Dilute-Solution Characterization of Poly(dihexoxyphosphazene)

J. Bravo, M. P. Tarazona, and E. Saiz*

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

Received October 8, 1990; Revised Manuscript Received January 22, 1991

ABSTRACT: A sample of poly(dihexoxyphosphazene) (PDHP) has been synthesized, purified, characterized, and fractionated according to standard procedures. Four fractions were separated and studied by light scattering, viscometry, and size-exclusion chromatography. The light scattering measurements, performed in THF solutions at 25 °C, gave $\bar{M}_w = 2.3, 0.92, 0.25$, and 0.026×10^6, respectively, for fractions 1–4; the values of the second virial coefficient decrease with increasing molecular weight, and thus $A_2 = 0.66, 1.27, 1.67$, and 3.98×10^{-4} mol cm^3 g^{-1}, respectively, for fractions 1–4; fraction 4 had a radius of gyration too small to be determined with accuracy; the results for the other three fractions were $\langle s^2 \rangle^{1/2} = 71, 30$, and 16 nm. Intrinsic viscosities of the four fractions, measured in THF solutions at 25 °C, were $[\eta] = 1.745, 1.151, 0.425$, and 0.064. Two iterative numerical procedures previously described in the literature were employed to combine all the experimental results, seeking the best choice of the parameters defining both the SEC calibration curve and the Mark–Houwink equation; both methods give approximately the same results. The K and a constants of the Mark–Houwink equation allow the determination of the viscosity-average molecular weight of the four fractions $\bar{M}_v$, and their molecular dimensions, that are concordant with those measured by light scattering.

Introduction

In recent years, many polyphosphazenes $(R_2PN)_n$ with different organic or organometallic side groups R have been prepared.[1-4] The special physical and chemical characteristics of this kind of polymer together with the useful properties of several of them are some of the reasons they are being extensively investigated.

One aspect of relevant importance in the study of the poly(organophosphazenes) is their characterization in dilute solution. A variety of standard dilute-solution techniques such as membrane osmometry, viscosity measurements, light scattering (LS), and size-exclusion chromatography (SEC) have been used in order to characterize the precursor poly(dichlorophosphazene) and numerous poly(organophosphazenes).[5-9]

The routine characterization of polyphosphazenes is usually hampered by their anomalous behavior in SEC.[10,11] In several cases severely tailing nonreproducible chromatograms were obtained, suggestive of an adsorption type of interaction between the polymer and the column materials. Moreover, the anomalous behavior is extended to viscosity measurements for some polyphosphazenes especially in the case of polymers with fluoroalkoxy side groups since the aggregation effect is enhanced by the fluorine.[5,12,13] It has been reported that the addition of small amounts of quaternary ammonium salts to the solvent in viscosity measurements or to the THF mobile phase in SEC eliminates the association in solution and the adsorption between polymers and column fillers; thus normal viscosity and SEC behavior are observed.[13,14] However, there are still several problems associated with the characterization in solution of most polyphosphazenes such as the high molecular weights, which cause concentration effects in SEC, isorefractivity with solvents used in LS, and especially the heterogeneous molecular weight distributions obtained in the synthesis, which makes difficult the determination of the Mark–Houwink parameters.[7,10,12,15]

In this paper we examine size-exclusion chromatography, dilute-solution viscosity measurements, and light scattering results of several samples of poly(dihexoxyphosphazene) synthesized following the method described by Allcock and co-workers[1,16] and fractionated using the solvent/nonsolvent technique. In order to minimize the problems aroused by the polydispersity of the samples, numerical methods that do not require monodisperse samples had been used to compute the parameters of the calibration curve for SEC and the Mark–Houwink constants. These results were then used to calculate viscosity-average molecular weights and molecular dimensions performing the extrapolation to unperturbed conditions.

Experimental Section

Materials. Poly(dihexoxyphosphazene) (PDHP) was synthesized by using the original method described by Allcock and co-workers.[1,16] Hexachlorocyclotriphosphazene (Fluka; 31.1 g, 0.089 mol) was resublimed and then polymerized in a sealed evacuated tube at 245 °C until the molten reaction mixture becomes so viscous that flows ceases. The poly(dichlorophosphazene) thus obtained was dissolved in benzene and added slowly over a benzene solution of sodium hexoxide prepared from hexanol (220 g, 2.55 mol) and sodium hydride (18.8 g of 80% oil dispersion, 0.6 mol). The reaction mixture was stirred for 120 h at room temperature and precipitated into 3 L of ethanol. Further purification was carried out by three successive precipitations of a polymer solution in THF into three 5-L batches of water. A total of 11.6 g of polymer was obtained.

