Characteristic numbers of polymers in dilute solution: a universal description of the cross-over effects

A. Dondos

To cite this version:


HAL Id: jpa-00210573
https://hal.archives-ouvertes.fr/jpa-00210573
Submitted on 1 Jan 1987

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Characteristic numbers of polymers in dilute solution: a universal description of the cross-over effects

A. Dondos

University of Patras, Department of Chemical Engineering, 26110 Patras, Greece

(Reçu le 29 décembre 1986, révisé le 12 mai 1987, accepté le 19 mai 1987)

Résumé. — Le comportement viscosimétrique de onze systèmes polymère-solvant a été analysé afin de déterminer les nombres caractéristiques au début et à la fin d'une zone de raccordement. Au début de cette zone les polymères passent d'un comportement gaussien à un comportement de volume exclu (masse moléculaire $M_c$) et à la fin de cette même zone les polymères passent d’un comportement partiellement obéissant au volume exclu à un comportement obéissant pleinement au volume exclu (masse moléculaire $M'_c$). A ce deuxième point on peut dire que nous avons une statistique de volume exclu à longue échelle et nous avons le début de la linéarité entre log $\eta$ et log $M$. Nous avons montré qu’au début et à la fin de la zone de raccordement le poids moléculaire ou le nombre des motifs monomères sont différents pour les différents polymères et il existe une relation linéaire entre les motifs monomères et la rigidité de la chaîne pour le deuxième point de raccordement. Par contre, le nombre des segments statistiques au début et à la fin de la zone de raccordement est presque le même pour tous les polymères et cela confirme la validité d’une description universelle de solutions des polymères.

Abstract. — The viscosimetric behaviour of eleven polymer-solvent systems is analysed in order to determine the characteristic numbers in the beginning and in the end of the cross-over region. In the beginning we have a cross-over between Gaussian and excluded volume behaviour and in the end a cross-over between partial excluded-volume and complete excluded-volume behaviour (in the second cross-over the chain exhibits an excluded volume statistics on a macroscopic scale and starts the linearity between log $\eta$ and log $M$). We show that in the beginning and in the end of the cross-over region the characteristic molecular weight or the characteristic number of monomers is different for different polymers and the second is related to the stiffness of the chain. In the contrary, the characteristic number of statistical segments in the beginning and in the end of the cross-over region are about the same for all the polymers, and this result confirms the validity of a universal description of polymer solutions.

1. Introduction.

In three previous articles [1-3] we have studied the viscosimetric behaviour of low molecular weight polymer samples. We were mostly interested in the deviation of the intrinsic viscosity of low molecular weight samples from the straight line which gives the representation of the solution of the Mark-Houwink-Sakurada (M-H-S) equation obtained with the polymer samples of higher molecular weights. This deviation leads to a wrong value of the molecular weight if we use the M-H-S equation constants and this wrong value can be of the order of 200% in the case of very low molecular weight sample ($M < 5000$).

A relation is proposed [3] which gives the error in the determination of the molecular weight of a polymer sample (of low molecular weight) and this error is directly related to the M-H-S equation exponent for a number of polymer-solvent systems. Another study [1, 2] has given a new relation between the intrinsic viscosity and the molecular weight of a polymer in the molecular weight region in which the relation log $\eta$ versus log $M$ is not a straight line. The proposed relation is:

$$\frac{1}{\eta} = -A_2 + \frac{A_1}{M^{1/2}}. \quad (1)$$

This semi-empirical relation is tightly related to the Stockmayer-Fixman-Burchard equation [4, 5] and provides a very good straight line between $[\eta]^{-1}$ and $M^{-1/2}$ in a molecular region from 1 000 to 100 000 or 200 000 [2].

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphys:019870048090143900
The principal aim of this article is to investigate for which molecular weight the deviation of the M-H-S equation starts for a number of polymer-solvent systems. In the case of polyoxymethylene glycol the log [\eta] versus log M relation is linear till a molecular weight of the order of 3000, while in the case of other polymers the log [\eta] versus log M relation is non-linear when the molecular weight is lower than 100000. We will try to correlate the point of the validity of the M-H-S equation for each polymer with the parameter \sigma which characterizes the stiffness of the macromolecular chain of the polymer. We will show that the point from which we have the beginning of the linearity between log [\eta] and log M starts in a different molecular weight or different number of monomers for the different polymers but the number of statistical segments in this point is about the same for all the polymers.

2. Experimental results.

The viscosimetric results of this article have been taken mostly from the literature or are our results presented in some of our previous articles [1-3, 6]. The intrinsic viscosity [\eta] of the macromolecular solutions will be given in cm^3/g.

