Dilute solution characterization of polyphosphazenes

María Pilar Tarazona
Departamento de Química Física, Universidad de Alcalá de Henares, 28871 Alcalá de Henares, Madrid, Spain
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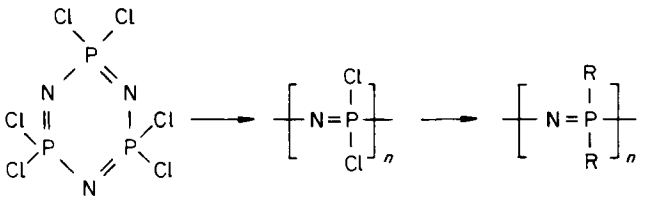
A survey of the data reported in the literature on the dilute solution characterization of polyphosphazenes is presented. There are relatively few studies dealing with this kind of characterization, at least in comparison with the enormous amount of work devoted to the synthesis, solid-state properties and possible practical applications of these materials. Furthermore the analyses published to date give surprising and often contradictory results which indicate that the solution properties of these polymers are difficult to measure and not yet well understood. High polydispersity of the samples, formation of intermolecular aggregations and branching are the problems more frequently invoked to explain the experimental results. Some conclusions are presented that could facilitate future characterizations of these polymers.

(Keywords: polyphosphazenes; solution properties; characterization)

INTRODUCTION

Poly(dichlorophosphazene) (PDCP) is one of the oldest known synthetic polymers. As far back as 1897, Stokes[1] reported the thermal conversion of hexachlorocyclotriphosphazene (HCTP) into highly crosslinked PDCP which was named *inorganic rubber* because of its elastomeric properties. However, the promising properties of this polymer were spoiled by its hydrolytic instability. Many attempts to obtain stable polyphosphazenes were carried out, but the first success was reported as late as 1965 when Allcock and co-workers[2,3] were able to perform the thermal polymerization of HCTP (I) with a very tight control of temperature and humidity, thus obtaining uncrosslinked and therefore soluble samples of PDCP (II). These samples were then dissolved and their chlorine atoms replaced by different organic groups through nucleophilic substitution. The poly(organophosphazene)s (POPNs) (III) thus obtained are hydrolytically stable polymers.



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A very wide range of organic side groups can be attached to the inorganic backbone of PDCP, and the physical and chemical properties of the resulting POPNs depend strongly on the substituents. Hence the POPNs form a new class of polymers with an extremely versatile adaptability for practical applications.

Considerable research efforts have been made to study the synthesis, properties and technological applications of POPN, and several excellent reviews on synthesis and applications can be found in the literature[4–12].

With respect to their properties, these polymers exhibit unique characteristics derived first from the inorganic skeletal backbone of alternating phosphorus and nitrogen atoms and second from the great variety of structures which can be attained just by choosing the appropriate organic side groups. The glass transition temperature, T_g, is the property most systematically studied for the over 300 different polyphosphazenes synthesized to date, and although T_g values depend strongly on the substituents, temperatures as low as $-105°C$ have been found[13,14]. This fact indicates that the chain has an inherent flexibility which can be restricted with appropriate rigid side groups.

Despite all the research work dedicated to these polymers since the 1960s, reports on the dilute solution properties of polyphosphazenes are scarce and sometimes surprisingly contradictory. Reports on very large dimensions of polyphosphazenes, which in a way seem unexpected due to the low values of T_g, are found in the literature. Moreover, very different values for the dimensions can be found depending on whether they are determined by light scattering or viscosity measurements. The problems associated with the peculiar behaviour of these polymers in solution have been explained in several ways by different authors; the presence of aggregates, branching, contamination by low-molecular-weight products, etc. are some of the explanations given in the literature. Very broad molecular-weight distributions and difficulties in obtaining narrow molecular-weight samples by fractionation have also contributed to mask the interpretation of the dilute solution properties of polyphosphazenes.

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In view of this situation, it is of interest to collect the data found in the literature about dilute solution properties and to try to organize and explain the results. Thus this paper presents a survey of the data published on the characterization of the precursor polymer PDCP and some POPNs, namely those having alkoxy and aryloxy side groups which are the most studied, although data for polyphosphazenes with amide and alkyl/aryl side groups found in the literature are also included. Some conclusions are drawn from this survey that could explain the differences in the experimental results reported to date and may be used to improve the consistency of future characterizations of this kind of polymer.

POLY(DICHLOROPHOSPHAZENE) (PDCP)

PDCP is by far the most frequently synthesized polyphosphazene, since it is used as a precursor for the preparation of many POPNs. The procedure most often used for obtaining PDCP has been the thermal polymerization of the cyclic trimer HCTP following the method described by Allcock and Kugel[2]. Nevertheless, some other procedures such as solution polymerization employing different catalysts[5,15–18], plasma initiated polymerization[19] or polycondensation of *N*-(dichlorophosphoryl)-*P*-trichlorophosphazene with elimination of phosphoryl chloride[12] have also been used. A lot of work has been devoted to the preparation of this polymer, seeking the best conditions under which samples of perfectly linear PDCP could be obtained with a good yield and reproducible results. Unfortunately, it seems that such an ideal procedure has not yet been found.

However, despite being the most common of all polyphosphazenes, PDCP is not the best characterized one. One of the reasons for this situation is the hydrolytic instability of PDCP which hampers most of the characterization procedures and encourages many authors to transform the obtained PDCP into a more stable POPN as soon as possible. An example is our work[20–24] on poly(dialkoxy/diaryloxyphosphazene)s which were obtained from the precursor PDCP trying to use the minimum possible manipulations of the unstable PDCP.

