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Solution properties of polyphosphazenes containing 2,2′-dioxybiphenyl groups

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Abstract

Dilute solution properties of four different polyphosphazenes containing 2,2′-dioxybiphenyl groups have been studied by size exclusion chromatography, using simultaneously multiangle light scattering and differential refractive index detectors. The polymers present broad molecular weight distributions and the dependence of the dimensions, i.e. radius of gyration, of the polymers on the molecular weight is discussed. Moreover, scaling laws and unperturbed dimensions have been calculated for the fractions with high molecular weight. The polymers behave as random coil chains, the characteristic ratios are in the range 12–17 in good accord with the results reported for other polyphosphazenes.

Keywords: Polyphosphazenes; Solution characterization; Unperturbed dimensions

1. Introduction

Poly(organophosphazene)s are an important class of polymers because of their unusual properties and potential applications [1,2]. Although there are several methods to synthesize these polymers, the more extended one is the substitution of chlorine atoms in the poly(dichlorophosphazene) $[NPCl_2]_n$ obtained by thermal polymerization of hexachlorocyclotriphosphazene $N_3P_3Cl_6$ either in melt [3] or in solution [4]. This procedure makes it possible to obtain a wide variety of polymers with different organic side groups and very diverse physical and chemical properties, that can be easily converted into useful materials [5].

Measurement of dilute solution properties and critical analysis of the results is a general and very powerful tool for the characterization of polymers, that could report a better knowledge of the structure and macroscopic behavior of this interesting kind of polymer. Recent efforts have concentrated on the study of the anomalous solution behavior of different polyphosphazenes, since the reports on solution properties of these polymers are scarce and even contradictory [6,7]. In this paper we extend the study to an interesting new type of polyphosphazene containing 2,2′-dioxybiphenyl groups whose synthesis has been reported recently [8].

The use of a widely employed technique, size exclusion chromatography (SEC) for the solution characterization of polyphosphazenes has the inconvenience that the reliability of the universal calibration technique [9] becomes questionable for these polymers. This problem can be avoided using a mass sensitive detector in addition to the concentration detector in the SEC measurements. Thus, a multiangle laser light scattering detector whose potential for the determination of both molecular weight distributions and dimensions of polymers has been demonstrated [10,11], has been used in this work. This experimental setup has permitted to obtain the absolute distributions of molecular weight and root mean square radius of gyration even for the broadly dispersed samples of polyphosphazenes. Moreover, the study of the dilute solution behavior of the polyphosphazenes with these techniques, yields information about their unperturbed dimensions.

2. Experimental

2.1. Materials

The samples were four different polyphosphazenes containing 2,2′-dioxybiphenyl groups of formula

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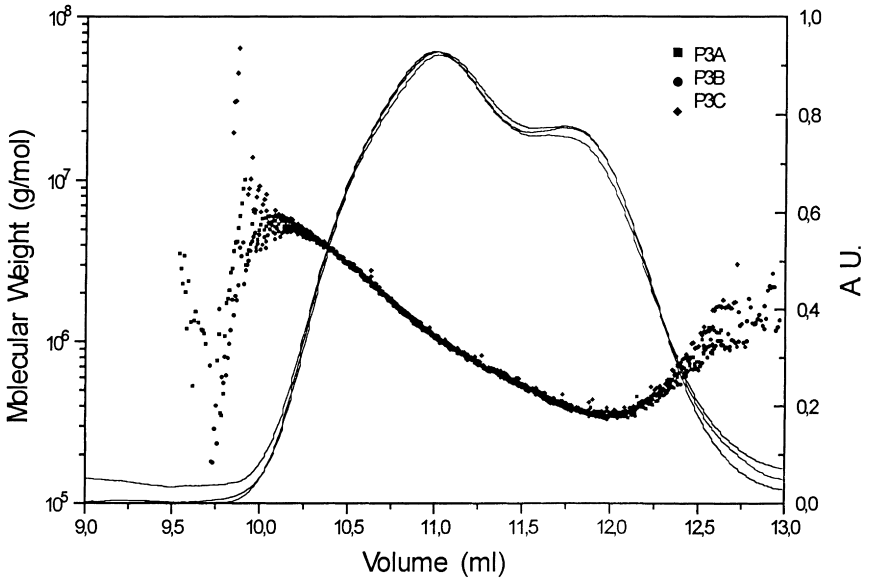
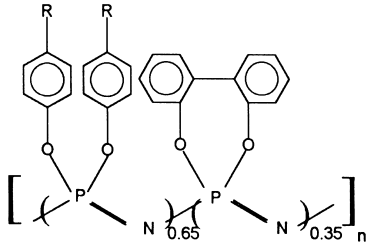


