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Scaling law for the radius of gyration of poly[bis(2-naphthoxyphosphazene)] (PBNP)

Maria P. Tarazona*, Julio Bravo, and Enrique Saiz

Departamento de Química Física, Universidad de Alcalá de Henares, 28871 Alcalá de Henares, Madrid, Spain

ABSTRACT

A numerical procedure that allows for the evaluation of the scaling law between radius of gyration and molecular weight, $\langle s^2\rangle_i^{1/2} = Q\ M_i^q$, of ideally monodisperse fractions of any polymer is proposed. The method is similar to that previously used to determine viscometric constants and chromatographic calibration functions and is based on the combination of experimental results obtained by Static Light Scattering and Size Exclusion Chromatography on polydisperse samples. The method is used to study poly[bis(2-naphthoxyphosphazene)] in THF solution at 25°C for which the relationship $\langle s^2\rangle_i^{1/2} = 0.557\ M_i^{0.29}$ is obtained. The comparison between the dimensions computed with this equation and those obtained by viscometric measurements, performed under the same experimental conditions, suggest the formation of intermolecular aggregates in the solutions of this polymer.

INTRODUCTION

It is a well known fact (1) that Static Light Scattering (LS) measurements provide weight-averaged molecular weights M_w and z-averaged values of mean squared radius of gyration $\langle s^2\rangle_z$. Thus, when experimental values of $\langle s^2\rangle_z$ and M_w are used to determine scaling laws (2) such as $\langle s^2\rangle^{1/2} = Q\ M^q$, the difference in the kind of average used for both magnitudes could somehow mask the actual variation of $\langle s^2\rangle$ with M. This effect is negligible when very well fractionated samples having polydispersity ratios $r = M_w/M_n \approx 1$ are used for the experimental measurements, but it becomes rather important when the fractionation of the sample is not so efficient, and even more, when the polydispersity of the measured fractions is very different. This is exactly the situation in the case of poly(organophosphazenes), that can be represented as [N-P(XX')-], where X and X' indicate two organic residues attached to every skeletal phosphorus atom. Indeed, serious experimental problems in the fractionation of this kind of polymers have been reported (3,4), and even very carefully fractionated samples (5,6) have

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*Corresponding author

polydispersity ratios ranging from 1.2 to 4.

Some semiempirical procedures (1,7) have been devised for transforming $\langle s^2\rangle_z$ into weight average $\langle s^2\rangle_w$. For instance, the relationship $\langle s^2\rangle_w/\langle s^2\rangle_z = (h+1)/(h+2)$ with $(1/h) = r-1$ is frequently used to compute the ratio $\langle s^2\rangle_w/M_w$, specially when these results have to be compared with values obtained by some other experimental techniques. An alternative procedure consists in evaluating M_z and use the ratio $\langle s^2\rangle_z/M_z$.

During the last years, we have been employing a numerical procedure designed to minimize the effect of polydispersity (3,5,8,9). The method uses the experimental results of Size Exclusion Chromatography (SEC), viscometry (VIS) and LS measurements performed on actual polydisperse samples and allows the evaluation of true values of viscometric parameters and SEC calibration functions for ideally monodisperse fractions (10-13). The procedure is extended in the present paper to the calculation of the parameters governing the relationship between radius of gyration and molecular weight and applied to the study of poly[bis(2-naphthoxy phosphazene)] (PBNP) (X = X' = 2-naphthoxy in the structure of polyphosphazenes given above) (5). Some conclusions about the structure of the polymer solution are then obtained through a comparison between the molecular dimensions calculated with this method and those previously obtained by viscometry.

