R_\theta \left(\frac{C}{C_\theta^*}\right)^{-1}. \quad (19)$$

As a function of temperature ξ_2 increases and ξ_θ decreases. Only ξ_θ obeys scaling laws :

$$\xi(t) \simeq \xi_\theta \left(\frac{\tau}{\tau^{**}}\right)^{-0.23}, \quad (20)$$

the exponent 0.23 was calculated using $\nu = 0.588$.

At high temperature we have :

$$\xi(t \to \infty) \equiv \xi_{BS} \approx \xi_{2BS}. \quad (21)$$

The scaling laws (19, 20) were directly verified by neutron scattering measurements [15] and through osmotic bulk modulus measurements [5] $\left(K = C\frac{\partial \pi}{\partial C} \sim \frac{1}{\xi^3}\right)$.

We note that it has been supposed in references [16, 17] that $\xi_2 < \xi_\theta$ but experimentally it has been shown directly by neutron scattering [15, 18] and indirectly by osmotic bulk modulus that $\xi_\theta > \xi_{BS}$. For the later case one finds $K_\theta \ll K_{BS}$ [5, 1] whatever the concentration.

In a earlier paper [19], we conjectured, based on the concentration dependence of the viscosity that :

1) The elastic shear modulus, which is proportional to the density of entanglements, is :

$$G_\theta \sim \frac{C}{p} \sim C^2 \quad [20].$$

2) The longest relaxation time, proportional to C^3, is sensible to ternary contact points which means that the distance ξ_θ is also a hydrodynamic screening length [21, 22] and, within the frame of reptation theory, proportional to the tube diameter. Using the main result of reptation theory that the molecular weight exponent is independent of the quality of the solvent [2], one can show that :

$$T_{R\theta} \simeq \frac{\eta_0}{k_B t}\left(\frac{N}{g}\right)^3 \xi_\theta^3 \sim N^3 C^3, \quad (22)$$

where N is the number of monomers in one chain and

$$\frac{T_{R\theta}}{T_{1\theta}} \simeq \left(\frac{C}{C_\theta^*}\right)^3. \quad (23)$$

Using the temperature dependence of ξ (20) one finds :

$$\frac{T_R}{T_{R\theta}} \simeq \left(\frac{\tau}{\tau^{**}}\right)^{1.4}, \quad (24)$$

so T_R increases with τ.

3) The zero shear viscosity is sensitive to both types of contact points.

Let us analyse the experimental facts that support this conjecture. We will begin with the elastic shear modulus because it is only related to the structure of the transient network.

The experimental fact that at a given concentration the elastic shear modulus is of the same order of magnitude in cyclohexane at 35 °C as in benzene indicates that the densities of entanglements are approximatively the same in both cases. Thus the transient networks seem to have mesh sizes ξ_2 (mean distances between two adjacent entanglements) which are of the same order of magnitude in a θ solvent and in a good solvent. At the θ temperature the mesh size of the transient network ξ_2 is much smaller than the correlation length ξ_θ. This is in agreement with the hypothesis made in references [16, 17] and with the experimental fact that the ratio between the shear modulus and bulk modulus in the θ region is of the order of unity instead of being equal to $\frac{1}{150}$ as in good solvent.

The experimental fact that G decreases when the temperature is increased from the θ temperature and that $\frac{\tau}{C}$ is not the reduced temperature variable of $\frac{G}{G_\theta}$ is also in agreement with this conjecture. Indeed the distance between binary contact increases with temperature because the excluded volume effects increase. But the reduced temperature variable for ξ_2 cannot be $\frac{\tau}{\tau^{**}} \sim \frac{\tau}{C}$.

However, the concentration exponent value found experimentally (2.5) is larger than that predicted (2). Is this discrepancy due to experimental imprecision or to a more complicated physical situation than the one described here ?

The concentration dependence of the longest relaxation time leads to an exponent value of 2.8 which is in agreement with the conjecture that $T_R \sim C^3$.