On the other hand, many authors[6,19,25–29] have performed different types of polymerizations of the trimer HCTP, trying to study the kinetics, mechanism, yields, etc. of the reaction. They characterized the resulting PDCP using several dilute solution techniques, especially size exclusion chromatography (s.e.c.) and viscometry, but since the aim of those works was not the dilute solution properties by themselves, the characterizations were not as detailed as would be desirable. Thus, some of them were based on the use of viscometric constants reported before in the literature, or on a universal calibration of s.e.c. using polystyrene standards, since, in general, the objective was to determine the relative values of molecular-weight distributions obtained in the different polymerizations. A good example is the work of Klein *et al.*[19] who carried out the polymerization of HCTP via the technique of plasma initiated polymerization and followed the molecular weight of the obtained PDCP by viscosity measurements in toluene containing 0.1% chlorotrimethylsilane as a water scavenger and polymer stabilizer. They used the Mark–Houwink relationship $[\eta]=KM_v^a$ to determine the viscosity-average molecular weights but the results of M_v are, as they state, only qualitative since they used the values of K and a from literature data reported by Knoesel *et al.*[30] and Hagnauer and co-workers[31–33]. Allcock *et al.*[25] studied the polymerization of HCTP; samples isolated after different reaction times were converted into the hydrolytically stable trifluoroethoxy derivative which was then characterized using s.e.c., calibrated with polystyrene standards, and viscosity measurements. Another example is provided by the work of Tur and co-workers[7,27] who studied the dependence of the intrinsic viscosity of polyphosphazenes on polymerization time and the polymerization–depolymerization equilibrium, based on the study of a poly(fluoroalkoxyphosphazene) derivative which will be presented in the next sections.

^{31}P n.m.r. spectroscopy has been used by some authors to characterize PDCP[18,19,25,34,35] and many other polyphosphazenes[13,36–38], trying to determine the presence of branching in the samples, which has been the object of considerable debate in the literature in recent years. This is obviously a very powerful technique, although its results are not always unquestionable. Thus, a spectrum containing a single signal such as those reported for some samples of PDCP is a very convincing proof that the sample is linear, but the presence of multiple peaks in the spectrum of a given sample could be explained in different ways. For instance, Klein *et al.*[19] attributed the appearance of several small peaks in the spectrum of a PDCP sample to the presence of unreacted trimer and the formation of cycles higher than tetramer and as high as octamer or nonamer. Ferrar *et al.*[34] proved that when a sample of PDCP was treated with an excess of sodium trifluoroethoxy in order to transform the precursor polymer into poly[bis(trifluoroethoxy)phosphazene], the sharp singlet of the original sample broadens and several other signals appear in the spectrum; they explained these changes by the formation of P–OH moieties and hydrogen bonding between the hydroxy groups or with other trifluoroethoxy side groups. On the contrary, Mujumdar *et al.*[18] explained the same behaviour by a crosslinking of the sample through the formation of intermolecular P–O–P linkages. Therefore, although ^{31}P n.m.r. is an excellent tool for detecting changes in the molecular structure of a given polyphosphazene sample, it needs the assistance of other techniques in order to determine the nature of those changes.

A more traditional technique is viscometry which, to our knowledge, was first employed for the characterization of PDCP in 1951 when Patat and Kollinsky[39] measured the intrinsic viscosities and number-average molecular weights (determined by osmometry) of several samples of PDCP in toluene solution fitting their data to the viscometric equation $[\eta]=KM_n^a$. The results obtained in this pioneer work, together with those reported later for some other authors, are summarized in *Table 1* and represented in graphic form in *Figure 1* which shows the values of $\log[\eta]$ *versus* $\log M$. The solid lines in this figure indicate the range of molecular weights and viscosities actually measured by each author while the broken lines represent extrapolations of the viscometric equations in order to facilitate the comparison between data from different sources.

It is difficult to reconcile the data shown in *Figure 1*. Thus, three of those papers report values determined in toluene solution, but neither ref. 39 (line b on *Figure 1*) nor ref. 30 (line c) indicate the temperature at which

Table 1 Viscometric experimental data for PDCP

Solvent	T (°C)	$10^5 M_n$	$10^5 M_w$	k_H	$[\eta]$ (dl g^{-1})	$10^4 K$	a	Ref.
Toluene	–	0.21–1.32			0.15–0.55	1.65	0.69	39
Toluene	–		1.15–14.2		0.14–0.82	0.389	0.71	30
Chloroform	–		0.29–5.12		0.31–2.04	13.2	0.56	30
Toluene	25	5.6–7.2	21.0–31.0	0.35–0.77	2.38–2.84			32
Toluene[a]	25	5.7	13.4	1.49	1.24			32
TCB	41		1.8–9.2		0.18–0.43	2.9	0.53	17

[a] The authors describe this sample as anomalous

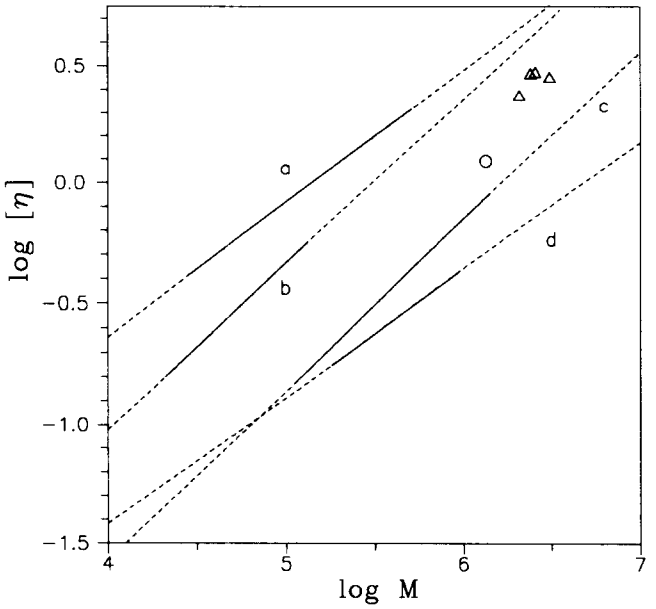

Figure 1 Summary of viscometric experimental data reported in the literature for PDCP. Solid lines represent the ranges of $[\eta]$ and M measured by different authors while the broken lines indicate extrapolations of the viscometric equations. Line a: ref. 30, solvent chloroform; b: ref. 39, solvent toluene; c: ref. 30, solvent toluene; d: ref. 17, solvent TCB, $T=41$°C; △: ref. 32, solvent toluene, $T=25$°C; ○: ref. 32, solvent toluene, t = 25°C, anomalous sample