The infrared, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were consistent with the literature.[16]

The fractionation of PDHP was carried out by the solvent/nonsolvent technique. A solution of the polymer in THF was cooled to 15 °C and ethanol added as the nonsolvent until a slight turbidity was observed. The solution was then warmed up to 35 °C until it was clear, allowed to slowly cool to 15 °C, and kept overnight at this temperature. The precipitated polymer was separated and the procedure repeated to obtain additional fractions. Four different samples were obtained, but since the first and second ones were still highly polydisperse, they were again precipitated by using the same solvent/nonsolvent system, discarding the polymer that remains in solution.

Viscometric Measurements. A Schott Gerate autoviscometer was employed to measure flow times of PDHP solution in THF. The bath temperature was controlled at 25 ± 0.1 °C. Intrinsic viscosity values, $[\eta]$, the Huggins constant, k_H, and the Kraemer constant, k_K, were estimated by the simultaneous extrapolation of η_{sp}/c and $(1/c) \ln \eta_{rel}$ (where η_{sp} and η_{rel} are the specific and relative viscosities, respectively) vs concentration plots to infinite dilution according to the Huggins[17] and Kraemer[18] equations using least-squares linear regression analysis.

Size-Exclusion Chromatography. Experiments were performed by using Waters Associates equipment consisting of a 510 reciprocating piston pump, a U6K injector, a 410 refractive index detector with an oven-temperature controller, and a Digital

0024-9297/91/2224-4089$02.50/0

Table I
Viscosity Parameters of PDHP in THF Solution at 25 °C

fraction	[η], dL/g	k_H	k_K
1	1.745 ± 0.001	0.344	−0.152
2	1.151 ± 0.002	0.301	−0.175
3	0.425 ± 0.001	0.236	−0.233
4	0.064 ● 0.001	0.0976	−0.381

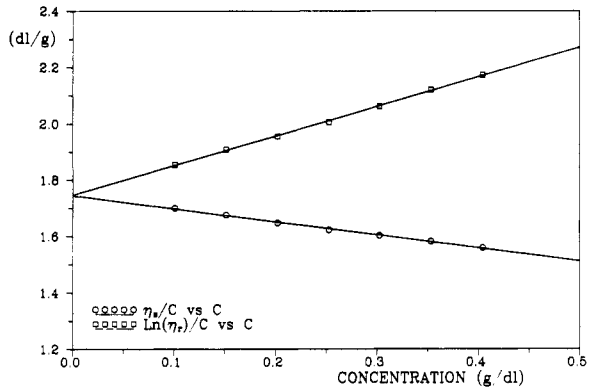

Figure 1. Huggins–Kraemer plot for fraction 1 in THF at 25 °C.

380 computer with an 840 data and chromatography control station. Two polystyrene gel columns packed in THF were used. Elutions were conducted with a flow rate of 1 mL min^{-1}. Freshly distilled THF with 0.1% of tetra-*n*-butyl ammonium bromide was used as eluent. Narrow molecular weight distribution polystyrene standards (Scharlau) were used.

Light Scattering. Scattering of solutions of PDHP in freshly distilled THF was measured with a Malvern light-scattering photometer Model K7027 with a He–Ne laser (λ = 632.8 nm). The solutions were passed through Millipore Teflon filters. The refractive index increments of the solutions were measured with a Brice Phoenix differential refractometer obtaining values of d*n*/dc ranging between 0.0666 and 0.0677 mL/g for the four fractions. Experimental values of the scattered intensities were represented in Zimm plots,[19] and values of weight-average molecular weight, $\bar{M}_w$, second virial coefficient, A_2, and radius of gyration, $\langle s^2 \rangle$, were determined from intercept and slopes.

Results

Results of the viscometric measurements are shown in Table I, and one of the Huggins–Kraemer plots showing the coincidence of intercepts is represented in Figure 1. The plots are linear and no anomalous behavior as reported previously for other polymers[5,13,20] was observed.

As can be seen in Table I, the Huggins and Kraemer slopes follow the theoretical relation[21] $k_K = k_H - 1/2$. Values of the Huggins constant usually range between 0.3 and 0.7 for flexible polymers,[22] although both much higher and lower values had been reported for polyphosphazenes.[5,10,15] For PDHP, the dependence of the Huggins constant with the intrinsic viscosity, and thus with the molecular weight of the sample, is very marked. However, the value obtained for the highest molecular weight fraction (0.34) is low enough as to suggest, within the limits of credibility of this analysis, that the chains are mainly linear.

