Molecular Characterization of Poly[bis(β-naphthoxy)phosphazene] by ^{31}P NMR, Viscometry, Light Scattering, and Size Exclusion Chromatography

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ABSTRACT: A sample of poly[bis(β-naphthoxy)phosphazene] (PBNP) has been synthesized, purified, fractionated, and characterized according to standard procedures. Seven fractions were separated and studied by light scattering, viscometry, and size exclusion chromatography (SEC). The light scattering measurements, performed in THF solutions at 25 °C, gave $\bar{M}_w$ = 140, 120, 54, 50, 42, 21, and 10 in 10^4 g/mol units, respectively, for fractions 1–7; the results for the radius of gyration for the fractions were $\langle s^2 \rangle^{1/2}$ = 48, 40, 31, 31, 31, 25, and 16 nm, and the intrinsic viscosities measured in THF solutions at 25 °C were $[\eta]$ = 0.72, 0.47, 0.38, 0.29, 0.25, 0.18, and 0.12 dL/g. An iterative numerical procedure previously described in the literature was 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. The results obtained for those functions were log M = 14.93 − 2.54V + 0.16V^2 and $[\eta]$ = 4.17 × $10^{-5}M^{0.69}$. The K and a constants of the Mark–Houwink equation allow the determination of the viscosity average molecular weight of the seven fractions, $\bar{M}_v$, and their molecular dimensions, which are smaller than those measured by light scattering. The analysis of the results obtained by light scattering and viscometry, together with the ^{31}P NMR spectra of the samples, allows one to reach some conclusions about the possible branching of this polymer.

Introduction

Since 1966, when Allcock first synthesized soluble poly(dichlorophosphazene) (PDCP) and substituted the chlorine atoms by organic groups,[1] many polyphosphazenes with a wide variety of substituents at the phosphorus atoms have been prepared, and the interest of this kind of polymer has increased rapidly not only because of the useful properties they often exhibit[2] but because they provide an excellent means for exploring the effects of changes in side group structure on the physical properties of flexible polymer chains.[3]

Recently[4-6] we have investigated the dilute solution characterization of two poly(dialkoxyphosphazenes), namely, those having hexoxy (PDHP) and ethoxy (PDEP) side groups by means of light scattering (LS), viscometry (VIS), and size exclusion chromatography (SEC). These two polymers have very flexible alkoxy residues as side groups, and as a consequence they are good elastomers with very low values of the glass transition temperature;[3] i.e., T_g = −104 and −84 °C, respectively, for PDHP and PDEP. We thought that it would be interesting to perform a similar study for a polyphosphazene having a rigid and bulky side group such as the naphthoxy residue which produces a very strong effect on the elastomeric properties of the chain, increasing the value of T_g by more than 100 °C; i.e., T_g = 47 °C when the two side groups are β-naphthoxy residues. Poly[bis(β-naphthoxy)phosphazene] (PBNP) was first synthesized by Allen et al.[7,8] and its photodegradation and photophysical behavior have been studied.[9-10] Although we also attempted the synthesis of poly[bis(α-naphthoxy)phosphazene], complete substitution of chlorine atoms by the α-naphthoxy group was not achieved neither in the polymer nor in the trimer hexachlorocyclotriphosphazene, presumably due to steric hindrance.[11] Consequently, we chose PBNP for the present work, and this paper presents the results obtained by LS, VIS, and SEC dilute solution measurements of seven samples of PBNP synthesized according to standard procedures and fractionated using the solvent–nonsolvent technique.[12]

Although extreme care was taken in the fractionation of PBNP, the fractions still had a great dispersity, with $\bar{M}_w/\bar{M}_n$ ratios as large as 3.4 for the most polydisperse fraction, as indicated by SEC. This result is a consequence of the severe problems associated with the fractionation of polyphosphazenes described in the literature.[5,8,13,14] Thus, a numerical method of analysis that does not require the use of monodisperse fractional samples has been applied to calculate SEC parameters and Mark–Houwink constants.

The analysis of the ^{31}P NMR spectra of the samples, together with a close examination of the present results of LS and VIS, provides information which can be used to decide on the possible branching of the sample.

Experimental Section

Materials. Poly[bis(β-naphthoxy)phosphazene] (PBNP) was synthesized by known procedures.[1,7] Hexachlorocyclotriphosphazene (Fluka; 29.5 g, 0.084 mol) was resublimed and then polymerized in a sealed evacuated tube at 250 °C until the molten reaction mixture became so viscous that flows ceased. The poly(dichlorophosphazene) thus obtained was dissolved in tetrahydrofuran, THF, and added slowly over a THF solution of sodium β-naphthoxide prepared from β-naphthol (100 g, 0.694 mol) THF solution and sodium hydride (23.6 g of 80% oil dispersion, 0.79 mol). The reaction mixture was stirred for 70 h at room temperature and was heated under reflux for 114 h. After the reaction was stopped, the reaction mixture was cooled to room temperature and precipitated in a large amount of water, and the product was isolated and purified in a Soxhlet apparatus with acetone for 24 h in order to extract the hexakis(β-naphthoxy)cyclotriphosphazene and other small cycles if present. Then the polymer was extracted with trichloromethane in the same Soxhlet apparatus to remove insoluble impurities. The polymer was purified by successive precipitations of a THF solution into water/acetone.

The fractionation of PBNP was carried out by the solvent–nonsolvent technique.[12] A solution of the polymer in THF was cooled to 10 °C, and hexane was then added as the nonsolvent until a slight turbidity was observed. The solution was then warmed to 40 °C until it was clear, allowed to slowly cool to 10 °C, and kept overnight at this temperature. The precipitated polymer was separated and the procedure repeated to obtain

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

fraction	$[\eta]$ (dL/g)	k_H	k_K
1	0.720	0.920	0.335
2	0.474	0.882	0.336
3	0.384	0.950	0.399
4	0.294	0.523	0.013
5	0.250	0.843	0.304
6	0.179	0.645	0.096
7	0.116	0.310	-0.188

additional fractions. Seven different fractions with quantities enough for the study were obtained, and the polymer that remained in solution was discarded. All the fractions were dissolved in THF and filtered, the solvent was then eliminated in a rotatory evaporator, and the polymer was further dried under vacuum at 50 °C. The polymer was characterized by elemental analysis and infrared, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra.

