

# High Performance Size Exclusion Chromatography of Poly(organo)phosphazenes

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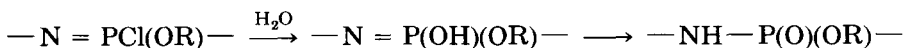
## Synopsis

The determination of the molecular weights of polyorganophosphazenes can only be achieved with great care. The nature of the substituents, the proportion of residual chlorine atoms after substitution, and also any traces of hydrolysis can considerably modify the behavior of these polymers in solution and thus lead to erroneous results. In our current research we have been developing a characterization method based on steric exclusion chromatography, coupled with a light scattering detector. We have used columns with styrene–divinylbenzene organic micropacking as the stationary phase and THF with added LiBr (0.1 mol/L) as the eluent. This method has enabled us to establish accurate correlations between molecular weight, hydrodynamic volume, and viscosimetric measurements for polyaryloxyphosphazenes of varying structures and origins. The method also provides results which agree very well with the variables for the preparation of polyphosphazenes, which is based on polycondensation of *P*-trichloro-*N*-dichlorophosphoryl monophosphazene  $\text{Cl}_3\text{P} = \text{N}-\text{P}(\text{O})\text{Cl}_2$ . Finally this method allows us to show that, despite their mineral backbone, these polymers obey Benoit's universal calibration concept.

## INTRODUCTION

Several eluent–stationary phase pairs have been described, but none of these provide a satisfactory solution for the application of steric exclusion chromatography (SEC) to polyphosphazenes as a whole. Although DMF–Styragel,<sup>1–4</sup> THF–Bondagel,<sup>5,6</sup> and chloroform–Styragel<sup>7</sup> are normally recommended for the characterization of polyfluoroalkoxy and polyaryloxyphosphazenes, most of the work was done with the THF–Styragel pair. However, the results obtained are not satisfactory since the chromatograms are asymmetric and frequently show a bimodal distribution which can be associated with a tail of very high masses.

For viscosimetric measurements the laws of Huggins and Kramer are not obeyed, whatever the solvent.<sup>8–10</sup> The authors explain these anomalies by the formation of aggregates.<sup>9</sup> These aggregates form because of the presence of residual P–Cl bonds or P–OH, P = O, and N–H bonds, which arise either from P–Cl bonds hydrolysis or from the classic phosphazene–phosphazane transposition according to the formula



In addition, Korshak, Vinogradova,<sup>11,12</sup> have shown that the proportion of residual chlorine directly controls both the conductivity of polyphosphazene solutions and whether or not Huggins and Kramer laws are obeyed. This proves that incompletely substituted polymers behave as polyelectrolytes and this behavior is responsible for the formation of aggregates.

The addition of a salt to the polymer solution is the method normally used to eliminate the aggregates since it neutralizes the charges on the polymer chain. For this reason several authors have recommended the addition of LiBr<sup>3</sup> or KI<sup>12</sup> to DMF and acetone solvents, respectively, when viscosimetrically characterizing polyfluoroalkoxyphosphazenes.

LiBr and KI are also used in the method suggested by Ferrar et al.<sup>10</sup> for the steric exclusion chromatography of polytrifluoroethoxyphosphazenes. However, the authors who have added tetrabutylammonium bromide to the THF eluent have pointed out that the anomalies related to interactions with the Bondagel packing still occur, although the addition of salt usually permits nonexclusion phenomena to be eliminated for industrial polymers.

Taking this data from the literature into account, we have tried to develop a reliable method for the determination of molecular weights in particular for polyaryloxyphosphazenes obtained by the substitution of polychlorophosphazenes from the polycondensation of P-trichloro-*N*-dichlorophosphorylmonophosphazene.

## EXPERIMENTAL

### Samples

The polyorganophosphazene samples used were mainly internal research products. Only a few materials were from external origin Firestone PNF200 commercial polymer, and samples from U.S. Army Research Laboratories (courtesy of Dr. G. L. Hagnauer and Dr. R. E. Singler, Army Materials and Mechanics Research Center, Watertown, MA 02172).