Light scattering data obtained in this study are shown in Table II. The Zimm plots showed no anomalies indicative of aggregation or gelification effects; one of them is represented in Figure 2 as an example. As can be seen in the last two rows of Table II, an increase or decrease of temperature does not influence the molecular weights, within experimental error, which is indicative of the absence of association, in accordance with viscometric results. The dependence of the second Virial coefficient A_2 on molecular weight is illustrated in Figure 3; as expected, it decreases with increasing molecular weight according to a relationship $A_2 = B\bar{M}^b$ where B is a constant

Table II
Light Scattering Data in THF at Several Temperatures

fraction	temp, °C	$10^{-6}\bar{M}_w$	$\langle s^2 \rangle^{1/2}$, nm	$10^4 A_2$, mol cm^3 g^{-1}
1	25	2.28	70.7	0.655
2	25	0.917	30.4	1.27
3	25	0.245	16.1	1.67
4	25	0.0263		3.98
1	18	2.34	73.4	0.758
1	32	2.26	71.9	0.576

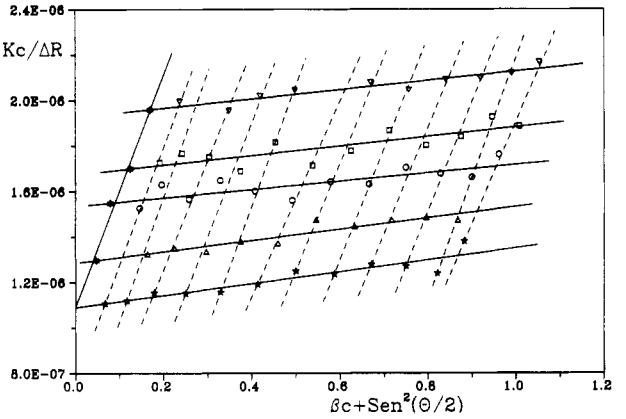

Figure 2. Zimm plot of fraction 2 in THF at 25 °C.

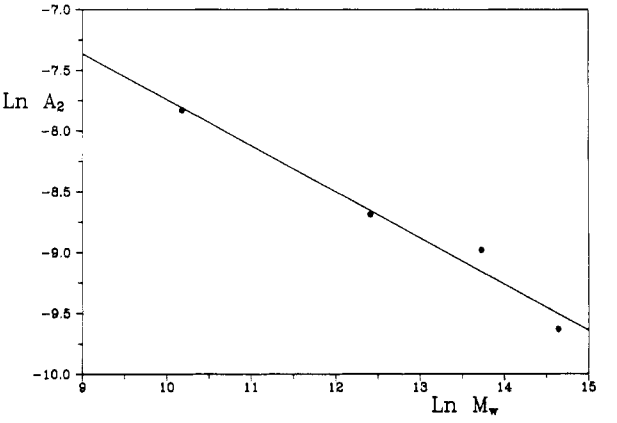

Figure 3. Dependence of the second coefficient of virial A_2 with the molecular weight.

that depends on the polymer solvent system. Krigbaum and Flory[23] predicted a value of b between −0.05 and −0.25 for random coils; experimentally values of b = −0.2 had been found for polymers with molecular weights higher than 10^5 in good solvents.[24] A value of b = −0.35 was obtained by Carlson et al.[25] for a polyphosphazene near Θ conditions, we found[9] a value of b = −0.37 for poly(diethoxyphosphazene). For PDHP a value of b = −0.38 is obtained. These values had been justified by the fact that increasing width of molecular weight distribution with increasing $\bar{M}_w$ will increase A_2[25] or by the proximity to Θ conditions.[9] In our opinion there is no contradiction between the two explanations, which can both contribute to the higher value of b. However, the value b = −0.38 is indicative of random-coil chains since the theory predicts values of b = −1 and b = 0, respectively, for rods and spheres.

