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Intrinsic viscosity of flexible macromolecules:
transition from theta to collapsed state

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Résumé. — Des mesures de viscosité intrinsèque [η] sont effectuées sur des solutions diluées de polystyrène dans le cyclohexane en fonction de la température (T ≈ θ) et de la masse moléculaire (8,2 × 10^4 ≪ M_w ≪ 2,06 × 10^7). Le facteur d'expansion (α^2 = [η]/[η_θ]) de la viscosité intrinsèque obéit à une loi d'échelle dont la variable réduite est (T - θ)/T · √M_w. Lorsque (T - θ)/T · √M_w ≈ 40, la viscosité intrinsèque d'une chaîne effondrée est indépendante de la masse moléculaire. L'indice β reliant la taille à la masse moléculaire est trouvé égal à 1/3.

Abstract. — Intrinsic viscosity measurements have been performed on polystyrene-cyclohexane system as a function of temperature T (T ≈ θ) and as a function of molecular weight (8.2 × 10^4 ≪ M_w ≪ 2.06 × 10^7). The expansion factor α^2 = [η]/[η_θ] of the intrinsic viscosity [η] scales with the reduced variable (T - θ)/T · √M_w. For (T - θ)/T · √M_w ≈ 40, the intrinsic viscosity of a collapsed macromolecule is found to be independent of molecular weight. A value v = 1/3 is therefore given to the index relating size to molecular weight.

Introduction.

Many experimental [1-10] works have been devoted to the collapse of a flexible polymer chain using a great number of different techniques, each experiment being performed on a limited molecular weight range. They lead to puzzling results [11]. Although intrinsic viscosity is very sensitive to chain contraction, as it is proportional to a volume, few measurements [7, 12-14, 9] have been carried out systematically to study the collapse. We have performed such measurements over a large range of molecular weights (M_w = 8.2 × 10^4 up to 2.06 × 10^7). We use the polystyrene-cyclohexane system below the θ temperature, in the dilute regime, with sample concentrations as low as possible in order to observe single chain behaviour over a temperature range as wide as possible.

In the first part of this paper we recall briefly the theoretical predictions of the intrinsic viscosity. In the second part we describe the experimental conditions. In parts three and four we present and discuss our results, respectively.

1. Theoretical background.

From the specific viscosity η_sp of a macromolecular solution, a molecular quantity can be derived: [η], the intrinsic viscosity of one macromolecule. η_sp is defined as:

$$\eta_{sp}(C, M, T) = \frac{\eta(C, M, T) - \eta_0(T)}{\eta_0(T)} ,$$

(1)

with η being the viscosity of the solution, η_0, the viscosity of the solvent, C, the monomer concentration of the solution, M, the molecular weight of the macromolecule, and T, the temperature. In dilute solution η_sp is written as a second order expansion in concentration [15]:

$$\eta_{sp} = [\eta] \cdot C \cdot (1 + K_q \cdot C) .$$

(2)
Usually \([K_t = K_H][\eta]\), with \(K_H\) being the Huggins interactions coefficient. From homogeneity arguments [16-18], \([\eta]\) can be written as:

\[
[\eta] \simeq R^3/M ,
\]

where \(R\) is the end to end distance of the macromolecule which scales with \(M\) as \(M^v\), then \([\eta] \sim M^{3v-1}\). At the \(\theta\) temperature, where thermodynamic interactions vanish, the macromolecule obeys Gaussian statistics, with \(v = 1/2\) and \([\eta_0] \sim R_0 \sim M^{0.5}\).

For the polystyrene-cyclohexane system when the temperature is decreased below \(\theta\), thermodynamic interactions are attractive and intrinsic viscosity decreases because macromolecules contract. This contraction can be described using the modified Flory equation [18, 19]:

\[
\alpha^5 - \alpha^3 - \frac{y}{\alpha^3} = cz ,
\]

where \(\alpha\) is the end-to-end expansion factor \((\alpha = R/R_0)\), \(c\) is a constant of order unity, \(z\) is the excluded volume parameter, \(y\) is a coefficient proportional to the ternary cluster integral frequently related to steric hindrance [18-20], which is constant and independent of \(T\). This mean field description, as well as scaling approach, lead to one universal reduced variable which is [19]:

\[
z \simeq \frac{v}{3}\sqrt{N} ,
\]

where \(v\) is the binary cluster integral, \(N\), the number of statistical units of length \(l\). Usually the following assumptions are made:

- \(N\) is proportional to the molecular weight \(M\),
- \(v\) is proportional to the relative temperature \(\tau = (T - \theta)/\theta\),
- \(l\) is a constant independent of \(N\) and \(T\).

