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Dilute solution properties of poly(dianilino phosphazene)

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Poly(dianilino phosphazene) has been synthesized from hexachlorocyclotriphosphazene by two different methods, bulk and solution. Several fractions, with polydispersity ratio ranging from 1.8 to 2.4, were obtained by fractional precipitation and characterized by viscometry and size exclusion chromatography (s.e.c.) using simultaneously refractive index and multi-angle light scattering detectors. From these data the solution behaviour of the polymer is discussed. © 1997 Elsevier Science Ltd. All rights reserved.

(keywords: poly(diaminophosphazene)s; poly(dianilino phosphazene); characterization)

INTRODUCTION

Poly(organophosphazene)s were first synthesized by Allcock and coworkers through nucleophilic substitution of the chlorine atoms on soluble samples of poly(dichlorophosphazene) (PDCP) obtained by thermal polymerization of hexachlorocyclotriphosphazene[1,2]. Thus, polymers with an inorganic chain of alternated phosphorous and nitrogen atoms and different organic side groups, whose properties depend strongly on the kind of substituents, can be obtained. The characterization of these polymers presents several problems due to their anomalous behaviour in solution that can mask a correct interpretation of results[3]. We have studied the solution properties of several poly(organophosphazene)s containing alkoxy or aryloxy side groups[4–7], and it seemed interesting to extend the study to other kind of polyphosphazenes with amino instead of alkoxy or aryloxy substituents, since the reports on solution properties of poly(diaminophosphazene)s are scarce. Poly(diaminophosphazene)s present a significant difference compared with their counterparts alkoxy or aryloxy phosphazenes, a much higher glass transition temperature (T_g) due to the lower torsional mobility of the amino group with a pendant hydrogen atom on the nitrogen that is not present on the oxygen atom of the alkoxy/aryloxy groups[8]. However, it is not yet clear whether or not this structural difference in the side groups modifies the molecular dimensions of the polymeric chains. This paper focuses on the study of the solution properties of poly(dianilinophosphazene) (PDAP) that has been synthesized, fractionated and characterized. Since branching or crosslinking can mask the correct interpretation of results, two different synthetic methods have been used, and special care has been taken in order to minimize the branching of the polymer.

EXPERIMENTAL

Synthesis

The synthesis of PDAP has been carried out through the intermediate PDCP by nucleophilic substitution of chlorine atoms by the amino groups. Two different synthetic procedures, bulk and solution, have been used in order to obtain the PDCP from hexachlorocyclotriphosphazene (HCTP). The first one is similar to the method described by Allcock and Kugel[1], although we have used a slightly lower temperature (240°C instead of 250°C), in order to prevent crosslinking. HCTP (Janssen Chimica) (10 g) carefully purified through recrystallization in hexane followed by two vacuum sublimations was polymerized in a sealed evacuated ampoule, in an oven at 240°C, until the molten reaction mixture became so viscous that flow ceased.

In the second method we have followed the procedure of Mujundar *et al.*[9] although we have omitted the addition of the promoter $CaSO_4.2H_2O$ in order to avoid branching and crosslinking. HCTP (8.8 g), purified as explained above, was dissolved in 1,2,4-trichlorobenzene (6.6 ml), 16 mg of sulfamic acid added, and the reaction mixture was refluxed (210°C), under nitrogen atmosphere, during 6 h.

The PDCP obtained in both procedures was immediately transformed into PDAP[8]. A solution of triethylamine (39.45 g) and aniline (24.2 g) in dry tetrahydrofuran (THF) was added dropwise to a stirred solution of the crude polymer (obtained from melt polymerization of HCTP) dissolved in anhydrous benzene, freshly distilled from sodium and benzophenone. After addition was complete, the reaction mixture was heated to reflux for 48 h under nitrogen atmosphere. The mixture is allowed to cool at room temperature, the triethylamine hydrochloride filtered off and the polymer (6.8 g) precipitated by adding the filtered solution dropwise to a large volume of methanol. The polymer obtained in the solution polymerization showed a broad molecular distribution in s.e.c. and was fractionated using THF/methanol as solvent/precipitant at temperatures of 30

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and 15°C, for solution and precipitation respectively. The polymer obtained in the melt polymerization showed a molecular weight distribution similar to the fractions separated from the solution polymer and was used without further fractionation.

