# On the Number of Blobs per Entanglement in Semidilute and Good Solvent Solution: Melt Influence

**E. Raspaud, D. Lairez,\* and M. Adam**

*Laboratoire Léon Brillouin, CEA-CNRS, CE-Saclay, 91191 Gif/Yvette Cedex, France*

**ABSTRACT:** Measurements of viscoelastic properties in good solvent semidilute solution are reported for three linear polymer species: polystyrene, polyisoprene, and polybutadiene. It is shown that using the same reduced concentration $C/C^*$ as for static properties, three different curves are obtained for the reduced viscosity $\eta/\eta_{\text{solvent}}$. The scaling used for static properties is no longer valid and a number $n_e$ of blobs per chains are needed for polymers to be entangled. This number, here determined by the ratio of the osmotic modulus to the elastic modulus $K/G = n_e$, is found to be different for the three kinds of polymer and identical to the number of monomers per entanglement measured in the melt. The reduced variables for the viscosity are $\eta/\eta_{\text{Rouse}}$ as a function of $C/C_e$ where $\eta_{\text{Rouse}} = \eta_{\text{solvent}}(C/C^*)^{1.30}$ is the viscosity predicted by the Rouse model and $C_e = n_e^{0.76}C^*$ is the concentration at which polymers begin to be entangled.

## Introduction

Linear polymers in solution are known to have universal physical properties at a macroscopic length scale. This is due to the scaling properties of these compounds, which can be described using a single length $\xi$ whatever the concentration is. Once this length scale is introduced, it is possible to define reduced variables allowing universal laws to be written. For example, in scattering experiments (light or neutron) the scattered intensity per monomer $I/C$ depends on the transfer vector $q$. The transfer vector corresponds in fact to the inverse length scale at which the polymer is observed. The scattered intensity per monomer is proportional to the mass of polymer viewed at this length scale. Plotting reduced scattered intensity $(I/C)/(I_{q\to0}/C)$ as a function of the reduced length scale $q\xi$, one obtains a single curve independent of the chemical nature of the polymer, its molecular mass, and its concentration. This is a manifestation of the self-similarity of the polymer conformations, which looks the same whatever the observation length scale in dilute solutions and which is preserved at length scales smaller than $\xi$ in semidilute solutions. Such laws which emphasize the universal behavior of polymers are called "scaling laws". In this paper, following refs 1−3, the term "scaling law" for a given physical property will imply that there is only one characteristic length relevant for the description of this property. As a consequence scaling requires that there is only one characteristic concentration. Using this strict definition, physical laws involving two (or more) characteristic concentrations will not be called here scaling laws. However, some authors would have called them "two (or more) parameters scaling".

Scaling laws for static properties have been fully verified for linear polymers over the past 20 years, due to extensive experimental work of several teams throughout the world.[4] However, until now scaling laws for dynamic properties were not well established;[5] this paper is concerned with this problem which suffers from a lack of experimental works. First, theoretical scaling laws for static properties will be presented, while for dynamic properties the notion of entanglement in semidilute regime will be introduced. This notion causes

scaling laws to fail by introducing a second length in order to describe polymer reptation in the semidilute concentration regime. In other words, the question is whether or not polymers begin to be entangled once a concentration simply proportional to the overlap is reached? Second, experimental evidence for the scaling of the osmotic pressure will be reported on three kinds of polymer. Both exponent value and prefactor are found to be in very good agreement with theory. In contrast, by using the same reduced variables as for the osmotic pressure, viscoelastic properties measured on polystyrene, polyisoprene, and polybutadiene samples do not scale on a single curve. In order to obtain a master curve reliable whatever the polymer species, one has to reduce the concentration by a quantity which cannot be derived from the dilute regime, as for static properties, but rather from the melt properties.

## Theory

**1. Static Properties.** Linear polymers in dilute solution have a fractal conformation which implies that the degree of polymerization $N$ is linked to the radius of gyration $R_g$ through the power law: $N = (R_g/a)^D$, where $a$ is the monomer size. Due to excluded volume interactions between monomers, polymers in good solvent adopt swollen conformations and the fractal dimension $D$ corresponds to that of a self-avoiding random walk: $D = 1.70$.[4,6] This self-similar conformation has an outstanding importance because it allows the establishment of scaling laws for physical properties of polymer solutions.

By analogy to a perfect gas, the osmotic pressure $\pi_0$ of $n$ independent particles per unit volume is proportional to $kTn$ where $k$ is the Boltzmann's constant and $T$ the temperature. In the case of a solution at a concentration $C$ of polymers having a degree of polymerization $N$, the osmotic pressure becomes $\pi_0 = kT(C/N)$.[7] However, in dilute solution, polymers interact and the osmotic pressure is expressed by a virial expansion: $\pi = kT(C/N)(1 + NA_2C + ...)$. In this expression, the second virial coefficient $A_2$ takes into account interactions between two monomers belonging to different chains. In the good solvent case, as correlations between monomers are mainly pair correlations, the second term $NA_2C$ is larger than the higher order terms. One can note that $NA_2$ has the dimension of the inverse

of a concentration. We will see in the Experimental Section that scattering experiments are sensitive to the derivative of osmotic pressure $(d\pi/dC)$ of polymer solutions. This can be written, for $NA_2C < 1$, as

$$(d\pi/dC) = (d\pi/dC)_0(1 + 2NA_2C) \qquad (1)$$

with

$$(d\pi/dC)_0 = kT/N \qquad (2)$$

By defining the internal concentration of polymer coils, as $C^* = N/R_g^3$, one obtains