The dependence of the radius of gyration $\langle s^2 \rangle^{1/2}$ with $\bar{M}_w$ found for PDHP is $\langle s^2 \rangle^{1/2} = 4.73 \times 10^{-3} \bar{M}_w^{0.65}$. However, only three data values have been used since the molecular weight of the fourth fraction is too small to allow the determination of $\langle s^2 \rangle^{1/2}$ by light scattering measurements. Since values of 0.5–0.6 are expected for random coils, whereas a value of 1 is expected for rods, our result is also indicative of a random-coil chain, in agreement

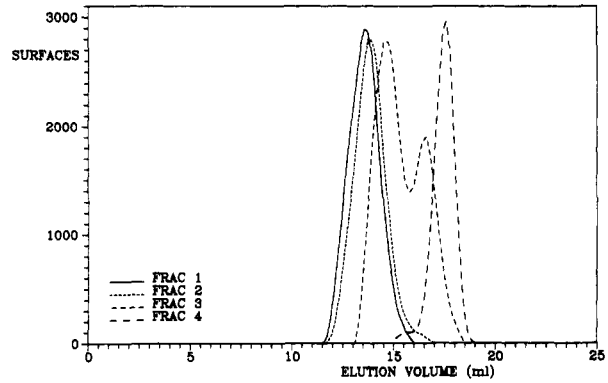

Figure 4. Results of the size-exclusion chromatography for the four fractions of PDHP.

with literature results for other polyphosphazenes.[5,8,9,25]

Initial attempts to obtain size-exclusion chromatograms of the polymer fractions solved in THF were unsuccessful since long tailing chromatograms inconsistent with LS and viscometric results were obtained. However, this problem was completely circumvented when, as reported by Neilson et al.,[14] a solution of tetra-*n*-butylammonium bromide (0.1 wt %) in THF was used as eluent. The chromatograms thus obtained are represented in Figure 4. As can be seen in this figure, three of the fractions show a broad unimodal distribution and fraction 3 is bimodal. The difficulties encountered in the fractionation of polyphosphazene samples and the presence of bimodal or even multimodal distributions have been reported.[5,6,12,13,25] Although we first tried a universal calibration plot generated for narrow molecular weight distribution polystyrenes, in our opinion, the SEC results obtained for PDHP suggest that instead it would be much better to apply a numerical analysis to the data, thus circumventing the necessity of having narrow distribution fractions of the PDHP.

Numerical Analysis

The chromatograms obtained by SEC, the weight-average molecular weights, $\bar{M}_w$, determined by LS, and the intrinsic viscosities, $[\eta]$, were combined to calculate the calibration curve for SEC, i.e., a function $\log M = f(V)$ relating the molecular weight and elution volume of ideally monodisperse fractions of the polymer, and the true values of the parameters on the Mark–Houwink equation,[21] i.e., the K and a parameters on the relationship $[\eta] = KM^a$.

The methods used for this analysis have been explained elsewhere.[26-30] In brief, they consist of applying iterative numerical procedures, seeking the best agreement between theoretical and experimental values of $\bar{M}_w$ and $[\eta]$. Thus, the calibration function for SEC can be explicitly written as

$$\log M = f(V) = \sum_{k=0}^{m} A_k V^k = A_0 + A_1 V + A_2 V^2 + \ldots + A_m V^m \quad (1)$$

where M and V represent the molecular weight and elution volume of an ideally monodisperse sample, while A_k are unknown polynomial coefficients that should be chosen to produce minimum root-mean-squared relative deviation σ_M between theoretical and experimental values of $\bar{M}_w$ for all the fractions of the polymer actually measured, i.e., the minimum value of the function

$$\sigma_M = \left[\frac{1}{n}\sum_{i=1}^{n}\left(1 - \frac{\bar{M}_{wi}(\text{calc})}{\bar{M}_{wi}(\text{exp})}\right)^2\right]^{1/2} \quad (2)$$

where n is the number of fractions used in the analysis and $\bar{M}_{wi}$ is the weight-average molecular weight of fraction i, whose experimental value was determined by light scattering while the theoretical one is calculated from the SEC chromatogram of the corresponding fraction as

$$\bar{M}_{wi}(\text{calc}) = \int_0^\infty H_i(V)\, M(V)\, dV = \int_0^\infty H_i(V)\, [\sum_{k=0}^{m} A_k V^k]\, dV \quad (3)$$

where $H_i(V)$ represents the normalized chromatogram of the ith fraction and the molecular weights of monodisperse species $M(V)$ are computed according to eq 1.