In figure 1 we give the log [\eta] versus log M representation for three polymer-solvent systems: polyethyleneglycol (POE)-dimethylformamide (DMF) [7], poly[2-(triphenylmethoxy) ethyl methacrylate] (PTEMA)-toluene [8] and polyvinylacetate (PVAc)-chloroform [9]. The deviation of [\eta] from the linearity of log [\eta] versus log M representation is appeared in a very different molecular weight for each polymer. So for the POE the deviation starts in the molecular weight region of 3 500 to 4 500, for the PTEMA the deviation starts in the molecular weight region from 160 000 to 180 000 and for the PVAc the deviation starts in the region of 20 000 to 24 000 (Fig. 1). For the above polymers the solvents are very good solvents of the polymers (exponent a of the M-H-S equation higher than 0.72, Tab. I).

If, in figure 1, M_c' is the critical molecular weight in which starts the linearity between log [\eta] and log M, the molecular weight region of 3 500 to 4 500, for the PTEMA the deviation starts in the molecular weight region from 160 000 to 180 000 and for the PVAc the deviation starts in the region of 20 000 to 24 000 (Fig. 1). For the above polymers the solvents are very good solvents of the polymers (exponent a of the M-H-S equation higher than 0.72, Tab. I).

Table I. — Exponent of the M-H-S equation a, K_o parameter, stiffness parameter \sigma, statistical segment length A, number of monomers in a statistical segment n_o, characteristic molecular weight M_e, characteristic number of monomers n_e, characteristic number of statistical segments N_e in the onset of excluded-volume behaviour, characteristic molecular weight M_c, characteristic number of monomers n_c and characteristic number of statistical segments N_c in the beginning of the complete excluded-volume behaviour and the ratio N_c/N_e for eleven polymer-solvent systems (the K_o, M_e and M_c are mean values).

<table>
<thead>
<tr>
<th>System</th>
<th>a</th>
<th>K_o x 10^2</th>
<th>\sigma (\AA)</th>
<th>n_o</th>
<th>M_e</th>
<th>n_e</th>
<th>N_e</th>
<th>M_c</th>
<th>n_c</th>
<th>N_c</th>
<th>N_e/N_c</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS-Toluene</td>
<td>0.71</td>
<td>6.4</td>
<td>1.3</td>
<td>10</td>
<td>3.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>POE-DMF</td>
<td>0.72</td>
<td>15</td>
<td>1.54</td>
<td>10.8</td>
<td>3.8</td>
<td>600</td>
<td>14</td>
<td>3.7</td>
<td>450</td>
<td>102</td>
<td>27</td>
</tr>
<tr>
<td>PP-Cyclohexane</td>
<td>0.82</td>
<td>16</td>
<td>1.72</td>
<td>12</td>
<td>4.8</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PMMA-benzene</td>
<td>0.69</td>
<td>5</td>
<td>1.8</td>
<td>12</td>
<td>4.8</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>18</td>
<td>000</td>
<td>37.5</td>
</tr>
<tr>
<td>PS-benzene (CCl_4)</td>
<td>0.73</td>
<td>8.1</td>
<td>2.1</td>
<td>19</td>
<td>7.6</td>
<td>3000</td>
<td>29</td>
<td>3.8</td>
<td>25000</td>
<td>240</td>
<td>31.5</td>
</tr>
<tr>
<td>PS-CHCl_3</td>
<td>0.78</td>
<td>8.2</td>
<td>2.2</td>
<td>19</td>
<td>7.6</td>
<td>2500</td>
<td>24</td>
<td>3.2</td>
<td>40000</td>
<td>384</td>
<td>51.0</td>
</tr>
<tr>
<td>PVAc-CHCl_3</td>
<td>0.75</td>
<td>10.2</td>
<td>2.2</td>
<td>18.5</td>
<td>7.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>22000</td>
<td>255</td>
<td>34.5</td>
</tr>
<tr>
<td>PaMS-toluene</td>
<td>0.72</td>
<td>7.6</td>
<td>2.3</td>
<td>21</td>
<td>8.4</td>
<td>3000</td>
<td>26</td>
<td>3.1</td>
<td>30000</td>
<td>255</td>
<td>30.3</td>
</tr>
<tr>
<td>PpCS-toluene</td>
<td>0.75</td>
<td>5.3</td>
<td>2.5</td>
<td>26</td>
<td>10.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>75000</td>
<td>375</td>
<td>36.0</td>
</tr>
<tr>
<td>PVC-PDP-THF</td>
<td>0.63</td>
<td>6.1</td>
<td>2.5</td>
<td>27</td>
<td>11</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>65000</td>
<td>360</td>
<td>34.5</td>
</tr>
<tr>
<td>PTEMA-toluene</td>
<td>0.74</td>
<td>3.1</td>
<td>3.0</td>
<td>36</td>
<td>14.5</td>
<td>30000</td>
<td>80</td>
<td>5.5</td>
<td>175000</td>
<td>470</td>
<td>32.5</td>
</tr>
</tbody>
</table>
log \( M \), \( M_e \) is the molecular weight in which we have the onset of the excluded volume behaviour. Drawing straight lines with slope equal to 0.5 (Fig. 1) we consider that the onset of the excluded volume behaviour \( (M_e) \) takes place at the point in which the curve \( \log [\eta] \) versus \( \log M \) begins to present a slope higher than the slope of these straight lines. Nevertheless the determination of \( M_e \) is less accurate than the determination of \( M'_e \) (large arrows in Fig. 1).