$$C^* = a^{-3}N^{(D-3)/D} \qquad (3)$$

with

$$(D-3)/D = -0.76$$

At the concentration $C^*$, polymer coils are in closed packing condition. It was shown theoretically that, in good solvent, the second virial term $NA_2$ is proportional to the inverse of the concentration $C^*$.[8] As the macroscopic concentration increases beyond $C^*$, the osmotic pressure is no longer given by a simple virial expansion. The semidilute regime corresponds to the concentration range $1/a^3 \gg C > C^*$. In this regime, chains overlap but solvent prevails and local properties as density or viscosity are governed by solvent properties. The chain overlap screens hydrodynamic and excluded-volume interactions at distances larger than the correlation length $\xi$.[9] Inside the volume of a blob $\xi^3$, there are only monomers belonging to one chain which consequently preserves its swollen conformation. If $g$ denotes the number of monomers per blob, one has $g = (\xi/a)^D$.[1,10] The internal concentration of the blob is equal to the macroscopic concentration:

$$C = g/\xi^3 \qquad (4)$$

This equation leads to

$$\xi = R_g(C/C^*)^{1/(D-3)} = a^{D/(D-3)}C^{1/(D-3)} \qquad (5)$$

with

$$1/(D-3) = -0.77$$

In a good solvent, $\xi$ corresponds to the average distance between two successive binary contacts. Semidilute solution is a compact set of independent blobs as the melt is the compact set of monomers. Thus the analogue of the degree of polymerization $N$ is in semidilute solution the number of blobs per chain $N/g$. This number is a function of the reduced concentration $C/C^*$:

$$N/g = (C/C^*)^{D/(3-D)} \qquad (6)$$

with

$$D/(3-D) = 1.31$$

As blobs are thermodynamically independent, the osmotic pressure is equal to $\pi = kT(C/g) = kT/\xi^3$. For the derivative of the osmotic pressure $(d\pi/dC) \simeq kT/g$, once reduced by $(d\pi/dC)_0$, one obtains the universal scaling law:

$$\frac{(d\pi/dC)}{(d\pi/dC)_0} = \beta(NA_2C)^{D/(3-D)} \qquad (7)$$

with

$$D/(3-D) = 1.31$$

the prefactor of this power law being theoretically independent of the polymer.[8] The osmotic modulus $K = C(d\pi/dC) \simeq kT/\xi^3$ is proportional to

$$K \simeq kTa^{3D/(3-D)}C^{3/(3-D)} \qquad (8)$$

with

$$3/(3-D) = 2.31$$

$K$ is expected to be independent of the degree of polymerization but depends on the kind of polymer through the prefactor $a^{3D/(3-D)}$.

**2. Dynamic Properties.** Let us first present dynamic properties in the dilute regime. In this regime, a polymer solution behaves like a solution of spheres having a hydrodynamic radius $R_h$. A concentration expansion is expected for the viscosity:

$$\eta = \eta_s(1 + [\eta]C + k_H([\eta]C)^2 + ...) \qquad (9)$$

where $\eta_s$ is the solvent viscosity, $k_H$ the Huggins coefficient, and $[\eta]$ the intrinsic viscosity of the polymer. The term $k_H([\eta]C)^2$ takes into account hydrodynamic interactions between two polymers. The intrinsic viscosity is proportional to $(R_g^2R_h)/N$ and would correspond to the inverse of the overlap concentration. However, it is predicted theoretically that $R_h$ reaches the asymptotic limit $(R_h \sim N^{1/D})$ at much larger values of $N$ than the radius of gyration $R_g$.[11] Thus the intrinsic viscosity will be proportional to $1/C^*$ only for large values of $N$. This limit will be considered in the following.

If the term $k_H([\eta]C)^2$ is negligible, the expression of the increment viscosity $\eta - \eta_s$ (eq 9) due to the presence of polymer can be also derived using the Zimm model.[12-13] In this model, $\tau$ the longest relaxation time, i.e. the first mode characteristic time is expressed as

$$\tau_{Zimm} = \tau_s(R_g/a)^3 \qquad (10)$$

where $\tau_s$ corresponds to the local relaxation time of the solvent. Assuming a stored energy equal to $kT$ per chain, the elastic modulus $G$, is equal to[14]

$$G = (C/N)kT \qquad (11)$$

The difference of viscosity between dilute solution and solvent $(\eta - \eta_s)$ is equal to the product $G\tau$. One obtains $(\eta - \eta_s) = \eta_sC[\eta]$.

In semidilute solution, polymers may be considered as a chain of $N/g$ hydrodynamically independent blobs. Dynamic properties of these solutions are derived from extension of dynamic properties of the melt using the reduced degree of polymerization $N/g$.[3,13] In the melt, depending on the degree of polymerization $N$, two regimes are observed for dynamical properties: unentangled and entangled. Theoretically, the unentangled regime corresponds to three-dimensional Brownian motion of monomers, while the entangled regime corresponds to reptation motion of high polymers, i.e. the

motion inside a tube caused by the presence of neighboring chains. Reptation motion appears for polymers having a degree of polymerization higher than a given value $N_e$ which depends only on the chemical nature of polymer. Let us introduce the same notion in semidilute solution, in which a given number of blobs per chain, $n_e$, is needed to observe reptation.[3,5] In order to predict concentration dependence of viscosity and relaxation time, $n_e$ is assumed to be a constant. The crossover concentration $C_e$ for which the number of blobs per chain, $N/g$, is equal to $n_e$ is obtained using eq 6:

$$C_e = C^* n_e^{(3-D)/D} \tag{12}$$

with

$$(3-D)/D = 0.76$$

For $C^* < C < C_e$, i.e. for $1 < N/g < n_e$, dynamic properties in the unentangled regime are described by the Rouse model.[13,15] The longest relaxation time $\tau_{Rouse}$ is written as the product $\tau_{blob}(N/g)^2$ with the blob relaxation time predicted by the Zimm model: $\tau_{blob} = \tau_s(\xi/a)^3$. Using relations 5, 6, and 10, $\tau_{Rouse}$ is written as a function of $C/C^*$:

$$\tau_{Rouse} = \tau_{Zimm}(C/C^*)^{(3-2D)/(D-3)} \tag{13}$$

with

$$(3-2D)/(D-3) = 0.31$$

As in dilute solution, the elastic modulus $G$ of the unentangled solution is proportional to the number of chains per unit volume:

$$G = \left(\frac{C}{N}\right)kT = \frac{kT}{(N/g)\xi^3} \tag{14}$$

The viscosity $\eta_{Rouse} = G\tau$ is found to be simply proportional to the number of blobs per chain $\eta_{Rouse} = \eta_s(N/g)$ and scales with $C/C^*$ (see eq 6) as

$$\eta_{Rouse} = \eta_s(C/C^*)^{D/(3-D)} \tag{15}$$

with

$$D/(3-D) = 1.31$$

In this regime, the reduced relaxation time and the viscosity are only functions of the reduced concentration $C/C^*$.

