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Viscosity and reptation time in polystyrene-benzene semidilute solutions

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Résumé. — Nous donnons quelques résultats expérimentaux préliminaires concernant la viscosité et le temps de reptation de solutions semi-diluées (polystyrène benzène).

Nous avons obtenu les résultats suivants :

$$\eta \sim M^{3 \pm 0,5} c^{4,5 \pm 0,1}$$

et

$$T_R \sim c^{2,8 \pm 0,4}.$$

Les valeurs des exposants de concentration ne sont pas en accord avec celles prévues par de Gennes.

Abstract. — We report some preliminary experimental results on Newtonian viscosity η and reptation time T_R in semidilute polystyrene-benzene solutions.

We have obtained the following results :

$$\eta \sim M^{3 \pm 0.5} c^{4.5 \pm 0.1}$$

and

$$T_R \sim c^{2.8 \pm 0.4}.$$

The concentration exponent values are not in agreement with de Gennes' theory.

It has been shown experimentally by many authors [1, 2, 3], that the viscosity of a *concentrated* solution of polystyrene in various good solvents can be described as :

$$\eta \sim M \quad \text{if } M < M_c$$

$$\eta \sim M^{3.4} \quad \text{if } M > M_c$$

M is the molecular weight of the macromolecule and M_c , the critical molecular weight for entanglements, is of the order of 2×10^4 daltons.

One of these authors has shown [2] that :

$$\eta \sim (c[\eta])^{4.7},$$

where $[\eta] \sim M^{0.72}$ is the intrinsic viscosity and c the monomer concentration.

Recent experimental and theoretical work [4] has shown the existence of three concentration regimes in polymer solutions : dilute, semidilute and concentrated. Here, our aim is to study the viscoelastic properties of polystyrene-benzene systems in a well defined semidilute regime. We recall briefly the

conformation of chains in semidilute solution [4] and theoretical predictions on their dynamical properties [5], and then, we give the description of the experiments and the experimental results obtained.

Let us consider a solution whose monomer concentration is higher than the overlap concentration, c^* , defined as :

$$c^* \simeq M/AR^3 \sim M^{-0.8} \quad (1)$$

A is the Avogadro number, R is the radius of gyration of an isolated macromolecule ($R \sim M^\nu$, $\nu = 0.6$ in good solvent). The semidilute regime is meaningful if the monomer concentration, c , follows the condition :

$$c^* \ll c \ll c_s$$

where c_s is the solvent concentration.

Then the macromolecules interpenetrate each other and have contact points; ξ , is the mean distance between these points and T_R their finite life time.

The length ξ , derived from an analogy with critical

phenomena, is molecular weight independent and decreases with concentration as :

$$\xi \sim c^{-0.75} . \quad (2)$$

This law has been checked experimentally by elastic neutron scattering [4].

The life time T_R is the time required for one macromolecule to change its conformation amongst the others. T_R has been calculated assuming that the molecule reptates along a *virtual* tube [5, 6, 7] of diameter ξ and length $[M/M(\xi)] \xi$. $M(\xi)$ is the molecular weight of a part of chain between two contact points.

This leads to :

$$T_R \sim M^3 c^{1.5} . \quad (3)$$

Now, let us consider the viscoelastic properties of such a system. At a time scale smaller than T_R but much bigger than T_ξ , it has a finite elasticity and thus behaves like a gel of mesh size $\xi - T_\xi$ is the time corresponding to the mesh first mode. The shear elastic modulus G_0 is proportional to the number of contact points per unit volume.

$$G_0 \simeq \frac{kT}{\xi^3} \sim c^{2.25} . \quad (4)$$

On a time scale larger than T_R the liquid is Newtonian with a viscosity η . From a dimensional argument [8] and for continuity between the two behaviours, we have :

$$\eta \simeq G_0 T_R \quad (5)$$

which becomes using expressions (3), (4) and (1) :

$$\eta \sim M^3 c^{3.75} \sim \left(\frac{c}{c^*} \right)^{3.75} . \quad (6)$$

In terms of phenomenological viscoelastic theory, this behaviour corresponds to a Maxwell model with a relaxation modulus [9] :

$$G(t) = G_0 e^{-t/\tilde{T}_R} . \quad (7)$$

\tilde{T}_R is the relaxation time of a stress when a sudden strain is imposed. In our case, we assume that \tilde{T}_R is proportional to the life time T_R , which is the longest time in the semidilute solution.