Once the coefficients A_k appearing in eq 1 have been obtained, the Mark–Houwink equation can be written as a function of the elution volume as

$$\log [\eta] = \log K + a \log M = \log K + a \log[\sum_{k=0}^{m} A_k V^k] \quad (4)$$

and the K and a coefficients can be adjusted to minimize the root-mean-squared relative deviation σ_η defined in a way similar to eq 2 as

$$\sigma_\eta = \left[\frac{1}{n}\sum_{i=1}^{n}\left(1 - \frac{[\eta]_i(\text{calc})}{[\eta]_i(\text{exp})}\right)^2\right]^{1/2} \quad (5)$$

with theoretical values of $[\eta]_i$ for each fraction computed from its own normalized chromatogram $H_i(V)$ according to

$$[\eta]_i(\text{calc}) = \int_0^\infty H_i(V)\, [\eta](V)\, dV = \int_0^\infty H_i(V)\, K[\sum_{k=0}^{m} A_k V^k]^a\, dV \quad (6)$$

We have used two numerical approaches, namely those proposed by Szewczyk[26] (method I in the present paper) and by McCrackin[27] (method II). Method I requires use of the inverse of eqs 1 and 4, i.e., the equations obtained by solving eq 1 for V and eq 4 for M as

$$V = f^{-1}(\log M) = \sum_{k=0}^{m} B_k (\log M)^k \quad (7)$$

$$\log M = \log K' + a' \log [\eta] \quad (8)$$

A least-squares regression is applied to compute the A_k coefficients on eq 1 by using the experimental values of $\bar{M}_{wi}$ of each fraction and their corresponding elution volumes at the peak of the chromatograms V_{pi} as first trial values. Theoretical results of $\bar{M}_{wi}(\text{calc})$ and σ_M are then computed with eqs 3 and 2, respectively. Next, the B_k coefficients in eq 7 are obtained by least-squares fitting of V_{pi} versus $\bar{M}_{wi}$, and a new set of volumes V_{2i} corresponding to ideally monodisperse samples having molecular weights equal to the weight average of the fraction $\bar{M}_{wi}$ are then computed. The set V_{2i} and $\bar{M}_{wi}$ is then used as a new trial value in eq 1 and the whole procedure is repeated in a cyclic way, monitoring the value of σ_M until this deviation reaches a minimum. The fitting of the K and a parameters in the Mark–Houwink equation is performed in a very similar way, assuming that analysis of the SEC calibration curve has been carried out previously, so that the set of coefficients A_k in eq 1 giving minimum deviation σ_M is known. Thus the first values of K and a are obtained by least-squares fitting of the experimental viscosities $[\eta]_i$ versus $\bar{M}_{wi}$ according to eq 4;

Table III
Best Values of the Coefficients A_k for the SEC Calibration Curve (Equation 1) and the Mark–Houwink K and a Parameters (Equation 4)

	method I		method II	
	order $m = 1$	order $m = 2$	order $m = 1$	order $m = 2$
A_0	12.46	24.17	12.01	21.13
A_1	−0.471	−2.06	−0.442	−1.66
A_2		0.053		0.040
σ_M	0.25	0.19	0.22	0.18
10^5K	3.47	2.39	2.09	2.00
a	0.75	0.78	0.79	0.80
σ_η	0.067	0.13	0.066	0.13

these values of K and a are used, together with the final set of A_k, to compute $[\eta]_i$(calc) and σ_η according to eqs 5 and 6, respectively; K' and a' are then obtained by fitting $\bar{M}_{wi}$ versus $\bar{M}_{wi}$ according to eq 8 and are used to compute the set of values M_{2i} that would correspond to ideally monodisperse samples having $[\eta]_i$. This new trial set of $[\eta]_i$ and M_{2i} is substituted into eq 4 to provide new values of K and a by least-squares fitting, and the whole procedure is repeated until the minimum value of σ_η is reached.

Method II is more simple, at least conceptually. It consists of imposing on the deviation σ the condition of minimum with respect to the adjustable parameters. Thus, in the case of the SEC calibration curve

$$\left[\frac{\delta(\sigma_M)}{\delta(A_i)}\right]_{A_{j\neq i}} = 0 \quad \text{for } i, j = 0, 1, ..., m \tag{9}$$

with σ_M and A_i given, respectively, by eqs 2 and 1, while for the Mark–Houwink equation

$$\left[\frac{\delta(\sigma_\eta)}{\delta(K)}\right]_a = \left[\frac{\delta(\sigma_\eta)}{\delta(a)}\right]_K = 0 \tag{10}$$

and σ_η, K, and a are given by eqs 5 and 4.