Viscometric Measurements. A Schott Gerate autoviscometer was employed to measure flow times of PBNP solution in THF. The bath temperature was controlled at 25 ± 0.1 °C. Values of the intrinsic viscosity, $[\eta]$, Huggins constant, k_H, and Kraemer constant, k_K, were estimated by the simultaneous extrapolation to infinite dilution of $\eta_{red} = \eta_{sp}/c$ and $\eta_{inh} = (1/c) \ln \eta_{rel}$ vs c, where c represents the concentration and η_{sp} and η_{rel} are the specific and relative viscosities, respectively, according to the Huggins[15] $\eta_{red} = [\eta] + k_H[\eta]^2 c$ and Kraemer[16] $\eta_{inh} = [\eta] + k_K[\eta]^2 c$ equations using least-squares linear regression analysis.

Size Exclusion Chromatography. Experiments were performed 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 380 computer with an 840 chromatography control and data acquisition station. The column used was a PLgel 10^5 Å. Elutions were conducted with a flow rate of 1 mL min^{-1}. It has been reported[17] that, in the case of polyphosphazenes, adsorption phenomena between polymer and the column fillers occur, producing anomalous and not reproducible chromatograms. The adsorption is eliminated by the addition of small amounts of quaternary ammonia salts to the mobile phase.[17] Thus, freshly distilled THF with a 0.1 % a tetrakis(n-butyl)ammonium bromide was used as the eluent in the present work, and reproducible chromatograms were obtained for all the fractions. However, pure THF was used as the solvent for all VIS and LS measurements in order to facilitate the comparison of the results with those previously reported for similar polymers in pure solvents.[5,17] The calibration curves obtained with narrow molecular weight distribution polystyrene standards (Scharlau) using either pure THF or THF with added salt as the mobile phase are indistinguishable. The universal calibration method fails when applied to the samples studied in this work.

Light Scattering. Scattering of solutions of PBNP 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 dn/dc ranging between 0.1858 and 0.1908 mL/g for the different fractions. Experimental values of the scattered intensities were represented in Zimm plots,[18] and values of the weight average molecular weight, $\bar{M}_w$, second virial coefficient, A_2, and radius of gyration, $\langle s^2 \rangle$, were determined from the intercept and slopes.

Results and Discussion

Dilute-Solution Measurements. Results of the viscometric measurements are shown in Table I, and the Huggins–Kraemer plots showing the coincidence of intercepts are represented in Figure 1. A rough estimation of the experimental uncertainty in the values of $[\eta]$ gives ca. 3%. Concentrations lower than 0.2 g/dL were used for the four fractions of higher molecular weight in order to avoid curvature on the plots. Huggins constants were in the range 0.3–0.9 which are somewhat larger than values expected for linear and flexible polymers in a good solvent
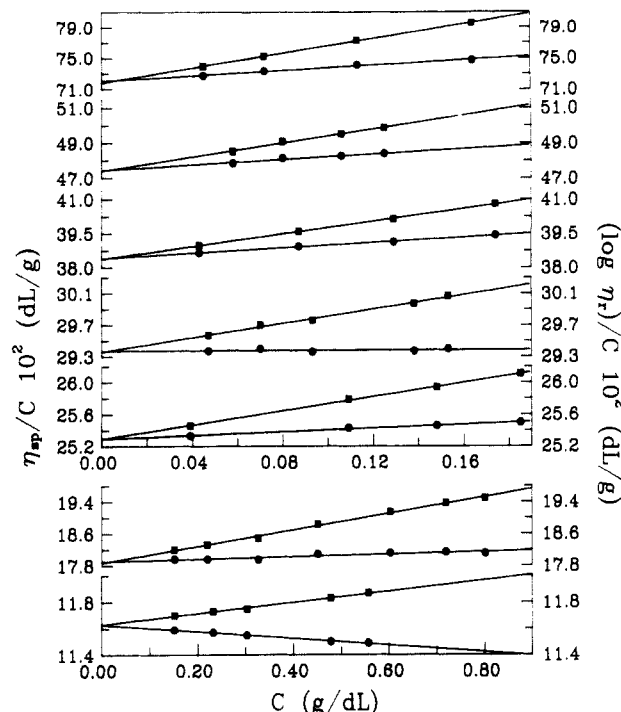

Figure 1. Huggins–Kraemer plots for seven fractions of PBNP in THF at 25 °C.

Table II
Light Scattering Data for the Seven Fractions of PBNP in THF at 25 °C

fraction	dn/dc (mL/g)	$10^{-4}\bar{M}_w$ (g/mol)	$\langle s^2 \rangle_z^{1/2}$ (nm)	$\langle s^2 \rangle_w^{1/2}$ (nm)
1	0.1908[a]	140	48	37
2	0.1908	120	40	31
3	0.1883	54	31	24
4	0.1883[a]	50	31	24
5	0.1883	42	31	26
6	0.1858[a]	21	25	21
7	0.1858	10	16	15

[a] Experimentally determined.

and larger than those obtained for PDHP.[5] Values of the Huggins and Kraemer constants found in the literature for other polyphosphazenes range from very low values, even negative Huggins constants, to very high ones[13,14,19] and do not normally follow the theoretical relation[20] $k_H - k_K = 1/2$. As Table I indicates, the values found for PBNP follow fairly well the above theoretical equation; i.e., $k_H - k_K = 0.5 \pm 0.09$ for the seven fractions.