For $C > C_e$, i.e. for $N/g > n_e$, chains relax via reptation. The number of entanglements per chain $(N/g)/n_e$ is

$$\frac{(N/g)}{n_e} = \left(\frac{C}{C_e}\right)^{D/(3-D)} \tag{16}$$

with

$$D/(3-D) = 1.31$$

The classical theory of elasticity[14] predicts the elastic modulus $G$ to be proportional to the number of entanglements per unit volume $G = kT/(n_e\xi^3)$:

$$G = (kT/n_e)a^{3D/(3-D)}C^{3/(3-D)} \tag{17}$$

with

$$3/(3-D) = 2.31$$

Following the reptation theory,[1,3] the longest relaxation time is expected to obey the relation $\tau = \tau_s(\xi/a)^3(N/g)^3/n_e$. Using eqs 13 and 16, one obtains

$$\tau = \tau_{Rouse}\left(\frac{(N/g)}{n_e}\right) = \tau_{Rouse}\left(\frac{C}{C_e}\right)^{D/(3-D)} \tag{18}$$

with

$$D/(3-D) = 1.31$$

From eqs 17 and 18, one deduces the expression for the viscosity $\eta = \eta_s(N/g)^3/n_e^2$ and it follows that

$$\eta = \eta_s(C/C^*)^{3D/(3-D)}/n_e^2 \tag{19}$$

with

$$3D/(3-D) = 3.93$$

In the same manner, the viscosity may be rewritten as a function of $C/C_e$:

$$\eta = \eta_{Rouse}\left(\frac{(N/g)}{n_e}\right)^2 = \eta_{Rouse}\left(\frac{C}{C_e}\right)^{2D/(3-D)} \tag{20}$$

with

$$2D/(3-D) = 2.62$$

It is important to stress that when the number $n_e$ differs from one polymer species to another, entanglements cause a failure of scaling laws. This is because the relaxation time and the viscosity depend on two characteristic concentrations $C^*$ and $C_e$, introduced by the Rouse and reptation modes of motion, respectively.

## Experimental Section

**1. Samples Characteristic and Experiment Conditions.** Experiments were performed on three kinds of polymers having quite a different number $N_e$ of monomers between entanglements in the melt: polybutadiene, polyisoprene, and polystyrene. Samples having a polydispersity less than 1.1 were examined. Polystyrene and polybutadiene samples were purchased from TOYO SODA and POLYMER LABORATORIES, respectively; polyisoprene samples were kindly provided by L. Fetters (Exxon Research & Engineering Co.). Solutions were prepared in cyclohexane for polybutadiene and polyisoprene, and in benzene for polystyrene. The chemical microstructure of polybutadiene and polyisoprene samples, i.e. their fraction of cis, trans, and vinyl monomers, were determined by NMR spectroscopy (see Table 2).

Samples were characterized in dilute solution by static light scattering measurements, which allowed the radius of gyration $R_g$ and the weight average molecular mass $M$ of polymer samples to be determined by a double extrapolation to zero transfer vector $q$ and to zero concentration:[16]

$$\frac{I}{C} \sim kT\left(\frac{d\pi}{dC}\right)^{-1}P(q) \sim M(1 - 2MA_2C - ...)\left(1 - \frac{(qR_g)^2}{3} - ...\right) \tag{21}$$

The second virial coefficient $A_2$ was determined by the concentration dependence of the apparent mass $M(1 - 2MA_2C - ...)$. Results are summarized in Table 1. Verification of the measurement quality is done by comparison of $1/MA_2$ with $C^* = M/(N_AR_g^3)$, $N_A$ being the Avogadro's number. The product

**Table 1. Static Light Scattering Characterization of Samples[a]**

|  | $10^{-5}M$ (g/mol) | $R_g$ (nm) | $MA_2$ (cm³/g) | $10^3C^*$ (g/cm³) | $MA_2C^*$ | $[\eta]$[b] (cm³/g) | $[\eta]C^*$ |
|---|---|---|---|---|---|---|---|
| polystyrene | 12.4 | 54 | 520 | 12.9 | 6.71 | 300(a) | 3.87 |
|  | 40.0 | 110 | 1270 | 4.99 | 6.32 | 700(a) | 3.49 |
| polyisoprene | 3.10 | 28 | 300 | 23.5 | 7.06 | 210(b) | 4.93 |
|  | 9.4 | 54 | 650 | 9.91 | 6.44 | 470(b) | 4.66 |
| polybutadiene | 9.6 | 53 | 610 | 10.7 | 6.53 | 600(c) | 6.42 |

[a] $M$ is the weight molecular mass; $R_g$ is the radius of gyration; $A_2$ the second virial coefficient; and $C^* = M/(N_A R_g^3)$ with $N_A$ the Avogadro's number. [b] Values of intrinsic viscosities $[\eta]$: (a) and (b) were determined from equations given in refs 19 and 20, (c) is measured using an Ubbelohde viscosimeter.

which is predicted to be a constant independent of the polymer species is found to be

$$MA_2C^* = 6.6 \pm 0.3 \tag{22}$$

for polystyrene, polyisoprene, and polybutadiene samples. This result, obtained on three different polymers, is in good agreement with experimental values determined on polystyrene samples.[17–18] In addition, this value has to be compared with the des Cloizeaux and Jannink theoretical value:[8]

$$MA_2C^* = 5.19 \tag{23}$$

In the following, because of its more accurate determination, the reduced concentration will be taken as $MA_2C$ instead of $C/C^*$.