The set of eqs 9 and 10 can be numerically solved to provide the values of the coefficients A_k, and K, and a that give the least deviation. More details about all these procedures can be found in the literature.[26–30]

Once the SEC calibration curve has been fitted, any average of the molecular weight can be obtained from the chromatogram with an equation similar to eq 3. Thus, for instance, the number-average molecular weight of each fraction $\bar{M}_{ni}$, is given by

$$\bar{M}_{ni}(\text{calc}) = \{\int_0^\infty H_i(V)[M(V)]^{-1}\,dV\}^{-1}$$
$$= \{\int_0^\infty H_i(V)[\sum_{k=0}^{m} A_k V^k]^{-1}\,dV\}^{-1} \tag{11}$$

The coefficients obtained by applying both methods of numerical analysis with polynomials of both first and second orders, i.e., $m = 1$ or 2 in eq 1, are summarized in Table III, in which it can be seen that both procedures give practically the same results and that, in both cases, the second-order polynomial gives a better fit for molecular weight (i.e., smaller values of σ_M), although the first-order fitting produces a better agreement for viscosity (i.e., smaller values of σ_η). Figures 5 and 6 show, respectively, the curves of log M and log $[\eta]$ versus V calculated with the coefficients obtained applying both methods to first and second order. The circles in Figures 5 and 6 represent, respectively, the experimental values of $\bar{M}_{wi}$ (measured by light scattering) and $[\eta]_i$ (obtained by viscometry) for each fraction versus the elution volume at the peak, V_{pi}, on their corresponding chromatograms. It is important to notice that the lines on Figures 5 and 6 *do not represent* least-squares fittings of the experimental results indicated by circles. Thus, the lines indicate the values of either $\bar{M}_{wi}$ or $[\eta]_i$ of *ideally monodisperse samples* as a function of the elution volumes that they would give in an *infinitely narrow chromatogram*; on the contrary, the circles are experimental values measured on polydisperse samples as a function of the elution volume in one particular point of the chromatogram, namely, that corresponding to the maximum height, i.e., the peak. Thus, the differences between the curves and the circles are due to the polydispersity of the samples used in the analysis and, as Figures 5 and 6 indicate, severe errors may be introduced when either the calibration curve for SEC or the Mark–Houwink parameters are obtained by a direct fitting of experimental values. Figure 5 also shows the good agreement between the experimental values of $\bar{M}_{wi}$ and the calculated $\bar{M}_{wi}$ (represented by triangles) according to method II at a second order.

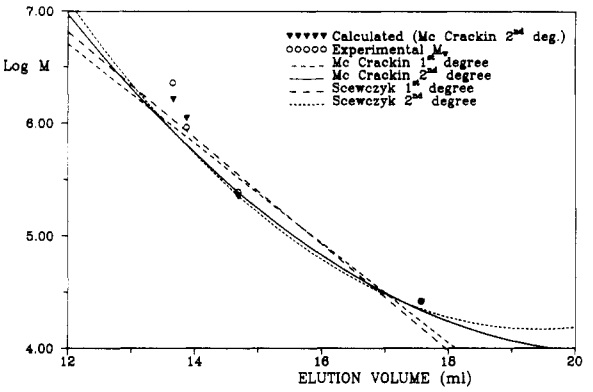

Figure 5. Calibration curves for SEC (eq 1) obtained with the A_k coefficients computed according to both Szewczyk and McCrackin methods at first and second degree. The circles represent experimental values of $\bar{M}_{wi}$, measured by light scattering, versus elution volumes at the peak of the SEC chromatogram for each fraction V_{pi}. The triangles represent the values of $\bar{M}_{wi}$ calculated with method II at the second degree.

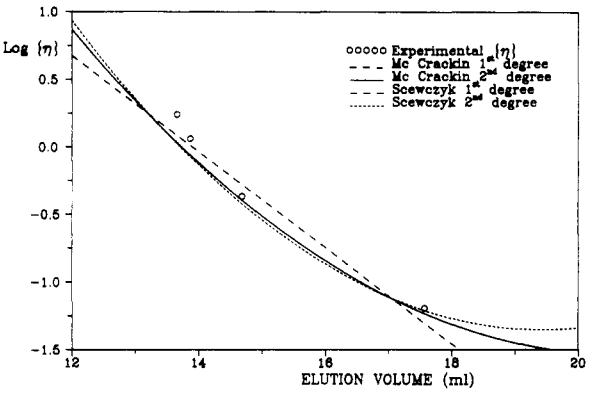

Figure 6. Representation of the Mark–Houwink equation (eq 4) according to the K and a coefficients obtained with both methods at first and second degree. The circles represent experimental values of $[\eta]_i$, measured by viscometry, versus elution volumes at the peak of the SEC chromatogram for each fraction V_{pi}.