Table II summarizes the light scattering data, namely, the value of dn/dc used for each fraction, weight-average molecular weight $\bar{M}_w$ with an experimental uncertainty of ca. 5%, and root-mean-square z-average radius of gyration $\langle s^2 \rangle_z^{1/2}$ whose experimental error is estimated to be ca. 10%. The last column in this table contains the root mean square of the weight average for the radius of gyration $\langle s^2 \rangle_w^{1/2}$, computed as[21,22]

$$\langle s^2 \rangle_w = \langle s^2 \rangle_z \left[\frac{h+1}{h+2} \right] \tag{1}$$

with the polydispersity index h defined as $1/h = \bar{M}_w/\bar{M}_n - 1$. Theoretical values of $\bar{M}_w$ and $\bar{M}_n$, obtained by integration of the SEC chromatogram (see below), were used to compute the h index.

The variation of the ratio $Kc/\Delta R$ with concentration was very poor, and therefore the determination of the second virial coefficient A_2 in the Zimm plots was affected by serious errors. Thus, values of A_2 ranging from -2.2 to +2.6 in units of 10^{-4} mol cm^3 g^{-1} were obtained. Although
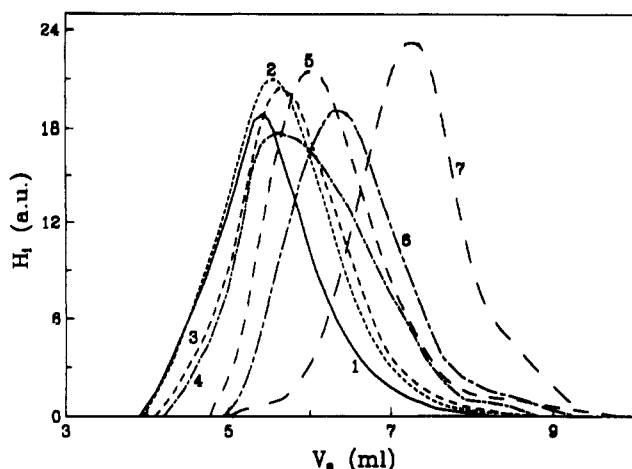
Figure 2. Size exclusion chromatograms for seven fractions of PBNP.

we try to plot $K/\Delta R$ versus $1/c$ and extrapolate to zero angle[23] to give an intercept of A_2, the plots do not improve very much. The results and the positive and negative values of A_2 obtained do not have much relation to the behavior of the polymer solution.

The chromatograms obtained in SEC are represented in Figure 2. As can be seen in this figure, the fractions show a broad distribution. Although we first tried a universal calibration plot generated for narrow molecular weight distribution polystyrenes, in our opinion, the SEC results obtained for PBNP suggest that it would be much better to apply a numerical analysis to the data, thus circumventing the necessity of having narrow distribution fractions of the PBNP.

Numerical Analysis. The numerical approach developed by McCrackin[24] was used to compute the parameters defining the calibration function for SEC and the Mark-Houwink[20] viscometric equation from the experimental results obtained with the actual polydisperse samples. This procedure has been employed before for other polymers,[25-27] including samples of PDHP.[5] Some calculations, not shown here, were also performed using the alternative procedure proposed by Szewczyk,[28] but the results were almost identical to those obtained with the much easier method of McCrackin.

The calibration function for SEC is written in a polynomial form as

$$\log M = f(V) = \sum_{k=0}^{m} A_k V^k =$$

$$A_0 + A_1 V + A_2 V^2 + ... + A_m V^m \quad (2)$$

where M and V are the molecular weight and elution volume of an ideally monodisperse sample while A_k represent the unknown polynomial coefficients to be determined by minimizing the root-mean-square relative deviation σ_M between experimental and calculated values of the weight-average molecular weights for all the fractions studied.

A standard routine using the Powell algorithm[29] was used to minimize the σ_M function taking the A_k coefficients of eq 2 as independent variables, thus allowing the computation of these parameters. Once the coefficients of the SEC calibration function have been obtained, the

Mark-Houwink viscometric equation can be written as a function of the elution volumes

$$\log [\eta] = \log K + a \log M = \log K + a[\sum_{k=0}^{m} A_k V^k] \quad (3)$$

so that theoretical values of intrinsic viscosities $[\eta]_i$(calcd) and viscosity-average molecular weights $\bar{M}_{vi}$(calcd) for the ith fraction can be computed by integration of the SEC chromatogram.

The K and a Mark-Houwink parameters appearing in eq 3 are computed by minimizing the root-mean-square relative deviation σ_η between experimental and calculated values of the intrinsic viscosities of all the fractions.

Polynomials of degree $k = 1-3$ have been tested as calibration functions of SEC according to eq 2. The results obtained with degree $k = 2$ are better, i.e., produce lower values of both σ_M and σ_η, than those computed with $k = 1$. However, increasing the degree of the polynomial to $k = 3$ does not give any noticeable decrease of those deviations. Consequently, it seems that a second-degree polynomial represents a good enough approximation for the SEC calibration function of PBNP.

All the results obtained in the present analysis, i.e., A_k, K, and a coefficients, molecular weight averages, and intrinsic viscosities, are summarized in Table III. The solid line of Figure 3 shows a graphic representation of the calibration curve for SEC drawn with the coefficients contained in Table III. The circles and triangles in this figure represent, respectively, experimental (measured by LS) and calculated (computed according to eq 4) values of the weight-average molecular weights $\bar{M}_{wi}$ of the seven fractions plotted versus the elution volumes at the peak of their respective SEC chromatograms. The solid line in this figure is *not* a least-squares fitting of the experimental points. Instead it is a calibration function that represents a relationship between molecular weight and elution volume for *ideally monodisperse samples* which allows the computation of averaged molecular weights for actually polydisperse samples. The accuracy of this relationship can be judged by the agreement between experimental (circles in Figure 3) and calculated (triangles in the same figure) values of $\bar{M}_{wi}$ for the actual fractions. If the calibration curve were obtained by a direct least-squares fitting of the experimental $\bar{M}_{wi}$ versus elution volume at any point of the chromatogram, at the peak for instance, a much poorer agreement between experimental and calculated values of $\bar{M}_{wi}$ would be obtained. Figure 4 shows a representation of the Mark-Houwink viscometric equation. The solid line was drawn with the K and a coefficients given in Table III. The circles represent values of log $[\eta]$ (experimental) versus log $\bar{M}_v$, with the viscosity-average molecular weight $\bar{M}_{vi}$ computed by integration of the SEC chromatogram. The agreement between theory and experience is very good.