Fig. 1. Logarithm of molecular weight versus elution volume for three different samples of polyphosphazene P3. The corresponding DRI signals are also shown. THF with 0.1% tetra-*n*-butyl ammonium bromide was used as eluent.

$[NP(O_2C_{12}H_8)]_{0.35}[NP(OC_6H_4R)_2]_{0.65}$, where $R = COC_6H_5$ (P1), $COCH_3$ (P2), CN (P3) and Br (P4):



The synthesis of these polymers has been described elsewhere [8].

2.2. Equipment

The absolute molecular weight distribution and radius of gyration were determined by SEC combined with multi-angle laser light scattering (MALLS). A Waters Associates differential refractive index detector Model 410, was used as concentration detector and a Dawn-DSP-F laser photometer from Wyatt Technology was the mass and size detector

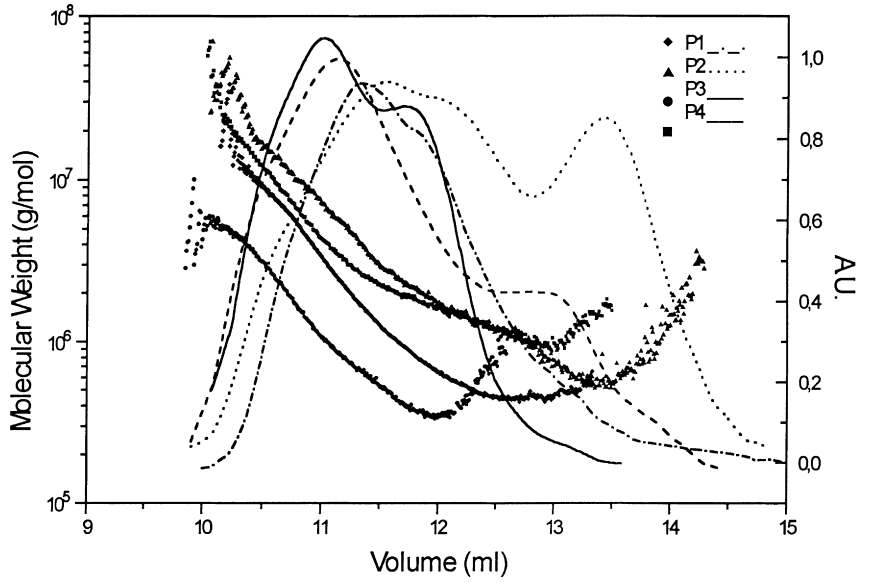


Fig. 2. Logarithm of molecular weight versus elution volume for the four polyphosphazenes. The corresponding DRI signals are also shown. THF with 0.1% tetra-*n*-butyl ammonium bromide was used as eluent.