### Chromatographic System

Size exclusion chromatography was carried out on a Water 150 ALC/GPC instrument. The columns used were a set of two similar Shodex 80 M. A Chromatix CMX 100 low angle laser light scattering (LALLS) detector was inserted on line between the outlet of the columns and the inlet of the refractometer. Tubing between the Waters 150 and the LALLS cell were thermostatted by means of the Chromatix high temperature accessory. A purpose-designed filter housing was connected in front of the cell inlet. Filters of adequate diameter were cut from 0.5  $\mu\text{m}$  pore size Millipore FHLP 04700 membranes. Consequently the LALLS signal was almost noise-free. HPLC grade THF was purchased from the Societe des Solvants (SDS, France). It was stabilized with 0.03% 2,6-di-*tert*-butyl-4-methylphenol and carefully filtered on Millipore membranes before use. LiBr and ethylene glycol were used as received from Prolabo (France). In all experiments the flow rate was 1 mL/min and the temperature was 30°C. Polyorganophosphazenes were dissolved in THF at 0.2% by gentle stirring at room temperature for a few hours. They were filtered on millipore SLSR G 25 NB Millex Filters (0.5  $\mu\text{m}$ )

before injection. The injection volume was typically 200  $\mu\text{L}$ . Eleven standards from Tosoh ranging from 1800 to 3.8M were used to calibrate the system in polystyrene units.

### Data Acquisition and Processing

The following equipment was used to build a complete system of automatic data acquisition and processing: Hewlett Packard HP 9836 S desktop computer (1 Mbyte memory); HP 7475 A plotter; HP Thinkjet; Keithley 705 scanner + Keithley 195 A digital multimeter. Highly efficient software for SEC/LALLS calculations was used courtesy of Dr. J. Lesec.

### Refractive Index Increment

A Chromatix KMX-16 differential refractometer operating with He/Ne 632.8 nm light (the same as in the CMX-100) was used to determine the  $dn/dc$  values in the conditions selected for the SEC analysis (where  $n$  is the refractive index of the solution and  $c$  is the concentration of the polymer in the solvent).

The following values were obtained:

$$dn/dc = 0.160 \pm 0.002 \text{ for poly(diphenoxy)phosphazenes}$$

$$dn/dc = 0.145 \pm 0.002 \text{ for poly(aryloxy)phosphazenes}$$

$$dn/dc = -0.029 \pm 0.004 \text{ for poly(fluoroalkoxy)phosphazenes}$$

with substantial changes within the latter group, probably related to problems of solubility.

### Viscosity Measurements

Dilute solution viscosities in THF and in THF-LiBr were measured using a conventional Ubbelohde type viscosimeter. The intrinsic viscosity was deduced from the classic extrapolation to zero concentration. The shear rate was about 1000  $\text{s}^{-1}$ . Later in this study, use was made of a home-made continuous viscosimeter which had been initially developed for SEC coupling.<sup>14</sup> Despite a higher shear rate, a good agreement between the two systems was definitely obtained. In all cases the temperature was kept constant at the desired value (30°C) by means of a thermostatted water bath.

## RESULTS

### Choice of the SEC Conditions

The SEC analysis of different polyorganophosphazenes (polydiphenoxy, polyaryloxy, and polytrifluoroethoxy phosphazenes which subsequently will be referred to as PPP, PAP, and PFP, respectively) was first tried in pure THF since this classic SEC eluent was apparently a good solvent for our products. In all cases the chromatograms were unusually shaped, suggesting adsorption phenomena, or other nonexclusion phenomena.

In analogy with the data in the literature as well as with other problems solved in our laboratory, polyethylene glycol 400, or ethylene glycol, was tested as a first additive to the THF. A notable improvement was obtained and the products were eluted in the order expected from their intrinsic viscosities.<sup>15</sup> However, the shapes of the chromatograms were not as typical as might have been expected.