the measurements were performed; probably these experiments were carried out at room temperature which should be somewhere around 20°C. Moreover, while Patat and Kollinsky[39] used M_n for the viscometric equation, Knoesel *et al.*[30] employed M_w determined by light scattering. Nevertheless, both authors obtained practically the same value of the exponent $a \approx 0.7$, which indicates that toluene at room temperature is a good solvent for PDCP. Most of the difference between lines b and c on *Figure 1* could be due to the use of different averages of molecular weights; in fact, both lines will superpose if b is redrawn using M_w instead of M_n and a polydispersity ratio $r = M_w/M_n \approx 9$ is assumed for the samples measured by Patat and Kollinsky[39].

The last set of values measured in toluene were reported by Hagnauer and Koulouris[32] who studied five samples of PDCP obtained by thermal polymerization of HCTP with different reaction times, ranging from 60 to 215 h using s.e.c., osmometry, light scattering and viscometry. All the dilute solution measurements were performed in toluene at 25°C, although s.e.c. analyses were also run with 1,2,4-trichlorobenzene (TCB) and tetrahydrofuran (THF) as eluents. Four of their samples are soluble and give molecular weights that increase with reaction time, both in the case of M_w and M_n, although the s.e.c. analysis indicates that the molecular weight distributions are bimodal, tailing to higher elution times with polydispersity ratios $r = M_w/M_n = 4.0 \pm 0.3$. The viscometric analysis shows that both $[\eta]$ and the Huggins constants k_H increase with increasing M_w (or with increasing reaction time). The values of k_H are within the usual range of about 0.3–0.8, but the results of $[\eta]$ do not give a good fit to the viscometric equation $[\eta] = KM^a$ using either M_n or M_w averages; the triangles on *Figure 1* represent the values of log $[\eta]$ *versus* log M_w for these four samples. The authors suggest that the poor fitting may be due to the different (and large) polydispersities of the samples. The fifth sample prepared by these authors was obtained with a reaction time of 180 h and contained some insoluble gel. The authors extracted the soluble part, around 40% of the total sample, and characterized it with the same procedures employed for the other samples. They describe the behaviour of this fifth sample as anomalous since, in the first place it does not follow the trend of increasing molecular weight with reaction time shown by the other four samples; indeed, M_n of this sample is roughly the same as for the sample obtained with a reaction time of 60 h. On the other hand, the Huggins constant k_H is much larger than that expected for random coil molecules, and finally, the intrinsic viscosity is half of that obtained for the 60 h sample despite having the same value of M_n. The circle on *Figure 1* shows the log $[\eta]$ *versus* log M_w for this anomalous sample.

Line a on *Figure 1* shows the results obtained by Knoesel *et al.*[30] in chloroform solutions while line d represents the values reported by Potts *et al.*[17] in TCB at 41°C. Intrinsic viscosities are much higher in the former case, but the exponent a of the viscometric equation is roughly the same in both cases and very close to the unperturbed value $a = 0.5$. Thus, the differences in $[\eta]$ are in the pre-exponential factor K which is roughly three times larger in chloroform than in TCB. As will be explained later, in the last case the PDCP has been obtained by solution polymerization and branching is present, according to the authors.

According to *Table 1*, there is a reasonable coincidence in the results for the viscometric parameter a, which represents the variation of intrinsic viscosities with molecular weights. Thus, the measurements performed in toluene give $a \approx 0.7$ which would indicate that toluene is a good solvent for PDCP. On the other hand, the measurements performed in more polar solvents such as chloroform or TCB give $a \approx 0.5$ and therefore

a straightforward conclusion would be that polar compounds are poor solvents for this polymer. However, there must be some failure in this reasoning since some authors claim that TCB is a good solvent for PDCP while others indicate that toluene is nearly a theta solvent.

These discrepancies can be shown more clearly by computing the characteristic ratio of the dimensions according to the expression

$$C_n=\frac{\langle r^2\rangle_0}{nl^2}=\left[\frac{M_r}{2l^2\Phi^{2/3}}\right]\left[\frac{[\eta]_\theta}{M^{1/2}}\right]^{2/3} \quad (1)$$

where n is the number of skeletal bonds, each of them having a length l which in this case was taken as 0.152 nm for the P–N bond. M is the averaged molecular weight of the polymer and M_r the molecular weight of the repeating unit; $M_r=115.9$ for the unit N–P(Cl)$_2$ that contains two skeletal bonds. Finally, Φ represents the hydrodynamic constant which was taken as 2.5 with l in nm and $[\eta]$ in dl g^{-1}. The results of C_n computed according to equation (1) using both weight M_w and number M_n molecular weight averages, are summarized in *Table 2*. Hagnauer and Koulouris[32] report the values of C_n calculated for their samples using M_n and give slightly different values from those indicated in *Table 2*; in fact they give values of 27 and 17 instead of the 30 and 19 shown in the table; the discrepancy is due to the use of slightly different values for l and Φ. In these calculations, as in the corresponding ones in ref. 17, the measured $[\eta]$ was used as the unperturbed value $[\eta]_\theta$ since the authors find $A_2\approx0$ for PDCP in toluene. The values corresponding to refs. 30 and 39 have been computed by calculating $K_\theta=[\eta]_\theta/M^{1/2}$ from data in the original papers using the Stockmayer–Fixman method. Again a naive explanation of these results could be that the values of C_n computed with M_w are ca. 14 ± 7 and the large uncertainty could be justified by thinking that the result is sensitive to the temperature, polydispersity and possible branching of the measured samples. However, this simple explanation fails because the dimensions computed for chloroform solutions, which, according to the exponent of the viscometric equation, $a=0.56$, should be close to unperturbed conditions, are almost twice those computed in toluene, which gives $a\approx0.7$ indicating a very good solvent.

