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Fractionation of Poly bis(p-Methylanilino)Phosphazene

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Dedicated to Prof. Dragutin Fleš on the occasion of his 60th birthday

SUMMARY

Eleven fractions, having M_w from $1,7\cdot10^5$ to $1,3\cdot10^7$, were obtained by fractional precipitation from a sample of poly bis(p-methylanilino)phosphazene . In THF solution, $[\eta]$ is proportional to the 0,70 power of M_w and $\langle S^2\rangle_z$, the z-average mean square gyration radius, to the 1,00 power of M_w. A substantially linear structure and a very large characteristic ratio is suggested for this polymer.

INTRODUCTION

A relatively large number of polyphosphazenes have been synthetized (ALLCOCK et al., 1966) in the last years (ALLCOCK, 1977) but their molecular structure is open to debate. ALLEN et al. (1970) reported solution data indicative of branched structure, HAGNAUER et al. (1972) and SINGLER et al. (1974) of a linear structure. The polyphosphazenes are known to have a bimodal or trimodal GPC distribution (BUSULINI et al. 1977; SINGLER et al., 1975) and a very large polydispersity, M_w and M_n being about 10^6 and 10^5. Previous attempts to fractionate polyphosphazenes have been largely unsuccessfull, owing possibly to the fact that a liquid-liquid equilibrium was not obtained in the fractional precipitation, and nevertheless fractions, rather than whole polymers, have to be investigated in dilute solutions, for a satisfactory characterization of molecular structure.
In this work, a successfull fractionation of a sample of poly bis(p-methylanilino)phosphazene by fractional precipitation is reported. A solution characterization of the fractions has been carried out, and the results are compared with similar literature data.

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EXPERIMENTAL

The preparation of the parent polymer, poly(dichlorophosphazene), and the chlorine substitution with p-methylaniline were carried out according to the procedure used in the previous work (BUSULINI et al., 1977). The final Cl content of the polymer was 0,5%. After a series of unsuccessfull attempts with different solvent-precipitant pairs, the fractionation was carried out in the tetrahydrofuran-diethyleneglycol system, at 25,0±0,1°C. The sample was initially dissolved in THF and precipitated with methanol to remove low MW species soluble in this system. 89,7% of the sample was recovered, and its characteristics in THF solution were: $[\eta]$ =201 ml/g, $M_n = 3\cdot10^5$, $M_w = 4\cdot10^6$. The polymer was dissolved in THF (7,09 g in 550 ml of solvent) and the fractional precipitation was carried out, in the darkness and in the absence of oxygen, with the technique of adding the precipitant at 25,0±0,1°C to the point of incipient turbidity, increasing T to about 28°C, and letting the system to equilibrate 24 hours at the lower temperature. The fractions were obtained as a liquid phase at the bottom of the vessel, which was separated and successively dissolved in THF for the precipitation and filtration.

The eleven fractions of polymer so obtained, representing 99,1% of the original sample, were characterized in THF at 25,0±0,1°C, with the conditions indicated previously (BUSULINI et al., 1977). Particular care was taken in the depulverization of the solution, which were also stored in the dark, to avoid photodegradation. Osmotic measurements on several fractions were also carried out at 37°C, in THF. The data are shown in Table I.

DISCUSSION

In this work, an effective fractionation has been achieved, as seen from the changes of the $[\eta]$ and M_w values of the fractions (the M_w is $1{,}3\cdot10^7$ for the first fraction, and $1{,}7\cdot10^5$ for the last). No extensive degradation took place during the fractionation, as shown by the summative $MW=\sum w_i\, M_{wi}$ whose value, $3{,}7\cdot10^6$, is only 7% lower than that measured directly on the unfractionated polymer. The very large polydispersity of the original polymer ($M_w/M_n = 13{,}3$) is substantially reduced in the fractions for which osmotic data are available ($1{,}6 \leqslant M_w/M_n \leqslant 4{,}1$); this can be taken as a further indication that the fractionation was reasonably effective.

TABLE I

Fraction	w%	$[\eta]$ ml/g	$M_w \cdot 10^{-6}$	$M_n \cdot 10^{-6}$	M_w/M_n	$\langle S^2 \rangle_z^{\frac{1}{2}}$ Å
1	1,85	520	13,0	-	-	-
2	6,89	435	9,1	-	-	1404
3	12,07	356	7,76	-	-	-
4	17,78	272	4,35	-	-	894
5	13,64	208	3,30	-	-	688
6	14,48	141	2,77	0,73	3,79	604
7	7,20	128	1,88	0,57	3,76	541
8	7,77	80,7	1,20	0,29	4,13	468
9	4,96	62,5	0,45	0,28	1,61	263
10	2,29	40,0	0,31	0,13	2,38	238
11	10,14	22,3	0,175	0,10	1,75	162