The intrinsic viscosities of polystyrene and polyisoprene samples reported in Table 1 are deduced from mass dependence of $[\eta]$ reported in refs 19–20. As the Huggins coefficient of polybutadiene in cyclohexane was unpublished to our knowledge, the intrinsic viscosity was measured using a Ubbelohde viscosimeter. The Huggins coefficient is found to be equal to 0.37. The values of $MA_2$ and $[\eta]$ here determined for polybutadiene are close to the values given in ref 21. From Table 1, one can note that the product $[\eta]C^*$ depends strongly on the polymer unlike the product $MA_2C^*$. This will be discussed later on.

Semidilute solutions for viscoelastic measurements were prepared by weighing and kept for homogenization several weeks at room temperature, until viscosities measured at the top and at the bottom of the cell were identical within experimental precision. Solutions for light scattering measurements were prepared in dilute conditions, filtered, and then evaporated to reach desired semidilute concentrations. In all the cases polymer concentration was less than 0.13 g/cm³, in order to ensure that local properties (density and viscosity) are those of the solvent. Measurement of the derivative of osmotic pressure $(d\pi/dC)$ were performed by light scattering. Results obtained on poly($\alpha$-methylstyrene) and polyisoprene have already been reported in refs 22–23. Actually, the scattered intensity per monomer $I/C$ is proportional to the osmotic compressibility:

$$\left(\frac{I}{C}\right)_{q\to0} \sim kT\left(\frac{d\pi}{dC}\right)^{-1} \sim kT\frac{C}{K} \tag{24}$$

The prefactor includes optical constant and contrast length, both vanishing using reduced variables $(I/C)_{q\to0}/(I/C)_{q\to0;C\to0} = (d\pi/dC)/(d\pi/dC)_0$.

Shear viscosities $\eta$ and longest relaxation times $\tau$ of semidilute solutions were measured using the magnetorheometer described in detail elsewhere.[24] This rheometer allows zero shear rate measurements on samples put in hermetically sealed cells avoiding solvent evaporation. Experiments were performed in a temperature range from 7 to 50 °C in order to verify that temperature dependences of viscosity and relaxation time are only due to the variation of solvent physical properties. Measurements of the viscosity carried out at 30 °C are presented in the following.

**2. Results and Discussion.** In Figure 1 the reduced derivative of the osmotic pressure $(d\pi/dC)/(d\pi/dC)_0$ as a function of the reduced concentration $MA_2C$ is plotted for poly($\alpha$-methylstyrene), polyisoprene, and polybutadiene. The expected theoretical scaling law is well verified: all the data lie
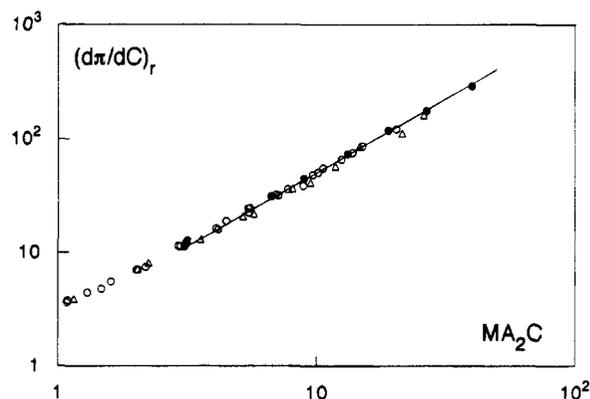


**Figure 1.** log–log plot of the reduced derivative of osmotic pressure $(d\pi/dC)_r = (d\pi/dC)/(d\pi/dC)_0$ versus the reduced concentration $MA_2C$ for poly($\alpha$-methylstyrene) (O), polyisoprene (●), and polybutadiene (△) samples. Straight line corresponds to the best fit (eq 25) of the high concentration part of data ($MA_2C > 3$) and has a slope equal to $1.30 \pm 0.02$.

on a single curve regardless of the mass and the polymer species. The best fit of the high concentration part of the data ($MA_2C > 3$) corresponds to the equation:

$$(d\pi/dC)/(d\pi/dC)_0 = (2.55 \pm 0.10) \times (MA_2C)^{1.30\pm0.02} \tag{25}$$

The exponent value is in very good agreement with the theoretical prediction (see eq 7). The prefactor 2.55 has to be compared to the universal values $\beta = 1.91$ and $\beta = 2.78$ predicted by des Cloizeaux and Jannink and by Duplantier, respectively.[8]

By using the values of $MA_2$ and $(d\pi/dC)_0$ of each sample being measured (see Table 1) and from relation 25, one can deduce the concentration dependence of the osmotic modulus $K = C(d\pi/dC)$ for each polymer species:

$$K = (1.75 \pm 0.10) \times 10^8 C^{2.30\pm0.02} \quad \text{(polystyrene)} \tag{26a}$$

$$K = (3.25 \pm 0.30) \times 10^8 C^{2.30\pm0.02} \quad \text{(polyisoprene)} \tag{26b}$$

$$K = (2.75 \pm 0.10) \times 10^8 C^{2.30\pm0.02} \quad \text{(polybutadiene)} \tag{26c}$$

$K$ being expressed in dyne/cm² and $C$ in g/cm³. As mentioned in the theoretical part, prefactors correspond to the dependence of the osmotic modulus $K$ on the parameter $a$ (eq 8).