The addition of LiBr (0.1 mol/L) (this concentration is usually employed for the most of complex polymers) proved much more satisfactory and led to very regular distributions. Calculations based on the value of the increment index proved that all the polymer injected came out of the column, whereas losses of 40% in pure THF and 25% with 0.5% ethylene glycol were observed. These results clearly confirm the adsorption phenomenon. The use of an LiBr type electrolyte makes it possible to seriously contemplate the precise characterization of polyorganophosphazenes by SEC/LALLS coupling, in the same way as for many other types of industrial polymers (polyimides, modified PAN, etc.).

Additionally, intrinsic viscosity measurements were carried out in order to separate the problems related to the choice of the polymer/solvent pair from the effects of the column packing. A series of  $[\eta]$  and  $K_H$  measurements were taken in pure THF, ethylene-glycol-containing THF and finally in the solvent chosen for the SEC analysis. No rule could be drawn about the Huggins constant, since it varies from 0.25 to 1.5 in pure THF, depending on the polymer studied. This phenomenon, which seems to confirm the presence of anomalies in the polyphosphazene chain, disappears completely when LiBr (0.1 mol/L) is added. For this reason, this eluent was used for the viscosity measurements.

### Characterization of Polyorganophosphazenes

Among the several hundred samples that have been analyzed over the past few years, less than 5% were PFP. This family presents a peculiar difficulty since it has a very low  $dn/dc$  value in THF, which makes the light scattering signal/noise ratio unfavorable. SEC/LALLS is still possible, as shown in Figure 1. In contrast with other families, PFP samples all exhibit a typically shaped RI chromatogram, with a high molecular weight tail. Two results seem to eliminate any analytical pitfalls: the calibration curve in PFP units deduced from both signals is regular, and a good agreement on  $\bar{M}_w$  between SEC/LALLS and static light scattering experiments has been stated on several occasions.

We are now particularly interested in the two other families (PPP and PAP) which gave very close results. Numerical values have been established mainly for PPP samples, but surprisingly they are valid for PAP too, despite their chemical difference.

For all new polymers, SEC/LALLS is an outstanding way of showing differences in the molecular weight distribution (MWD) of samples. The effects, if any, of various synthesis parameters (duration, temperature, solvents, additives, recovery of the polymer, etc.) have been well stated for our processes. As an example, the comparison of the two samples from our laboratory is given in Figure 2. A small difference in the polycondensation

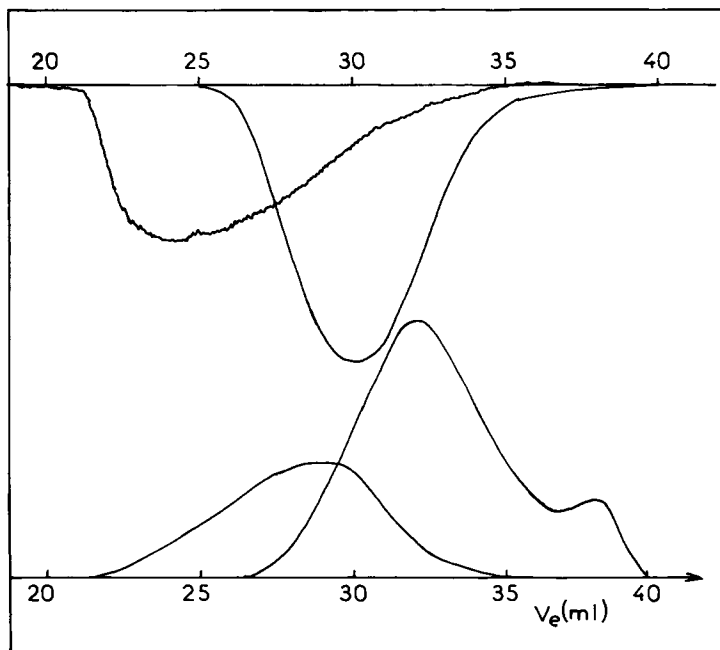


Fig. 1. Typical chromatograms of two polyorganophosphazenes: PFP (left) and PPP (right) (upper trace: LALLS signal; lower trace: RI).

process has noticeably changed the weight average molecular weight  $\bar{M}_w$  as well as the polydispersity  $I$ . Moreover, Figure 3 clearly illustrates that although RI is the proper detector for showing low molecular weight species, the LALLS signal will significantly enhance the differences in the high molecular weight region.