Table 2 Characteristic ratio of the dimensions $C_n=\langle r^2\rangle_0/nl^2$ of PDCP obtained from viscometric data[a]

Solvent	C_n with M_w	C_n with M_n	Ref.
Toluene	19	30	32
Toluene	14[b]	19[b]	32
Toluene		12	39
Toluene	7		30
Toluene	8[b]		17
Chloroform	21		30

[a] Values computed for this work are from data appearing in the original papers (see text)
[b] Possible branched samples

Light scattering measurements have also been used for the characterization of PDCP. The values reported in the literature are summarized in *Table 3*. Thus, Chu and Lee[40] have performed both static and dynamic measurements of PDCP in a mixture of the trimer HCTP and TCB that behaves as a good solvent. They found scaling laws of the type $y=QM_w^q$ where y represents one of the following magnitudes: second virial coefficient A_2 in units of mol cm^3 g^{-2} for which $Q=2.6\times10^{-3}$ and $q=-0.14$; radius of gyration $\langle s^2\rangle^{1/2}$ in nm that gives $Q=1.2\times10^{-2}$ to 3.0×10^{-2} and $q=0.58\pm0.04$; diffusion coefficient $\mathcal{D}$ in cm^2 s^{-1}, $Q=5.49\times10^{-4}$ and $q=-0.58$ and the hydrodynamic radius R_h in nm for which $Q=1.25\times10^{-2}$, $q=0.58$. Therefore, there is an excellent concordance between the exponents for $\langle s\rangle^{1/2}$ and R_h determined respectively by static and dynamic measurements. This exponent is also in good concordance with the value that would be obtained for randomly coiled chains in a good solvent in which the expansion coefficient α increases with M^ε with values of ε of ca. 0.2.

Hagnauer and Koulouris[32] performed static light scattering measurements in toluene solutions at 25°C and obtained a value for the second virial coefficient $A_2\approx0$ and an exponent $q=0.46$ for the scaling law of $\langle s^2\rangle^{1/2}$. Both results would indicate proximity to unperturbed dimensions. However, viscometric measurements on the same solvent gave an exponent of $a\approx0.70$ for the viscometric equation which is typical of good solvents. The authors calculated the z-average molecular weight M_z from their s.e.c. analysis and used this result to compute the ratio $\langle s^2\rangle_z/M_z$ and the characteristic ratio of the dimensions:

$$C_n=\frac{\langle r^2\rangle_0}{nl^2}=\left[\frac{3M_r}{l^2}\right]\left[\frac{\langle s^2\rangle_z}{M_z}\right] \quad (2)$$

obtaining the values $C_n=23$ for the four normal samples and $C_n=8$ for the anomalous one. Correction of these

Table 3 Static light scattering data for PDCP[a]

Solvent	A_2 (mol cm^3 g^{-2})	$\langle s^2\rangle^{1/2}=QM_w^q$ (nm) Q	q	$10^2\langle s^2\rangle/M_w$	Ref.
HTCP/TCB	$(3.7–5.0)\times10^{-4}$[c]	0.03–0.01	0.58	0.25–0.36[c]	40
Toluene	≈0	0.10*	0.46*	0.23–0.33	32
Toluene[b]				0.23	32
Toluene	≈0	0.305*	0.36*	0.13	17
Toluene		0.0048*	0.73*	1.0	30
Chloroform	<0	0.173*	0.51*	3.6	30

[a] Values computed for this work from data appearing in the original papers are marked with an asterisk
[b] The authors describe this sample as anomalous
[c] Computed from the scaling laws of A_2 and $\langle s^2\rangle^{1/2}$ for the range of molecular weights 10^5–10^6

results for the bond length $l = 0.152$ nm used in the present work gives values of 25 and 9 respectively for the normal and anomalous samples. Both results are smaller than those obtained from viscometric measurements using M_n, as shown in *Table 2*, although the difference is larger for the anomalous sample. The authors conclude that the fact that the dimensions obtained from light scattering are smaller than those calculated from viscometry may be due to branching of the polymeric chains. This explanation would be in concordance with the fact that the difference is larger for the anomalous sample which, at the same time, originally contained a large amount of insoluble gel and therefore it seems reasonable to assume than even the soluble part that was extracted for these measurements was more heavily crosslinked than the other four samples.

The same explanation is employed by Potts *et al.*[17] to rationalize the results of static light scattering performed in toluene solutions of PDCP obtained by a catalysed reaction that gave $A_2 \approx 0$, an exponent $q = 0.36$ for the scaling law of $\langle s^2 \rangle^{1/2}$ and a very small value of the ratio $\langle s^2 \rangle / M_w$ (see *Table 3*). Thus, the authors conclude that this sample contains branched chains and suggest that the catalytic reaction produces more branching than the thermal polymerization. It is noteworthy that an exponent $a = 1/3$ in the relationship between $\langle s^2 \rangle^{1/2}$ and M_w is characteristic of spherical particles and therefore may indicate highly branched polymer chains, but it may also be due to the presence of globular particles produced by intermolecular association, although in this second case, the ratio $\langle s^2 \rangle / M_w$ should be very large.