The major assumption in the theoretical derivation of viscoelastic properties in the semidilute regime is that the number $n_e$ of blobs per entanglement is independent of the concentration. This number can be determined through the ratio of the osmotic modulus $K$ to the shear elastic modulus $G$. As a matter of fact according to eqs 8 and 17 one has

$$K/G = n_e \tag{27}$$

the dependence of the moduli to the monomer size $a$ being eliminated. In Figure 2, the ratio $K/G$ is plotted as a function of the concentration for the three kinds of polymer. The shear elastic modulus $G$ is deduced from the ratio of the measured viscosity to the longest relaxation time at a given concentration
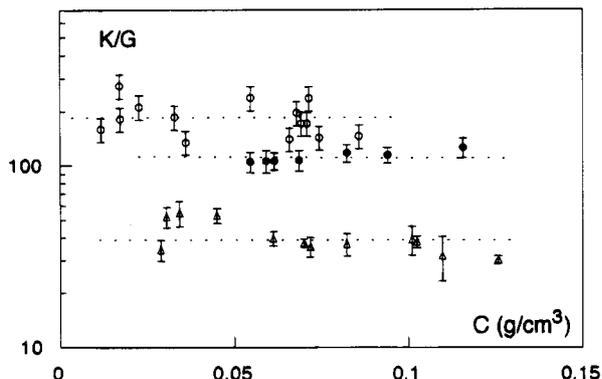
**Figure 2.** Concentration dependence of the ratio of the osmotic modulus to the shear elastic modulus, $K/G = n_e$, for the polymer species (log−ln scale): polystyrene (O), polyisoprene (●), and polybutadiene (△). Straight lines correspond to average values reported in Table 2.
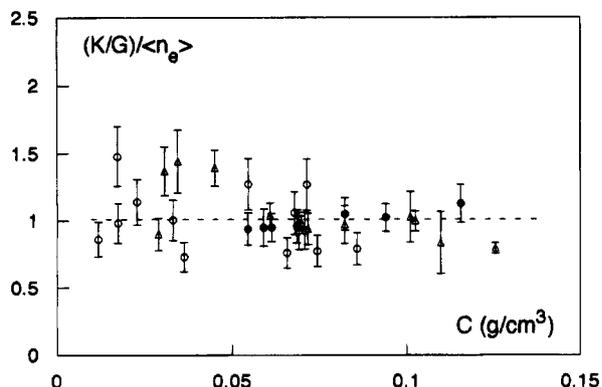


**Figure 3.** Comparison of the ratio $(K/G)/\langle n_e \rangle$ vs the concentration $C$ for the three polymer species, with $\langle n_e \rangle$ given in Table 2: polystyrene (O), polyisoprene (●), and polybutadiene (△).

**Table 2. Comparison between the Number $n_e$ of Blobs per Entanglement[a] and the Number $N_e$ of Monomers per Entanglement Measured in the Melt and Given in Refs 14 and 31**

|  | polystyrene | polyisoprene | polybutadiene |
|---|---|---|---|
| $\langle n_e \rangle$ | 185 ± 40 | 112 ± 8<br>cis:trans:vinyl =<br>84.2:12.3:3.3 | 38 ± 6<br>cis:trans:vinyl =<br>56.8:37.6:5.5 |
| $N_e$ | 165[b] | 94[c]<br>cis:trans:vinyl =<br>78:14:8 | 35[b]<br>cis:trans:vinyl =<br>43:50:7 |

[a] Here determined in semidilute solutions through the ratio of the osmotic modulus to the shear elastic modulus K/G. [b] From ref 14. [c] From ref 31.

and the osmotic modulus $K$ is calculated from eq 26 at the same concentration. One can see that $K/G = n_e$ is independent of the concentration compared to the variation by a factor $10^4$ of the viscosity in the same concentration range. In Figure 3 the ratio $(K/G)/\langle n_e \rangle$ is plotted as a function of the concentration in order to outline that no systematic concentration dependence is observed. These results are in agreement with the observation reported in ref 25 that $K$ and $G$ have the same concentration dependence; some data published in ref 25 are included in Figures 2 and 3. Moreover, the number $n_e$ is different for each kind of polymer, the mean values $\langle n_e \rangle$ being listed in Table 2. One of the major results obtained in this study concerns the equality between the number $n_e$ of blobs per entanglement here determined in semidilute solution and the number $N_e$ of monomers per entanglement determined in the melt. Actually, one can see in Table 2 that

$$n_e/N_e = 1.15 \pm 0.05 \qquad (28)$$

for the three polymers species.
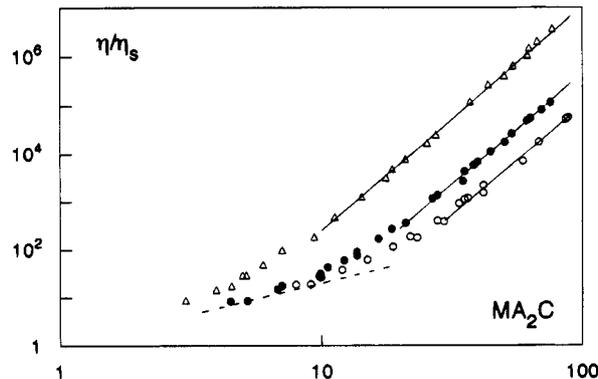


**Figure 4.** Reduced viscosity $\eta/\eta_s$ as a function of the reduced concentration $MA_2C$ (log−log scale) of polystyrene (O), polyisoprene (●), and polybutadiene (△) samples. The straight line superimposed on polybutadiene data corresponds to the best fit of high $MA_2C$ values ($MA_2C > 7$) and has a slope equal to 4.65 ± 0.05. The other ones are guides for the eyes having the same slope. Dashed line is also a guide for the eyes having a slope 1.3.