If the second virial coefficient  $A_2$  cannot be easily determined using the CMX 100 LALLS detector, the way to establish whether it plays a role in the calculations has been well established.<sup>16</sup> Since perfect linearity of the LALLS signal area vs. the injected quantity was observed within the range of SEC concentrations,  $A_2$  was neglected. Taken together, the results which were

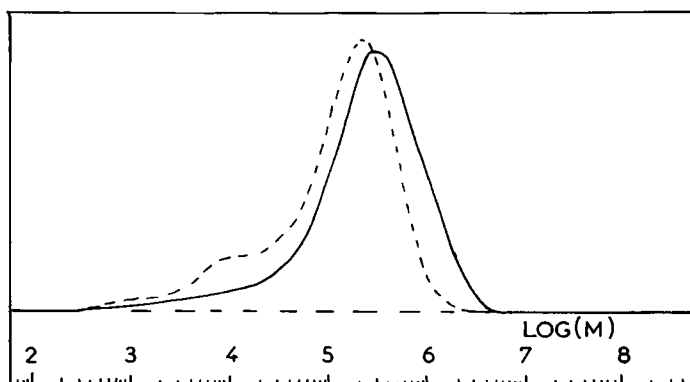


Fig. 2. Comparison of two PPP samples showing the effect on the molecular weight distribution of some changes in the process.

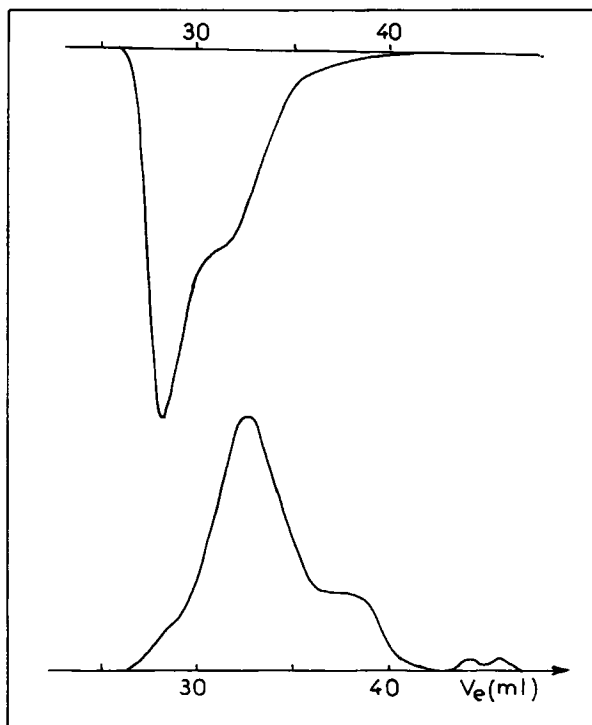


Fig. 3. PPP samples illustrating the synergy of the two detectors. LALLS (upper trace) is highly sensitive to high molecular weight species, whereas only RI (lower trace) shows a low molecular weight peak.

progressively accumulated (Table I is the collection of 10 runs over the past 6 months) have allowed us to show a very simple relationship between the absolute  $\bar{M}_w$  (from LALLS) and the same average in polystyrene units  $\bar{M}_{PS}$ :

$$\bar{M}_w/\bar{M}_{PS} = 2.0 \pm 0.1 \quad (1)$$

This rule applies to the entire range of molecular weights ( $10^5 < \bar{M}_w < 10^6$ ). Only a few samples gave higher values (2.3–3). An excess of light scattered by aggregates or similar species is a plausible explanation, knowing the unusual shape of the LALLS signal (Fig. 4). These findings lead us to recommend that results in polystyrene units should never be neglected whatever the type of polymer studied, despite the nonabsolute nature of these data. This is an additional advantage of the SEC/LALLS coupling compared to a conventional light scattering experiment.

