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Characterization of poly(diethoxyphosphazene) by size exclusion chromatography and viscometry

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ABSTRACT

Two samples of poly(diethoxyphosphazene) (PDEP) having very different molecular weights have been studied by viscometry and size exclusion chromatography in THF solution. The results obtained, together with light scattering data of these samples, allow the calculation of the Mark-Houwink constants a = 0.65 and K = 2.5 10^{-4} in THF at 25°C. The method of calculation employed takes into account the great polydispersity of the samples. The characteristic ratio of the unperturbed dimensions was also calculated giving $C_n = \langle r^2\rangle_0/n\ell^2 \approx 18$, a value slightly higher than those previously reported for poly(dihexoxyphosphazene), $C_n \approx 13$ and poly (dichlorophosphazene), $C_n \approx 13.5$.

INTRODUCTION

Poly(diethoxyphosphazene) (PDEP) was one of the first poly(organophosphazenes) synthesized by Allcock and co.(1) through substitution of chlorine atoms of poly(dichlorophosphazene) by organic groups thus yielding hydrolytically stable polymers having inorganic chain and organic substituents. More than 300 poly(organophosphazenes) with a wide variety of polymer structures and properties have been prepared since then (2-5).

The study of properties of poly(organophosphazenes) in dilute solution has been hampered by many factors: The great polydispersity of the synthesized polymers which present broad, and sometimes multinodal, molecular weight distributions (6-8) together with the difficulties for the fractionation of these polymers (9,10) and their anomalous behavior in size exclusion chromatography (SEC) characteristic of adsorption phenomena in the column (11,12). Recently it has been reported (13) that the addition of quaternary ammonium salts to the mobile phase allows the elimination of the adsorption phenomena, thus yielding reproducible chromatograms.

We have studied the properties of poly(dihexoxyphosphazene) (PDHP) in dilute

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*To whom offprint requests should be sent solution by SEC, light scattering (LS) and viscometry (14), and present here a similar study for PDEP, whose light scattering analysis has been reported elsewhere (15), with the aim of investigate the influence of the length of the side groups in the behavior of the solutions of these poly(organophosphazenes).

EXPERIMENTAL PART

The synthesis of PDEP, according to the procedure described by Allcock and co., has been described elsewhere (1,15). In brief, two batches, A and B, of hexachlorocyclotriphosphazene $(NPCl_2)_3$ were thermally polymerized at 230°C during 24 and 46 hours respectively for samples A and B. The poly (dichlorophosphazene) thus obtained was dissolved in benzene and converted into PDEP by treatment with a solution of sodium ethoxide in ethanol. The resulting PDEP was characterized by IR, ^1H, ^{13}C, and ^{31}P NMR spectroscopies.

Viscometric measurements

A Schott Gerate autoviscometer was employed to measure flow times of PDEP solutions in THF. The bath temperature was controlled at 25 ± 0.1 °C. Values of intrinsic viscosity $[\eta]$, Huggins constant, k_H, and Kraemer constant, k_K, were obtained by the simultaneous extrapolation to infinite dilution of η_{sp}/c and $(1/c)\ln(\eta_r)$, where η_{sp} and η_r are the specific and relative viscosities respectively, vs. concentration plots according to the Huggins (16) and Kraemer (17) equations using least-squares linear regression analysis.

Size-Exclusion Chromatography

Experiments were performed using a Waters Associated equipment consisting of a 510 reciprocating piston pump, a U6K injector, a 410 refractive index detector with oven temperature controller and a Digital 380 computer with 840 data and chromatography control station. Polystyrene gel columns packed in THF were used. Elutions were conducted with a flow rate of 1mL min^{-1}. Freshly distilled THF with a 0.1% of tetra(n-butyl ammonium) bromide was used as eluent. The performance of the whole equipment was checked with narrow molecular weight distribution polystyrene standards (Scharlau).

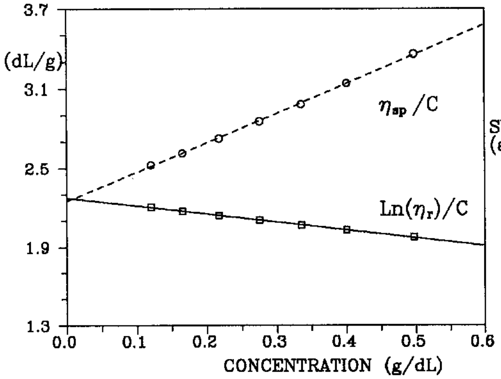
RESULTS

Results of the viscometric measurements are shown in Table 1, and one of the Huggins-Kraemer plots showing the coincidence of intercepts is represented in Fig. 1. The plots are linear and no anomalous behavior was observed.