Since, for small strain and simple shear, the effects of mechanical history are linearly additive, the stress is given by :

$$\sigma(t) = G_0 \int_{-\infty}^t \exp \left\{ -\frac{t-t'}{\tilde{T}_R} \right\} \dot{\gamma}(t') dt' \quad (8)$$

where $\dot{\gamma}$ is the shear rate.

Measurements of stresses and strains allow the viscosity and the relaxation time, T_R , of the semidilute solution to be determined.

In our experiments we measure the shear stress with the help of a magnetic sphere immersed in the solution. The principle of the apparatus [10] is schematically represented in figure 1. The sphere is located in a region where the magnetic field created by a coil is not uniform and thus it experiences a magnetic force. The current intensity, I , in the coil is adjusted in such a way that the sphere holds at a fixed position when the solution is displaced by δ .

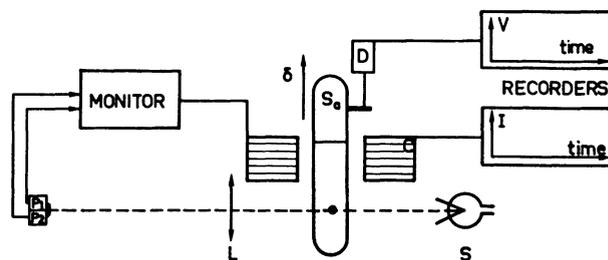


Fig. 1. — By means of light source, S, and a lens, L, the image of the sphere projected to the surface of the photodiodes $P_1 P_2$. The differential current of photodiodes $P_1 P_2$, is fed to the monitor which adjusts the intensity current, I , of the coil, C, in such a way that the sphere remains at the same place in the cell (S_a) which contains the polymer solution studied. The displacement, δ , is measured by recording the output voltage of a displacement detector, D.

We measure the intensity I and the displacement δ which are proportional to σ and γ respectively.

The *viscosity* of the solution is obtained if a constant shear rate $\dot{\gamma}$ is applied at time 0. From the expressions (8) and (5) we have :

$$\sigma = G_0 \tilde{T}_R \dot{\gamma} = \eta \dot{\gamma} \quad \text{if } t \gg \tilde{T}_R$$

which corresponds in our experiments to :

$$\eta = \alpha(I/\dot{\delta})$$

where I is the stationary magnetic coil intensity measured at a time much longer than T_R ($t > 5 \tilde{T}_R$), and α is a factor related to the magnetic moment of the sphere and to the geometry of the experiment. In order to determine the factor α , we also measure I/δ for a reference solution of viscosity η_r in the same experimental conditions. This allows us to obtain the relative viscosity η/η_r .

As shown in figure 2, for each solution, we verify that the viscosity is Newtonian.

This apparatus allows one to measure viscosities ranging from 0.3 poises to 10^4 poises, reproducible to about 8 %.

The viscosity of polystyrene-benzene solutions is studied as a function of the concentration for different molecular weights ranging from 4×10^6 to 24×10^6 daltons, at 32 °C. The concentration range investigated corresponds to $c/c^* > 4$ and c smaller than 10^{-1} (g/g) in order to satisfy the inequality

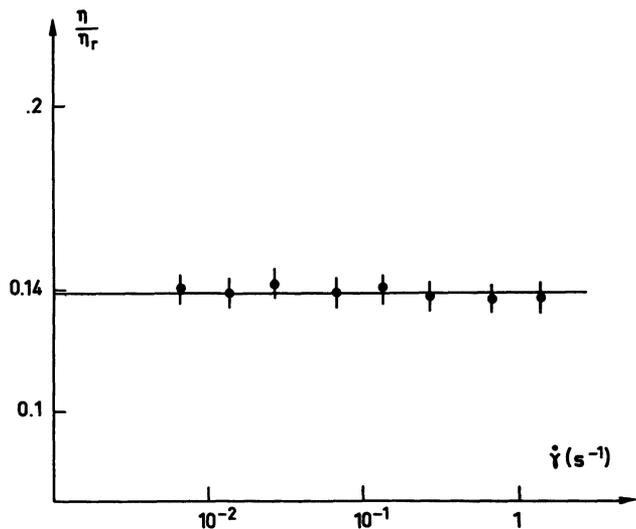


Fig. 2. — Relative viscosity versus shear rate $\dot{\gamma}$ defined as $\dot{\gamma} = \dot{\delta}/a$, where a (≈ 0.5 mm) is the radius of the sphere.