Chain Dimensions. The molecular dimensions of the polymeric chains can be computed according to the Flory-Fox equation:

$$\langle r^2 \rangle^{3/2} = [\eta] M_v / \Phi \quad (4)$$

where Flory's constant $\Phi = 2.5$ when r is expressed in nanometers and $[\eta]$ in deciliters per gram. The results obtained using the data of Table III for experimental values of $[\eta]$ and calculated $\bar{M}_v$'s are summarized in Table IV together with the dimensions computed as $\langle r^2 \rangle \approx 6\langle s^2 \rangle$, with the values of the radius of gyration measured by LS and summarized in Table II.
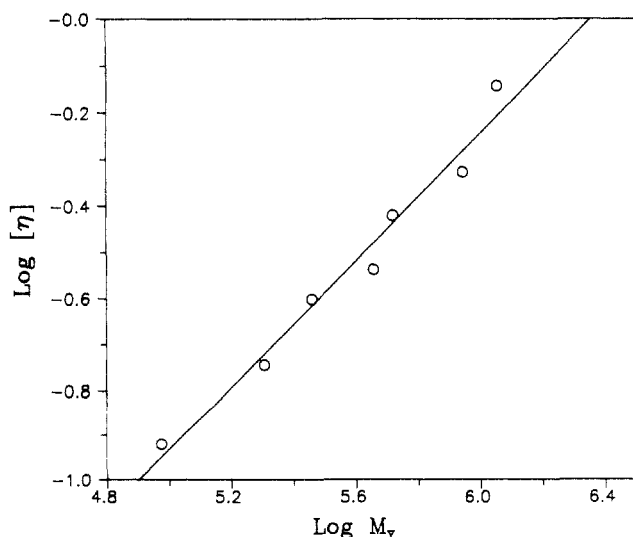
Table III
SEC Calibration Function, Viscometric Parameters, Molecular Weight Averages, and Intrinsic Viscosities (dL/g) Obtained for Seven Fractions of PBNP in THF at 25 °C

	SEC calibration function		$\log M = 14.93 - 2.54V + 0.16V^2$			$\sigma_M = 0.11$	
	viscometric equation		$\log [\eta] = -4.38 + 0.69 \log M$			$\sigma_\eta = 0.09$	
fraction	$\log \bar{M}_{wi}$(exptl)	$\log \bar{M}_{wi}$(calcd)	$\log \bar{M}_{ni}$(calcd)	r^a	$\log \bar{M}_{vi}$(calcd)	$[\eta]_i$(exptl)	$[\eta]_i$(calcd)
1	6.146	6.137	5.648	3.07	6.053	0.72	0.61
2	6.078	6.041	5.510	3.41	5.943	0.47	0.52
3	5.731	5.784	5.408	2.43	5.719	0.38	0.36
4	5.695	5.729	5.320	2.66	5.656	0.29	0.33
5	5.623	5.502	5.250	1.86	5.458	0.25	0.24
6	5.330	5.343	5.156	1.60	5.307	0.18	0.19
7	4.991	4.996	4.915	1.26	4.975	0.12	0.11

^{a} Calculated polydispersity ratio: $r = \bar{M}_{wi}$(calcd)$/\bar{M}_{ni}$(calcd).
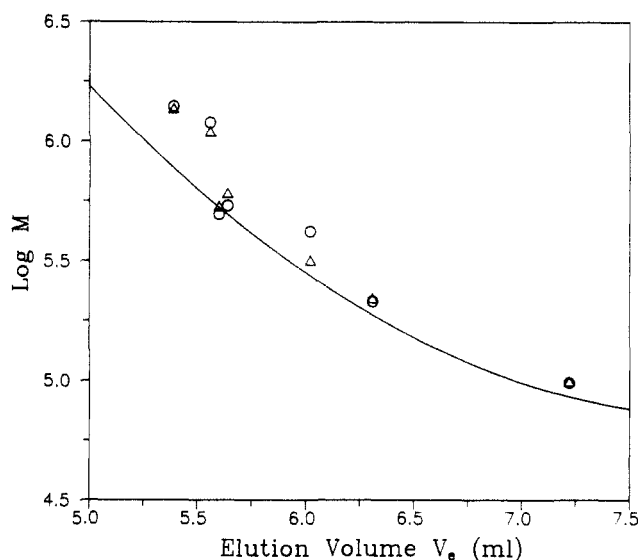
Figure 3. Calibration curve for SEC (eq 2) at second degree. The circles represent experimental values of $\bar{M}_{wi}$ measured by light scattering versus the elution volumes at the peak of the SEC chromatogram for each fraction. The triangles indicate calculated values of $\bar{M}_{wi}$ computed by integration of the chromatogram.

Figure 4. Representation of the Mark–Houwink viscometer equation. The solid line was drawn with the K and a coefficients given in Table I. The circles represent values of $\log [\eta]$(exptl) versus $\log \bar{M}_v$ with the viscosity-average molecular weight $\bar{M}_{vi}$ computed by integration of the SEC chromatogram.

