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Viscosity of semi-dilute polymer solutions

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Résumé. — Nous présentons des résultats de viscosité obtenus dans des solutions semi-diluées de polymères \((c^* < c < 10\%)\).
La variation de la viscosité est indépendante de la température de transition vitreuse du polymère et compatible avec un coefficient de frottement du monomère proportionnel à la viscosité du solvant.
En fonction de la concentration dans différents systèmes, les relations suivantes sont obtenues :
— PIB-toluène, \(\eta_r \sim c^{4.1}\), qui est proche de la théorie de la viscosité de de Gennes,
— PS-benzène et PIB-cyclohexane, \(\eta_r \sim c^{4.6}\), qui peut être expliquée par la structure locale de la chaîne,
— solution semi-diluée à la température \(\theta\), \(\eta_r \sim c^{5}\), qui peut être interprétée avec un temps de reptation analogue à celui introduit dans le modèle de de Gennes et une élasticité déduite de la théorie de champ moyen.
En fonction de la masse moléculaire, nous obtenons :
\[ \eta_r \sim M_w^{3.1} \]
en accord avec le modèle de reptation.
Toutefois, il semble que les lois d’échelle en température ne peuvent expliquer la décroissance de la viscosité relative lorsque la température croît.

Abstract. — We report viscosity measurements on semi-dilute solutions \((c^* < c < 10\%)\).
The viscosity variation is independent of the glass transition temperature of the undiluted polymer and consistent with monomer friction proportional to the solvent viscosity.
With concentration, the following variations were observed :
— for PIB-toluene, \(\eta_r \sim c^{4.1}\), close to de Gennes’ viscosity theory,
— for PS-benzene and PIB-cyclohexane, \(\eta_r \sim c^{4.6}\) which seems to be influenced by local statistics in the chains,
— for semi-dilute \(\theta\) solvent conditions, \(\eta_r \sim c^{5}\) which could be interpreted using de Gennes’ theory of reptation and mean field theory of elasticity.
With molecular weight we observe :
\[ \eta_r \sim M_w^{3.1} \]
in agreement with reptation model.
However temperature scaling laws do not seem to be applicable. The interpretation of the temperature dependence of the viscosity remains open question.

Introduction. — Zero shear viscosity of polymer solutions and melts have been intensively studied for many years. A good review article on the subject was written by Fox and Berry [1](1968).
Our purpose is to compare de Gennes’ viscosity theory [2], which gives a new approach on the problem, to experimental results obtained with semi-dilute solutions. A semi-dilute solution may be considered as a transient network, the monomer concentration \(c^*\) being higher than the overlap concentration \(c^* \simeq N/R^3 [3]\) but much lower than the solvent concentration. In order to be able to compare theory with experiments we have performed some new experiments on very high molecular weight polymer.
First, we review de Gennes’ theory of semi-dilute (S.D) polymer solutions. Then we define the experimental conditions at which the experiments were performed. Finally, we present and discuss the experimental results obtained in both, good and \(\theta\) solvents.

1. Theory. — The main term in the expression for the viscosity \(\eta\) is the product of the longest relaxation time \(T_R\) and the shear elastic modulus \(E\) of the transient network :
\[ \eta \simeq ET_R. \]
Let us successively derive the two quantities $E$ and $T_R$ from de Gennes’ theory in the simplest case
of an athermal solvent (Flory-Huggins parameter $\chi = 0$).

The main hypothesis of the de Gennes’ theory is to consider a chain (in a S.D. solution) as formed by
a succession of subchains of mean size $\bar{\xi}$, each subchain having $g$ monomers.

Inside a subchain, the $g$ monomers are subject to
excluded volume effects and to hydrodynamic interactions. Such interactions do not take place between
two subchains; $\bar{\xi}$ is a screening length for both excluded volume and hydrodynamic effects.

Edwards [4] and de Gennes [5] imagine that the motion of a particular chain is a reptation in a fictitious
tube, defined by all the surrounded chains. The diameter of this tube is the screening length $\xi$:

$$\xi \approx l (l^3 \sigma)^{(1-v)/(3v-1)}.$$  \hspace{1cm} (2)

where $l$ is an effective length per monomer.