NUMERICAL METHOD

Let us represent by $R_i = \langle s_i^2\rangle^{1/2}$ the root of the mean square radius of gyration of a polymer chain having molecular weight M_i averaged over all the conformations available to this particular chain. We further assume that R_i follows a variation with M_i that can be represented by a scaling law (2) such as:

$$R_i = Q\, M_i^q \tag{1}$$

When the *radius of gyration* is determined by LS measurements, the magnitude actually obtained, which usually is represented by $\langle s^2\rangle$ or $\langle s^2\rangle_z$, is the z-average of the values of R_i^2 for all the chains contained in the sample. This average can be computed as (1):

$$\langle s^2\rangle_z = \frac{1}{M_w}\sum \omega_i M_i R_i^2 = \frac{\sum \omega_i M_i R_i^2}{\sum \omega_i M_i} \tag{2}$$

where ω_i represent the weight fraction of molecules having molecular weight M_i and the sums expand over all the molecular sizes contained in the sample.

If a SEC chromatogram of this sample is available, and the calibration function

$$\log M = A_o + A_1 V + A_2 V^2 + \ldots.. \tag{3}$$

has been previously determined so that the A_j coefficients are known, any average of $\langle s^2 \rangle$ can be calculated by numerical integration of this chromatogram. Thus, for instance, weight and z averages are given by:

$$\langle s^2 \rangle_w = \sum \omega_i R_i^2 = Q^2 \sum_{i=1}^{m} \omega_i M_i^{2q} \tag{4}$$

$$\langle s^2 \rangle_z = Q^2 \left[\sum_{i=1}^{m} \omega_i M_i^{1+2q} \right] \left[\sum_{i=1}^{m} \omega_i M_i \right]^{-1} \tag{5}$$

where it was assumed that the integration is performed by dividing the chromatogram in m slices and representing by h_i and V_i the height and elution volume of the i-th slice so that its weight fraction is $\omega_i = h_i/\Sigma h_i$ and its molecular weight M_i can be computed by substitution of V_i into eq. 3.

The Q and q coefficients appearing on eq. 1 can be calculated with the same procedure previously used to determine the Mark-Houwink parameters of the viscometric equation $[\eta] = KM^a$ (5,8-13). Thus, assuming that experimental values of $\langle s^2 \rangle_z$ for n fractions of the polymer have been measured by LS, the root mean square relative deviation σ_s between theoretical values computed according to eq. 5 and those experimentally determined can be written as:

$$\sigma_s = \left[\frac{1}{n} \sum_{i=1}^{n} \left(1 - \frac{\langle s^2 \rangle_z(\mathrm{cal})}{\langle s^2 \rangle_z(\mathrm{exp})} \right)^2 \right]^{1/2} \tag{6}$$

Imposing on the deviation σ_s the condition of minimum with respect to the two adjustable parameters appearing on eq. 1, i.e.

$$[\delta(\sigma_s)/\delta Q] = [\delta(\sigma_s)/\delta q] = 0 \tag{7}$$

two equations are obtained that can be solved by any numerical procedure (14) to provide the values of Q and q giving the best fit between experimental and theoretical results of $\langle s^2 \rangle_z$.

ANALYSIS OF PBNP

The numerical method explained above was employed for the analysis of a sample of PBNP whose synthesis and characterization have been reported elsewhere (5). In brief, the sample was obtained by thermal polymerization of the cyclic trimer

$[NP(Cl_2)]_3$ followed by a nucleophilic substitution of chlorine atoms by 2-naphthoxi groups. Fractional precipitation of the sample provided seven fractions that were characterized by SEC, LS and VIS measurements performed in THF solutions at 25°C. A 0.1 wt% of tetra(n-butylammomium)bromide was added to the THF used as eluent for SEC experiments in order to obtain reproducible chromatograms (15) that are shown in Fig. 1.

All the pertinent data are summarized in table I in which columns one through seven were taken from reference 5, while the two last columns contains data calculated in the present work. Thus, second and third columns represent data experimentally obtained by LS. The fourth column contains the calculated values of polydispersity ratios. Columns five to seven summarize the viscometric data, i.e. experimental results of intrinsic viscosities and calculated values M_v and end to end distance.