Then the reduced variable of the end-to-end expansion factor is written as:

\[
z \sim \tau \sqrt{M} .
\]

The intrinsic viscosity expansion factor, defined as \(\alpha_\eta^3 = [\eta]/[\eta]_0\), is also an universal function of the same reduced variable. \(\alpha_\eta^3 \simeq \alpha^3\) is expected to have the following behaviour.

1) In the vicinity of the \(\theta\) temperature, the so-called \(\theta\) domain, \(\alpha_\eta^3\) can be developed as a linear function of \(\tau \sqrt{M}\). Experimentally it is found that for the hydrodynamic radius \([9]\) the \(\theta\) domain extends down to \(\tau \sqrt{M} \approx -10\).

2) In the collapsed regime which corresponds to

high negative values of \(\tau \sqrt{M}\) and \(x < 1\) in formula (4), \(\alpha_\eta^3\) can be expressed as a power law in \(\tau \sqrt{M}\):

\[
\alpha_\eta^3 \sim (\tau \sqrt{M})^x, \quad \text{with} \quad x = 3(2v - 1) = -1 ,
\]

and

\[
v = 1/3 .
\]

In the collapsed regime the volume of the macromolecule is proportional to \(M\), the intrinsic viscosity is molecular weight independent and decreases as the temperature decreases:

\[
[\eta] \sim M^{0} \tau^{-1}. \tag{7}
\]

2. Experimental conditions and procedures.

The viscosity \(\eta\) was measured with a capillary or a microcapillary viscometer (Viscosboy from Lauda) immersed in a regulated water bath (see the table). The viscosity was deduced from the flow time \(t\) in the capillary which was measured by means of two photodiodes; the reproducibility on the flow time was \(10^{-4}\). The specific viscosity of the solution is \(\eta_{sp} = (t - t_0)/t_0\) [21] with \(t\) and \(t_0\) being equal to the flow time of the solution and of the pure solvent, respectively. We limited our study to temperatures lower than 36 °C, slightly above the \(\theta\) temperature of the polystyrene-cyclohexane system (35 °C). At low temperatures the experimental range is limited from below by the demixing temperature of the solution, previously determined by light scattering experiments. The temperature was measured close to the capillary by a thermometer with an accuracy of 0.05 °C.

We use polystyrene (PS) of the narrowest polydispersity available (see the table) and cyclohexane from Prolabo without any purification. We did not filter the solutions because, within the experimental accuracy, the measured specific viscosity of a solution \((M_w = 1.71 \times 10^5, C = 10^{-3} \text{g/cm}^3)\) was the same with or without a filtration on a 0.22 μm Millipore filter.

Measurements were performed with sample concentrations as low as possible. In this way:

- we have enlarged the temperature range because the demixing temperature is concentration dependent,
- we have minimized the influence of the interaction term on \(\eta_{sp}\) (see Eq. (1)).

But as the concentration is lowered \(\eta_{sp}\) decreases and the determination of \([\eta]\) becomes more and more inaccurate. In the case of the highest molecular weights, for which measurements with samples of very low concentrations are necessary, we used a differential method. We measured simultaneously both \(t\) and \(t_0\) at the same temperature, with two viscometers immersed in the same bath and previously calibrated with pure solvent.

Measurements were performed on solutions of con-
### Characteristics of samples and capillaries.