In figure 2 we give the viscosimetric results for PS in benzene or \( \text{CCl}_4 \) (the PS presents a same value of intrinsic viscosity in these two solvents), for PS in \( \text{CHCl}_3 \) and for the copolymer polyvinylchloride-polydiphenylpropane (PVC-PDP) in THF. All the viscosimetric results of figure 2 are our results [1-3, 6].

In figure 3 the relation \( \log [\eta] \) versus \( \log M \) is given for three polymer-solvent systems: PMMA-benzene [10], polypropylene (PP)-hexane [11] and poly-p-cyclohexylstyrene (PpCS)-toluene [12]. The system polydimethylsiloxane (PDMS)-toluene [13] and poly-\( \alpha \)-methylstyrene (PaMS)-toluene [14] are also studied and the \( M_e \) and \( M'_e \) values are given in table I.

3. Discussion and conclusions.

It is clear from figures 1 to 3 that the molecular weight \( M'_e \), above of which a polymer obeys to the M-H-S equation, is different for the different polymers. So for the POE \( M'_e \) is equal to 4 000 and for the PTEMA \( M'_e \) is the order of 175 000.

It is known, according to the scaling theory of macromolecular solutions [15], that above the molecular weight \( M'_e \) the polymer exhibits a complete excluded-volume behaviour or a excluded-volume statistics on a macroscopic scale and the excluded volume index \( v \) presents its asymptotic limit value. According to the renormalization theory the asymptotic limit value of \( v \) is equal to 0.588 [16], instead of the value 0.6 which was proposed by Flory. For the systems polymer-solvent studied in this article the solvents are very good solvents of the polymers, because the exponent \( a \) of the M-H-S equation lies, in general, near the limit value 0.76 as it is predicted by the relation:

\[ [\eta] \sim M^{3\nu-1} \sim M^a. \]

In the molecular weight region below \( M'_e \) we have a continuous variation of the value of exponent \( a \) and we reach finally \( a = 0.5 \) for the molecular weight \( M_e \). As we have already pointed out determination of \( M_e \) is less accurate than that of \( M'_e \). From the critical values \( M'_e \) and \( M_e \) we calculate the critical number of monomers \( n'_c \) and \( n_c \) (Tab. I).

According to the scaling theory, above the critical number \( n_c \), the macromolecular chain starts to present an excluded volume behaviour while below
\( n_c \) the chain is presented as a unique blob and obeys a Gaussian statistics.

We will try now to correlate \( n'_c \) (complete excluded volume behaviour) with the stiffness of the chain as it is expressed by the parameter \( \sigma \) which is obtained by the relation:

\[
\sigma = \left( \frac{R_0^2}{R_0^2} \right)^{1/2}
\]

where \( R_0 \) is the radius of gyration of the chain in the case of free rotation and \( R_0 \) is the unperturbed value of radius of gyration in the considered solvent. The value of \( R_0 \) (or the ratio \( R_0^2/M \)) is calculated from the value of \( K_\theta \) parameter which is determined for all the polymer-solvent systems using the Stockmayer-Fixman-Burchard equation [4, 5] or the relation 1 [1, 2] and which is equal to \( [\eta]_0/M^{1/2} \), where \( [\eta]_0 \) is the intrinsic viscosity at the \( \theta \) conditions. Between \( K_\theta \) and \( R_0 \) there exist the relation

\[
K_\theta = \phi_0 \left( \frac{R_0^2}{M} \right)^{3/2}
\]

where \( \phi_0 \) is Flory’s constant (\( \phi_0 = 2.6 \times 10^{23} \)). The value of \( R_0 \) is calculated from the valance bond angle of each polymer and it is given in « Polymer Handbook » as \( R_0/M^{1/2} \).