The length of the tube is :

$$L \approx \left(\frac{N}{g}\right) \cdot \bar{\xi},$$  \hspace{1cm} (3)

where $N$ is the number of monomers in a chain and

$$g \approx c \bar{\xi}^3,$$  \hspace{1cm} (4)

since a S.D. solution is a closely packed system of subchains units.

The time $T_R$ necessary for a complete renewal of
the tube is the time required for chain to reptate the length of the tube [6] :

$$T_R \approx \frac{L^2}{D_t},$$  \hspace{1cm} (5)

where $D_t$ is the diffusion coefficient of the Rouse chain along its tube. Thus :

$$D_t \approx \frac{1}{\eta_0} \frac{kT}{L},$$  \hspace{1cm} (6)

where $\eta_0$ is the solvent viscosity.

Combining equations (3), (5) and (6), we have :

$$T_R \approx \frac{\eta_0}{kT} \frac{N}{g}$$

thus :

$$T_R \approx \frac{\eta_0}{kT} \left(\frac{N}{g}\right)^3 \bar{\xi}^3.$$  \hspace{1cm} (7)

Substituting the expressions (4) and (2) for $g$ and $\xi$ in the expression of $T_R$ (7) we have :

$$T_R \approx \frac{\eta_0}{kT} l^3 N^3(l^3 \sigma)^{3(1-v)/(3v-1)}.$$  \hspace{1cm} (8)

Following rubber elasticity theory (7), the elastic modulus of the transient network is proportional to
the volume number density of strands $c/g$. Using the expressions (2) and (4) we obtain:

$$E \approx \frac{kT}{T^3} (l^3 \sigma)^{3v/(3v-1)}.$$  \hspace{1cm} (9)

From the expressions of $T_R$ (8) and $E$ (9) we obtain for the viscosity [10] :

$$\eta \approx \eta_0 N^3(l^3 \sigma)^{3(3v-1)}$$

or

$$\eta \approx \eta_0 N^3(c \bar{\xi}^3)^3.$$  \hspace{1cm} (10)

Using the most accurate experimental value of $v$
[8], which corresponds to the prediction of the $n$
vector model [9],

$$v = 0.588$$

one finds :

$$\eta \sim \eta_0 N^3 c^{3.95}.$$  

We have considered above the case of an athermal solvent ($\chi = 0, \nu = 0.588$) where only one characteristic length $\xi$ exists. The quality of the solvent should have no influence on the viscosity molecular weight exponent, but it must influence strongly the concentration dependence. One may remark that, since the length $\xi$ decreases when the quality of the solvent increases (Ref [2], p. 119, 11, 12), the viscosity given by equation (10) must increase.

In the case of a $\theta$ solvent [13] the theory of the viscosity is much more difficult because there exist two lengths [14] :

— the correlation length, which is the screening length of the density-density correlation function :

$$\xi \approx \frac{l}{c \bar{\xi}},$$  \hspace{1cm} (11)

— and the mean distance between two consecutive entanglements :

$$\bar{\xi}_2 \approx l(l^3 \sigma)^{-1/2}.$$  \hspace{1cm} (12)

The problem is : how the shear modulus and the longest relaxation time depend on $\xi$ and $\bar{\xi}_2$. In section 3.2, we will discuss our experimental results obtained in $\theta$ conditions and compared them with different theoretical possibilities.

2. Experimental procedure. — The principle of the viscometer was given in our earlier paper [15]. We
measure the viscous force $F$ to which a sphere (radius $r = 5 \times 10^{-2}$ cm) is submitted when the fluid is
displaced at a velocity $v$ :