<table>
<thead>
<tr>
<th>( M_w )</th>
<th>( M_w/M_n )</th>
<th>from</th>
<th>( \dot{\gamma}(1) )</th>
<th>( \dot{\gamma}(2) )</th>
<th>( \dot{\gamma}(3) )</th>
<th>Symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4 ( \times 10^4 )</td>
<td>1.02</td>
<td>1</td>
<td>n.m.</td>
<td>n.m.</td>
<td>6.0 ( \times 10^{-5} )</td>
<td></td>
</tr>
<tr>
<td>4.39 ( \times 10^4 )</td>
<td>1.01</td>
<td>2</td>
<td>n.m.</td>
<td>n.m.</td>
<td>1.4 ( \times 10^{-4} )</td>
<td></td>
</tr>
<tr>
<td>8.2 ( \times 10^4 )</td>
<td>1.08</td>
<td>1</td>
<td>1.0 ( \times 10^{-4} )</td>
<td>n.m.</td>
<td>3.6 ( \times 10^{-4} )</td>
<td></td>
</tr>
<tr>
<td>1.71 ( \times 10^5 )</td>
<td>1.02</td>
<td>1</td>
<td>3.0 ( \times 10^{-4} )</td>
<td>6.8 ( \times 10^{-4} )</td>
<td>1.1 ( \times 10^{-3} )</td>
<td>( \nabla )</td>
</tr>
<tr>
<td>4.22 ( \times 10^5 )</td>
<td>1.05</td>
<td>2</td>
<td>n.m.</td>
<td>n.m.</td>
<td>4.2 ( \times 10^{-3} )</td>
<td></td>
</tr>
<tr>
<td>7.75 ( \times 10^5 )</td>
<td>1.01</td>
<td>2</td>
<td>n.m.</td>
<td>n.m.</td>
<td>1.1 ( \times 10^{-2} )</td>
<td></td>
</tr>
<tr>
<td>1.26 ( \times 10^6 )</td>
<td>1.05</td>
<td>2</td>
<td>n.m.</td>
<td>n.m.</td>
<td>2.2 ( \times 10^{-2} )</td>
<td>( x )</td>
</tr>
<tr>
<td>3.84 ( \times 10^6 )</td>
<td>1.05</td>
<td>2</td>
<td>3.2 ( \times 10^{-2} )</td>
<td>n.m.</td>
<td>1.1 ( \times 10^{-1} )</td>
<td>( \bullet )</td>
</tr>
<tr>
<td>6.77 ( \times 10^6 )</td>
<td>1.14</td>
<td>2</td>
<td>7.6 ( \times 10^{-2} )</td>
<td>n.m.</td>
<td>2.6 ( \times 10^{-1} )</td>
<td>( + )</td>
</tr>
<tr>
<td>20.6 ( \times 10^6 )</td>
<td>—</td>
<td>2</td>
<td>0.4</td>
<td>n.m.</td>
<td>n.m.</td>
<td></td>
</tr>
</tbody>
</table>

\( M_w \) : weight average molecular weight.
\( M_w/M_n \) : polydispersity index.
Polystyrene furnished by 1 : CRM Strasbourg (France)
2 : Toyo Soda Inc. (Japan).
\( \dot{\gamma}(1) \) : reduced shear rate at \( \theta \) temperature of capillary 1 (microviscometer I).
\( \dot{\gamma}(2) \) : capillary 2 (viscometer OB).
\( \dot{\gamma}(3) \) : capillary 3 (viscometer OC).
The viscometers are KPG Ubbelohde viscometers with suspended level bulb from Schött Geräte (West Germany).

The molecular weight symbols are those used on figures 4, 5, 6.
n.m. indicates that no measurement has been performed in the capillary.

The overlap concentration \( C^* \) at the \( \theta \) temperature is taken to be equal to 40\( \sqrt{M} \) (g/cm\(^3\)) which corresponds to:

- the usual order of magnitude \( 3[\eta]_0 \) [22, 23],
- the limit between dilute and semi-dilute behaviour of the osmotic bulk modulus from light scattering measurements [24].

To check experimentally the absence of shear rate effect we used different capillaries with same solutions. The usual parameter is the reduced shear rate \( \dot{\gamma} = \eta_0[\eta] M_w \Gamma/RT \) where \( \Gamma \) is the shear rate calculated from the viscometer characteristics (see the Table), \( R \) is the gas constant and \( \eta_0[\eta] M_w/RT \) is proportional to the relaxation time of the first mode of a single macromolecule. Reduced shear rates at the \( \theta \) temperature are listed in the table. All the measurements, except with the 2.06 \( \times 10^7 \) molecular weight, were performed with \( \dot{\gamma}(\theta) \leq 0.3 \). No shear rate dependence of \( \eta_{sp} \) was observed at the \( \theta \) temperature, in agreement with reference [25]. At lower temperatures some difficulties were encountered, which we shall discuss in the next section.