However, the following points should be noted :

1) The high value of the molecular weight exponent x_M (3.75),

2) T_R only slightly influenced by the quality of the solvent while the correlation length is strongly dependent,

3) The non universality of the curve $\frac{T_{R\theta}}{T_{1\theta}} = f\left(\frac{C}{C_\theta^*}\right)$.

4) The decrease of $\frac{\tilde{T}_R}{\tilde{T}_{R\theta}}\left(\tilde{T}_R = \frac{t}{\eta_0} T_R\right)$ when τ increases. They invalidate the conjecture that $T_{R\theta}$ depends only on ternary contact points.

In order to explain these experimental results in the framework of reptation theory (Eqs. (22, 23, 24)) one has to invoke an additional hindrance to the longitudinal motion of the chain in the tube. This hindrance, which must increase with the molecular weight, enhances the absolute value of T_R. The

hindrance decreases as τ increases because in a good solvent its effect is not dominant and its temperature behaviour inverses the temperature dependence expected for $\frac{\tilde{T}_R}{\tilde{T}_{R\theta}}$.

This additive hindrance could explain that η_r and T_R have the same behaviour as a function of τ or $\frac{C}{C^*_\theta}$ because the hindrance has the same dissipative effect on both quantities.

Is it the residual effect of the hindrance in a good solvent which increases the x_M value (3.4 instead of 3) ?

The discussion remains qualitative, we cannot determine experimentally the dependence of the hindrance as a function of molecular weight and temperature because :

1) the longest relaxation time and the viscosity decrease by only a factor 2 in the range of temperatures (35 °C to 65 °C) where experiments can be performed on our system, polystyrene cyclohexane.

2) The temperature behaviour of η_r and $\tilde{T}_R$ observed, is due to two opposite effects :

— an increase of the reptation time with τ as predicted by equation (24),

— a decrease of the hindrance.

At low values of $\frac{C}{C^*}$ one observes successively those two effects.

5. Conclusion.

The experimental results, obtained on polystyrene in semi-dilute cyclohexane solutions at the θ point and as a function of temperature and concentration, show that the main features of viscoelastic properties do not obey scaling laws.

We interpret those results by the presence of two lengths :

— the correlation length ξ_θ which is also a dynamic screening length,

— the mean distance ξ_2 between two adjacent entanglements.

With such a simple model : reptation in a tube having a diameter ξ_θ, and entanglements taking place at distance ξ_2, one can explain the concentration dependence of viscosity, longest relaxation time and shear modulus.

However there are three experimental facts which cannot be explained using such a naive model :

1) the absolute values of the measured quantity T_R and η_r do not differ substantially between polystyrene cyclohexane at 35 °C and polystyrene benzene at a given molecular weight.

2) $\frac{t}{\eta_0} T_R$ and η_r are decreasing functions of temperature.

3) $\frac{C}{C^*_\theta}$ is not a reduced variable of η_r and $\frac{T_{R\theta}}{T_{1\theta}}$, i.e. the molecular weight exponent x_M of the viscosity and the reptation time are much larger (3.75) than the value predicted by the reptation model (3). In order to explain these facts one can invoke an additional molecular weight dependent hindrance but there is no strong experimental evidence for this assumption. This additive hindrance may be due to :

— self entanglements in the chain, proportional to $M^{1/2}$ [16], at the θ temperature,

— entanglements between two different chains in a blob of size ξ_θ.

But, at the θ temperature, this hindrance has a greater influence than the tube itself on the motion of the chain.

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Appendix.

Raw results of the zero shear viscosity η_θ and the longest relaxation time $T_{R\theta}$ of polystyrene cyclohexane solutions at θ temperature (35 °C).