$$F = 6 \pi r v \eta,$$
Table I. — Characteristics of polymer solutions studied. Tg is the glass transition temperature of the undiluted polymer and \( \chi \) the Flory-Huggins parameter. Indexes \( v \) and \( t \) refer to \( \chi \) deduced from intrinsic viscosity and thermodynamic measurements, respectively.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( T_{g\text{soln}} ) [K]</th>
<th>Temperature [°C]</th>
<th>( \chi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-cyclohexane</td>
<td>373</td>
<td>35</td>
<td>0.5 (37)</td>
</tr>
<tr>
<td>PS-benzene</td>
<td>205</td>
<td>25</td>
<td>0.5 (38)</td>
</tr>
<tr>
<td>PIB-benzene</td>
<td>205</td>
<td>25</td>
<td>0.45 (37)</td>
</tr>
<tr>
<td>PIB-cyclohexane</td>
<td>205</td>
<td>30</td>
<td>0.44 (39)</td>
</tr>
<tr>
<td>PIB-toluene</td>
<td>205</td>
<td>25</td>
<td>0.45 (7)</td>
</tr>
</tbody>
</table>

We measure the ratio \( F/v \) as a function of \( v \) and verify that \( F/v \) has a constant value, thus we determine the zero shear viscosity of the sample.

We have made various improvements [16] upon the viscometer specifications as compared to reference [15]. The force maintaining the sphere in place is transmitted magnetically and we have improved the feedback control of the current driving the field coils. This current is of the order of 1 mA and it is now measured to within 1 %. The sample flow is now driven by a stepper motor and its velocity is measured to an accuracy better than 0.1 %.

We made an absolute calibration of the apparatus by measuring a standard silicon oil (\( \eta = 50 \, \text{P} \) at 25 °C) and our new overall precision is 2 %.

From the measured viscosity, we have deduced the relative viscosity \( \eta' \) as the ratio of polymer solution viscosity to that of the solvent [17], given in appendix 2.

Two kinds of polymer were used: poly-isobutylene and polystyrene in three different solvents whose characteristics are given in table I.

In figure 1 we plot the different concentrations of the samples at which the viscosity was measured. We represent also the variation of the overlap concentration \( c^* \) as a function of molecular weight. As usual [12, 15, 18] we use for \( c^* \):

\[ c^*(g/g) = \frac{M_w}{\rho A R_G^2} \]

where \( A \) is Avogadro’s number, \( \rho \) is the density of the solvent, and \( R_G \) is the radius of gyration measured by light scattering [19]. For comparison, we plot (dashed line) the value of \( c_c \) for PS system:

\[ c_c M = 3.8 \times 10^4 \]

where \( c_c (g/g) \) define the boundary between the entangled and non entangled regime [20]. We can note that:

- the \( c_c \sim M^{-1} \), in good solvent cannot be justified using de Gennes’ theory,
- for PS good solvent (Fig. 1a), with our range of molecular weight, \( 1.5 < c_c/c^* < 3 \)
- for PS-\( \theta \) solvent (Fig. 1b), \( c_c \) is smaller than \( c^* \) and \( 1.3 < c^*/c_c < 6 \).

Thus for such high molecular weight polymers \((M > 10^6)\), we find no significant range of concentration where the system is semi-dilute but not entangled [20].

3. Experimental results and discussions. — 3.1 GOOD SOLVENT. — 3.1.1 Concentration dependence.

In the PS-benzene and PIB-cyclohexane systems, the dependence of relative viscosity on concentration is, at 32 °C, identical for both systems:

For PIB-cyclohexane the exponent decreases slightly as the temperature increases, at 64 °C, the exponent value is 4.4 ± 0.1. This has to be checked on PS-benzene at high temperature.

For PIB-toluene the viscosity, for a given concentration, is much lower than for PIB-cyclohexane:

\[ \frac{\eta_{\text{PB-toluene}}}{\eta_{\text{PB-cyclohexane}}} \approx 2. \]
In the PIB-toluene system, the concentration dependence of the relative viscosity is:

\[ \eta_r \sim c^{4.1 \pm 0.1} \], see figure 3,

in agreement with reference [21]. The concentration exponent, close to theoretical value of 3.95, is independent of the temperature.

3.1.2 Temperature dependence. — The main effect, observed on S.D. solutions, PS-benzene and PIB-cyclohexane, is that the relative viscosity \( \eta_r \) decreases as we increase the temperature.