Since the capillaries were not sealed, there was a slight evaporation of the solvent when the experiment took a few days. With a cathetometer we measured the variation of volume of the solution and then we controlled the variation of concentration \( dC \).

We made a correction of the specific viscosity \( \frac{d \eta_{sp}}{\eta_{sp}} = \frac{dC}{C} \) with \( dC/C \) always smaller than 5\%. To check the validity of the correction the solution were always divided in two, and we performed:

- an experiment beginning from \( \theta \) and decreasing \( T \),
- another one beginning with low temperature and increasing \( T \).

After evaporation corrections we found the same results in both cases.

Measurements, performed with concentrations \( C \) such that \( \frac{C}{C^*} > 10^{-3} \), lead to an intrinsic viscosity accuracy of 5\%, the main error comes from the determination of the concentration. By a normalization at the \( \theta \) temperature, \( \eta_{sp}^3 \) is obtained with more precision (2\%):

\[
\frac{\eta_{sp}(C, T)}{\eta_{sp}(C, \theta)} = \eta_{sp}^3 \left( \frac{1 + K_4(T) C}{1 + K_4(\theta) C} \right). \tag{8}
\]

On the other hand with concentrations such that \( C/C^* < 10^{-3} \) the main error comes from the flow time determination and the intrinsic viscosity accuracy is such that:

\[
\frac{\Delta[\eta]}{[\eta]} \cdot \frac{C}{C^*} \approx 5 \times 10^{-5}.
\]
3. Experimental results.

We take 35 °C as the θ temperature: it is the temperature at which the second virial coefficient of the osmotic pressure vanishes [26]. For the whole range of molecular weight and concentration and for the three capillaries, the theta specific viscosity is always proportional to the concentration: \( K_\eta(\theta) \) (see form (2)) is not detectable and \( \eta_\eta(C, \theta) = \eta_\eta(C, 0) \).

For \( 2.4 \times 10^4 \leq M_w \leq 6.77 \times 10^6 \) we find

\[
\frac{[\eta]_\theta}{\sqrt{M_w}} = (9.04 \pm 0.24) \times 10^{-2}
\]

in agreement with other measurements [7, 23]. One must note that a fit to a power low leads to (see Fig. 1):

\[
[\eta]_\theta = 7.7 \times 10^{-2} M_w^{0.51 \pm 0.01} \text{ (cm}^3/\text{g)}.
\]

(9)

This result confirms that:
- the evaporation corrections are valid,
- there is no shear rate effect in these measurements at the θ temperature.

![Fig. 1. Log Log plot of the intrinsic viscosity (cm³/g) as a function of molecular weight. The point marked ⊗ is not used in the fitting of formula (9).](image)

We could not check experimentally the absence of shear rate dependence for the sample of molecular weight \( M_w = 2.06 \times 10^7 \). The reduced shear rate at the θ temperature (cf. Table) of this sample in the microcapillary corresponds to the onset of shear rate effect in [25], but the corresponding correction is estimated to be less than 2 % undetectable in our experiment.

One can see in figure 1, that for this sample the measured value of \( [\eta]_\theta = 360 \pm 20 \text{ cm}^3/\text{g} \), in agreement with Toyo Soda’s value 340 cm³/g, is smaller than that expected from formula (9). This is related to the polydispersity of the sample, which viscosity averaged molecular weight \( M_e \) is equal to \( 1.6 \times 10^7 \).

3.1 Concentration dependence at \( T < \theta \). — For a given sample, the two capillaries with lowest shear rates (Cap. 1 and 2 cf. Table) lead to the same determination of the specific viscosity \( \eta_\sp{sp}(C) \) which is proportional to the concentration for the whole range of \( T \) and \( M_w \). On the contrary with capillary 3 (cf. Table) for \( T < 27 \) °C and whatever the molecular weight, the evaluation of \( \eta_\sp{sp} \) is different and presents a second order concentration dependence (\( \sim K_\eta \) term in formula (2)). It seems that this effect cannot be understood from an exclusively hydrodynamic point of view. Hydrodynamic interactions are proportional to the occupied volume of the macromolecules and decrease as the temperature is lowered. This effect is related to the increase of thermodynamic interactions as the temperature is lowered. The phenomena involved could be, for instance:
- a macromolecular adsorption on the wall of the capillary leading to a concentration variation of the sample.
- a chain deformation induced by the flow.