Table IV shows values of the averaged molecular weights (computed according to eqs 3 and 11 and the similar one for $\bar{M}_{vi}$) and intrinsic viscosities of the four fractions studied in the present work. As the table indicates, the polydispersity ratios of these fractions, r, range from 1.14 to 2.87.

Once the viscosity-average molecular weights $\bar{M}_{vi}$ have been computed, the Flory–Fox[31–32] relationship can be used to calculate the molecular dimensions from the viscosity

Table IV
Molecular Weight Averages and Intrinsic Viscosities (in dL/g) for the Four Fractions of PDHP[a]

	fraction 1	fraction 2	fraction 3	fraction 4
log ($\bar{M}_{wi}$)(exp)	6.357	5.962	5.389	4.420
log ($\bar{M}_{wi}$)(calc)	6.216	6.047	5.354	4.423
log ($\bar{M}_{ni}$)(calc)	5.813	5.647	4.896	4.365
$r = \bar{M}_{wi}$(calc)/$\bar{M}_{ni}$(calc)	2.53	2.51	2.87	1.14
log ($\bar{M}_{vi}$)(calc)	6.184	5.957	5.416	4.387
$[\eta]_i$(exp)	1.75	1.15	0.43	0.06
$[\eta]_i$(calc)	1.72	1.26	0.35	0.07

[a] Theoretical values were computed with the coefficients obtained by method II at the second degree.

Table V
Comparison of Experimental (LS) and Theoretical (FF) Values of $\langle r^2\rangle^{1/2}$ Calculated by LS or by Using the Flory–Fox Relationship, Respectively

	$\langle r^2\rangle^{1/2}$, nm			$\langle r^2\rangle^{1/2}$, nm	
fraction	LS	FF	fraction	LS	FF
1	173.1	102.1	3	34.2	35.4
2	74.5	74.7	4		8.5

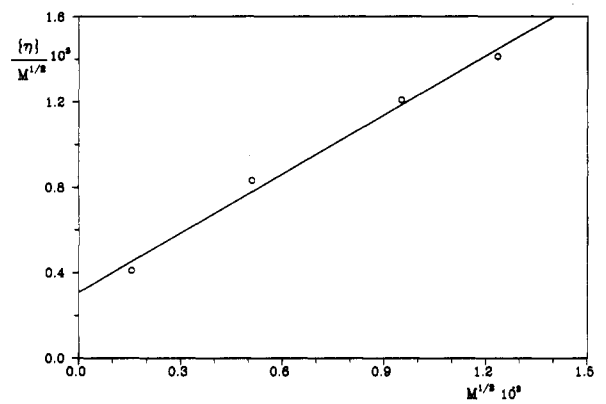

Figure 7. Plot of the Stockmayer–Fixman equation.

results as

$$\langle r^2\rangle^{3/2} = [\eta]\bar{M}_v/\phi \quad (12)$$

where ϕ is 2.5 and $\langle r^2\rangle^{3/2}$ is in cubic nanometers and $[\eta]$ is in deciliters per gram.

Table V shows the experimental (calculated as $\langle r^2\rangle = 6\langle s^2\rangle$ from the radius of gyration measured by LS) and theoretical (FF) values of $\langle r^2\rangle$. It is worthy to point out that experimentally determined values are similar to or lower than the values calculated by using the Flory–Fox relationship, which indicates the absence of branching, in good agreement with other authors.[8,25]

The characteristic ratio of the unperturbed dimensions relative to the number of skeletal bonds and the square of their length $C_n = \langle r^2\rangle_0/nl^2$ has been calculated by using the Stockmayer–Fixman relationship

$$[\eta]/M^{1/2} = K_\theta + CK_\theta M^{1/2} \quad (13)$$

The plot of $[\eta]M^{-1/2}$ vs $M^{1/2}$ is represented in Figure 7. Least-squares fitting of the points gives a value of $K_\theta = 0.308 \times 10^{-3}$. Taking into account the Flory–Fox and Mark–Houwink relationships, the characteristic ratio can be calculated as

$$C_n = \frac{\langle r^2\rangle_0}{nl^2} = \frac{\langle r^2\rangle_0 M_r}{2l^2 M} = \frac{M_r K_\theta^{2/3}}{2l^2\Phi^{2/3}} \quad (14)$$

where l is the P–N bond length (0.152 nm), n the number of bonds of the chain, and M_r the molecular weight of the repeat unit. The value of C_n thus obtained is 13.2. Very different values of characteristic ratios ranging between 6 and more than 100 have been reported[9,15] for polyphosphazenes of the type $-[P(OR)(OR')N^-]_n$. The value obtained in the present work for PDHP suggests a rather flexible chain molecule in the random-coil state. It is noteworthy to point out the good agreement between values of the molecular dimensions obtained for this polymer by LS and viscometry.