An example of the decrease of the viscosity as a function of temperature is given in figure 4. This variation can be considered as linear and parameterizing it as:

\[ \frac{\eta_r(T) - \eta_r(313)}{\eta_r(313)} = -\Gamma(T - 313) \]

we find: \( \Gamma = 9 \times 10^{-3} \) in the case of figure 4.

In figure 5 we present the variation of \( \Gamma \) as a function of concentration for different systems (some numerical values of \( \eta_r \) as a function of temperature are given in appendix 3).

In a dilute regime with short chains at high concentration (\( c = 9 \times 10^{-2} \text{ g/g}, c/c^* = 0.6, M_w = 4 \times 10^4 \)) the relative viscosity is very small and within experimental accuracy, independent of the temperature (20°C < \( T < 60 \text{ °C} \), see figure 5. Even with 9% solution concentration, the viscosity dependence on temperature is that of the solvent. This proves that for a monomer concentration less than 10% the monomer friction is proportional to the viscosity of the solvent (monomer-monomer friction can be neglected).

In figure 5, one observes that:

— PS-benzene and PIB-cyclohexane systems present the same variation of \( \Gamma \) with concentration,
\( \Gamma \) being independent of the molecular weight. This temperature behaviour is not a glass transition temperature effect, because one set of experiments (on PS) was performed below, the other (on PIB) above the \( T_g \) of the respective undiluted polymer.

- the PIB-toluene system presents a variation of the relative viscosity with temperature which is independent of concentration. The \( \Gamma \) values are very small compared to those obtained on PIB-cyclohexane.

In the systems studied (\( \chi \approx 0.44 \)) the concentration exponent values found are larger than the theoretical value developed in section 1 for an athermal solvent. In the systems PS-benzene and PIB-cyclohexane, the relative viscosity decreases as we increase the temperature.

If the first result can be interpreted as due to high \( \chi \) values, the second result cannot be interpreted using usual temperature scaling laws [2, 11, 12] which predict a thermal effect opposite to that observed. Indeed increasing the temperature, the quality of the solvent increases and thus the viscosity should increase (see section 1).

3.1.3 Qualitative interpretation of the results. — In the polymeric systems studied (\( \chi \approx 0.44 \)) the effective length \( l \) is much larger than the size of a monomer \( a \). Let us suppose that:

i) at very short distance \( r (r < ma) \), the chain is rigid [22, 23], \( m \) being the number of monomers affected by rigidity;

ii) at larger distance \( r > ma \) the subchain \( \xi \) has a Gaussian conformation if \( m \ll g < g_r \). The excluded volume effects are dominant if \( g > g_r \) [24].

In the range of molecular weight studied, we have low values of \( g/g_r \) in the semi-dilute range. For instance, in a PS-benzene solution, at room temperature, \( g_r \) corresponds to a molecular weight \( M_g \) of \( \approx 10^7 \) [25]. By comparison of diffusion coefficient at zero concentration and cooperative diffusion coefficient in semidilute solution [18], having a monomer concentration of \( 2\% < c < 10\% \) the corresponding \( M_g \) values are:

\[
10^5 > M_g > 10^4
\]

Thus, for \( c \approx 10\% \), the ratio \( g/g_r \) is of the order of unity. In other words, at room temperature and for \( 2\% < c < 10\% \), the effective value of the exponent \( \nu \) has not reached its asymptotic value.

Using the assumptions i) and ii) the expressions \( g/g_r \) (A.5) and \( \eta_r \) (A.6) are developed in appendix 1. In those expressions \( \alpha \) is a constant because the systems studied (PS-benzene and PIB-cyclohexane) have very low \( \theta \) temperatures [7] and small change near room temperature does not affect the quality of solvents (\( \alpha = \text{const} \)). If we suppose that \( m \) is inversely proportional to the temperature we obtain the following temperature dependences:

\[
\frac{\theta}{g_r} \sim T^{3(3\nu-1)} \quad \text{and} \quad \eta_r \sim T^{-\frac{9\nu^2-3\nu}{3\nu-1}}
\]

When \( T \) increases, \( g/g_r \) and \( \eta_r \) increase and decrease, respectively. This seems to justify that in the case of PS-benzene and PIB-cyclohexane:

- \( \Gamma \) is independent of the molecular weight (see Fig. 5).