Measurements presented further on are not affected by this problem, and there is no \( K_\eta \) interaction coefficient for the entire range of temperature; thus \( \eta_\sp{sp}/C \) is always independent of \( C \).

3.2 Intrinsic viscosity. — For \( M_w = 1.71 \times 10^5 \) and \( 6.77 \times 10^6 \), \( \eta_\sp{sp}/\eta_\sp{po} \) is plotted in figures 2 and 3 versus temperature. In each case the experimental points are obtained with two different concentrations and two capillaries of different shear rate. Neither of these two parameters has an influence on the viscosity expansion factor \( c_\eta \).

Figure 4 is a linear representation of the intrinsic viscosity expansion factor \( c_\eta^2 \), as a function of \( \tau\sqrt{M_w} \) for molecular weights ranging from \( 8.2 \times 10^4 \) to \( 6.77 \times 10^6 \). All the experimental points lie on a master curve down to \( \tau\sqrt{M_w} \approx -50 \). Our measurements are in agreement with those of reference [7].

![Fig. 2. Viscosity expansion factor versus temperature (°C) obtained with \( M_w = 1.71 \times 10^5 \) and \( \times \) cap. 1, ○ cap. 2, \( C = 10^{-3} \text{ C}^* \), \( \times \) cap. 1, \( \times \) cap. 2, \( C = 10^{-2} \text{ C}^* \). Characteristics of the capillaries (cap.) are given in the table.](image)
Fig. 3. — Viscosity expansion factor *versus* temperature (°C) obtained with $M_w = 6.77 \times 10^6$ and $\eta + \text{cap. 1, 0 \text{ \cap. 3, } C = 3 \times 10^{-4} C^3 }$; $\times$ cap. 1, $\sqrt{\text{cap. 3, } C = 10^{-2} C^3}$. Characteristics of the capillaries (cap.) are given in the table.

Fig. 4. — Intrinsic viscosity expansion factor as a function of the reduced temperature variable $\tau \sqrt{M_w}$ obtained with $8.2 \times 10^4 \leq M_w \leq 6.77 \times 10^6$ (for symbols see the Table).

Fig. 5. — Plot of $\alpha^2_\eta \times |\tau \sqrt{M_w}|$ *versus* the reduced temperature variable $\tau \sqrt{M_w}$. The collapsed regime appears at $\tau \sqrt{M_w} \approx -40$ (for symbols see the Table).

Measurements performed on the sample $2.06 \times 10^7$ are omitted in the former treatment which is very sensitive to polydispersity. One can easily show that the mean molecular weight $\bar{M}$ to be used in the reduced temperature variable $\tau \sqrt{M_w}$ is:

- near the $\theta$ temperature $|\tau \sqrt{\bar{M}}| < 10$,
  $$\bar{M} = \frac{M_w^2}{\bar{M}_e}$$
- far from the $\theta$ temperature $|\tau \sqrt{\bar{M}}| > 40$,
  $$\bar{M} = M_w.$$

Thus a polydispersity effect may explain that the experimental results obtained with $M_w = 2.06 \times 10^7$ do not fit with the function of $\tau \sqrt{\bar{M}}$ shown in figure 4.

As a definitive demonstration of the collapse regime, $[\eta]$ is plotted, in figure 6, *versus* the relative tempera-

Fig. 6. — Log Log representation of the intrinsic viscosity (cm$^3$/g) *versus* the relative temperature $\tau$ for $M_w = 3.84 \times 10^6$, $6.77 \times 10^6$, $2.06 \times 10^7$ (for symbols see the Table).

obtained with a molecular weight of $3.19 \times 10^7$ on a smaller range at $\tau \sqrt{M_w}$. Thus $\alpha^2_\eta$ is a universal function of the reduced variable $\tau \sqrt{M_w}$, whatever the molecular weight.