Viscometric measurements

A Schott Gerate autoviscometer was employed to measure flow times of PDHP using THF and *N,N*-dimethylformamide DMF as solvents. The bath temperature was controlled at 25 ± 0.1°C. Intrinsic viscosity $[\eta]$ values were estimated by the simultaneous extrapolations of Huggins and Kraemer as reported elsewhere[10].

Light scattering and size exclusion chromatography

A Waters Associates equipment consisting of a 510 pump, a U6K injector and a 410 refractive index detector was used. THF with 0.1% of tetra-*n*-butyl ammonium bromide was used as eluent. A Dawn Laser Photometer from Wyatt Technology Co. equipped with a flow cell was placed between the separating columns and the refractive index detector. When the eluent leaving the column flows through the cell, light scattering measurements are made simultaneously at different angles, allowing the determination of absolute molecular weights.

RESULTS AND DISCUSSION

S.e.c. chromatograms of the PDAP obtained by melt polymerization (sample 1) and several fractions (samples 2–4) of the PDAP obtained in solution are represented in *Figure 1*, and the averaged molecular weights together with the polidispersity ratio are presented in *Table 1*. The fractions are still broad, with polydispersity ratios ranging between 1.7 and 2.4, although they are suitable for polymer characterization. It is a well known fact that very broad molecular weight distributions, many times multimodals, are found in the synthesis of polyphosphazenes. Thus Busulini *et al.*[11] synthesized several poly[bis(phenylamino)phosphazene]s including PDAP with ratios M_w/M_n ranging between 13 and 16 and bimodal distributions. Moreover, difficulties encountered in the fractionation of polyphosphazenes have already been reported. Several attempts to fractionate these polymers have been unsuccessful, and nevertheless narrow fractions or numerical analysis of data of broad fractions have to be used for a satisfactory characterization of molecular structure[3]. To our knowledge the only poly(diaminophosphazene) successfully fractionated is poly[bis(*p*-methylanilino) phosphazene] with fractions having polydispersities between 1.6 and 4.1[12].

Viscosity measurements of PDAP fractions presented more difficulties than polyalkoxy/aryloxy phosphazenes. Two solvents, THF and DMF, have been used because the low solubility of PDAP in THF originates large errors in the determination of intrinsic viscosities. On the contrary DMF proved to be a very good solvent for PDAP. Problems with viscosity measurements, which in some cases prevented the determination of intrinsic viscosity, have been reported[8]. *Table 2* presents the intrinsic viscosities $[\eta]$, and Huggins and Kraemer constants obtained in the present study. As can be seen in the table, higher values of intrinsic viscosity are found in DMF and the Huggins and Kraemer constants follow the theoretical relationship $k_K = k_H - 0.5$. Although one must be very careful interpreting Huggins constants, the lower values encountered in DMF compared with those in THF can indicate that the polymer behaves in DMF in a more flexible manner than in THF.

Weight-averaged molecular weights M_w and intrinsic viscosities $[\eta]$ were combined to obtain the parameters K and a of the Mark–Houwink equation, $[\eta] = KM_v^a$, yielding the values $K = 1.11 \times 10^{-6}$, $a = 0.94$ and $K = 8.98 \times 10^{-6}$, $a = 0.84$, with $[\eta]$ in dl g^{-1}, in THF and DMF solutions respectively. The value of a obtained in DMF corresponds to a random coil polymer in a good solvent, in good agreement with the results obtained for the Huggins constants, whereas the one found in THF is higher than the expected for a random coil polymer and indicates a more rigid conformation.