The dilute solution characteristics of the fractions were "regular"; the Huggins constants were in the range 0,3-0,5, and the dependence on concentration of the osmotic and light-scattering data used to extrapolate the M_n and M_w values were linear. Similarly, the Zimm plots were regular, so that the z-average radius of gyration $\langle S^2 \rangle_z^{\frac{1}{2}}$ could be evaluated. The relation between $[\eta]$ and M_w is shown in Figure 1. The linear log-log dependence corresponds to the equations:

$$[\eta] = 5,2 \cdot 10^{-3} \; M_w^{0,70} \quad \text{ml/g} \qquad 1)$$

The exponent of the Mark-Houwink equation,0,70, is therefore close to the upper of the two limits (0,5 and 0,8) between which it is expected to lie (TOMPA, 1956). In the literature, only two sets of data on polyphosphazene fractions are available; that of TATE (1974) on 7 fractions of a fluoroalkoxyphosphazene copolymer, and that of HAGNAUER et al. (1976) on 13 fractions of a m-chlorophenoxy polymer. The method used by the former author to fractionate the fluoroalkoxy copolymer is not indicated, but light scattering and osmotic measurements in methylisobutylketone (MIBK) show that the fractions are very polydisperse, (M_w/M_n from 7 to 23). From TATE's data, the equation of Mark-Houwink has been evaluated (in MIBK) and found to be:

$$[\eta] = 6{,}6\cdot 10^{-2}\ M_w^{0{,}53} \quad \text{ml/g} \qquad 2)$$

Equation 2) corresponds to the dotted line in Fig.1. The exponent is close to 0,5, which could indicate either than MIBK is a ϑ solvent for the fluoroalkoxyphosphazene copolymer, or that the fractions are branched.

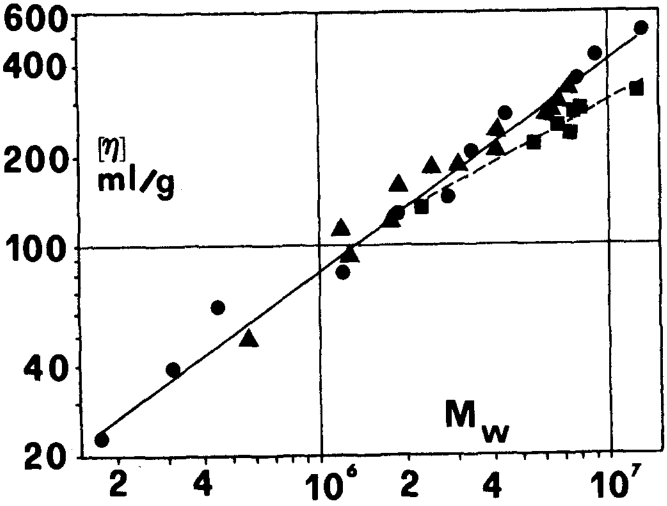

FIGURE 1: Plot of $|\eta|$ vs. M_w (● This work; ▲ HAGNAUER et al. (1976); ■ TATE (1974)).

The data of HAGNAUER et al. (1976) on chloroform solutions of the m-chlorophenoxy substituted polymer fractions are also plotted in the figure. They are rather close to our data, and are described by the equation:

$$[\eta] = 8{,}3\cdot 10^{-3}\ M_w^{0{,}67} \quad \text{ml/g} \qquad 3)$$

Equation 1) and equation 3) are rather similar; a higher value of K in the second compensate for the slightly lower exponent. Apparently, the difference in the substituents of the polyphosphazene chain (m-chlorophenoxy groups in one case and p-methylanilino groups in the other) does not change appreciably the $[\eta]$ -M_w relationship, altough the solvents used are different. The z-average radii of gyration measured in this work, as well as those of the above papers, are plotted as a function of M_w in Figure 2.

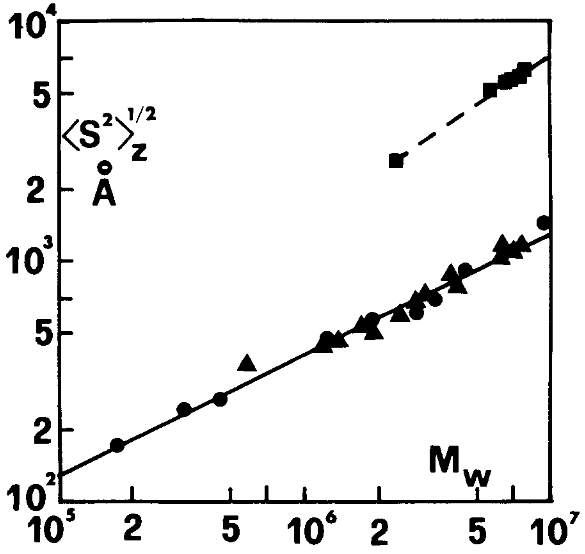

FIGURE 2: Gyration radius vs. M_w (Simbols as in Fig.1)