From $\theta$ down to $\tau \sqrt{M_w} \approx -10$, $\alpha^2_\eta$ decreases linearly as:

$$\alpha^2_\eta = 1 + 8 \times 10^{-3} \tau \sqrt{M_w}.$$  

The power law (6) is tested in the representation of figure 5. For $-60 < \tau \sqrt{M_w} < -40$, the quantity $|\alpha^2_\eta \times \tau \sqrt{M_w}|$ is a constant equal to 27 thus:

$$\alpha^2_\eta = \frac{27}{|\tau \sqrt{M_w}|} \text{ for } -60 < \tau \sqrt{M_w} < -40.$$  

This corresponds to the collapsed regime with $v = 1/3$.  

 obtains 6.77 x 10^6 and $\eta + \text{cap. 1, 0 \text{ \cap. 3, } C = 3 \times 10^{-4} C^3 }$; $\times$ cap. 1, $\sqrt{\text{cap. 3, } C = 10^{-2} C^3}$. Characteristics of the capillaries (cap.) are given in the table.

Fig. 4. — Intrinsic viscosity expansion factor as a function of the reduced temperature variable $\tau \sqrt{M_w}$ obtained with $8.2 \times 10^4 \leq M_w \leq 6.77 \times 10^6$ (for symbols see the Table).

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Measurements performed on the sample $2.06 \times 10^7$ are omitted in the former treatment which is very sensitive to polydispersity. One can easily show that the mean molecular weight $\bar{M}$ to be used in the reduced temperature variable $\tau \sqrt{M_w}$ is:

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Thus a polydispersity effect may explain that the experimental results obtained with $M_w = 2.06 \times 10^7$ do not fit with the function of $\tau \sqrt{\bar{M}}$ shown in figure 4.

As a definitive demonstration of the collapse regime, $[\eta]$ is plotted, in figure 6, *versus* the relative tempera-
ture $\tau$ for $M_u = 3.84 \times 10^6$ and $6.77 \times 10^6$. The intrinsic viscosity, inversely proportional to the relative temperature $\tau$, is molecular weight independent; both molecular weight ($3.84 \times 10^6$ and $6.77 \times 10^6$) have same mean value of the intrinsic viscosity:

$$[\eta] = 117 \pm 12 \text{ cm}^3/\text{g} \quad \text{for} \quad T = 28^\circ \text{C}.$$  

In the same figure 6 we report measurements obtained with $M_w = 2.06 \times 10^7$, one can see that, at a given temperature ($T = 29.5^\circ \text{C}$), both molecular weights $6.77 \times 10^6$ and $2.07 \times 10^7$ have same mean value of intrinsic viscosity:

$$[\eta] = 158 \mp 16 \text{ cm}^3/\text{g}.$$  

This fact demonstrates that for $\tau \sqrt{M_w} \leq -40$ the chain is collapsed: intrinsic viscosity does not depend on molecular weight and consequently on polydispersity index, at a given $T$.

4. Discussion.

In the previous section, we have determined that for $\tau \sqrt{M_w} \leq -40$ a collapsed macromolecule is observed. We discuss here how this collapsed regime is reached using:

1) a Flory mean field approach with $[\eta]$ proportional to a global volume,

2) a scaling approach distinguishing between static and dynamic lengths.

For $T > \theta$ experimental results below the $\theta$ temperature can be described phenomenologically by:

- near $\theta$, $\tau \sqrt{M_w} > -10$,
  $$\alpha_\theta^3 \approx 1 + 8 \times 10^{-3} \tau \sqrt{M_w}$$  

- in the collapsed regime, $\tau \sqrt{M_w} < -40$,
  $$\alpha_\sigma^3 \approx -\frac{27}{\tau \sqrt{M_w}}$$

4.1 Mean-field approach. — Near $\theta$ and for $T > \theta$ it is known [28, 16] that the intrinsic viscosity measurements are in agreement with a linear expansion in $z$ ($\alpha_\theta^3 = 1 + 1.05 z$) for $0 \leq z \leq 0.6$ with:

$$z \approx 8 \times 10^{-3} \tau \sqrt{M_w} [29].$$  

Such a behaviour is well predicted by an original Flory equation (Eq. (4) with $y = 0$) in the context of the two parameter theory where $\alpha = 1$ for $\tau = 0$. The expansion (10.a) is an experimental extension of this linear expansion to negative values of $z$ valid till $z \approx -8 \times 10^{-2}$.

In order to prevent the instability of the chain at $T < \theta$ (in the theoretical description), the three body interaction term is introduced, leading to the modified Flory equation (Eq. (4) with $y \neq 0$).