The light scattering measurements give weight-averaged molecular weights, M_w, and the Mark–Houwink relationship uses viscous averaged molecular weights, M_v. These averages are identical only if the polymer is monodisperse whereas M_v is smaller than M_w for polydisperse samples. Since the fractions of PDAP obtained in this work are polydisperse, a numerical analysis[13] which has proved to be very useful in the characterization of polyphosphazenes[4,5] since it minimizes the error due to the broadness of the fractions, has been

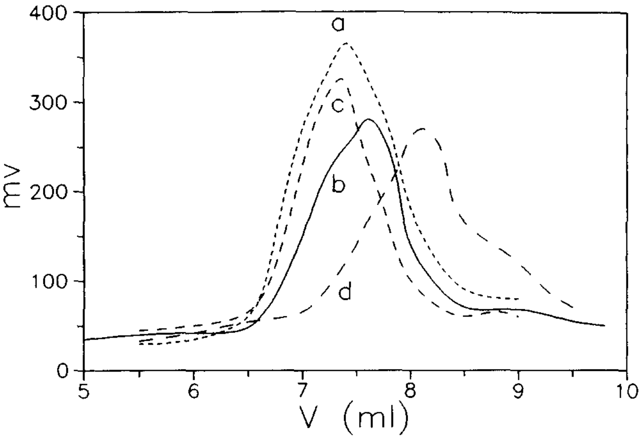

Figure 1 S.e.c. chromatograms of PDAP fractions. Sample 1, a; Sample 2, b; Sample 3, c; Sample 4, d

Table 1 Averaged molecular weights of PDAP fractions

Sample	$10^{-3}M_n$	$10^{-3}M_w$	$10^{-5}M_z$	M_w/M_n
1	114	198	1.1	1.7
2	84	176	30	2.1
3	127	237	293	1.9
4	35	86	7.0	2.4

Table 2 Viscometric results

Fraction	Solvent	$[\eta]$ (dl g)$^{-1}$	k_H	k_K
4	THF	0.0596	0.11	−0.38
2	THF	0.112	1.19	0.63
1	THF	0.138	1.34	0.72
3	DMF	0.312	0.020	−0.45
1	DMF	0.268	−0.016	−0.47

performed with the results obtained in THF solutions. The method here used shows an important difference with previous ones since the light scattering measurements have been done on line with s.e.c. and the s.e.c. software used, ASTRA, allows the evaluation of absolute molecular weights as well as the concentration (height) of each slice in the chromatogram. In brief the method consists of applying iterative numerical procedures seeking the best agreement between theoretical and experimental values of $[\eta]$. The s.e.c. chromatogram of each fraction can be split into s slices whose intrinsic viscosities can be calculated through the Mark–Houwink relationship as $[\eta_i] = KM_i^a$, where M_i is the molecular weight of the slice. Thus, the viscosity of a polydisperse sample can be calculated by adding the contributions of each slice multiplied by the concentration of the slice:

$$[\eta]_{\text{calc}} = \sum_{i=1}^{s} h_i[\eta_i] = \sum_{i=1}^{s} h_i K\ M_i^a$$

and the K and a coefficients can be adjusted to minimize the root mean squared relative deviation defined as

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

where n is the number of different fractions of the polymer used in the analysis. Imposing on the deviation σ the condition of minimum with respect to the parameters a and K, and using a numerical procedure such as the Powell algorithm[14], we have obtained $K = 1.64 \times 10^{-5}$, with $[\eta]$ in dl g^{-1}, and $a = 0.92$. Since these values presumably are not affected by the broadness of the peaks and the a value is still higher than that expected for a random chain coil, we can conclude that the polymer shows rather rigid conformations in THF solutions.