The last line of Table IV contains the values of characteristic ratios of unperturbed dimensions C_∞ = $\lim_{n\to0}[\langle r^2\rangle_0/nl^2]$ obtained from both LS and VIS data. Viscometric results were extrapolated to unperturbed

Table IV
Comparison between the Molecular Dimensions of PBNP in THF Solution at 25 °C Obtained by LS (with the Relationship $\langle r^2\rangle \approx 6\langle s^2\rangle$) and Viscometry (Using the Flory–Fox Equation) Techniques

|	$\langle r^2\rangle^{1/2}$ (nm)	
fraction	LS	Flory–Fox
1	90	69
2	75	55
3	60	43
4	60	37
5	64	31
6	52	24
7	37	17
C_∞	103 ± 10	18 ± 2

conditions by using the Stockmayer–Fixman equation:[30]

$$[\eta]\bar{M}^{-1/2} = K_\theta + A\bar{M}^{1/2} \qquad (5)$$

where A contains the Φ constant and a function of the polymer–solvent interaction parameters that do not depend on molecular weight. The circles in Figure 5 and their least-squares regression line indicated by a dot line show the fitting of eq 5 using experimental values of $[\eta]$ and experimental results of $\bar{M}_w$. The quality of the fitting is improved by using experimental values of $[\eta]$ and theoretical values of M_m obtained as $M_m = ([\eta]/K)^{1/a}$ with the K and a coefficients obtained before; thus, M_m represents the molecular weight of a monodisperse sample having the same intrinsic viscosity measured for each actual fraction. This second kind of representation is indicated by the triangles and the solid line of Figure 5. Despite the difference in quality of the two fitting procedures, both of them give almost identical values for the intercept K_θ = 3.02×10^{-4} which can be converted into a characteristic ratio using the relationship

$$C_\infty = \frac{M_r K_\theta^{2/3}}{2l^2\Phi^{2/3}} \qquad (6)$$

with $l = 0.152$ nm for the length of the P–N bond and M_r = 331.3 g/mol for the molecular weight of the repeating unit of PBNP.

Several procedures have been proposed for the extrapolation of the radius of gyration to unperturbed conditions. We have used three of these procedures that consist in plotting the ratio $\langle s^2\rangle_w/\bar{M}_w$ versus a function containing $\bar{M}_w$ and extrapolate it to $\bar{M}_w \to 0$. The first of these procedures is due to Stockmayer[31] and Flory[32] and is represented by eq 7. The second one, proposed by Fixman,[33] is given by eq 8. Finally, eq 9 represents the procedure of Kurata–Stockmayer–Roig,[34] where the B constant contains magnitudes such as the partial specific volume of polymer and the molar volume of solvent. The factor $G(\alpha)$ appearing in eq 9 is defined as a function of
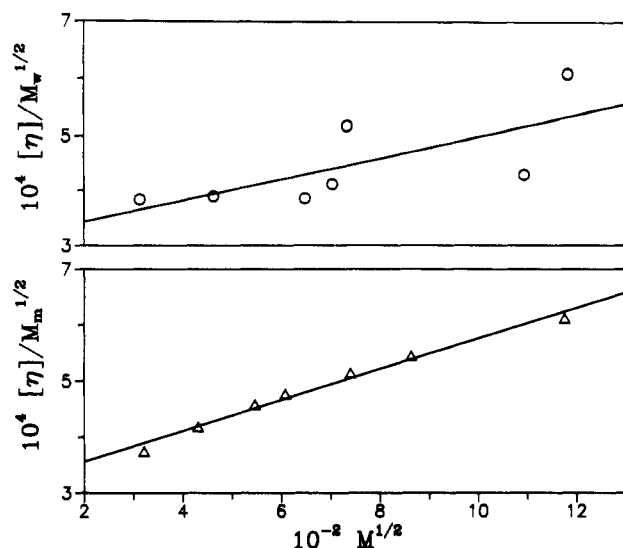
Figure 5. Representation of the Stockmayer–Fixman extrapolation to unperturbed conditions. Experimental values of intrinsic viscosities [η] were always employed. The circles and the solid line representing their least-squares fitting line were obtained using experimental values of weight-average molecular weight $\bar{M}_{wi}$. The triangles and their least-squares fitting were obtained using M_m defined as the molecular weight of monodisperse samples having the same intrinsic viscosities measured for the actual fractions; i.e., $M_m = ([\eta]/K)^{1/a}$.
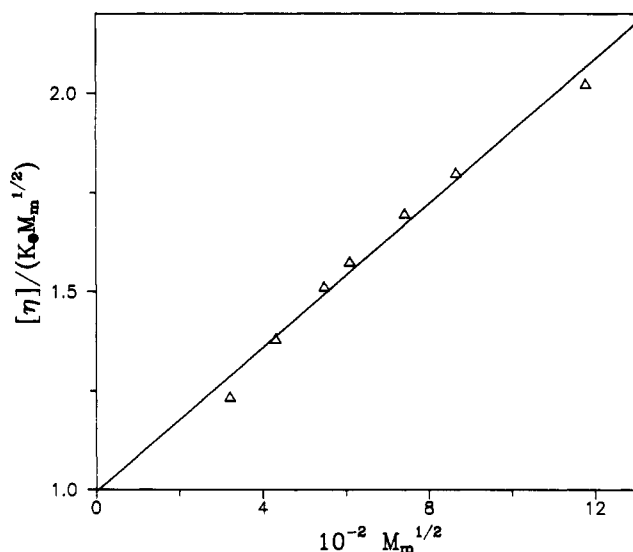
Figure 6. Expansion coefficient of the chain $\alpha^3 = [\eta]/[\eta]_\theta$ as a function of the molecular weight.
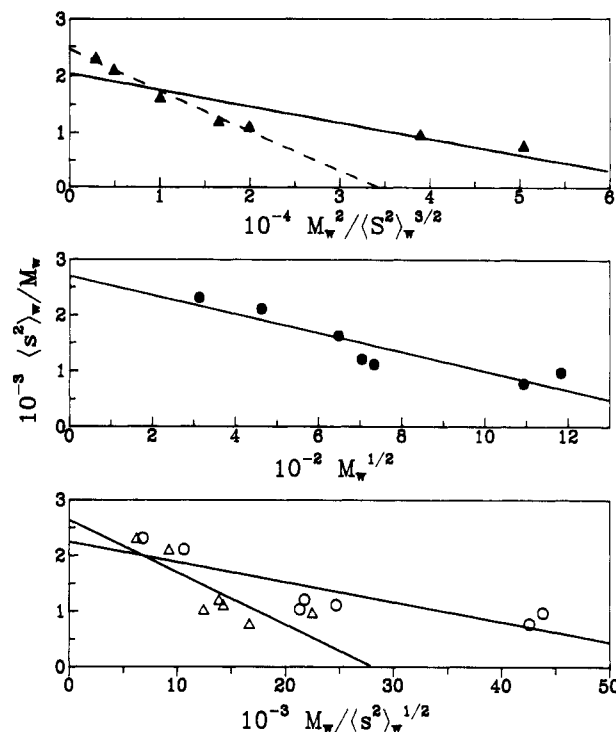
$$\frac{\langle s^2 \rangle_w}{\bar{M}_w} = \frac{\langle s^2 \rangle_{0w}}{\bar{M}_w} + 0.056B\left(\frac{\langle s^2 \rangle_{0w}}{\bar{M}_w}\right)\left(\frac{\bar{M}_w^2}{\langle s^2 \rangle_w^{3/2}}\right) \quad (7)$$