TABLE I

Results for PBNP. Experimental data measured in THF solutions at 25°C. Molecular weights in 10^4 g/mol. Intrinsic viscosities in dL/g. Dimensions in nm SEC calibration function: $\log M = 14.93 - 2.54\ V + 0.16\ V^2$

Fr.	M_w	$\langle s^2\rangle_z^{1/2}$	r	$[\eta]$	M_v	$\langle r^2\rangle^{1/2}$	$\langle s^2\rangle_z^{1/2}$	$\langle s^2\rangle_w^{1/2}$
1	139.9	47.8	3.1	0.72	112.9	68.7	43.2	30.6
2	119.6	39.8	3.4	0.47	87.8	55.0	42.2	28.3
3	53.8	30.8	2.4	0.38	52.3	43.2	32.1	24.6
4	49.6	31.1	2.6	0.29	45.2	37.6	31.9	23.5
5	42.0	25.0	1.8	0.25	28.7	30.8	25.1	20.8
6	21.4	24.7	1.5	0.18	20.3	24.4	22.1	18.8
7	9.8	16.3	1.2	0.12	9.5	16.4	17.0	15.2

Application of the numerical procedure to the data collected in Table I and the SEC chromatograms represented in Fig. 1 gives the following scaling law between radius of gyration and molecular weights of ideally monodisperse fractions:

$$\langle s_i^2\rangle^{1/2} = 0.557\ M_i^{0.29} \qquad \text{with} \qquad \sigma_s = 0.12 \qquad (8)$$

This scaling law is graphically represented by the solid line of Fig. 2 while the filled circles on this Fig. show the values of $(\langle s^2\rangle_z)^{1/2}$ computed for the seven fractions according to eq. 5 as function of the experimental M_w. The open circles indicate the experimental values of $(\langle s^2\rangle_z)^{1/2}$ versus M_w, both magnitudes being obtained by LS. Finally, the broken line shows the least squares fitting of experimental data. It is important to notice that the solid line on Fig. 2 *is not*

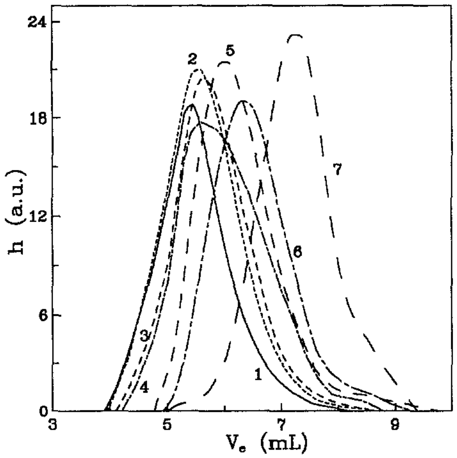

Fig.1. SEC chromatograms for the seven fractions of PBNP.

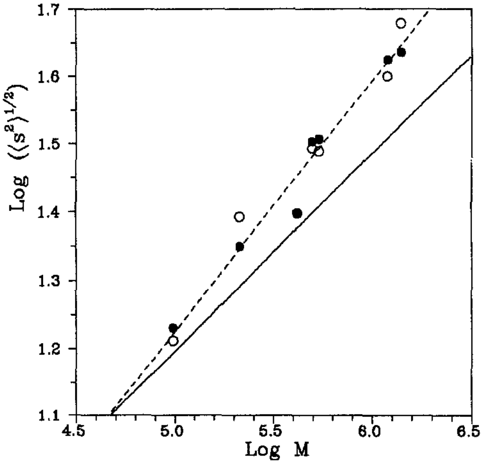

Fig.2. Radius of gyration as function of molecular weights. See text for details.

a *least squares fitting* of the filled circles, instead it represents a scaling law for magnitudes corresponding to ideally monodisperse samples. The goodness of this scaling law can be judged by comparing open and filled circles that represent, respectively, experimental and theoretical values obtained for actual polydisperse fractions. As Fig. 2 indicates, when experimental magnitudes are directly employed in the fitting, the use of different averages for radius of gyration and molecular weights produce an overestimation of the slope.