$c^* \ll c \ll c_s$. The c^* values for polystyrene-benzene systems are determined using the expression given in reference [11]. The characteristics of the samples and the viscosity measurements are listed in table I and reported on a log-log scale in figure 3.

For $c/c^* > 7$, it is found that the viscosity behaviour can be described by a power law :

$$\frac{\eta}{\eta_r} = F(M) c^{x_\eta}$$

where the prefactor $F(M)$ depends only on the molecular weight.

As shown in table II, a least square fit gives

$$x_\eta = 4.5 \mp 0.1$$

which is larger than the exponent obtained from the reptation model (eq. (6)) but compatible with exponent

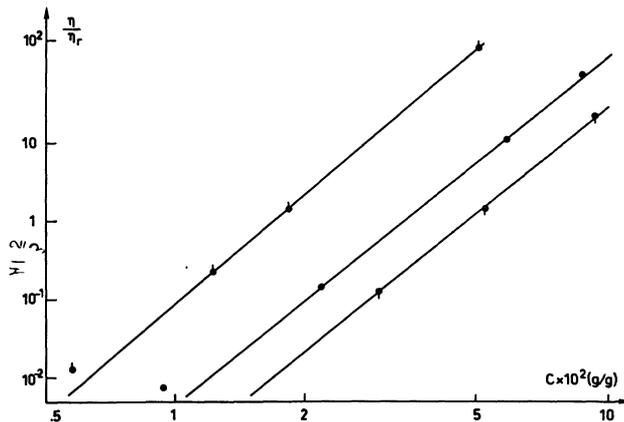


Fig. 3. — Variation of the relative viscosity versus concentration for the 3 molecular weights used :

• $M_w = 24 \times 10^6$, • $M_w = 7.1 \times 10^6$, • $M_w = 4.1 \times 10^6$.

Table II. — Calculated values of $F(M)$ and the concentration exponent x_η defined in the text.

Sample	$F(M)$	x_η
1, 2, 3	$(1.44 \pm 0.02) 10^8$	4.61 ± 0.01
5, 6, 7	$(3.27 \pm 0.6) 10^6$	4.44 ± 0.06
9, 10, 11	$(7.34 \pm 1) 10^5$	4.43 ± 0.07

values previously found from experiments in concentrated regime [2].

For $c/c^* < 7$ the experimental points deviate systematically from this law.

If we assume that the prefactor $F(M)$ varies with the molecular weight (Fig. 4) as a power law : $F(M) \sim M^x$, we obtain :

$$x = 3 \pm 0.5$$

the poor accuracy of this exponent is due to the high polydispersity of the samples.

Table I. — Characteristics of the samples used and experimental results on viscosity and relaxation time. The symbols used are defined in the text, except M_w/M_n which is the polydispersity index as given by the supplier and η_r which is the viscosity of the reference solution (silicon oil, $\eta_r \approx 50$ poise).

Sample	M_w	M_w/M_n	$c \times 10^2$ (g/g)	c/c^*	η/η_r	\tilde{T}_R (s)
1			5.06	51	1.53×10^2	—
2	24×10^6	—	1.83	18	1.40	—
3			1.22	12	2.17×10^{-1}	—
4			0.573	6	1.29×10^{-2}	—
5			8.70	33	6.65×10^1	3.68
6	7.1×10^6	1.15	5.86	22	1.06×10^1	6.79×10^{-1}
7			2.18	8	1.40×10^{-1}	6.28×10^{-2}
8			0.936	4	7.41×10^{-3}	—
9			9.37	23	2.07×10^1	—
10	4.1×10^6	1.15	5.22	13	1.44	—
11			2.96	7	1.25×10^{-1}	—

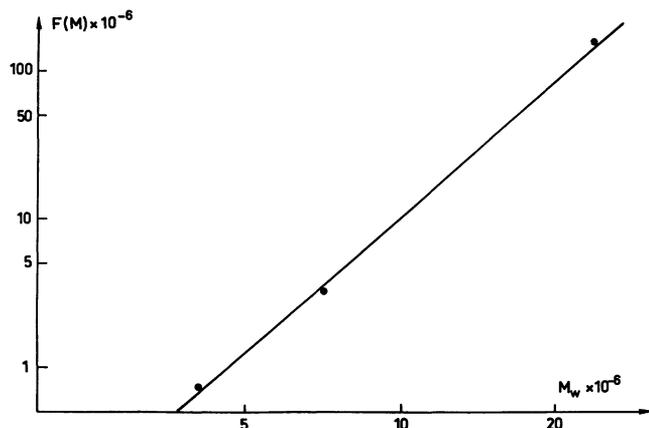


Fig. 4. — Variation of the prefactor $F(M)$ as a function of the molecular weight.