$M_w \times 10^{-6}$	w %	η_θ (poises)	$T_{R\theta}$ (s)
2.89	4.89	6.4	
	5.11	8.26	
	5.95	16.52	
3.84	2.63	0.798	
	5.02	19.33	4.36×10^{-2}
	6.401	66.1	8.77×10^{-2}
	10.85	9.02×10^{2}	0.34
6.77	3.18	11.97	8.37×10^{-2}
	5.01	1.57×10^{2}	0.316
	5.32	1.80×10^{2}	0.33
	5.39	1.92×10^{2}	0.335
	7.05	8.72×10^{2}	0.72
	7.38	1.03×10^{3}	0.89
	10.75	8.11×10^{3}	3.06
20.6	2.38	1.48×10^{2}	2.99
	3.98	2.34×10^{3}	14
	4.09	3.08×10^{3}	14.3
	5.00	7.41×10^{3}	25.0
	5.21	8.56×10^{3}	27
	7.37	4.90×10^{4}	63
	10.85	3.34×10^{5}	164

References

[1] ADAM, M., DELSANTI, M., *J. Physique* **44** (1983) 1185.

[2] DE GENNES, P. G., *Scaling concept in polymer physics* (Cornell University Press) 1979.
DE GENNES, P. G., *Macromolecules* **9** (1976) 587.

[3] ADAM, M., DELSANTI, M., *Revue Phys. Appl.* **19** (1984) 253.

[4] STRAZIELLE, C., BENOIT, H., *Macromolecules* **8** (1975) 203.

[5] STEPANEK, P., PERZYNKI, R., DELSANTI, M., ADAM, M., to appear in *Macromolecules*.

[6] SCHOLTE, Th. G., *Eur. Poly. J.* **6** (1970) 1063.

[7] TIMMERMANS, J., *Physics Chemical constants of pure organic compounds* (Elsevier, Amsterdam) 1950.
BANDRUP, J., IMMERGUT, E. H., *Polymer Handbook* (1975).

[8] VIDAKOVIC, P., Private Communication.

[9] *Scaling laws* $\left(\frac{D}{D_0} = f\left(\frac{C}{C_\theta^*}\right)\right)$ obtained from results of reference [21].

[10] GRAESSLEY, W. W., *Advanves in polymer Sci.*, Volume 16 (Springer-Verlag, Berlin) 1974.

[11] ISONO, Y., NAGASAWA, M., *Macromolecules* **13** (1980) 862.

[12] BAUER, D. B., BRAUMAN, J. I., PECORA, R., *Macromolecules* **8** (1975) 443.

[13] EINAGA, Y., MIYAKI, Y., FUJITA, H., *J. Polym. Sci. Polym. Phys.* **17** (1979) 2103.

[14] RAJU, V. R., MENEZES, E. V., MARIN, G., GRAESSLEY, W. W., Fetters, L. J., *Macromolecules* **14** (1981) 1668.

[15] COTTON, J. P., NIERLICH, M., BOUÉ, F., DAOUD, M., FARNOUX, B., JANNINK, G., DUPPLESSIX, R., PICOT, C., *J. Chem. Phys.* **65** (1976) 1101.

[16] BROCHARD, F., DE GENNES, P. G., *Macromolecules* **10** (1977) 1157.

[17] BROCHARD, F., *J. Physique* **44** (1983) 39.

[18] DAOUD, M., COTTON, J. P., FARNOUX, B., JANNINK, G., SARMA, G., BENOIT, H., DUPPLESSIX, R., PICOT, C., DE GENNES, P. G., *Macromolecules* **8** (1975) 804.

[19] ADAM, M., DELSANTI, M., *J. Physique* **43** (1982) 549.

[20] DE GENNES, P. G., *J. Physique Lett.* **35** (1974) L-133.

[21] ROOTS, J., NYSTRÖM, B., *Macromolecules* **13** (1980) 1595.

[22] VIDAKOVIC, P., ALLAIN, C., RONDELEZ, R., *J. Physique Lett.* **42** (1981) L-323.