The straight line describing our data is given by the leastsquare equation:

$$\langle S^2 \rangle_z^{\frac{1}{2}} = 0{,}403 \cdot M_w^{0{,}50} \quad \text{Å} \qquad 4)$$

whose square is:

$$\langle S^2 \rangle_z = 0{,}162 \cdot M_w^{1{,}0} \quad \text{Å}^2 \qquad 5)$$

Plotted in the Figure as triangles, are HAGNAUER et al. (1976) data, that again are very close to ours. On the contrary TATE's results lie on the upper right part of the Figure, the gyration radii of his fractions being about 5 times larger than ours. The great heterogeneity of TATE's fractions ($M_w/M_n \cong 12$) cannot possibly explain the difference, since the unfractionated polymer studied in this work ($M_w/M_n = 13$) has $\langle S^2 \rangle_z^{\frac{1}{2}} = 1000$ Å, i.e. only 25% larger than that predicted by equation 4).

From equation 5) it is possible to estimate the characteristic ratios (uncorrected for perturbation and heterogeneity) of all the fractions:

$$C = \frac{\langle R^2 \rangle_z}{n\, l^2} = \left[\frac{6 \langle s^2 \rangle_z}{l^2} \right] \frac{M_o}{M_w} \qquad 6)$$

where the symbols have their usual meanings (MARK, 1978). Taking the P-N bond length as 1,6 Å, one obtains C=50, a value almost one order of magnitude greater than that of other polymers, including polyphosphates and polysiloxanes (MARK, 1978), and suggesting a very high spatial extension for polyphosphazenes. Further information on this problem can be obtained, according to KURATA et al. (1963) from a plot of viscosity and M_w data according to equation:

$$\frac{[\eta]^{2/3}}{M_w^{1/3}} = K^{2/3} + 0{,}363\, \Phi_o\, B\, g(\alpha_\eta) \frac{M_w^{2/3}}{[\eta]^{1/3}} \qquad 7)$$

The least-square equation obtained from this plot, Figure 3, gives, for the intercept, $6{,}76 \cdot 10^{-3}$, and for the slope, $1{,}73 \cdot 10^{-7}$ ($[\eta]$ in dl/g), from which, ignoring the uncertainty caused by the effect of the fractions heterogeneity, and taking $\Phi_o = 2{,}5 \cdot 10^{21}$, one obtains:

$$K = 56 \cdot 10^{-5}$$

$$B = 0{,}19 \cdot 10^{-27}$$

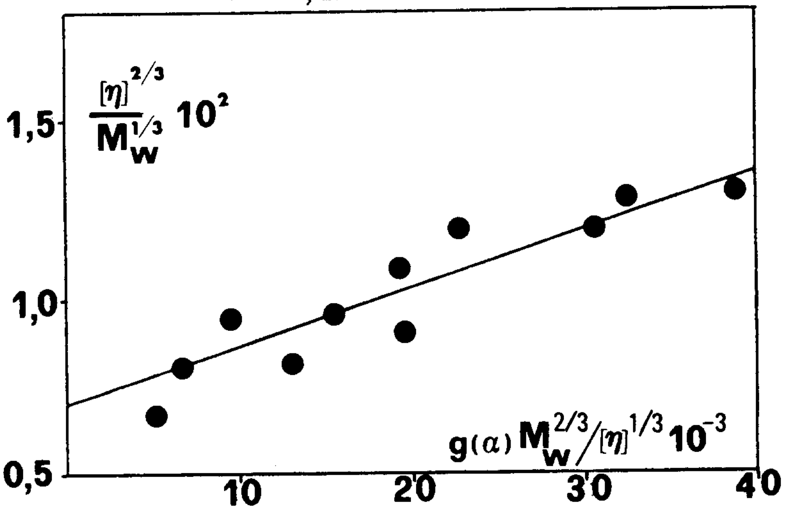

FIGURE 3: KURATA-STOCKMAYER plot ($[\eta]$ in dl/g).

The unperturbed mean square radii of gyration $\langle s^2\rangle_o$ can readily be calculated from K, with the aid of the Flory-Fox equation. The result is:

$$\langle s^2\rangle_o = 0{,}061\ M \qquad Å^2 \qquad 8)$$

From a comparison with equation 5) it is seen that the measured z-average radii of gyration are about 2,65 times larger than the unperturbed ones, and therefore the expansion factor α should be of the order of 1,6. Although this results is only approximate, due to the possible influence of polydispersity, the "regular" value of α seems to confirm that the polyphosphazene samples here investigated have indeed a very large characteristic ratio in the unperturbed solution. The direct proportionality existing between $\langle s^2\rangle_z$ and M_w (equation 5) and the normal behaviour in solution of the fractions, seem moreover to confirm that branching is absent, as suggested by other workers (SINGLER et al., 1974).

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