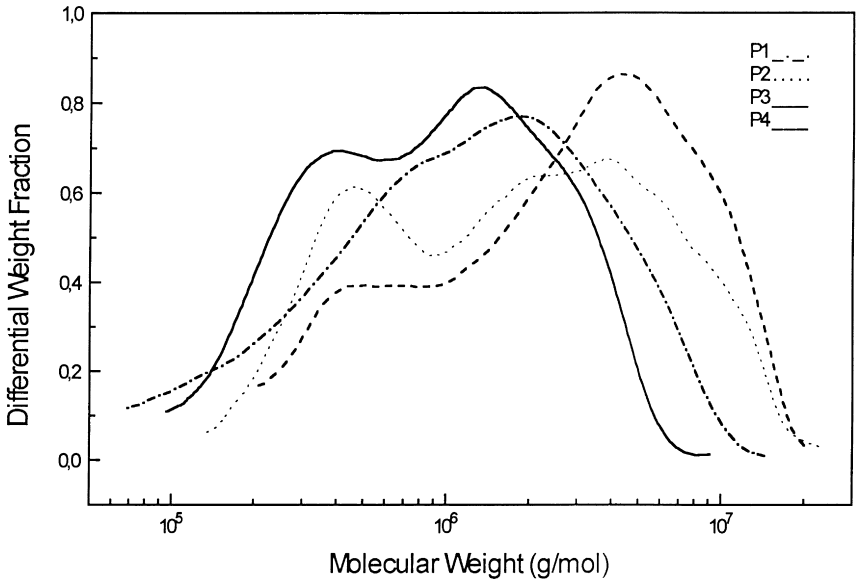


Fig. 3. Differential molecular weight distributions for the four polyphosphazenes.

used. A Model 510 pump, a U6K injector (Waters Associates) and two columns PLgel mixed B (Polymer Laboratories) in series completed the equipment. Tetrahydrofurane (THF) freshly distilled from sodium and benzophenone, filtered through a 0.2 μm Fluoropore filter and degassed, with 0.1% tetra-*n*-butyl ammonium bromide was used as eluent at a flow rate of 1.0 ml/min.

The Dawn photometer was calibrated with spectrometric grade toluene freshly distilled from sodium and benzophenone, and the normalization of the detectors was performed with standard monodispersed polystyrene of low molecular weight which did not show angular dependence on the light scattering signal. Standard monodispersed polystyrene was also used to determine the interdetector volume using the 'spider' plot method [10].

3. Results and discussion

3.1. Molecular weight distributions of polymers

The use of a multiangle light scattering detector enables the weight average molecular weight and the mean square radius of gyration $\langle s^2 \rangle$ to be calculated for each slice across a sample peak of the size exclusion chromatogram. Assuming that each slice contains molecules of a single molecular weight, or at least a very narrow distribution, a value of M is obtained for each elution volume V. Fig. 1 shows the molecular weight calculated from the scattered light for three samples of the same polyphosphazene P3 plotted versus the elution volume, i.e. absolute calibration curves for SEC. The signals from the differential refractive index detector, proportional to the concentration, have also been plotted. As can be seen in this figure, the results are consistent in the range between 10 and 13 ml; out of this region, the signals from the detectors are so feeble that the points are meaningless. The uncertainties in the tails or heads of the molecular weight distributions are more easily discernable from the plot of the calibration curve than from the raw chromatograms. Fig. 2 shows the values of molecular weight versus elution volume for all four polyphosphazenes, measured individually, together with the respective differential refractive index signal. All four polymers exhibit the same behavior, the molecular weight diminishes as the elution volume increases until they reach a point for which the molecular weight starts to increase. As can be

Table 1
Averaged molecular weights, polydispersities and root mean square radii of gyration of polyphosphazenes obtained in THF with a 0.1% tetra-*n*-butyl ammonium bromide as eluent

	$10^{-5} M_n$ (g/mol)	$10^{-6} M_w$ (g/mol)	$10^{-6} M_z$ (g/mol)	M_w/M_n	$\langle s^2 \rangle_n^{1/2}$ (nm)	$\langle s^2 \rangle_w^{1/2}$ (nm)	$\langle s^2 \rangle_z^{1/2}$ (nm)
P1	9.5 ± 0.1	2.08 ± 0.04	4.7 ± 0.4	2.17 ± 0.05	35 ± 1	38 ± 1	48 ± 1
P2	13.6 ± 0.5	3.64 ± 0.2	11.4 ± 2.0	2.68 ± 0.2	51 ± 2	54 ± 2	74 ± 1
P3	7.2 ± 0.2	1.38 ± 0.03	2.58 ± 0.2	1.91 ± 0.06	41 ± 1	44 ± 1	51 ± 1
P4	21.9 ± 0.6	4.56 ± 0.1	11.9 ± 3.0	2.08 ± 0.08	53 ± 2	55 ± 1	67 ± 1