Finally, a Mark-Houwink relationship has been established. Figure 5 clearly shows again that PAP and PPP can be considered together. The following equation was thus obtained after least-square regression on a selection of about 40 values ( $[\eta]$  in mL/g):

$$\text{THF}/30^\circ\text{C}: [\eta] = 0.0119 M_w^{0.649} \quad (2)$$

TABLE I  
Collect of SEC/LALLS Data over a Period of 6 Months.<sup>a</sup>

Sample no.	$\bar{M}_{PS} \times 10^{-3}$	$\bar{M}_W \times 10^{-3}$	$\bar{M}_W/\bar{M}_{PS}$
1	200	428	2.1
2	200	450	2.3
3	218	460	2.1
4	223	445	2.0
5	288	572	2.0
6	236	464	2.0
7	158	312	2.0
8	207	376	1.8
9	111	246	2.2
10	166	312	1.9
11	170	360	2.1
12	240	478	2.0
13	346	670	1.9
14	421	819	1.9
15	171	393	2.3
16	236	521	2.2
17	124	240	1.9
18	131	266	2.0
19	176	358	2.0
20	160	331	2.1
21	135	243	1.8
22	122	242	2.0
23	151	332	2.2
24	154	311	2.0
25	220	457	2.1
26	229	451	2.0
27	161	324	2.0
28	169	347	2.1
29	197	367	1.9
30	278	471	1.7
31	356	644	1.8
32	298	544	1.8
33	328	590	1.8
34	273	513	1.9
35	251	484	1.9
Mean value (1 standard deviation)	—	—	2.0 ( $\pm 7\%$ )

<sup>a</sup>Comparison of the absolute weight-average molecular weight  $\bar{M}_W$  with the weight-average molecular weight in polystyrene units  $\bar{M}_{PS}$

As polydispersities of samples ranged between 2 and 10, the validity of (2) is limited to similar products. Any isomolecular polyorganophosphazenes would not obey the same equation. To complete this work on the SEC of polyphosphazene derivatives, it was interesting to check whether or not the universal calibration concept<sup>17</sup> applies for such unusual polymers. If we assume that the hydrodynamic volume at a given elution volume is the same for polystyrene and for PPP,

$$[\eta]_{PS} \cdot M_{PS} = [\eta]_{PPP} \cdot M_{PPP} \quad (3)$$

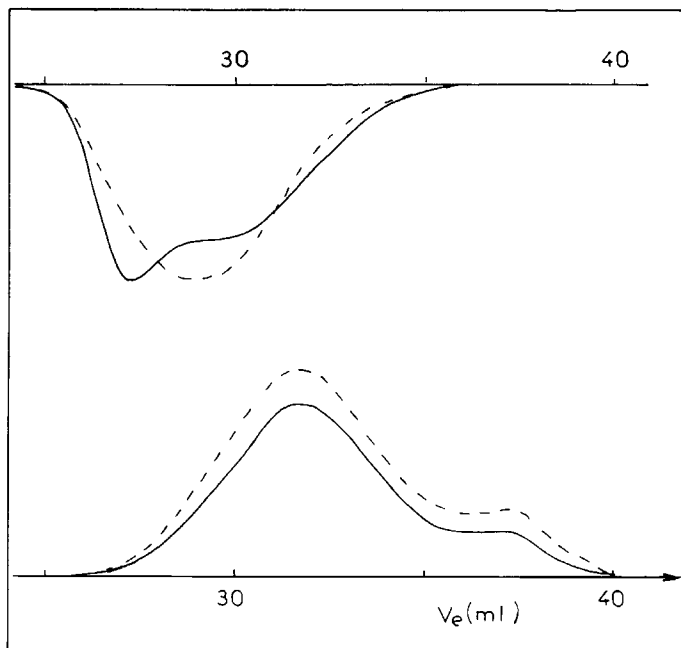


Fig. 4. Comparison of two PPP samples of very similar RI chromatogram (lower trace). The LALLS detector seems to reveal some aggregates for one of them.