$$\frac{\langle s^2 \rangle_w}{\bar{M}_w} = \frac{\langle s^2 \rangle_{0w}}{\bar{M}_w} + 0.0299B\left(\frac{\bar{M}_w}{\langle s^2 \rangle_{0w}}\right)^{1/2}\bar{M}_w^{1/2} \quad (8)$$

$$\frac{\langle s^2 \rangle_w}{\bar{M}_w} = \frac{\langle s^2 \rangle_{0w}}{\bar{M}_w} + 0.0286BG(\alpha)\left(\frac{\bar{M}_w}{\langle s^2 \rangle_w^{1/2}}\right) \quad (9)$$

the expansion coefficient of the chain α as $G(\alpha) = 8\alpha^3/(1 + 2\alpha^2)^{3/2}$. The value of α can be computed by the ratio $\alpha^3 = [\eta]/[\eta]_\theta$ from the results obtained with eq 5 that can be written as

$$\alpha^3 = \frac{[\eta]}{[\eta]_\theta} = \frac{[\eta]}{K_\theta M^{1/2}} = 1 + (A/K_\theta)M^{1/2} \quad (10)$$

Figure 7. Extrapolation of the radius of gyration to unperturbed conditions according to eqs 7 (filled triangles), 8 (filled circles), and 9 (open circles and triangles); see text.

The plot of α^3 versus $M_m^{1/2}$ is shown in Figure 6 from which one obtains $\alpha^3 = 1 + 9.1 \times 10^{-4}M_m^{1/2}$.

Figure 7 contains the three extrapolations represented by eqs 7–9. As this figure shows, none of these procedures provides a good extrapolation. For instance, the data of eq 7 show a noticeable curvature, and the fitting is considerably improved if the two last points are discarded. Equation 9 is in fact an iterative procedure; the results of $\langle s^2 \rangle_{0w}/\bar{M}_w$ can be used to compute new values of α^2 which allow a new iteration. Figure 7 contains two of these iterations, namely, the first one with values of α computed from eq 10 and the third one after which the intercept remains unchanged. Although the extrapolations are rather poor, all their intercepts are in the range $(2.4 \pm 0.2) \times 10^{-3}$, and this is the only parameter required for the evaluation of C_∞ by the equation

$$C_\infty = \left[\frac{6M_r}{2l^2}\right]\left[\frac{\langle s^2 \rangle_{0w}}{\bar{M}_w}\right] \quad (11)$$

in which $\langle s^2 \rangle_{0w}/\bar{M}_w = 2.4 \times 10^{-3}$ with uncertainties of ca. 10%.

31P NMR Spectrum. The existence of branching in phosphazene chains has been the subject of considerable debate in the literature.[7,13,14,35–39] We have not found any evidence of branching in the poly(alkoxyphosphazenes) studied so far,[4–6] but there are a few points in the case of PBNP that deserve a more detailed study.

The 31P NMR spectrum of PBNP taking phosphoric acid as a reference is depicted in Figure 8. As can be seen in this figure, there is not a unique singlet as could be expected from a linear completely substituted polymer formed with chains long enough so that chain ends would not affect the spectrum. The main signal is centered at −17.7 ppm and shows some fine splitting and a shoulder downfield, but there is also a smaller signal centered at −14.82 which indicates that not all the P atoms are equivalent. Several researchers have found more than one signal in the 31P NMR spectra of some polyphosphazenes which have been attributed to different reasons.

Figure 9. Logarithmic plot of the dependence of $\langle s^2 \rangle_z^{1/2}$ (circles) and $\langle s^2 \rangle_w^{1/2}$ (triangles) on $\bar{M}_w$.

Figure 8. ^{31}P NMR spectrum of PBNP.

For thermally polymerized PDCP Klein et al.[40] found a signal at -18.7 ppm with a shoulder on the downfield side and several small peaks at $+19.7$ (produced by unreacted trimer), -16.1, and -17.9 ppm that they attributed to cycles higher than a tetramer and as high as an octamer or nonamer. In our case, one could think that those cycles were transformed into substituted cyclic compounds during the nucleophilic substitution reaction from PDCP to PBNP; thus, the spectrum shows the peaks corresponding to these cycles. However, this explanation does not seem valid for several reasons. In the first place, we have purified and fractionated the polymer; thus, it is not probable that some cycles still remain in the sample. Morevoer, the spectra of PDEP and PDHP samples, prepared from PDCP polymerized in conditions very similar to those used for the present work, show only a sharp singlet in both cases. But the strongest reason for ruling out the presence of cycles in the PBNP sample is that the spectra of the several fractions studied, whose molecular weights expand more than 2 orders of magnitude, are almost identical. If the sample contained low molecular weight cyclic compounds, there would presumably be a different proportion of them in the different fractions and the relative intensity of the second signal would decrease with increasing molecular weight of the fraction.