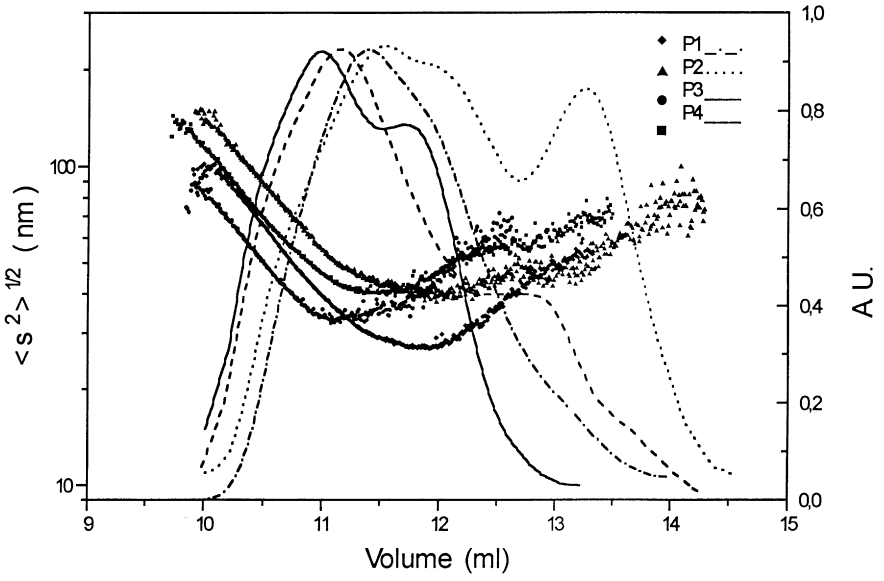


Fig. 4. Logarithm of root mean squared radius of gyration versus elution volume for the four polyphosphazenes. The corresponding DRI signals are also shown. THF with 0.1% tetra-*n*-butyl ammonium bromide was used as eluent.

seen in this figure the absolute calibration curves for SEC are not linear. This fact is in agreement with our previous results for other polyphosphazenes for which we calculated the calibration curves using several fractionated samples of polyphosphazenes and a numerical procedure [12,13]. There are also similarities between our results and the study of poly[bis(trifluoroethoxy)phosphazene] by Mourey et al. [14] using SEC and on-line low angle light scattering and differential viscometry since they found that the polymer was structurally heterogeneous across the molecular weight distributions and the Mark–Houwink plot deviated from linearity at low molecular weights.

The combined measurements of molecular weight, obtained with the MALLS detector, and concentration, obtained with a differential refractive index (DRI) detector for each elution volume, allows to determine the absolute molecular weight distributions for the polymer samples [11].

Fig. 3 presents the absolute molecular weight distributions of the polymers. It can be seen that the polydispersity is high and the distributions are multimodal, a repetitive characteristic in polyphosphazenes. Mean values of molecular weights, polydispersities and the corresponding standard deviations, obtained using ASTRA software, are listed in Table 1.

3.2. Dimensions

The *z* average root mean square radius of gyration $\langle s^2\rangle^{1/2}$ can be derived from the angular dependence of the intensity of the scattered light. At the very low concentrations used in SEC, the calculation of the values for this magnitude is independent [15] of both d*n*/d*c* (assumed constant) and M_w and therefore, if the normalization constants of the different detectors have been measured with care, it offers an excellent form to study the dimensions of the polymer. The only problem is that the size of the polymer must be larger than $\lambda/20$ in order to observe the angular dependence of the scattered light intensity [16]. Thus the accuracy of the radius of gyration obtained in the region of low molecular weights begins to deteriorate rapidly. Fig. 4 shows the root mean square radius of gyration versus the elution volume for the four polyphosphazenes; the signals from the DRI detector are also shown. The radius of gyration is proportional to the hydrodynamic radius [9,17] and therefore to the product $([\eta]M)^{1/3}$; consequently, the dimensions of the polymer diminish as the elution volume increases, as expected, until they reach a point at which they start to increase as can be noticed on Fig. 4. The values of $\log\langle s^2\rangle^{1/2}$ versus volume are linear, for the four polymers only in the region of low volumes ($V < 11$ ml), i.e. very high molecular weights. At higher values of the elution volume the linearity is lost and also the accuracy in the determination of the radius of gyration is lower than that of molecular weight, as can be seen from the comparison between the plots of molecular weight (Fig. 2) and radius of gyration (Fig. 4) versus volume. The increase in radius of gyration and the corresponding increase in molecular weight at high elution volumes, explained above, can explain why the polyphosphazenes do not always follow the universal calibration assumptions [9] and also the difficulties usually found in the fractionation of these polymers [6].