- the viscosity and the experimental concentration exponent decrease as \( T \) increases.

In the case of PIB-toluene the independence of the relative viscosity with temperature and the low value of concentration exponent could be due to high flexibility of the polymer in this system giving a high value of \( g/g_r \).

This agreement is only qualitative, we cannot go further because the effective \( \nu \) is an unknown function of concentration and temperature.

This assumption (that \( \nu \) has not reached its asymptotic value) seems in contradiction with neutron measurements on \( \xi \) in PS-benzene solutions [26]. But one must note that the law

\[
\xi \sim c^{-0.72 \pm 0.06},
\]

in which the exponent value corresponds to the asymptotic value of \( \nu \), was measured in a concentration range (0.5 \% \( < c < 5\% \)) lower than that of our viscosity measurements, hence in a higher range of \( g/g_r \).

Self-diffusion measurements on PS-benzene solutions are reported in reference [27] (2 \% \( < c < 20\% \)), they give

\[
D_s \sim c^{-1.7 \pm 0.1}.
\]

Using the relation : \( D_s \sim R^2/T \eta \) with \( R^2 \sim c^{-1/4} \) and \( E \sim c^{2.25} \) (corresponding to \( \nu = 0.6 \)) leads to \( \eta \sim c^{3.7} \). This exponent (3.7), in agreement with de Gennes’ prediction, is much lower than our 4.6 concentration exponent. Is the concentration exponent of the self diffusion coefficient very sensitive to the effective value of \( \nu \) [28]?

Due to the low value of \( g/g_r \), the PS-benzene system might be used as an experimental model of mean field theory. However this theory leads to a viscosity concentration exponent of 3.5, smaller than the good solvent exponent (3.95) and thus in contradiction with our experimental results.

In short, the value of the concentration exponent may be interpreted as due to a non athermal solvent polymer system. However, the decrease of the relative viscosity with increasing temperature could not be understood in terms of the classical temperature dependence of \( \xi \), but in terms of local rigidity.

3.2 \( \theta \) Solvent : PS-cyclohexane, PIB-benzene solutions. — The viscosity of S.D. solutions, at \( \theta \) temperature and at a given concentration is not very different from that of S.D. solutions in good solvents. This contrasts with what is observed in dilute solutions, (Ref. [29]). On both our systems, when we increase the temperature from the \( \theta \) point, \( (T - \theta = 16^\circ) \) the relative viscosity, for a 9 \% monomer concentration, decreases by a factor 1.6.
In both cases, PS-cyclohexane (35 °C) and PIB-benzene (25 °C) the relative viscosity varies with concentration as:

$$\eta_r \sim c^5 \pm 0.1$$, see figure 6.

In figure 6 the arrows represent the $c^*$ values on both systems. As soon as $c > c^*$, the experimental points, on log log scale, lie on a straight line of slope 5.

Starting from these experimental results ($\eta_r \sim c^5$) we want to examine the contribution of the two characteristic lengths which are present in the system, at the $\theta$ temperature.

The first length is the mean distance between two consecutive entanglements or contacts:

$$\xi_2 \simeq l(c\ell)^{-1/2},$$

using this distance it was found [14, 30]:

$$E \sim c^2, \quad T_R \sim N^3 c^{1.5}.$$  \hspace{1cm} (14)

The second length is the correlation length of density-density correlation function:

$$\xi \simeq l(c\ell)^{-1}$$  \hspace{1cm} [11, 31, 32], note that $\xi > \xi_2$.

$\xi \sim c^{-1}$ corresponds to the expression (2) of $\xi$ where $v$ is set equal to $1/2$. Using $v = 1/2$ in the expressions of the shear modulus (9) and of the longest relaxation time (8) one find:

$$E \sim c^3, \quad T_R \sim N^3 c^3.$$  \hspace{1cm} (15)

Combining the expressions of $T_R$ and $E$ given, the different resulting viscosity expressions are reported in table II.