The exponent found lies between the value given by the theory [5] (eq. (6)) and that determined experimentally [1] ($x = 3.4$).

The relaxation time \tilde{T}_R is obtained if a constant shear strain γ , is imposed at a time 0, during a period ε (≈ 50 ms) much shorter than \tilde{T}_R , for which equation (8) becomes

$$\sigma(t) = G_0 \cdot \gamma \cdot e^{-t/\tilde{T}_R}$$

which corresponds in our experiment to :

$$I(t) = I_0 e^{-t/\tilde{T}_R} \quad \text{if } t \gg \varepsilon$$

where I_0 is proportional to the shear modulus multiplied by the displacement.

Fitting the time dependence of the coil intensity $I(t)$ to an exponential function of time we determined \tilde{T}_R [12]. \tilde{T}_R has been studied (table I) for a given molecular weight — 7.1×10^6 daltons — as a function of the concentration ($c/c^* > 8, c < 10^{-1}$ g/g)

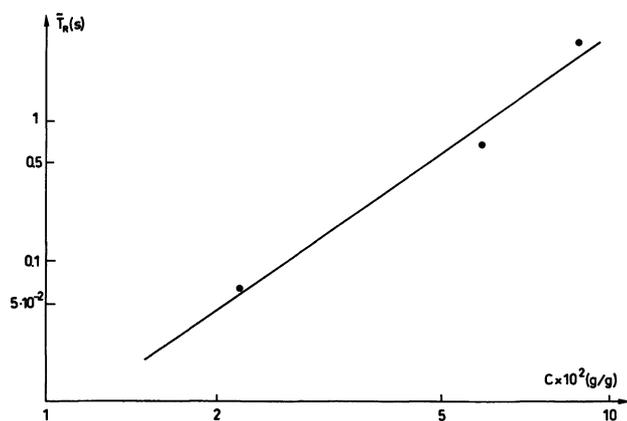


Fig. 5. — Variation of the relaxation time as a function of concentration.

at 32 °C. The experimental points \tilde{T}_R , plotted on a log-log scale (Fig. 5) can be approximated to the power law :

$$\tilde{T}_R \sim c^{x_T} \quad \text{with } x_T = 2.8 \mp 0.4$$

which is larger than the theoretical value 1.5 [5]. One must compare our exponent value x_T , to that determined by using a forced Rayleigh scattering technique [13], which, via concentration dependence of the self diffusion coefficient ($D_s \sim c^{1.7 \mp 0.1}$) yields $T_R \sim c^{1.5}$, in agreement with theoretical prediction. We have no satisfactory explanation concerning the discrepancy between the results given by these two methods.

From the general relation $\eta = G_0 \tilde{T}_R$ and the concentration exponents x_η, x_T we can deduce the exponent of the shear modulus :

$$G_0 \sim c^{x_G} \quad \text{with } x_G = 1.7 \mp 0.5$$

This exponent is compatible with theory and mechanical measurements on polystyrene gel swollen by benzene [14].

These experiments, performed on systems which corresponds to the hypothesis of de Gennes' theory, show clearly that the viscosity of a semidilute polystyrene-benzene solution does not obey to the scaling law : $\eta \sim (c/c^*)^{3.75}$. However the relation $\eta \approx G_0 T_R$ seems to be valid.

It is useful to note here, that, one of the experiments [15] done on semi-dilute polyisobutylene (PIB) toluene solutions ($c < 10\%$) yields :

$$\eta \sim M^{2.9 \pm 0.4} c^{3.8 \mp 0.2}$$

in agreement with expression (6).

However, the two systems (PIB toluene-PS benzene) present a number of mismatching features (such as : quality of the solvent, flexibility of the macromolecule, glass temperature transition of the melt, value of M_0) which may result in somewhat different respective values of the exponents x_η and x_T .

On the other hand, by some improvements of the apparatus it should be possible to measure the shear modulus and to determine its variation as a function of both concentration and molecular weight. By increasing the \tilde{T}_R precision we hope to be able to determine the origin of the discrepancy between experiments and theory for the viscosity of polystyrene-benzene semidilute solutions.

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