Thus, it seems that the nucleophilic substitution reaction is responsible for the two different chemical shifts of the phosphorus atoms in PBNP. The first difference between the reactions when the nucleophile is an alkoxy or an aryloxy group is the necessity of stronger conditions in the last case. Thus, there was no reflux for PDEP[4,6] and only 6 h for PDHP[5] whereas in the case of PBNP the reaction was refluxed for 114 h.

Ferrar et al.[41] showed that if an excess of sodium trifluoroethoxy nucleophile was used in the preparation of poly[bis(trifluoroethoxy)phosphazene] from PDCP, changes were observed in the ^{31}P NMR spectrum of the polymer. Thus, the original sharp singlet centered at -7.5
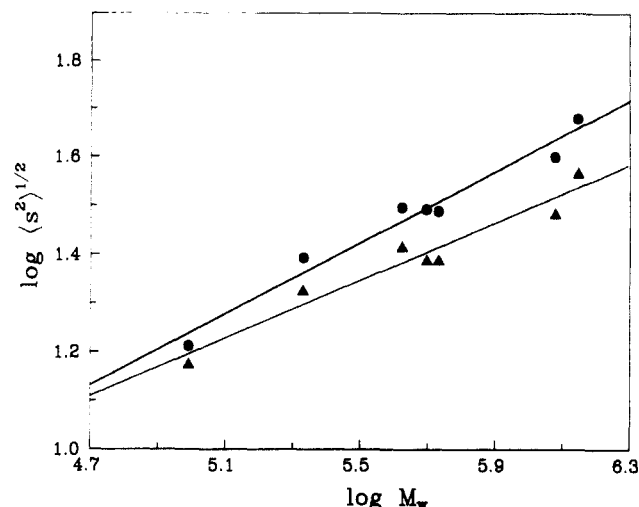
ppm having a 7-Hz width at half-peak height broadened to 21 Hz, keeping the same chemical shift, and several broad bands from -2 to -11 ppm appeared, indicating that not all the phosphorus atoms were in the same environment. They suggested the formation of P–OH moieties and hydrogen bonding between the hydroxy groups or with trifluoroethoxy side groups. Although the variation in physical properties could also be attributed to branching, hydrogen bonding was their preferred explanation because (1) branched polymers would be much less soluble and (2) their work on the corresponding trimer suggested the formation of a hydroxy compound and not a phosphazene dimer.

Recently Magill and co-workers[42] have reported that branching in the nucleophilic substitution reaction of PDCP with sodium trifluoroethoxy can occur if the reaction is heated to reflux for several hours. Also they reported branching in the polyphosphazenes obtained in solution when large quantities of $CaSO_4 \cdot 2H_2O$ were added to the reaction mixture, since the ^{31}P NMR spectra of substituted polyphosphazenes showed several small broad signals besides the expected singlet. They suggest that P–OH bonds may form P–O–P linkages between two chains.

Gabler and Haw[43] have studied the hydrolysis of PDCP by ^{31}P NMR, and they propose that gel formation is the result of hydrogen bonding between ClPOH groups rather than POP cross-linking, and with a majority of the hyrogen bonds being intramolecular and thus not contributing to gel formation which is due only to the small proportion of bonds that are intermolecular.

The above arguments will be in agreement with the fact that the multiple ^{31}P NMR resonances for PBNP are originated in the nucleophilic substitution reaction, and the problem is to elucidate whether they are due to branching or to hydrogen bonding between POH groups. With this purpose we can examine more carefully the VIS and LS data.

A first hint on the possible existence of branching can be obtained by analyzing the dependence of the radius of gyration on molecular weight. Thus, Figure 9 shows a logarithmic plot of both $\langle s^2 \rangle_z^{1/2}$ (determined by LS) and $\langle s^2 \rangle_w^{1/2}$ (computed according to eq 1) versus M_w. The fitting is similar for both magnitudes, and the slopes are ca. 0.3 which indicates a dependence of $\langle s^2 \rangle^{1/2} \approx M^{0.3}$. Values of ca. 0.5–0.6 are expected for the exponent of M in the case of linear chains in the random coil state, and we found a value of 0.65 for PDHP.[5] Thus, the low value

of the exponent found for PBNP could be indicative of branching. However, the formation of molecular aggregates would also produce a low value of this exponent. Indeed if the aggregates had roughly a globular shape, their volume would increase with M, and therefore their radius would depend on $M^{1/3}$ just as we obtained.[44] Furthermore, if branching exists, the dimensions determined by LS should be considerably lower than the values calculated from the Flory–Fox relationship while aggregation will produce just the opposite effect. As Table IV shows, the dimensions obtained from VIS data are lower than those of LS for all the fractions.

On the other hand, the PBNP showed a normal viscosity behavior; the only noteworthy feature is that the Huggins constants are higher than 0.3–0.4, and this fact has been related for some researchers to the presence of aggregation or branching; however, since several factors can influence this constant, this is not a conclusive point. A more interesting feature is that the Mark–Houwink plot is linear and there is no curvature for higher molecular weights as one would expect if branching were present. Moreover, the exponent in the Mark–Houwink relationship $a = 0.69$ is indicative of a random coil chain in a rather good solvent.