Values of the root mean square radii of gyration for the four polyphosphazenes, calculated using ASTRA software are shown in the last three columns of Table 1. These mean values have been computed from the *z* averaged mean square radius of each slice of the chromatogram and thus number and weight averages are not accurate [10].

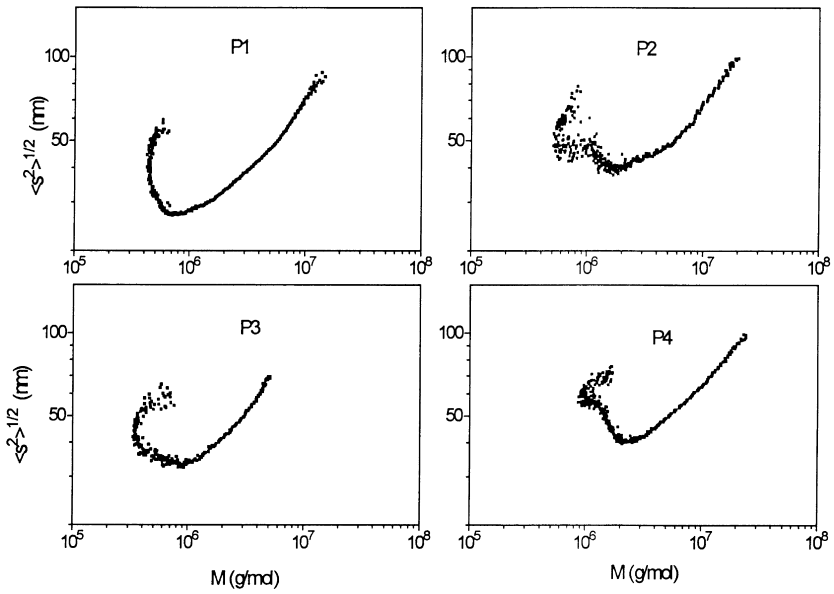


Fig. 5. Log–log plot of root mean squared radius of gyration versus molecular weight for the four polyphosphazenes in the whole range of molecular weights.

3.3. Scaling laws

The study of the dependence of radius of gyration on molecular weight can give additional information on the polymer structure. Thus, the value of the q parameter in the scaling law $\langle s^2\rangle^{1/2} = QM^q$ may provide a hint about the shape of the polymeric chain since values of $q \simeq 0.3$ are expected for globular polymers, $q \simeq 0.5$ would indicate theta conditions and $0.5 < q \leq 0.6$ are obtained for random coil polymers in good solvents [18]. Fig. 5 shows the log–log plot of the radius of gyration versus molecular weight, that is the scaling law $\langle s^2\rangle^{1/2} = QM^q$ for the four polyphosphazenes. Although at high molecular weights the plots are linear, they deviate from linearity in the region of lower molecular weights; this behavior is a consequence of the molecular weight and dimension versus elution volume results implicit in Figs. 2 and 4. As can be seen in Fig. 5 the values obtained for Q and q depend on the chosen range of molecular weights. This fact can explain why the scarce values [19–22] for the scaling law reported for polyphosphazenes are very different [6], with values ranging from 0.3 to 0.6. To our knowledge the scaling laws for other polyphosphazenes have been obtained through the measurements of a few fractionated samples of polymers, and, if their behavior were similar to those studied here, the values obtained will depend strongly on the range of