On the contrary, Knoesel *et al.*[30] found values of $\langle s^2 \rangle / M_w$ that are between 5 and 10 times larger than those reported later by Hagnauer and Koulouris[32]. Moreover, they obtained negative values of A_2 in chloroform solutions. They explained these results by assuming the formation of intermolecular aggregates that would increase the intensity of the scattered light and therefore produce very large values of $\langle s^2 \rangle$; at the same time, the proportion of these aggregates would diminish when the concentration goes to zero thus simulating a negative value of A_2.

Therefore, it seems that it is rather difficult to characterize PDCP by measuring its properties in solution, owing to several factors:

(1) The samples usually have very broad molecular-weight distributions with multimodal distributions and therefore many results are very sensitive to the kind of molecular-weight averages used in the analysis of the experimental data.

(2) Samples of PDCP obtained in different batches can be different, especially those obtained by catalysed polymerization, which may be branched and could produce surprising results in some of the measured properties such as very large Huggins constants in viscometric analysis or rather small dimensions in light scattering measurements.

(3) However, intermolecular aggregates may be formed sometimes, so that, although this will not modify the intrinsic viscosities, it will affect the values of the Huggins constants and produce serious overestimations of the dimensions determined by light scattering.

(4) The hydrolytic instability of PDCP not only renders the measurements difficult, which explains the scarce number of data available, but also the hydrolysis of even a very few chlorine atoms can contribute to enhance points b and/or c through the possible formation of P–O–P links and/or P–OH moieties respectively.

Unfortunately, there is not yet a simple way of avoiding those problems. Thus, for instance, an obvious solution to the problem of having broad molecular-weight distributions would be to fractionate the sample, but it seems that the procedures employed so far for this fractionation are difficult and not very efficient when applied to this polymer. Something similar happens with the branching of the samples, which could be solved by using a method of synthesis that gives linear chains; however, although a lot of work has been devoted to looking for a correlation between the conditions of synthesis and the degree of branching, the results are not clear.

The only point which can be surmounted, in principle, is the instability problem. In fact, the substitution of chlorine atoms by organic groups produces stable POPNs which can be measured much more easily and, consequently, a greater amount of data is available in the literature for these polymers. Thus the study of POPNs can also give information, with the pertinent differences, on the polyphosphazene chains. However, some problems still remain and new ones appear which will be discussed in the next sections, before obtaining more general conclusions.

POLY(ORGANOPHOSPHAZENE)S

Poly(dialkoxy/diaryloxyphosphazene)s

The substitution of the chlorine atoms in PDCP by alkoxy or aryloxy groups by treatment of PDCP with the corresponding alcoholates or phenolates improves the hydrolytic stability of polyphosphazenes and is, in general, easily achieved following the procedure described by Allcock *et al.*[3]. Thus, a large number of polyphosphazenes with different alkoxy or aryloxy side groups are found in the literature[13,25,36,41,42].

^{31}P n.m.r. spectroscopy is used frequently as a routine technique for the characterization of these polymers. A spectrum containing just one signal proves not only that the sample is linear, it also indicates that the nucleophilic substitution was quantitative and that all the chlorine atoms were replaced by the desired groups. The problem is that, as was indicated above, the presence of multiple peaks can be explained in different ways. Among the possible explanations for the multiple signals, the presence of unreacted trimer and the incomplete substitution of chlorine atoms can be confirmed or ruled out with a careful elemental analysis. As for the presence of low-molecular material such as cyclic oligomers, this seems quite unlikely, at least in fractionated samples. Thus, for instance, we have reported the analysis of seven fractions of poly[bis(2-naphthoxy)phosphazene] (PBNP) with molecular weights expanding over more than two orders of magnitude and whose spectra were almost identical, containing a main signal with some fine splitting centred at -17.7 ppm and a smaller signal centred at -14.82 ppm. Both the splitting and the ratios between the intensities of the two signals were almost identical for all seven fractions studied, whereas if the second signal was due to the presence of low-molecular oligomers, their proportion would decrease with increasing molecular weight of the fraction.

On the contrary, there seems to be enough experimental evidence for the idea that, when carried out under strong

conditions, the nucleophilic substitution could produce multiple signals in the spectrum, probably due to the formation of P–OH moieties. As well as the work on poly[bis(trifluoroethoxy)phosphazene] carried out by Ferrar *et al.*[34] and Mujumdar *et al.*[18], indicated above, our own experience on the preparation of polyphosphazenes from samples of PDCP obtained under similar conditions shows a good correlation between the splitting of the signals and the severity of the conditions used for the nucleophilic substitution. It is a matter of controversy at present, as to whether those P–OH groups produce only intermolecular aggregates via hydrogen bonding or lead to the formation of intermolecular P–O–P linkages and thus to branching of the sample.

S.e.c. is a technique often used for the characterization of POPNs, many of which seem to produce interactions with the stationary phase, and several anomalous, non-reproducible chromatograms showing long tails have been reported. This problem can be eliminated by the addition of small amounts of a quaternary ammonium salt to the eluent, ca. 0.1 wt% tetrabutylammonium bromide, and reproducible chromatograms can then be obtained, as has been reported by Neilson *et al.*[43] and confirmed by several workers[21,44]. In general, the molecular-weight distributions obtained are multimodal and very broad, with polydispersity ratios $r = M_w/M_n$ as high as 31 reported by Allen *et al.*[45] for poly[bis(*p*-phenoxy)phosphazene]. Furthermore, it seems that the fractionation procedures are difficult and not very efficient and even if they are successful, they still give fractions with broad molecular-weight distributions[23]. A good example is the work of Tate[46] and Carlson *et al.*[47] who analysed a copoly(fluoralkoxyphosphazene) containing 64 mol% CF_3CH_2O and 36 mol% $H(CF_2)_4CH_2O$ as pendent groups; the s.e.c. chromatogram showed a very broad molecular distribution ($r \approx 28$) with a long tail to high elution volumes and, although fractionation was achieved, the eight fractions obtained still showed a large polydispersity with values of r ranging from 7 to 23. We have studied poly(diethoxy-[20,22] and poly(dihexoxyphosphazene)[21,23] and poly[bis(2-naphthoxy)phosphazene][24]. In the case of poly(diethoxyphosphazene), fractionation was not attempted, although the samples were dissolved and precipitated in order to eliminate heads and tails of the molecular-weight distribution; the polydispersity ratios of the two samples prepared were 7.5 and 27: in the other two cases, extremely careful fractional precipitations were performed and yet the values of r for the fractions thus obtained ranged from 1.1 to 3.4.