On the contrary, DMF seems to be a good solvent, and the polymer shows random coil configuration. Thus, it is possible to apply the Stockmayer–Fixman equation[15]

$$\frac{[\eta]}{M^{\frac{1}{2}}} = K_\theta + 0.51B\theta M^{\frac{1}{2}}$$

to these solutions and a value of $K_\theta = 1.9 \pm 0.2 \times 10^{-4}$ dl g$^{-\frac{3}{2}}$ mol$^{\frac{1}{2}}$, is obtained when M_w is used. The characteristic ratio of the unperturbed dimensions C_N relative to the number of skeletal bonds (N), and the square of their length, 1, can be calculated taking into account the Flory–Fox relationship

$$C_N = \frac{\langle r^2\rangle_o}{Nl^2} = \frac{\langle r^2\rangle_o M_r}{2l^2 M} = \frac{M_r K_\theta^{\frac{2}{3}}}{2l^2\Phi^{\frac{2}{3}}}$$

where M_r is the molecular weight of the repeating unit (229.2 g mol^{-1}) and l is the P–N bond length (0.152 nm). A value of 2.5×10^{23} mol^{-1} was taken for the Flory constant Φ. The value of C_N obtained for PDAP is 9.0, which is in the range of those obtained for other polyphosphazenes, which vary between 6 and 20[3].

The experimental results obtained in the present work can be explained, at least at the qualitative level, by performing a theoretical calculation of the unperturbed dimensions of this polymer by employing the rotational isomeric state model developed several years ago for PCDP[16]. In brief, this model uses four rotational isomers (*trans*, *gauche*, *cis* and *negative gauche*, located at the positions $\phi \approx 0$, 130, 180, 230° for the rotation over the skeletal bonds). The statistical weight matrices assigned to the allowed orientations of P–N–P (U matrix) and N–P–N (U′ matrix) pairs of skeletal bonds are:

$$\mathrm{U} = \begin{bmatrix} 1 & \sigma & \sigma & \sigma \\ \sigma & \sigma' & \sigma' & \sigma' \\ \sigma & \sigma' & 0 & \sigma' \\ \sigma & \sigma' & \sigma' & \sigma' \end{bmatrix} \qquad \mathrm{U}' = \begin{bmatrix} 1 & \omega & \omega & \omega \\ \omega & 0 & 0 & 0 \\ \omega & 0 & 0 & 0 \\ \omega & 0 & 0 & 0 \end{bmatrix}$$

where the statistical weights σ, σ' and ω are the Boltzmann factors of their relative conformational energies whose values, in kcal mol^{-1}, are $E_\sigma = -1.4$, $E_{\sigma'} = -1.6$ and $E_\omega = -1.0$. The characteristic ratio of the unperturbed dimensions calculated with these parameters is $C_N = 13.5$ for PDCP chains containing $N = 400$ skeletal bonds, i.e. $x = 200$ repeating units.

As far as the molecular dimensions are concerned, the value of ω is almost irrelevant. Thus, a variation of 1 kcal mol^{-1} in E_ω modifies C_N by *ca* 0.3%. The reason is that the U′ matrix forces at least one of the two bonds in the N–P–N pair to be in *trans*. On the contrary, C_N is very sensitive to σ as shown in *Figure 2*, where the values of C_N are represented as a function of E_σ. The reason for