We conclude that the multiple resonances in the ^{31}P NMR spectra of PBNP are due to different chemical environments produced during the nucleophilic substitution reaction, presumably by formation of P–OH moieties in addition to the regular P–O–β-$C_{10}H_7$ species. Our results of viscosity and light scattering measurements suggest that these P–OH groups produce intermolecular aggregates roughly globular in shape which do not influence the viscosity behavior of the sample but have a marked effect on the light scattering measurements, in the sense of overestimating the molecular size.

References and Notes

(1) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
(2) Potin, Ph.; De Jaeger, R. *Eur. Polym. J.* **1991**, *27*, 341.
(3) Allcock, H. R.; Connolly, M. S.; Sisko, J. T.; Al-Shali, S. *Macromolecules* **1988**, *21*, 334.
(4) Bravo, J.; Tarazona, M. P.; Roig, A.; Saiz, E. *An. Quim.* **1991**, *87*, 27.
(5) Bravo, J.; Tarazona, M. P.; Saiz, E. *Macromolecules* **1991**, *24*, 4089.
(6) Tarazona, M. P.; Bravo, J.; Rodrigo, M. M.; Saiz, E. *Polym. Bull.* **1991**, *26*, 465.
(7) Allen, G.; Lewis, C. J.; Todd, S. M. *Polymer* **1970**, *11*, 31.
(8) Allen, G.; Lewis, C. J.; Todd, S. M. *Polymer* **1970**, *11*, 44.
(9) Gleria, M.; Minto, F.; Lora, S.; Bortolus, P. *Eur. Polym. J.* **1979**, *15*, 671.
(10) Flamigni, L.; Camaioni, N.; Bortolus, P.; Minto, F.; Gleria, M. *J. Phys. Chem.* **1991**, *95*, 971.
(11) Gleria, M.; Barigelletti, S.; Dellonte, S.; Lora, S.; Minto, F.; Bortolus, P. *Chem. Phys. Lett.* **1981**, *83*, 559.
(12) Rabek, J. F. *Experimental Methods in Polymer Chemistry*; Wiley: Chichester, 1980.
(13) Hagnauer, G. L.; Schneider, N. S. *J. Polym. Sci., Part A-2* **1972**, *10*, 699.
(14) Carlson, D. W.; O'Rourke, E.; Valaitis, J. K.; Alternau, A. G. *J. Polymn. Sci., Polym. Chem. Ed.* **1976**, *14*, 1379.
(15) Huggins, M. L. *J. Am. Chem. Soc.* **1942**, *64*, 2716.
(16) Kraemer, E. O. *Ind. Eng. Chem.* **1938**, *30*, 1200.
(17) Neilson, R. H.; Hani, R.; Wisian Neilson, P.; Meister, J. S.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* **1987**, *20*, 910.
(18) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.
(19) Andrady, A. L.; Mark, J. E. *Eur. Polym J.* **1981**, *17*, 323.
(20) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Thiaca, NY, 1953.
(21) Evans, J. M. In *Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic Press: London, 1972; Chapter 5.
(22) Huglin, M. B.; Radwan, M. A. *Polymer* **1991**, *32*, 1293.
(23) Cowie, J. M. G. In *Light Scattering from Polymer Solutions*; Huglin, M. B. Ed.; Academic Press, London, 1972; Chapter 14.
(24) McCrackin, F. L. *J. Appl. Polym. Sci.* **1977**, *21*, 191.
(25) Barrales-Rienda, J. M.; Romero-Galicia, C.; Horta, A. *Macromolecules* **1983**, *16*, 932.
(26) Barrales-Rienda, J. M.; Galera-Gómez, P. A.; Horta, A.; Saiz, E. *Macromolecules* **1985**, *18*, 2572.
(27) Horta, A.; Saiz, E.; Barrales-Rienda, J. M.; Galera-Gómez, P. A.; *Polymer* **1986**, *27*, 139.
(28) Szewczyk, P. *Polymer* **1976**, *17*, 90.
(29) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes. The Art of Scientific Computing*; Cambridge University Press: Cambridge, 1986.
(30) Stockmayer, W. H.; Fixman, M. *J. Polym. Sci., Part C* **1963**, *1*, 137.
(31) Stockmayer, W. H. *J. Polym. Sci.* **1955**, *15*, 595.
(32) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303.
(33) Fixman, M. *J. Chem. Phys.* **1955**, *23*, 1656.
(34) Kurata, M.; Stockmayer, W. H.; Roig, A. *J. Chem. Phys.* **1960**, *33*, 151.
(35) Singler, R. E.; Hagnauer, G. L.; Schneider, N. S.; Laliberte, E. R.; Sacher, E. R.; Matton, R. W. *J. Polym. Sci., Polym Chem. Ed.* **1974**, *12*, 433.
(36) Busulini, L.; Osellame, M.; Lora, S.; Pezzin, G. *Makromol. Chem.* **1977**, *178*, 277.
(37) Hagnauer, G. L. *ACS Symp. Ser.* **1980**, *138*, 239.
(38) Adams, H. E.; Valaitis, J.; K. Henderson, C. W.; Strauss, E. J. *ACS Symp. Ser.* **1980**, *138*, 255.
(39) Kayser Potts, M.; Hagnauer, G. L.; Sennett, M. S.; Davies, G. *Macromolecules* **1989**, *22*, 4235.
(40) Klein, J. A.; Bell, A. T.; Soong, D. S. *Macromolecules* **1987**, *20*, 782.
(41) Ferrar, W. T.; Marshall, A. S.; Whitefield, J. *Macromolecules* **1987**, *20*, 317.
(42) Mujumdar, A. N.; Young, S. G.; Merker, R. L. R.; Magill, J. H. *Macromolecules* **1990**, *23*, 14.
(43) Gabler, D. G.; Haw, J. F. *Macromolecules* **1991**, *24*, 4218.
(44) Rey, A.; Freire, J. J.; Garcia de la Torre, J. *Macromolecules* **1987**, *20*, 2385.