Thus the only way to match the experimental results is to have:

- **Shear modulus** $E \sim c^2$
- **Longest relaxation time** $T_R \sim N^3 c^3$.

Physically: the elastic modulus corresponds to probability of contact of two monomers, belonging to a Gaussian chain, because the coils are real and cannot cross each other.

The longest relaxation time ($T_R \sim N^3 c^3$) corresponds to a screening length proportional to $c^{-1}$.

In that case the fictitious tube has a length:

$$L \sim N c$$ because $L \sim (T_R)^{1/3}$

and thus a diameter proportional to $\xi$.

At the $\theta$ temperature, they are contact points (entanglements) which define the transient network, but which do no show up in the correlations because the pair interaction vanishes. In order to define a correlation length $\xi$ in the density-density correlation function, one must invoke higher order interactions.

However the sign of the variation of the relative viscosity with temperature cannot be rationalized with the usual temperature dependence of the characteristic length in S.D. solutions. Using this temperature dependence [11, 12], we find a relative viscosity which increases with temperature.

### 3.3 Molecular Weight Dependence in PS-Benzene Solutions.

The polydispersity of PS samples makes the determination of the value of the molecular weight exponent very delicate. We have used the best commercial samples available.

The molecular weight exponent value is independent of the quality of the solvent, thus of the concentration exponent value (see section 3.1.1). Taking the experimental value $\eta \sim c^{4.6}$ for PS-benzene samples at 32 °C we find:

$$\frac{\eta_r}{c^{4.6}} \sim M_w^{2.1 \pm 0.1}$$  \hspace{1cm} (Fig. 7)

with samples from Toyo Soda company, having a polydispersity of 1.04 and 1.14 for $M_w = 3.84 \times 10^6$ and $M_w = 6.77 \times 10^6$, respectively; and,

$$\frac{\eta_r}{c^{4.6}} \sim M_w^{2.7 \pm 0.1}$$

with samples from pressure chemical having a polydispersity of 1.15 for both $M_w = 4.1 \times 10^6$ and $7.1 \times 10^6$.

This exponent value is very sensitive to polydisper-
Fig. 7. — Molecular weight dependence of the relative viscosity from Toyo Soda samples, at c = 5 x 10^{-3} g/g [41].

sity. In fact if we use the viscosity average molecular weight \( M_v \) we find instead of 3.1, an exponent value of 3.5. There is no reason to use the \( M_v \) mean value. Making the assumption that the mean longest relaxation time of a polydisperse sample is the weight average of \( T_R \) [6], since the elastic modulus is independent of the molecular weight, we have:

\[
\eta \sim \frac{\sum w_i M_i^3}{\sum w_i},
\]

where \( w_i \) is the weight fraction of species having a molecular weight \( M_i \) the mean molecular weight to be used is closer to \( M_n \) than \( M_v \).

In fact, to our knowledge, most of the authors [33], except references [21, 34] measured the viscosity molecular weight dependence using the \( M_v \) mean value. They determine the molecular weight of their samples through the Mark Houwink equation.

The molecular weight exponent value (3.1) seems to be closer to reptation prediction (3) than the 3.5 Bueche prediction [35], in the case of high molecular weight (\( M > 10^6 \)).

4. Conclusion. — These sets of experiments have demonstrated a certain number of facts concerning the viscosity behaviour of semi-dilute solutions for which the monomer concentration is less than 10 % but still higher than \( c^* \).

a) The relative viscosity does not depend on the glass transition temperature of the undiluted polymer.

b) Since the temperature variation of a 9 % PS-benzene solution, having a ratio of \( \frac{c}{c^*} \approx \frac{1}{2} \), is identical to that of the solvent viscosity, we may conclude that the local viscosity is that of the solvent. This confirms the NMR experimental results [36].

c) The relative viscosity of semi-dilute solution in good solvent, seems to be, in the case of PIB-toluene, in agreement with de Gennes theory. This fact confirms the experimental results [21] obtained a long time ago.

d) The viscosity of the PS-benzene and PIB-cyclohexane seems to be influenced by local conformation.

e) The viscosity at the \( \theta \) temperature is much more complex than in good solvent — scaling laws do not seem to be applicable.

f) The molecular weight dependence of the viscosity (\( \sim M_n^{-1} \)) is close to reptation model.