TABLE I

Weight average molecular weight (taken from ref. 15) and viscosity parameters of PDEP in THF solution at 25^o C

Sample	$10^{-5}\ \bar{M}_w$	$[\eta]$ (dL/g)	k_H	k_K
A	2.0	0.576	0.46	-0.08
B	20.0	2.26	0.44	-0.11



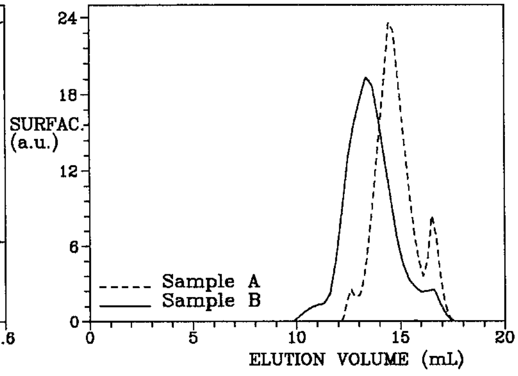


Fig.1.– Huggins–Kraemer plot for sample B in THF at 25°C.

Fig.2.– Size exclusion chromatograms for the two samples of PDEP.

As can be seen in Table 1, the Huggins and Kraemer slopes follow the theoretical relation (18) $k_K = k_H - 1/2$. Values of the Huggins constant usually range between 0.3 and 0.4 in systems with good solvents and increase, up to about 0.55 for θ conditions (19), although both much higher and lower values had been reported for polyphosphazenes (7,11,20) which can be attributed to the presence of supermolecular configurations or associates in solution. The values of the two samples are close enough to indicate that the Huggins constant for PDEP will be molecular weight independent within the limits of credibility of this analysis.

Initial attempts to obtain size exclusion chromatograms of poly(phosphazene) samples 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. (13), a solution of tetra-n-butylammonium bromide (0.1 wt %) in THF was used as eluent. The chromatograms obtained in the present work are represented in Fig. 2. As can be seen in this figure, the fractions show a broad distribution and therefore can not be used as monodisperse samples neither for a regular calibration of SEC chromatograms by fitting molecular weight versus elution volume, nor for the evaluation of the Mark-Houwink constants in the viscometric equation $[\eta] = KM^a$. Thus, a numerical analysis circumventing the necessity of using narrow distribution fractions (14) has been used for the calculation of all these parameters.

NUMERICAL ANALYSIS

The chromatograms obtained by SEC, the weight-average molecular weights $\bar{M}_w$ determined by LS (15), and the intrinsic viscosities $[\eta]$, were combined to calculate the calibration curve for SEC, ie. 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 (18), ie. the K and a parameters in the relationship $[\eta] = KM^a$.

Since we have only two fractions, it is important that the experimental conditions for SEC gave a linear variation of log M_i versus elution volume V_{ie}. This behavior was checked by calibrating the column with a set of narrow molecular weight distribution polystyrene standards. Thus, in the hypothetical case of *ideally monodisperse samples*, their molecular weights M_i and elution volumes V_{ie} will follow the relationship (21):

$$\log (M_i) = A_o - A_1V_{ie} \tag{1}$$

Then, the weight average molecular weight $\bar{M}_w$ of a sample having a broad distribution, like the fractions actually measured, can be calculated as:

$$\bar{M}_w = \sum_{i=1}^{n} w_iM_i = \sum_{i=1}^{n} w_i\ 10^{[A_o - A_1V_{ie}]} \tag{2}$$

The weight fractions w_i appearing on Eq. 2 are proportional to the height of the chromatogram at a given elution volume V_{ie} while A_o and A_1 are the unknown polynomial coefficients of the SEC calibration function (Eq. 1). n = 25 pairs of values w_i, V_{ie} were read from the chromatogram of each fraction A and B. Substitution of these pairs of values, together with the experimental results of $\bar{M}_w$ of each fraction, into Eq. 2 gives a system of two equations that allows the calculation of the two unknown A_o and A_1. The values of these coefficients for our experimental conditions were $A_o = 14.41$ and $A_1 = 0.643$.

Once the parameters for the SEC calibration function have been calculated, an equation similar to 2 can be written for the bulk viscosity of the actual polymer fractions $[\eta]$ as function of the viscosities of *ideally monodisperse samples* $[\eta_i]$

$$[\eta] = \sum_{i=1}^{n} w_i\ [\eta_i] = K \sum_{i=1}^{n} w_i\ M_i^a = K \sum_{i=1}^{n} w_i\ 10^{a[A_o - A_1V_{ie}]} \tag{3}$$

Substitution of the two values of $[\eta]$ measured for samples A and B into Eq. 3 gives a system of two equations from which the true values of the Mark-Houwink parameters K and a relating viscosity $[\eta_i]$ and molecular weight M_i of *ideally monodisperse samples* can be calculated.

The results obtained are a = 0.65 and K = 2.506 10^{-4}. The value of a found in the present work for PDEP is smaller than that reported for PDHP under the same experimental conditions (THF solution at 25°C), a = 0.79 which indicates that PDEP is closer to theta conditions than PDHP. It is worthy to point out that the substitution of the averaged molecular weight values directly in the Mark-Houwink equation would yield erroneous values (a = 0.60, K = 3.930 10^{-4}), different from those here obtained, since the samples can not be considered narrow under any circumstance.