There are some viscometric analyses of these polymers, although some of the studies give very disappointing results. Thus, for instance, Allen *et al.*[45] studied the solution properties of poly[bis(2,2,2-trifluorethoxy)-, poly[bis(*p*-chlorophenoxy)- and poly[bis(*p*-phenylphenoxy)phosphazene]s using viscometry, osmometry and light scattering techniques. They found serious problems in the fractionation of the samples and no correlation between the values of $[\eta]$ and M_w and concluded that the polymers were highly branched. Mourey *et al.*[44] examined the dilute solution behaviour of poly[bis(2,2,2-trifluoroethoxy)phosphazene] in acetone, THF and cyclohexanone in the presence of tetrabutylammonium nitrate using s.e.c. and on-line low-angle laser-light scattering (LALLS) or differential viscometry (DV) detection. They do not give quantitative values of the Mark–Houwink coefficients since they state that these coefficients change across the molecular-weight distribution as a result of a structurally heterogeneous sample.

The results of more quantitative studies are summarized in *Table 4*. The first lines on this table correspond to poly(fluoroalkoxyphosphazene)s which have been studied by several authors since, in the first place, it is relatively simple to transform PDCP into fluoroalkoxy derivatives, so that some authors, who studied either thermal or solution polymerizations of HCTP, transformed the PDCP thus obtained into fluoroalkoxy derivatives, especially poly[bis(trifluoroethoxy)phosphazene], and performed some characterizations of the resulting polymers. In addition, some of these derivatives have interesting technological properties[8,48] and this is also a good reason for trying to characterize them. However, the anomalous behaviour in s.e.c., as explained before, is extended to the viscosity measurements in some of these fluoroalkoxyphosphazenes since the fluorine atoms seem to enhance the aggregation effect[47,49,50].

Tur and co-workers[27,51,52] have studied the synthesis of PDCP, trying to determine the mechanism, products obtained and the possibilities of formation of anomalous units in the reaction of PDCP with nucleophilic agents such as sodium 2,2,3,3-tetrafluoropropylate. Although they present some measurements on PDCP as explained above, most data are for derived fluoroalkoxyphosphazenes such as [bis(2,2,3,3-tetrafluoropropoxy)phosphazene] for which they found an exponent of the Mark–Houwink relationship $a = 0.85$, slightly larger than the limiting value $a = 0.8$ customarily attributed to random coils in very good solvents.

The viscometric data reported for the fluoroalkoxy copolymers A and B indicated in lines five to seven in *Table 4* are very interesting. Copolymer A was studied using methyl isobutyl ketone (MIBK) as solvent, and anomalous behaviour was encountered with values of the Huggins and Kraemer constants ranging from negative to very high positive numbers, although good correlation between intrinsic viscosities and molecular weight was found. Thus the fitting of M_w and $[\eta]$ data measured at 25°C to the Mark–Houwink equation gives an exponent $a = 0.52$ that the authors attributed to proximity to unperturbed conditions. Studies in other solvents show that the addition of LiBr to the solvent in order to eliminate possible intermolecular aggregations decreased the values of the Huggins constants. Something similar happens in the case of copolymer B which was studied by Hagnauer and Schneider[49] using the freon solvent E2, $F[C(CF_3)F–CF_2O]_2CHFCH_3$, finding anomalous behaviour that was explained by the formation of a gel phase. Addition of acetone to the solvent produced a good fitting to the viscometric equation with an exponent $a \approx 0.5$, although the authors stated that their results are only tentative due to the high polydispersity of the measured samples; thus they obtained values of K ranging from 3×10^{-3} to 3×10^{-4} depending on the samples and whether the values of M_n or M_w were used for the fitting.

Lines eight to eleven in *Table 4* summarize the analysis performed by Bravo and co-workers[20–24] on alkoxy and aryloxy polymers using either THF or benzene as solvents. The polydispersities of the samples were very different; thus, whereas in the case of ethoxy the samples

Table 4 Summary of viscometric experimental data for poly(organophosphazene)s

Sidegroups	Solvent	$10^5 M_n$	$10^5 M_w$	k_H	$[\eta]$ (dl g^{-1})	$10^4 K$	a	Ref.
Fluoroalkoxy groups								
bis TFE	Acetone		15.4	0.30	1.17			44
bis TFE	THF		14.8	0.02	2.24			44
bis TFE	CHexanone		14.2	0.42	0.78	Change across distribution		44
bis TFP	THF					0.062	0.85	27, 51, 52
Co. A	MIBK	3.0–6.0	23–126	(−0.001)–15	0.6–2.5	7.52	0.52	47
Co. B	E2	0.4–6.8	3.1–31	0.40–3.62	0.46–2.34	No correlation		49
Co. B	E2/acetone	0.4–6.8	3.1–31	0.38–0.48	0.48–1.91	3.0–30	0.50	49
Alkoxy or aryloxy groups								
di Ethoxy	THF		2.0–20	0.44–0.46	0.57–2.26	2.51	0.65	20, 22
di Hexoxy	THF		0.26–22.8	0.10–0.34	0.064–1.75	0.21	0.79	21
di Hexoxy	Benzene		0.26–22.8	0.35–0.46	0.057–1.61	0.20	0.79	23
bis Naph	THF		0.98–14	0.34–0.92	0.12–0.72	0.42	0.69	24
di Benzoxy	Chloroform		0.36–10		0.087–1.0	0.68	0.68	53
bis *m*ClPh	Chloroform		5.6–71	0.35–0.5	0.49–3.37	0.83	0.67	54
Ph; *p*EthylPh	THF	10–15		0.23–0.46	3.59–3.84			55
Ph; 2,4diClPh	THF	4–13		0.71–2.69	0.875–1.46			55
Ph; Naph	THF	10–13		1.22–1.37	0.70–1.78			55
Other groups								
bis *p*MeAn	THF		2–130	0.30–0.50	0.2–5.2	0.52	0.70	61
Methyl/phenyl	THF		0.73–2.02	0.30–0.45	0.22–0.44	1.44	0.66	43