It appears that the concentration dependence of the relative viscosity could be interpreted using de Gennes’ theory of semi-dilute solutions. The problem posed by these experiments is the decrease of the viscosity when the temperature increases. The classical temperature dependence of the characteristic length could not account for this variation.

Acknowledgments. — The authors gratefully thank J. P. Cohen Addad for the Precious PIB-sample; P. G. de Gennes, P. Pincus and R. Ball for helpful and stimulating discussions.

Appendix 1

Let us suppose that a chain follows — on \( m \) monomers a local rigidity:

\[
b = m a, \quad a \text{ being the length of a monomer and } b \text{ the persistence length},
\]

— on \( g_r \) monomers a Gaussian conformation whose end to end distance \( \psi \) is:

\[
\psi = \left( \frac{g_r}{m} \right)^{1/2} b \quad \text{(A.1)}
\]

Using the Flory equation for the expansion factor, or following reference [29], near \( \theta \) temperature, the variation of \( g_r \) with the reduced temperature \( \tau \):

\[
\t = \frac{T - \theta}{T} = 1 - 2 \chi
\]

is

\[
g_r \approx \frac{m^3}{\tau^2}. \quad \text{(A.2)}
\]

In part 1, we have considered that the effective length of a monomer was defined through \( \xi = l g^2 \) and that the excluded volume effect is effective at any scale. In particular

\[
\psi = l g^2. \quad \text{(A.3)}
\]

(A.1) and (A.3) are compatible only if:

\[
l \approx m (3/3) \tau^{3/3}. \quad \text{(A.4)}
\]

Substituting this expression of \( l \) (A.4) in the formula (2) giving \( \xi \) as a function of \( c \) and \( l \) we obtain:

\[
\xi \approx a (c a^3)^{1/3} \tau^{2/3} m^{1/3} \tau^{1/3}.
\]

using

\[
\theta \approx c a^3, \quad g_r \approx \frac{m^3}{\tau^2} \quad \text{and } \eta \approx \left( \frac{N}{g} \right)^3
\]

\[
\frac{g}{g_r} = (c a^3)^{1/3} m^{1/3} \tau^{2/3} \tau^{1/3} \quad \text{(A.5)}
\]
and 
\[ \eta_r \approx N^3 (ca^2)^{3 \nu - 1} m \frac{q_{(2-\xi)}^{2-\xi} q_{(2-\xi)}^{1-1}}{\tau^{3\nu-1}} \]  
(A.6)

Usually \( m = U/kT \), \( k \) is the Boltzmann’s constant and \( U \) the bending energy per monomer. The temperature dependence of the quantities \( g/g_r \) and \( \eta_r \) are:

\[ \frac{g}{g_r} \sim T^{3\nu - 1} \tau^{3\nu - 1} \]

\[ \eta_r \sim T^{-\frac{q_{(2-\xi)}^{2-\xi} q_{(2-\xi)}^{1-1}}{\tau^{3\nu - 1}}} \]

Appendix 2
NUMERICAL VALUES CORRESPONDING TO FIGURES 2, 3, 6, 7; THE RELATIVE VISCOSITY ACCURACY IS 2 %.