Acknowledgment. The assistance provided by Dr. E. Riande and Dr. J. Guzmán of the Instituto de Ciencia y Tecnología de Polímeros is gratefully acknowledged. This work was supported by the Universidad de Alcalá de Henares through Grant No. UAH-89-A3.

References and Notes

(1) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(2) Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22.
(3) Wisian Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848.
(4) Neilson, R. H.; Wisian Neilson, P. *J. Macromol. Sci., Chem.* **1981**, *A16*, 425.
(5) Hagnauer, G. L.; Schneider, N. S. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 699.
(6) Tate, D. P. *J. Polym. Sci., Polym. Symp.* **1974**, *48*, 33.
(7) Hagnauer, G. L.; La Liberte, B. R. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 367.
(8) Singler, R. E.; Hagnauer, G. L.; Schneider, N. S.; Laliberte, B. R.; Sacher, R. E.; Matton, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 433.
(9) Bravo, J.; Tarazona, M. P.; Roig, A.; Saiz, E. *An. Quim.*, in press.
(10) Mourey, T. H.; Miller, S. M.; Ferrar, W. T.; Molaire, T. R. *Macromolecules* **1989**, *22*, 4286.
(11) Neilson, R. H.; Ford, R. R.; Hani, R.; Roy, A. K.; Scheide, G. M.; Wettermark, U. G.; Wisian Neilson, P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 442.
(12) Allen, G.; Lewis, C. J.; Todd, S. M. *Polymer* **1970**, *11*, 44.
(13) Ferrar, W. T.; Marshall, A. S.; Flood, E. C.; Goppert, K. E.; Myers, D. I. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 444.
(14) Neilson, R. H.; Hani, R.; Wisian Neilson, P.; Meister, J. S.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* **1987**, *20*, 910.
(15) Andrady, A. L.; Mark, J. E. *Europ. Polym. J.* **1981**, *17*, 323.
(16) Allcock, H. R.; Connolly, M. S.; Sisko, J. T.; Al-Shali, S. *Macromolecules* **1988**, *21*, 323.
(17) Huggins, M. L. *J. Am. Chem. Soc.* **1942**, *64*, 2716.
(18) Kraemer, E. O. *Ind. Eng. Chem.* **1938**, *30*, 1200.
(19) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.
(20) Kamide, K.; Saito, M. In *Determination of Molecular Weight*; Cooper, R., Ed.; Wiley: New York, 1989; Chapter 8.
(21) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(22) Bandrup, J.; Immergut, E. H. *Polymer Handbook*; Wiley-Interscience: New York, 1969.
(23) Krigbaum, W. L.; Flory, P. J. *J. Am. Chem. Soc.* **1953**, *75*, 1775, 5254.
(24) Fuyita, H.; Norisuye, T. *Macromolecules* **1985**, *18*, 1637.
(25) Carlson, D. W.; O'Rourke, E.; Valaitis, J. K.; Altenau, A. G. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1379.
(26) Szewczyk, P. *Polymer* **1976**, *17*, 90.
(27) McCrackin, F. L. *J. Appl. Polym. Sci.* **1977**, *21*, 191.
(28) Barrales-Rienda, J. M.; Romero-Galicia, C.; Horta, A. *Macromolecules* **1983**, *16*, 932.
(29) Barrales-Rienda, J. M.; Galera-Gómez, P. A.; Horta, A.; Saiz, E. *Macromolecules* **1985**, *18*, 2572.
(30) Horta, A.; Saiz, E.; Barrales-Rienda, J. M.; Galera-Gómez, P. A. *Polymer* **1986**, *27*, 139.
(31) Fox, T. G.; Flory, P. J. *J. Phys. Colloid Chem.* **1949**, *53*, 197.
(32) Flory, P. J.; Fox, T. G. *J. Am. Chem. Soc.* **1951**, *73*, 1904.