TFE: 2,2,2-trifluoroethoxy; TFP: 2,2,3,3-tetrafluoropropoxy; Co. A: 2,2,2-trifluoroethoxy, 2,2,3,3,4,4,5,5-octafluoropentoxy; Co. B: 2,2,2-trifluoroethoxy, 2,2,3,3,4,4,4-heptafluorobutoxy; Ph: phenoxy; Naph: 2-naphthoxy; *p*MeAn: *p*-methylanilino

were unfractionated and their polydispersity ratio ranged from ca. 8 to 27, the other two polymers were carefully fractionated and some of the fractions had values of r as low as 1.1. A numerical analysis was used to combine the results of s.e.c., light scattering and viscometry measurements in an attempt to eliminate the effect of polydispersity and obtain *true values* of the parameters for the s.e.c. calibration function and the viscometric equation. In all the cases, the samples behave as random coils in a good solvent and indeed the values obtained for the a parameter ranged from 0.65 to 0.79.

The next two polymers contained in *Table 4* are dibenzoxyl and bis(*m*-chlorophenoxy) phosphazenes investigated at 25°C in chloroform solution respectively by Sulkowski *et al.*[53] and Hagnauer and LaLiberte[54]. The viscometric behaviour of both polymers is very similar and indeed *Table 4* shows that both of them have almost identical values for the Mark–Houwink parameters which correspond to random coils in a good solvent. However, Hagnauer and LaLiberte[54] reported some problems with the fractionation of the samples; thus the original polymer had a very broad and bimodal molecular-weight distribution and the 13 fractions obtained still showed great dispersity with values of r ranging from 2 to 10. The authors indicated that this effect together with the limited molecular-weight range of the samples measured (0.5×10^6 to 7×10^6) could mask some of the results.

Andrady and Mark[55] studied three poly(aryloxyphosphazene) copolymers which are summarized in lines fourteen to seventeen in *Table 4*. They used osmometry and viscometry techniques for the characterization of the samples. However, since they studied only two fractions of each polymer, their experimental results are not enough for an accurate determination of the K and a parameters. Thus, for instance, fitting of the values of $[\eta]$ and M_n indicated in *Table 4* gives values of 0.16, 0.43 and 3.6 for the a parameter of the three polymers. Furthermore, the authors report some experimental difficulties in the measurements of these kinds of polymers. Consequently, these results can only be taken as a qualitative approach that seems to indicate a surprisingly high value for the viscosity in the case of the *p*-ethylphenoxy polymer.

Poly(aminophosphazene)s

Different alkylamino and arylamino phosphazenes have been synthesized[56–60] by replacing the chlorine atoms of the PDCP by amino groups using a procedure very similar to that employed in the preparation of alkoxy or aryloxy derivatives. Several dilute solution measurements have been carried out on unfractionated samples[59], but to our knowledge, the only values of Mark–Houwink constants found in the literature are in the study of Pezzin *et al.*[61] who fractionated a sample of poly[bis(*p*-methylanilino)phosphazene] obtaining eleven fractions that were characterized by dilute solution measurements performed in THF. Their results are summarized in the next to the last line in *Table 4*. It has been reported that the introduction of amino groups instead of alkoxy or aryloxy substituents produces a substantial increase in the value of T_g. However, according to the values shown in *Table 4*, the viscometric behaviour of the only amino polymer studied so far is very similar to that of its aryloxy analogues; in fact, the Mark–Houwink parameters for *p*-methylanilino and 2-naphthoxy polymers, both of them obtained under the same conditions, are almost identical.

Poly(alkyl/arylphosphazene)s

POGNs bearing alkyl or aryl groups directly attached to the phosphorus atoms have been much less studied since the reaction of PDCP with nucleophiles such as Grignard or organolithium reagents are accompanied by skeletal cleavage or crosslinking reactions[62]. Modifications of Allcock's original procedure have been used to obtain polyphosphazenes in which parts of the side groups are alkyl or aryl groups[63].

Neilson and Wisian-Neilson[11,64,65] have developed a different method of synthesis consisting of a condensation reaction of suitable *N*-silylphosphoranimines that produces cyclic or linear polyphosphazenes through elimination of substituted silane molecules, according to the scheme:

$$Me_3SiN{=}PRR'X \rightarrow Me_3SiX + {-}(N{=}PRR')_n{-}$$

where R and R′ are alkyl or aryl groups. The polymers thus obtained have much lower molecular weights than those obtained by thermal polymerization of PDCP, typical values range from ca. 25 000 to 200 000, and also lower polydispersities[43] ($M_w/M_n \approx 2$). Several polymers have been characterized in solution[43] including four samples of poly(methylphenylphosphazene) which allow the estimation of the Mark–Houwink constants that are presented in the last line in *Table 4*.