In figure 4, we present the variation of the characteristic number of monomers \( n'_c \) as a function of the stiffness coefficient \( \sigma \) for a number of polymers. We can see that there exist a relatively good linear relation between \( n'_c \) and \( \sigma \). This result indicates that, in the case of a polymer presenting a high rigidity (high value of the volume of the side group), we need a high number of monomers in order to arrive to a complete excluded-volume behaviour. On the contrary, in the case of a polymer presenting a high flexibility, the number of monomers in the critical point in which the complete excluded-volume behaviour is obtained, is very low. We may say that the straight line displayed in figure 4 acts as a guide in deciding which equation (M-H-S or Eq. (1)) is to be used depending on the molecular weight of the polymer samples.

In the following, we will show that, even though we have for the different polymers different characteristic numbers of monomers, \( n_c \) and \( n'_c \), the characteristic numbers \( N_c \) and \( N'_c \) of statistical segments are about the same for all polymers. The numbers \( N_c \) and \( N'_c \) are obtained from the relations:

\[
N_c = n_c/n_0 \quad \text{and} \quad N'_c = n'_c/n_0
\]

where \( n_0 \) is the number of monomers in a statistical segment. The value of \( n_0 \) is obtained from the length of statistical segments \( A \) which is calculated from the following equation

\[
A = (K_\theta/[\eta]_0)^{3/2} \frac{m_0}{I}
\]

where \( m_0 \) is the molecular weight of the monomer and \( I \) the monomer projection length. Dividing now the value of the statistical segment length \( A \) by the monomer projection length \( I \), we obtain the number of monomers per statistical segment \( n_0 \). The values of \( n_0, N_c \) and \( N'_c \) are given in table I.

It is very interesting to see that the characteristic numbers \( N'_c \) and \( N_c \) for all the polymers are about the same. This means that according to the chain stiffness we need at the critical points a low or high number of monomers \( n_c \) and \( n'_c \); this number divided by \( n_0 \) gives always the same number of statistical segments at these two critical points; (specifically, 3 to 4 statistical segments in the onset of the excluded volume behaviour and about 31 statistical segments in the onset of the complete excluded-volume statistics, excepts for the system PS-CHCl, Tab. I). This result confirms the validity of a universal description of polymer solutions as it was already predicted [15] and verified [17, 18]. We must point out that the characteristic numbers given here are quite different from the numbers given by Norisuye and Fujita [17] but are very close to the number given for PS by Nystrom and Roots [19].

We can say that we have not two cross-over points but a cross-over region between two different regimes (Gaussian behaviour to complete excluded-volume behaviour). The values of the statistical segments \( N_c \) and \( N'_c \) are the limits of this cross-over region.

Another interesting result obtained here is that the value of the ratio \( x' = N'_c/N_c = n'_c/n_c \) lies for all the polymers between 5 and 10 and this is in accordance with the theoretical predictions of Weill and des Cloizeaux [20] who indicated that the asymptotic limit values of the effective indices \( \nu_c \) and \( \nu_0 \) (especially \( \nu_c \)) are obtained in the same domain of values for \( x (5 < x < 10) \). In other words for \( x > 10 \) or \( M > M_c \) we must have a linearity between \( \log [\eta] \) and \( \log M^{2/3} + \nu_0 \) and this is what we observe in figures 1 to 3. The exponent \( a \) of M-H-
S equation in most cases is also very close to the theoretical value of 0.73 predicted for the good solvents [20] (Tab. I). This value of the exponent \(a\) can be considered as a parameter which permits the universality for the ratio \(n'_c/n_c\) (Tab. I) and the relation between \(\sigma\) and \(n_c\) (Fig. 4). A higher value of the exponent \(a\) observed for the system PS-CCI\(_3\) gives for this system a different value for the ratio \(n'_c/n_c\) and a value for \(n'_c\) which lies out of the straight line of figure 4. On the other hand it is already observed that in the case of a value for \(a\) lower than 0.73 (marginal solvents) the obtained value of \(N_c\) is also very different from the value of 4 [19]. Finally, we must note that the limiting values of the exponents in the variation of polymer dimensions as a function of the ratio \(N/N'_c\), introduced by the scaling theory, are obtained when the ratio \(N/N'_c\) lies between 5 to 10 [18, 21]. Considering that \(N/N'_c\) and \(n'_c/n_c\) express the same quantity for the macromolecular chains our results confirm also the predictions of the theory [21] and the experimental findings [18].

References