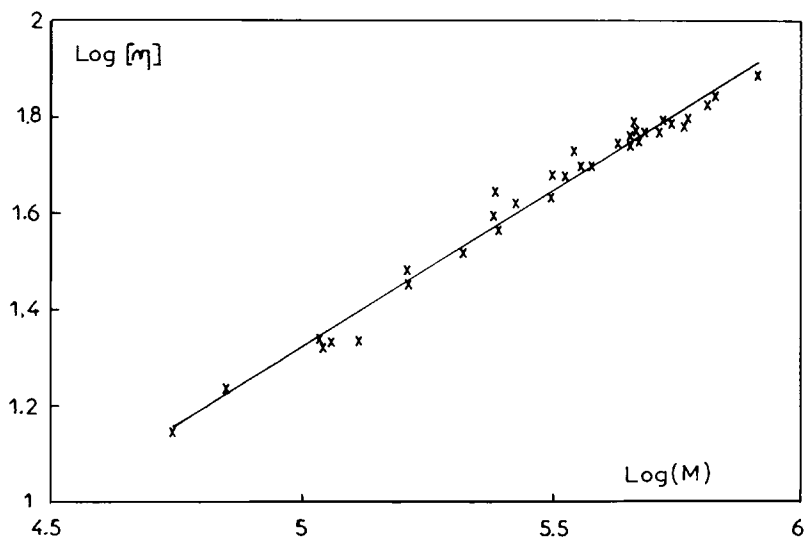


Fig. 5. Mark-Houwink relationship for PAP and PPP in THF at 30°C.



This is equivalent to

$$\bar{M}_w/\bar{M}_{PS} = [\eta]_{PS}/[\eta]_{PPP} \quad (4)$$

If the relationship  $[\eta] = 0.0162 M^{0.701}$  is used to calculate  $[\eta]_{PS}^{18}$ , and  $[\eta]_{PPP}$  is deduced from eq. (2), it follows that

$$\log(\bar{M}_w/\bar{M}_{PS}) = 0.031 \log \bar{M}_{PS} + 0.081 \quad (5)$$

The only benefit of this numerical relationship is to give  $\bar{M}_w/\bar{M}_{PS}$  values when the universal calibration concept is obeyed.

The following values are obtained:

$$\bar{M}_w/\bar{M}_{PS} = 1.7 \text{ for } \bar{M}_{PS} = 10^5$$

$$\bar{M}_w/\bar{M}_{PS} = 1.8 \text{ for } \bar{M}_{PS} = 10^6$$

Considering all sources of experimental error, these results can be considered in good agreement with our constant ratio of 2.

### CONCLUSION

In this study we have tried to show that SEC/LALLS coupling is a very effective characterization technique. For this we have used polyorganophosphazenes, the synthesis of which is based on the polycondensation of *P*-trichloro-*N*-dichlorophosphorylmonophosphazene  $\text{Cl}_3\text{P} = \text{N} - \text{P}(\text{O})\text{Cl}_2$ .

A simple relationship has been shown between the hydrodynamic volume in THF/LiBr and the absolute mass of the polymer. We have also shown that a departure from this rule is the proof of the presence of aggregates.

The following Mark-Houwink relationship has been established for this solvent in the case of polydiphenoxy- and polyaryloxyphosphazenes:

$$[\eta] = 0.0119 \bar{M}_w^{0.649}$$

In short, in spite of their mineral backbone, these polymers also confirm the universality of Benoit's calibration concept. Thus an SEC apparatus equipped with the RI/continuous viscosimeter coupling would equally work for the precise control of polyorganophosphazenes.

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