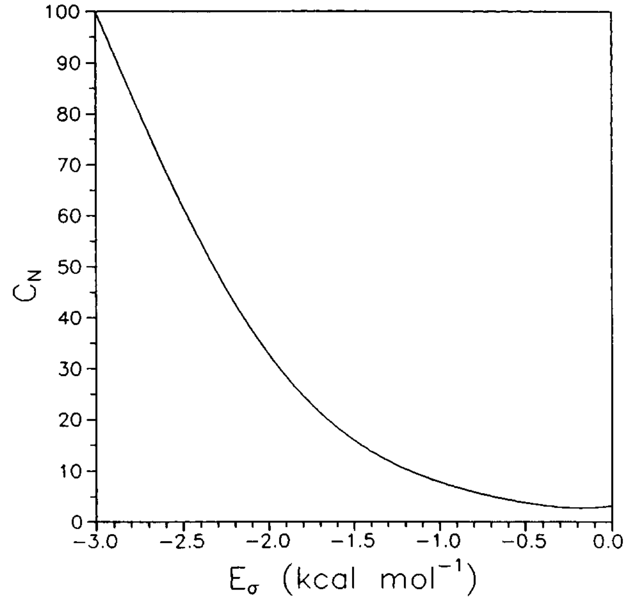

Figure 2 Characteristic ratio of the unperturbed dimensions (C_N) as a function of the conformational energy E_σ. Calculations where performed at 25°C for chains containing $N = 400$ skeletal bonds with $E_{\sigma'} = -1.6$, $E_\omega = 1.0$ kcal mol^{-1}, θ(N–P–N) = 118°, θ'(P–N–P) = 130°, $\phi_t = 0$, $\phi_g = 130$, $\phi_c = 180$, $\phi_{g-} = 230°$

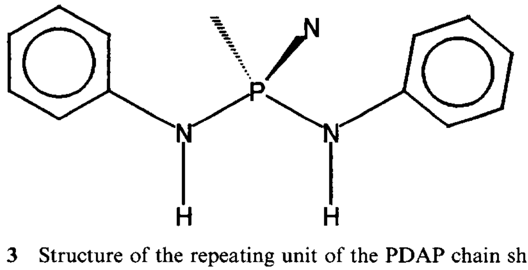

Figure 3 Structure of the repeating unit of the PDAP chain showing the planar conformation of the side groups attached to the P skeletal atom

this behaviour lies in the large difference between the skeletal bond angles. Thus a value of $\theta = 118°$ is used for the N–P–N angle, while P–N–P has a value of $\theta' = 130°$. This difference forces the *all trans* conformation to describe a spiral line having a rather small dimension, while sequences like $/tg/tg/tg/\ldots, /tc/tc/tc/\ldots$ etc., where the slashes represent the skeletal P atoms, produce a helix with a well defined direction of propagation and very large molecular dimensions. For instance, a chain containing $N = 400$ skeletal bonds will have $C_N = 0.5$ when it is in the *all trans* conformation, and $C_N = 242$ in the helicoidal $/tg/tg/tg/\ldots$ structure. Consequently, the molecular dimensions of the chain are strongly dependent on the amount of $/tt/$ conformations on the P–N–P pair of bonds which is controlled by the statistical weight σ. These kinds of conformations act as disruptions of the extended $/tg/tg/tg/\ldots$ conformations, and the value of C_N sharply decreases as the proportion of those conformations increase, i.e. as the statistical weight σ increases or the energy E_σ decreases, as shown in *Figure 2*.

Figure 3 shows the repeating unit of the PDAP with the two side groups attached to the P skeletal atom in their planar conformations, which is not far away from the lowest energy structure. Two consecutive units in the $/tt/$ conformation would place the two pairs of phenyl rings roughly parallel to each other at distances at which the non-bonded interactions will be attractive, while the dipole moments of the phenyl–nitrogen groups attached to the consecutive P atoms would be almost parallel and therefore produce repulsive interactions. Therefore, non-bonded interactions between phenyl rings will produce stabilization of the $/tt/$ conformation, and will therefore lower the molecular dimensions of the PDAP chain as compared to those of PDCP. On the contrary, dipole interactions will produce the opposite effect and result in an increase of the dimensions.

Dipole interactions are very sensitive to the polarity of the solvent. Thus in a very polar solvent such as DMF dipole interactions will be rather small, to the point of being overcome by non-bonded interactions, and therefore the $/tt/$ conformation will be stabilized producing a smaller value of the molecular dimensions. On the contrary, less polar solvents such as THF will enhance the dipole interactions, thus lowering the fraction of $/tt/$ conformations and increasing the molecular dimensions.

The experimental value of C_N measured in DMF solutions is 9.0, which is noticeably smaller than the value of 13.5 obtained for PDCP. Examination of *Figure 2* shows that $C_N = 9.0$ is obtained with $E_\sigma \approx -1.1$, i.e. with a stabilization of the $/tt/$ conformation by *ca* 0.3 kcal mol^{-1} with respect to PDCP.

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