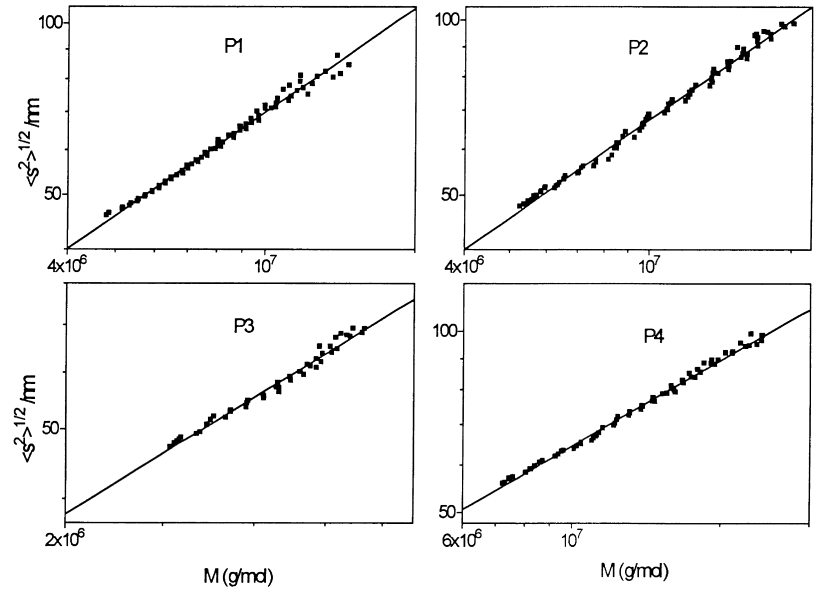


Fig. 6. Linear part, in the range of high molecular weight, of the log–log plot of root mean squared radius of gyration versus molecular weight for the four polyphosphazenes.

Table 2
Scaling law parameters and unperturbed dimensions of polyphosphazenes

	$10^3\ Q^a$	q^a	$10^4\ \langle s^2\rangle_o/M^b$ (nm^2 mol g)	$10^4\ \langle s^2\rangle_o/M^c$ (nm^2 mol g)	C_n
P1	4.0 ± 0.3	0.60 ± 0.01	2.7 ± 0.2	2.5 ± 0.2	12 ± 1
P2	7.5 ± 0.2	0.57 ± 0.01	3.3 ± 0.1	3.2 ± 0.1	12.0 ± 0.3
P3	4.2 ± 0.5	0.62 ± 0.01	4.0 ± 0.1	2.9 ± 0.1	12 ± 2
P4	30 ± 2	0.48 ± 0.01	4.10 ± 0.01	4.05 ± 0.01	17.6 ± 0.2

[a] With $\langle s^2\rangle^{1/2}$ in nm and M in g/mol.
[b] Fixman extrapolation.
[c] Stockmayer–Fixman extrapolation.

molecular weight of the samples used, as can be easily seen in Fig. 5. In this work, the scaling law is obtained for broad peaks of polymer divided into more than 300 slices and therefore it is equivalent to the measurement of more than 300 almost monodispersed samples, and the behavior of the polymer can be monitored through the whole range of molecular weights.

As can be seen in the four plots of Fig. 5, there is a linear part at high molecular weight, corresponding to the first eluted fractions of the polymers. Fig. 6 shows the enlarged linear part and the corresponding values of the q and Q coefficients are shown in the first two columns of Table 2. It is noteworthy that curvature appears if the range is expanded towards lower molecular weights. The values of the q parameter show that three polymers, P1, P2 and P3, behave as random coils in a good solvent, whereas the fourth polymer, P4, is closer to θ conditions.

3.4. Unperturbed dimensions

Unperturbed dimensions can be evaluated from measurements of dimensions of the polymers as a function of molecular weight in a good solvent, using several extrapolation procedures. Since, as can be seen in Fig. 6, we have values of the radius of gyration for different monodispersed samples (slices) of polyphosphazenes, we have tried to compute the unperturbed dimensions using two different extrapolation procedures. The first one, due to Fixman [23], is defined in Eq. (1), which affords $\langle s^2\rangle_o/M$ as the intercept:

$$\frac{\langle s^2\rangle}{M} = \frac{\langle s^2\rangle_o}{M} + 0.0299B\left(\frac{\langle s^2\rangle_o}{M}\right)^{-1/2} M^{1/2} \tag{1}$$