Once the values of a and K are obtained, the viscosity average molecular weights can be computed using the Mark-Houwink equation. The results are 1.484 10^5 and 1.216 10^6 for samples A and B respectively. These values together with the experimental bulk viscosities allow the calculation of the dimensions according to the Flory-Fox equation (22,23) $\langle r^2\rangle^{3/2} = [\eta]\ \bar{M}_v \Phi^{-1}$ where Φ is 2.5 when $\langle r^2\rangle^{3/2}$ is given in nm^3 and $[\eta]$ in dL/g. Values of $\langle r^2\rangle^{1/2}$ equal to 32 and 103 nm^3 are thus obtained for samples A and B respectively.

Application of the Flory-Fox equation to theta conditions in which a = 0.5 allows the evaluation of the unperturbed dimensions $\langle r^2\rangle_o$ as:

$$\langle r^2\rangle_o^{3/2} = [\eta]_\theta \bar{M}_v \Phi^{-1} = K_\theta \bar{M}_v^{3/2} \Phi^{-1} \tag{4}$$

And then, the characteristic ratio $C_n = \langle r^2\rangle_o / n\ell^2$, where n is the number of skeletal bonds, each of them having a length ℓ (0.152 nm for P-N bonds), can be calculated as:

$$C_n = \frac{\langle r^2\rangle_o}{n\ \ell^2} = \frac{\langle r^2\rangle_o\ M_r}{2\ \ell^2\ M} = \frac{M_r\ K_\theta^{2/3}}{2\ \ell^2\ \Phi^{2/3}} \tag{5}$$

where $M_r = 2M/n$ is the molecular weight of the repeating unit (135 for PDEP) and the K_θ constant can be evaluated by substitution of $\bar{M}_v$ and $[\eta]$ of the two fractions into the Stockmayer-Fixman relationship:

$$\frac{[\eta]}{\bar{M}^{1/2}} = K_\theta + C\ K_\theta\ \bar{M}^{1/2} \tag{6}$$

which gives K_θ = 1.14 10^{-3}. Substitution of this value into Eq. 5 provides C_n = 17.4. The calculated values of the chain expansion factor $\alpha = [\langle r^2\rangle / \langle r^2\rangle_o]^{1/2}$ are

1.1 and 1.2 for samples A and B respectively.

Very different values of characteristic ratios, ranging between 6 to more than 100, have been reported (9,20) for polyphosphazenes of type $-[P(OR)(OR')-N-]_n$. The result obtained in the present work for PDEP suggests a rather flexible chain molecule in the random-coil state. The values obtained for dimensions are similar to those obtained for PDHP with the same experimental procedure (C_n = 13) (14) and those calculated for the fully inorganic polymer poly(dichlorophosphazene) (PDClP) (C_n = 13.5) (24). The difference between the unperturbed dimensions of PDEP and PDHP chains can be explained by a small modification of the statistical weights of the conformations allowed to the pair of bonds P-N-P in the sense of a slight stabilization of the *tt* conformation in the case of PDHP due to attractive interactions between the aliphatic part of the side chains. Thus, the theoretical analysis of PDClP (24) indicates that the *tt* conformation for P-N-P bonds is disfavored about 1.4 kcal mol^{-1} over the alternative $tg^{\pm}$ and *tc* conformations (ie. $E_{\sigma} \approx -1.4$ kcal mol^{-1} taking *tt* as reference). Since the valence angles in the chain backbone are very different, (N-P-N ≈ 118^{o} and P-N-P ≈ 130^{o}), the *all trans* conformation describes a spiral line that produces a very small value of C_n; on the contrary, perpetuation of $tg^{\pm}$ conformations give a helix with very large molecular dimensions. Consequently, the value of C_n increases sharply as the energy difference between *tt* and $tg^{\pm}$ increases (ie. with decreasing value of E_{σ}, see Fig. 4 on Ref. 24). The dimensions of PDEP are larger than those of PDClP suggesting a value of $E_{\sigma} \approx -1.7$ kcal mol^{-1} which would indicate that the interaction between the side groups $-O-CH_2-CH_3$ on PDEP are slightly stronger than those between -Cl in PDClP; however, an increase of the length of the side group to $-O-(CH_2)_5CH_3$ in PDHP produces dimensions, and therefore values of E_{σ}, matching those of PDClP. The easiest explanation would be that the long tails of the side chains adjust themselves to positions in which the interactions are minimized producing attractions between side chains of consecutive units.

Finally, we should point out that the dimensions of PDEP obtained in the present work by a joint application of viscometry, SEC and LS thecniques are considerable lower than those measured by LS (15). The discrepancy between the results obtained with these two procedures has been reported by other authors and can be attributed to the formation of molecular aggregates that produces severe overestimations of the dimensions measured by LS, and/or the differences between viscosity and weight average molecular weights in these broad distribution polymers (20).

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