The number $n_e$ being independent of the concentration, the viscosity and the relaxation time in unentangled and entangled regimes are expected to follow two different behaviors as the concentration increases above $1/MA_2$. The crossover concentration $C_e$ depends on $n_e$ as $MA_2C_e \cong n_e^{0.76}$. In Figure 4, the reduced viscosity $\eta_r = \eta/\eta_s$ of the three polymers here studied is plotted as a function of the reduced concentration $MA_2/C$. While the reduced derivative of osmotic pressure scales on a single curve in the same range of $MA_2C$ and moreover has a power law behavior for $MA_2C > 3$ (see Figure 1), the reduced viscosity data do not lie on a single curve. For a given polymer species, regardless of the degree of polymerization, $MA_2C$ is the reduced variable, in agreement with ref 25. However a power law behavior is reached at different values of $MA_2C$ for polystyrene, polyisoprene, and polybutadiene samples, values compatible with the crossover reduced concentrations $MA_2C_e$ peculiar to each polymer species.

In the low reduced concentration part, Figure 4 shows that measurements performed on polystyrene and polyisoprene samples join together as the concentration decreases, the dashed line corresponding to eq 15. Those results are compatible with a Rouse regime within which a unique curve for $\eta_r = \eta/\eta_s$ versus $MA_2C$ and a $C^{1.3}$ concentration dependence are predicted. As for the polybutadiene sample, this regime is difficult to observe due to the small value of $MA_2C_e$, i.e. the small value of $n_e$ compared to polystyrene and polyisoprene (cf. Table 2).

At higher reduced concentration values, curves in Figure 4 are distinct, as suggested by eq 19. This regime is expected to correspond to the entangled regime described by the reptation model. For the same reason that the Rouse regime cannot be observed for polybutadiene, the reptation behavior is reached for lower value of $MA_2C$ than for polystyrene and polyisoprene. Thus, the $MA_2C$ exponent value is determined on polybutadiene data. It is found equal to 4.65 ± 0.05 which leads using expression 6, to a viscosity varying as $M^{3.57\pm0.07}$. As in the melt, this value is higher than the value predicted by reptation theory.[26] Figure 3 clearly demonstrates that dynamic properties cannot be described by scaling laws. This failure is due to entanglement effects and thus the reduced concentration $C/C_e = MA_2C/n_e^{0.76}$ has to be used for data superposition.

For concentration higher than $C_e$, polymers are entangled and the viscosity predicted by the reptation theory is written as $\eta/\eta_{Rouse} = (C/C_e)^{2.6}$ (see eq 20). At concentrations lower than $C_e$, $\eta/\eta_{Rouse}$ is a constant, independent of the concentration and of the polymer. Therefore $\eta/\eta_{Rouse}$ and $C/C_e$ are expected to be the reduced variables of the viscosity concentration behavior. In Figure 5 the ratio $\eta/\eta_{Rouse}$ with $\eta_{Rouse} = \eta_s(MA_2C)^{1.3}$ is plotted as a function of $C/C_e$ for the three polymers here studied and for the two higher mass polystyrene studied in ref 25 (see note 27) but the data superposition is not perfect. One may note
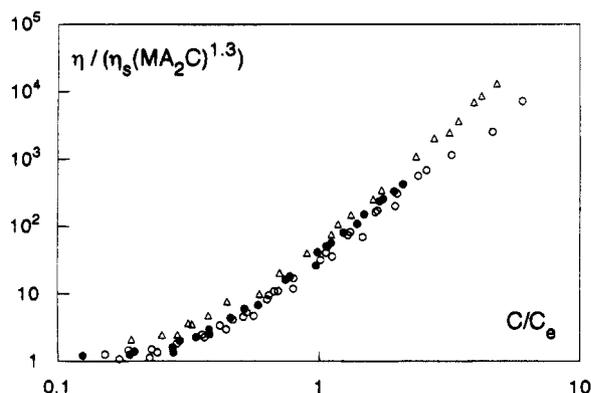
**Figure 5.** log–log plot of the reduced viscosity $\eta/\eta_{Rouse}$ with $\eta_{Rouse} = \eta_s(MA_2C)^{1.3}$ vs $C/C_e = n_e^{-0.76}MA_2C$: polystyrene (O), polyisoprene (●), and polybutadiene (△).
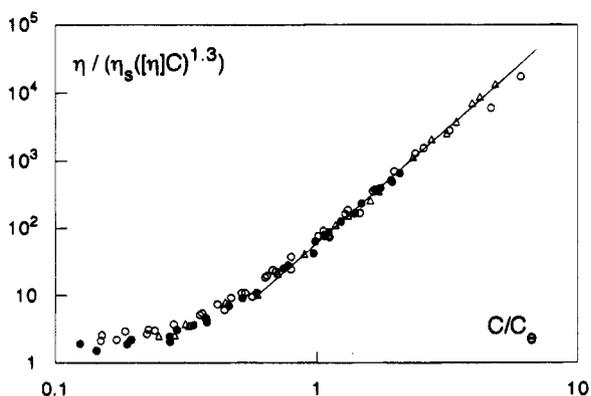


**Figure 6.** log–log plot of the reduced viscosity $\eta/\eta_{Rouse}$ with $\eta_{Rouse} = \eta_s([\eta]C)^{1.3}$ vs $C/C_e = n_e^{-0.76}MA_2C$: polystyrene (O), polyisoprene (●), and polybutadiene (△). The straight line corresponds to the best fit for $C > C_e$ and has a slope equal to 3.4 (eq 29).

that, regardless of $C/C_e$, polybutadiene data are weakly higher than the others. Because this is observed even for $C/C_e < 1$, entanglements are not responsible for this lack of superposition. This is better due to the fact that $[\eta]$ and $MA_2$ are not proportional (see Table 1). As a matter of fact, the reduced variable for the dilute regime is $[\eta]C$, and thus $\eta_{Rouse}$ has to be written as a function of the reduced variable $[\eta]C$ in order to ensure a continuity between dilute and Rouse semidilute regime. The ratio $\eta/\eta_{Rouse}$ with $\eta_{Rouse} = \eta_s([\eta]C)^{1.3}$ as a function of $C/C_e$ is plotted in Figure 6.[28] The data superposition is much better than the one in Figure 5. For $C/C_e < 0.3$, the ratio $\eta/\eta_{Rouse}$ tends to be a constant, which seems to indicate that the Rouse model describes the viscosity behavior in this regime. However the concentration range $C^* < C < C_e$ is too narrow to ascertain this result. The straight line in Figure 6 corresponds to the best fit of data obtained at $C > C_e$ on polybutadiene, polyisoprene, and polystyrene all together. It is found to be

$$\eta/\eta_{Rouse} = 60 \times (C/C_e)^{3.4} \tag{29}$$

In terms of the number $N/g$ of blobs per chain eq 29 can be rewritten as

$$\eta/\eta_{Rouse} = 60 \times \left(\frac{N/g}{n_e}\right)^{2.6} \tag{30}$$

Equation 30 emphasizes explicitly the $n_e$ power law dependence of the viscosity.