The other procedure used is similar to the extrapolation of Stockmayer and Fixman [24] for viscosity measurements. Since the perturbed and unperturbed mean square radius of gyration are related though the chain expansion factor, α:

$$\langle s^2\rangle = \alpha^2\langle s^2\rangle_o \tag{2}$$

and the expansion factor is related to molecular weight M by:

$$\alpha^3 = 1 + \mathrm{C}M^{1/2} \tag{3}$$

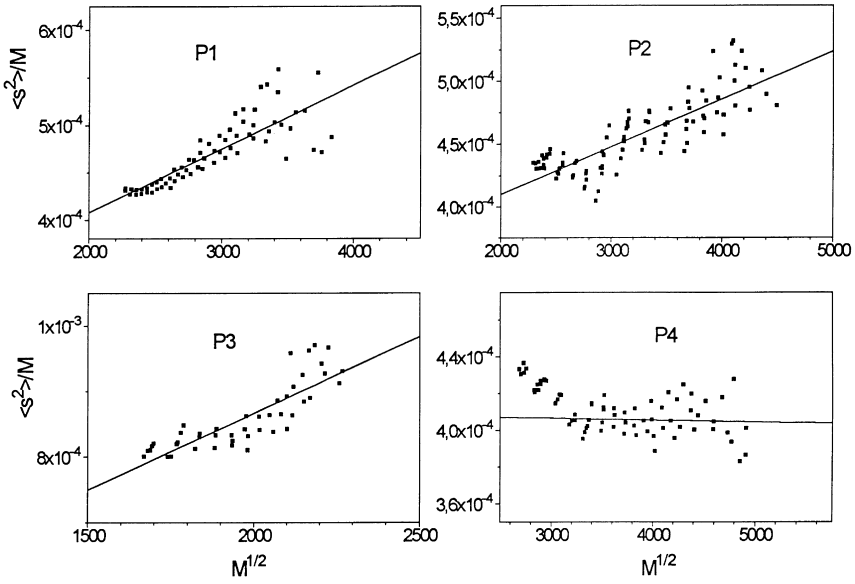


Fig. 7. Fixman extrpolations for the four polyphoshazenes.

An extrapolation equation may be written as:

$$\left(\frac{\langle s^2\rangle}{M}\right)^{3/2} = \left(\frac{\langle s^2\rangle_o}{M}\right)^{3/2}\left(1 + CM^{1/2}\right) \quad (4)$$

and the intercept provides $(\langle s^2\rangle_o/M)^{3/2}$.

The Fixman plots of the four polymers in the linear regions (the same ones shown in Fig. 6) are represented in Fig. 7. The Stockmayer–Fixman plots are very similar and are not shown. The derived values of $\langle s^2\rangle_o/M$, in $nm^2\ mol\ g^{-1}$, for both extrapolations are listed in Table 2; it is worth noting that, despite the dispersion of the points, the errors in the intercepts are not too large and there is good accord between the two extrapolations. The results obtained for the polyphosphazene P4 which show a line with zero slope, are in accordance with the exponent q close to 0.5, thus the polymer seems to be in unperturbed dimensions and there is no variation of the ratio $\langle s^2\rangle/M$ with molecular weight. The characteristic ratio C_n can be calculated from the extrapolated values of $\langle s^2\rangle_o/M$ as:

$$C_n = \frac{\langle r^2\rangle_o}{nl^2} = \frac{6M_o}{2l^2}\frac{\langle s^2\rangle_o}{M} \quad (5)$$

where n is the number of bonds, M_o is the molecular weight of the repetitive unit for each polymer, which contains two P–N bonds of length $l = 0.152$ nm, and $\langle r^2\rangle_o$ the unperturbed value of the mean square end to end distance, which for flexible chains is $\langle r^2\rangle_o = 6\langle s^2\rangle_o$. The mean values of C_n are listed in the last column of Table 2, these results are in good agreement with the values obtained for most polyphosphazenes [6]. Finally we want to stress the point that unperturbed values of chain dimensions can be obtained with experimental results of SEC for a single sample in a good solvent even if it is broadly dispersed as polyphosphazenes tend to be, provided that both MALLS and DRI detectors are used.

Acknowledgements

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