For $\tau = 0$, $\alpha_\theta$ is not equal to 1 and obeys the equation:

$$\alpha_\theta^3 - \alpha_\theta^3 - \frac{y}{\alpha_\sigma^3} = 0.$$  

The modified Flory equation can be expanded as:

- for $\alpha \approx 1$
  $$\left(\frac{\alpha}{\alpha_\theta}\right)^{3} = 1 + \frac{3}{2 + 3 \eta} \alpha_\sigma^3,$$  

- for $\alpha \ll 1$
  $$\left(\frac{\alpha}{\alpha_\theta}\right)^{3} = -\frac{y}{\alpha_\sigma^3 \cdot c z}.$$  

Using formulae (10), (11), (12) and an identification of $\left(\frac{\alpha}{\alpha_\theta}\right)^{3}$ with $\alpha_\sigma^3$, we determine an order of magnitude of $y$ and $\alpha_\sigma$:

$$0.5 \leq y \leq 1$$

$$1.1 \leq \alpha_\sigma \leq 1.2.$$  

This $y$ value corresponds to a smooth shrinking of the chain [19] and is compatible with experimental observation and with the measurements of reference [30]. But there is a shift $\Delta \theta$ between the two definitions of the $\theta$ temperature, $\tau = 0$ and $\alpha = 1$, $(\Delta \theta \cdot M_w^{0.5} \approx 10^6)$, which is molecular weight dependent. $\Delta \theta$ may be due to an artifact of the mean field calculation [19].

4.2 Scaling approach. — This theory considers the asymptotic regimes. In order to describe the cross over from $\theta$ to good solvent regimes, the blob model [17] has been introduced using the reduced temperature variable $\tau \sqrt{M}$.

It has been suggested [17] that the intrinsic viscosity is:

$$[\eta] \approx \frac{R_H \cdot R_G^2}{M}.$$  

$R_G$ being the radius of gyration of the chain and $R_H$ its hydrodynamic radius. This expression is well verified in very good solvents (cf. [17]). Considering the radius of gyration expansion factor $\alpha_G$ and the hydrodynamic radius expansion factor $\alpha_H$, $\alpha_\sigma^3$ may be expressed as:

$$\alpha_\sigma^3 \approx \alpha_G^3 \cdot \alpha_H.$$  

Below $\theta$ we use the same approach. Figure 7 is a plot of $\alpha_G^3 \cdot \alpha_H$ versus $\tau \sqrt{M_w}$, where $\alpha_G^3 \cdot \alpha_H$ values are interpolated from light scattering measurements of $R_G$ [7, 8] and $R_H$ [9] on the PS-cyclohexane system [31]. In the range of $\tau \sqrt{M_w} (-35 \leq \tau \sqrt{M_w} \leq 0)$ where such measurements are available. We do not find good agreement between $\alpha_G^3 \cdot \alpha_H$ and $\alpha_G^3 \cdot \alpha_H$. In figure 7...
Conclusion.

Intrinsic viscosity measurements have been performed on polystyrene-cyclohexane system for $T < \theta$. To perform measurements in the collapsed regime the following conditions must be fulfilled:

- high molecular weight samples ($M_w \gtrsim 3.84 \times 10^6$)
- low concentration ($C/C_0 \lesssim 5 \times 10^{-4}$).

Thus a precise viscosity measurement is required $\frac{\delta \eta}{\eta} = \pm 10^{-4}$. The intrinsic viscosity expansion factor scales with a single reduced variable $\tau \sqrt{M_w}$ whatever the molecular weight ($8.2 \times 10^4 \leq M_w \leq 6.77 \times 10^6$) from the $\theta$ to the collapsed regime ($\tau \sqrt{M_w} \lesssim 40$). In this asymptotic regime, $[\eta]^{-1}$ is independent of molecular weight and is then directly proportional to the internal concentration of a chain of infinite molecular weight.

An index relating size to molecular weight $v = 1/3$ is derived at several temperatures through the asymptotic behaviour $[\eta] \sim |\tau|^{-1} M_w^v$ with $M_w = 3.84 \times 10^6$, $6.77 \times 10^6$, and $2.06 \times 10^7$.

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References and notes

This $\theta$ shift would only affect by 10% the coefficients in the $\alpha_4$ expressions which are given without error bars and rather as order of magnitude.

We chose measurements for which the $\tau M_w$ conservation is clearly established.