The data superposition of $\eta/\eta_{Rouse}$, as a function of $C/C_e$ in the whole concentration range and for the three polymers here studied, demonstrates the validity of the relations derived in

the theoretical part which introduce a number $n_e$ of blobs between entanglements.

## Conclusion

In this paper, experimental evidence for the nonscaling of viscoelastic properties is reported. The reduced viscosity $\eta/\eta_s$ is actually a unique function of $C/C^*$ for a given polymer, but differs from one polymer species to another. A given number $n_e$ of blobs is needed for polymers to be entangled. This number was determined through the ratio of the osmotic modulus to the shear elastic modulus $K/G$ and is found to be identical to the number $N_e$ of monomers per entanglement measured in the melt. The concentration behavior of viscoelastic properties can be derived from the relations established in the melt for the Rouse and reptation regimes, replacing the degree of polymerization $N$ by the reduced variable $N/g$ i.e. the number of blobs per chain. Consequently, as for the melt two concentration regimes are expected in semidilute solutions:[29] entangled and unentangled. These expectations were fully verified, by plotting the reduced viscosity $\eta/\eta_{Rouse}$, with $\eta_{Rouse} = \eta_s(C/C^*)^{1.30} = \eta_s(C[\eta])^{1.30}$, as a function of the reduced concentration $C/(n_e^{0.76}C^*)$ one superimposes the data obtained on the three kinds of polymer here studied. However, such a master curve is not properly speaking a scaling law because the reduced concentration is written using two quantities $C^*$ and $n_e$ coming from the zero concentration limit and from the melt, respectively.

At first glance, this experimental result seems to be very strange. Static properties obey scaling laws and this seems to indicate that in semidilute solution all the specific features of polymers due to the chemical nature of their monomers are forgotten. On the contrary, in the melt, the number $N_e$ of monomers between entanglements is often viewed as linked to the local flexibility of the polymer.[30] Blobs being fully "flexible", this notion has no meaning in semidilute solution and one could have expected that viscoelastic properties scale in the same manner as static properties. Here we have shown experimentally that this is not the case and that there is a melt influence on the number of blobs per entanglement. Thus, it is necessary to conceive of entanglements in another way. This can be done by considering, in the melt, the number of entanglements per unit volume as the probability $1/N_e$ for a monomer to act as an entanglement. In semidilute solution, this probability has to be multiplied by the probability $1/\xi^3$ for this monomer to concur with a binary contact between polymers. Thus, the entanglement probability, i.e. the number of entanglements per unit volume, becomes $1/N_e\xi^3$. Within this simple picture, the number of blobs per entanglement is due to the property of monomers to adopt a specific conformation leading to reptation hindrance, this conformation, and its inherent probability being independent of the concentration. In this context, measurements at and near the $\Theta$ temperature would be fruitful and are planned in the near future.

## Appendix

Relative viscosity $\eta/\eta_s$ measured at 30 °C for the three polymer species are shown in Table 3.

**Table 3$^a$**

| $10^2C$ (g/cm$^3$) | $\eta/\eta_s$ | $10^2C$ (g/cm$^3$) | $\eta/\eta_s$ |
|---|---|---|---|
| Polystyrene, $M = 4.00 \times 10^6$ g/mol | | | |
| 1.73 | $1.88 \times 10^2$ | 5.35 | $1.79 \times 10^4$ |
| 2.80 | $1.13 \times 10^3$ | 6.79 | $5.35 \times 10^4$ |
| 3.31 | $2.21 \times 10^3$ | 6.93 | $5.83 \times 10^4$ |
| Polystyrene, $M = 1.24 \times 10^6$ g/mol | | | |
| 1.54 | $1.88 \times 10^1$ | 5.38 | $4.02 \times 10^2$ |
| 1.75 | $1.89 \times 10^1$ | 5.71 | $3.83 \times 10^2$ |
| 1.89 | $2.78 \times 10^1$ | 6.52 | $9.28 \times 10^2$ |
| 2.31 | $3.81 \times 10^1$ | 7.05 | $1.19 \times 10^3$ |
| 2.89 | $6.13 \times 10^1$ | 8.06 | $1.53 \times 10^3$ |
| 3.63 | $1.14 \times 10^2$ | 11.4 | $7.17 \times 10^3$ |
| 4.50 | $1.78 \times 10^2$ | | |
| Polyisoprene $M = 9.40 \times 10^5$ g/mol | | | |
| 0.80 | 8.49 | 5.91 | $5.85 \times 10^3$ |
| 1.05 | $1.50 \times 10^1$ | 5.96 | $5.80 \times 10^3$ |
| 1.52 | $3.14 \times 10^1$ | 6.14 | $6.87 \times 10^3$ |
| 1.53 | $2.67 \times 10^1$ | 6.86 | $1.13 \times 10^4$ |
| 1.62 | $4.33 \times 10^1$ | 7.75 | $1.78 \times 10^4$ |
| 2.11 | $8.85 \times 10^1$ | 8.23 | $2.68 \times 10^4$ |
| 2.88 | $2.71 \times 10^2$ | 9.40 | $4.97 \times 10^4$ |
| 4.12 | $1.17 \times 10^3$ | 9.72 | $5.63 \times 10^4$ |
| 4.29 | $1.38 \times 10^3$ | 10.7 | $8.27 \times 10^4$ |
| 5.46 | $4.30 \times 10^3$ | 11.6 | $1.17 \times 10^5$ |
| Polyisoprene $M = 3.10 \times 10^5$ g/mol | | | |
| 1.50 | 8.47 | 5.53 | $1.69 \times 10^2$ |
| 2.36 | $1.76 \times 10^1$ | 7.04 | $3.58 \times 10^2$ |
| 4.07 | $5.90 \times 10^1$ | 11.7 | $2.67 \times 10^3$ |
| 4.58 | $7.58 \times 10^1$ | | |
| 0.50 | 8.90 | 3.44 | $7.85 \times 10^3$ |
| 0.65 | $1.48 \times 10^1$ | 4.18 | $1.71 \times 10^4$ |
| 0.75 | $1.78 \times 10^1$ | 4.51 | $2.57 \times 10^4$ |
| 0.82 | $2.96 \times 10^1$ | 6.10 | $1.21 \times 10^5$ |
| 0.85 | $2.96 \times 10^1$ | 7.17 | $2.77 \times 10^5$ |
| 0.98 | $4.87 \times 10^1$ | 8.23 | $4.06 \times 10^5$ |
| 1.16 | $9.75 \times 10^1$ | 8.90 | $6.59 \times 10^5$ |
| 1.54 | $1.83 \times 10^2$ | 10.1 | $1.06 \times 10^6$ |
| 1.84 | $4.75 \times 10^2$ | 10.2 | $1.51 \times 10^6$ |
| 2.33 | $1.28 \times 10^3$ | 11.0 | $2.05 \times 10^6$ |
| 2.90 | $3.18 \times 10^3$ | 12.6 | $3.76 \times 10^6$ |
| 3.07 | $4.85 \times 10^3$ | | |