Radius of gyration determined by LS are frequently converted into end to end distances $\langle r^2\rangle$ by the relationship $\langle r^2\rangle \approx 6\langle s^2\rangle$ and compared with the results

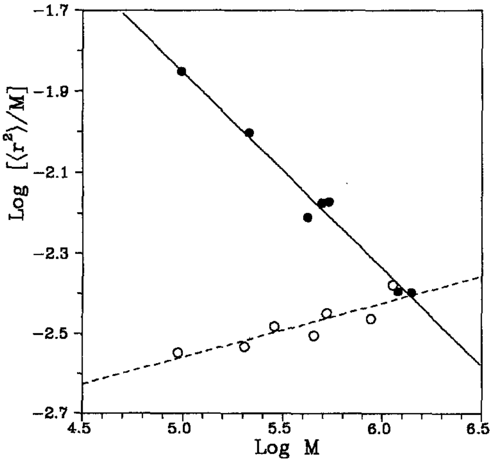

Fig.3. Ratio between end to end distances and molecular weights as function of M.

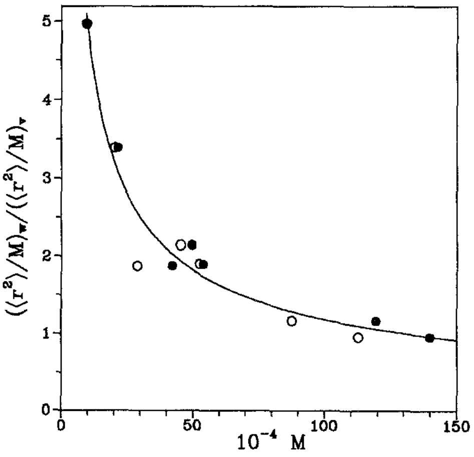

Fig.4. Ratio between LS and VIS magnitudes as function of M.

obtained by VIS. This comparison is shown in Fig. 3 that represents the values of $\text{Log}(\langle r^2\rangle/M)$ versus Log(M). The open circles indicate the viscometric results, i.e. the dimensions were computed with the Flory-Fox equation $[\eta]M_v = \Phi\langle r^2\rangle^{3/2}$ and values of M_v were used for the horizontal axis. Least squares fitting of these data, represented by the dot line, gives $\langle r^2\rangle/M = 5.90\ 10^{-4}\ M^{0.13}$, or written in another form, $\langle r^2\rangle \sim M^{1.13}$ which indicates a normal behavior of a random coil in a good solvent (2,16). Filled circles represent weight averages obtained by using eq. 4 to compute $\langle s^2\rangle_w$ and experimental values of M_w for the evaluation of $\langle r^2\rangle/M_w = 6\langle s^2\rangle_w/M_w$ whose logarithm is represented versus $\text{Log}(M_w)$. The least square fitting is represented by the solid line and gives $\langle r^2\rangle \sim M_w^{0.52}$. The discrepancy between viscosity and weight averages is more clearly shown in Fig. 4 where the ratio $\gamma = [\langle r^2\rangle/M]_w/[\langle r^2\rangle/M]_v$ is plotted against the molecular weight. The open circles represent values of γ versus $\text{Log}(M_v)$ while filled circles were drawn using $\text{Log}(M_w)$ in the horizontal axis. However, the differences between both kind of representations are rather minor and the solid line indicates the fitting of all the points to the power function $\gamma = 6.06\ 10^3\ M^{-0.62}$.

The behavior represented in Figs. 3 and 4 can be easily explained by assuming that intermolecular aggregates are formed in the solution. The presence of these aggregates do not perturb the viscosity measurements but leads to overestimations on the radius of gyration determined by LS that become larger with decreasing molecular size. For this reason, the extrapolation to M → 0 in order to evaluate unperturbed dimensions is good when performed with VIS results and rather poor when obtained from LS values. Moreover, the differences in characteristic ratios $C_n = \langle r^2\rangle_0/n\ell^2$ obtained with this extrapolation are much larger than the differences in perturbed dimensions actually measured for most of the fractions, specially for those of higher molecular weight.

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