<table>
<thead>
<tr>
<th>System</th>
<th>( M_w )</th>
<th>( c \times 10^2 ) g/g</th>
<th>( \eta_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-benzene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( T = 32 \degree C )</td>
<td>24 \times 10^6</td>
<td>0.573</td>
<td>1.11 \times 10^2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.22</td>
<td>1.87 \times 10^3</td>
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<tr>
<td></td>
<td></td>
<td>1.83</td>
<td>1.20 \times 10^4</td>
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<tr>
<td></td>
<td></td>
<td>5.06</td>
<td>1.32 \times 10^6</td>
</tr>
<tr>
<td>PIB-cyclohexane</td>
<td></td>
<td>1.17 \times 10^6</td>
<td>1.43</td>
</tr>
<tr>
<td>( T = 32 \degree C )</td>
<td></td>
<td>3.30</td>
<td>3.16 \times 10^2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.39</td>
<td>2.11 \times 10^3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.00</td>
<td>7.05 \times 10^3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.29</td>
<td>2.49 \times 10^4</td>
</tr>
<tr>
<td>PS-cyclohexane</td>
<td></td>
<td>7.1 \times 10^6</td>
<td>1.44</td>
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<tr>
<td>( T = 35 \degree C )</td>
<td></td>
<td>2.50</td>
<td>3.73 \times 10^2</td>
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<tr>
<td></td>
<td></td>
<td>5.56</td>
<td>2.36 \times 10^4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.13</td>
<td>6.95 \times 10^4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.97</td>
<td>2.68 \times 10^5</td>
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<tr>
<td>PIB-benzene</td>
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<td>1.17 \times 10^6</td>
<td>2.47</td>
</tr>
<tr>
<td>( T = 25 \degree C )</td>
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<td>5.39</td>
<td>1.92 \times 10^3</td>
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<td></td>
<td></td>
<td>9.39</td>
<td>3.49 \times 10^4</td>
</tr>
<tr>
<td>PIB-toluene</td>
<td></td>
<td>1.17 \times 10^6</td>
<td>2.26</td>
</tr>
<tr>
<td>( T = 64 \degree C )</td>
<td></td>
<td>3.26</td>
<td>1.65 \times 10^2</td>
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<td>4.75</td>
<td>7.82 \times 10^2</td>
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<td>6.02</td>
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<td>8.70</td>
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<tr>
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<tr>
<td>( T = 32 \degree C )</td>
<td></td>
<td>6.77 \times 10^6</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.60 \times 10^6</td>
<td>5</td>
</tr>
</tbody>
</table>

The viscosity of the solvent was calculated using the values given in reference [17]. We obtain the following relations:

\[ \eta_0 \text{ benzene} = 1.0603 \times 10^{-4} \exp \left( \frac{1204.5}{T+273} \right) \]

\[ \eta_0 \text{ cyclohexane} = 6.1739 \times 10^{-5} \exp \left( \frac{481.6}{T+273} \right) \]

\[ \eta_0 \text{ toluene} = 1.7321 \times 10^{-4} \exp \left( \frac{1032.7}{T+273} \right) \]

Appendix 3
TEMPERATURE DEPENDENCE OF THE RELATIVE VISCOSITY OF PIB-CYCLOHEXANE SYSTEMS AT DIFFERENT CONCENTRATIONS.

<table>
<thead>
<tr>
<th>( c \times 10^2 ) (g/g)</th>
<th>( T ) (\degree C)</th>
<th>( \eta_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.30</td>
<td>3.15 \times 10^2</td>
</tr>
<tr>
<td></td>
<td>5.39</td>
<td>2.11 \times 10^3</td>
</tr>
<tr>
<td></td>
<td>7.00</td>
<td>7.01 \times 10^3</td>
</tr>
<tr>
<td></td>
<td>9.29</td>
<td>2.48 \times 10^4</td>
</tr>
</tbody>
</table>

References and notes

[3] \( c^* \approx \frac{N}{R^3} \), \( N \) is the number of monomers in a chain of radius \( R \). The concentration in section 1 is expressed in volume number density of monomers, in sections 2 and 3.3 is expressed in g/g.
Here we do not make a distinction between the static exponent, \( v \), and the effective dynamic exponent, \( \nu_D \), because the latter plays a minor role in the concentration exponent value.


One defines the \( \theta \) temperature as the temperature at which the second virial coefficient is zero, for an infinite dilute solution.


Details on the apparatus will be published:


For each solvent we have used the viscosity temperature dependence tabulated in:


PS-benzene and PS-cyclohexane:


PIB-cyclohexane and PIB-\( \theta \) solvent (IAIV):


We are indebted to R. Ball for pointing out this effect.


We know from reference [12] that the concentration exponent value of the cooperative diffusion coefficient is insensitive to the exact value of effective exponents \( \nu_D \) and \( v \).


See for instance:


For numerical values corresponding to figures 2-3-6-7, see appendix 2.