$^a$ Solvent viscosity $\eta_s$ at 30 °C: benzene, $\eta_s = 5.646 \times 10^3$ P, cyclohexane, $\eta_s = 8.206 \times 10^{-3}$ P.

## References and Notes

(1) de Gennes, P. G. *Scaling Concept in Polymer Physics*; Cornell University Press: London, 1979.
(2) Doi, M.; Edwards, S. F. *The theory of polymer dynamics*; Clarendon Press: Oxford, 1986.
(3) Grosberg, A. Y.; Khokhlov, A. R. *Statistical physics of macromolecules*; A.I.P. Press: New York, 1994.
(4) Adam, M.; Lairez, D. *Fractals* **1993**, *1*, 149.
(5) Adam, M.; Lairez, D.; Raspaud, E. *J. Phys. II* **1992**, *2*, 2067.
(6) Le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.
(7) Flory, P. J. *Principles of polymer chemistry*; Cornell University Press: London, 1953.
(8) des Cloizeaux, J.; Jannink, G. *Les Polymères en solution* (*Polymers in solution*); Les Editions de Physique: France, 1987.
(9) de Gennes, P. G. *Macromolecules* **1976**, *9*, 587–598.
(10) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.
(11) Weill, G.; des Cloizeaux, J. *J. Phys. France* **1979**, *40*, 99.
(12) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(13) Colby, R. H.; Rubinstein, M. *Macromolecules* **1990**, *23*, 2753. Colby, R. H.; Rubinstein, M.; Daoud, M. *J. Phys. II* **1994**, *4*, 1299.
(14) Ferry, J. D. *Viscoelastic properties of polymers*; J. Wiley & Sons Inc.: New York, 1980.
(15) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(16) Chu, B. *Laser light scattering*, 2nd ed.; Academic Press: San Diego, 1991.
(17) Cotton, J. P. *J. Phys. Lett.* **1980**, *41*, L-231.
(18) Berry, G. C.; Casassa, E. F. *J. Polym. Sci. D* **1970**, *4*, 1.
(19) Delsanti, M. Thesis, Orsay, France, 1978.
(20) Davidson, N. S.; Fetters, L. J.; Funk, W. G.; Hadjichristidis, N.; Graessley, W. W. *Macromolecules* **1987**, *20*, 2614.
(21) Colby, R. H.; Fetters, L. J.; Graessley, W. W. *Macromolecules* **1987**, *20*, 2226.
(22) Adam, M.; Fetters, L. J.; Graessley, W. W.; Witten, T. A. *Macromolecules* **1991**, *24*, 2434.
(23) Noda, I.; Kato, N.; Kitano, T.; Nagasawa, M. *Macromolecules* **1981**, *14*, 668.
(24) Adam, M.; Delsanti, M. *Rev. Phys. Appl. France* **1984**, *19*, 253.
(25) Adam, M.; Delsanti, M. *J. Phys. France* **1983**, *44*, 1185.
(26) Pearson, D. S. *Rubber Chem. Technol.* **1987**, *60*, 439.
(27) Assuming a fractal dimension equal to 1.7 and calculating prefactors of the eq 5 with measurements of $M$ and $MA_2$ given in Table 1, we have estimated the $MA_2$ value of two polymers of ref 25. We find for $M = 6.77 \times 10^6$, $MA_2 = 1900$ and for $M = 20.6 \times 10^6$, $MA_2 = 4450$.
(28) Values of intrinsic viscosities [$\eta$] for polystyrene samples studied in ref 25 were determined from equations given in ref 19. We find for $M = 6.77 \times 10^6$, [$\eta$] = 1020 and for $M = 20.6 \times 10^6$, [$\eta$] = 2270.
(29) Graessley, W. W. *Polymer* **1980**, *21*, 258.
(30) Rault, J. C. *R. Acad. Sci. Paris* **1985**, *300*, 433.
(31) Gotro, J. T.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2767.

MA941183A