DISCUSSION AND CONCLUSION

It seems that the characterization of POPNs by measurement of dilute solution properties is rather difficult owing to multiple factors such as differences in the samples obtained with different polymerization procedures, broad molecular-weight distributions and problems in fractionating samples, etc., already mentioned for PDCP. Although the instability problem of PDCP is in general surmounted, some depolymerization can occur even at low temperatures if residual phosphorus–chlorine bonds are still present[66]. Probably for these reasons, the number of such characterizations reported in the literature is relatively small, although sufficient for obtaining some important conclusions which are analysed in the next paragraphs.

Dependence of viscosity on molecular weight

Table 4 clearly shows a fairly clear distinction between POPNs with and without fluorinated side groups. The fluorine atoms seem to enhance the aggregation effect showing, in general, abnormal values for the Huggins constants and difficulties in obtaining correlation between $[\eta]$ and M in the Mark–Houwink equation. The few cases in which correlation has been found seem to indicate that THF is, as in the rest of the POGNs shown in the table, a good solvent, whereas ketones are closer to theta solvents.

For the remaining POPNs of *Table 4*, the values of the a exponent range from 0.65 to 0.79 indicating that THF, benzene and chloroform are good solvents. The pre-exponential K parameter ranges from 2 to 8×10^{-5} for fractionated samples whereas higher values are obtained for the diethoxy and methyl/phenyl substituted polymers which were not fractionated. This fact is in agreement with the sensitivity of the K parameter to the polydispersity of the sample and to the shape of its molecular-weight distribution.

Although the interpretation of the Huggins constants is difficult[14], because they depend on multiple factors, they can at least be used in a qualitative form to provide supplementary information about the polymer. Values of k_H between 0.3 and 0.6 are found for random coils, whereas higher values of 0.8 are often encountered for aggregated molecules. As can be seen in *Table 4* and as has been explained before, there seems to be a good correspondence between abnormal values for the Huggins constants and problems in obtaining correlation between viscosity and molecular weights.

Thus, in brief, the data of *Table 4* indicate that many POPNs exhibit normal viscometric behaviour typical of random-coil chains in good solvents. However, in some cases, unusual results can be obtained, distinguished by either negative or abnormally high values of the Huggins constant and lack of correlation between intrinsic viscosities and molecular weights. This situation has been explained as a consequence of the formation of aggregates which sometimes can be destroyed with the use of additives or mixed solvents, thus restoring normal behaviour.

Scaling laws

The scaling laws of the second virial coefficient A_2 and radius of gyration $\langle s^2 \rangle^{1/2}$ obtained by light scattering measurements are summarized in *Table 5*. In several cases, the authors do not give the coefficients of the scaling laws, but provide enough data as to allow their calculation; the values obtained in this fashion are marked with an asterisk in *Table 5*.

Table 5 Scaling laws for the second virial coefficient A_2 (in mol cm^3 g^{-2}) and radius of gyration $\langle s^2 \rangle^{1/2}$ (in nm) of POPN: data determined from light scattering measurements[a]

		$A_2 = B\bar{M}_w^b$		$\langle s^2 \rangle^{1/2} = Q\bar{M}_w^q$		
Side groups	Solvent	$10^2 B$	b	$10^2 Q$	q	Ref.
Co. A	MIBK	0.132*	−0.35*	0.81*	0.57*	47
di Ethoxy	THF	4.0	−0.37	8.9	0.48	20
di Hexoxy	THF	1.93	−0.38	0.47	0.65	21
bis (2-Naphthoxy)	THF			25.6	0.36	24
di Benzyloxy	Cl_3CH	109.7*	−0.84*	9.95*	0.5*	53
bis (*m*-ClPhenoxy)	Cl_3CH				0.58	54
bis *p*MAm	THF			4.03	0.50	61

[a] Values computed from data appearing on the original paper are marked with an asterisk
Co. A: 2,2,2-trifluoroethoxy, 2,2,3,3,4,4,5,5-octafluoropentoxy; *p*MAm: *p*-methylanilino

The dependence of A_2 on molecular weight can be expressed as $A_2 = BM^b$ where B is a constant that depends on the polymer solvent system. Krigbaum and Flory[67] predicted a value of b between -0.05 and 0.25 for random coils while values of $b=-1$ and $b=0$ are predicted for rods and spheres respectively. Values of $b=-0.2$ have been found for polymers with molecular weights higher than 10^5 in good solvents[68], and have been explained theoretically[69] on the basis that for flexible polymers in good solvents the interpenetration function $\Psi(\bar{z})$ first decreases with increasing molecular weight reaching a limit for very large molecular weights and thus becoming independent.

In the case of A_2 only the values for three polymers are accurate enough as to allow a reasonable fitting as a function of molecular weight and in the three cases the value of the exponent is not far away from the expected result for random coils in good solvents. The value indicated in the table for poly(dibenzyloxyphosphazene) may not be significant, since the data reported by Sulkowski *et al.*[53] have a lot of scatter and the correlation between A_2 and M_w is not good; for instance, elimination of one of the fractions from the fitting changes the values of the parameters to $B=5.2$, $b=-0.60$. Something similar happens in the analysis of the 2-naphthoxy polymer performed by Bravo *et al.*[24] who found values of A_2 ranging from -2.2 to 2.6 in units of 10^{-4} mol cm^3 g^{-2} and concluded that the results were too inaccurate to determine the variation with molecular weight.

Difficulties in obtaining accurate values of A_2 are, as we have been explaining above, encountered frequently by different researchers of POPN. Some of them even state that a value of $A_2 \approx 0$ may not be sufficient condition for assuming theta conditions which is important for determining the unperturbed dimensions, as will be explained later.

The dependence of the radius of gyration on molecular weight can give additional information on the polyphosphazene structure. Values of $q=0.5$ in the scaling law $\langle s^2\rangle^{1/2} = QM^q$ are expected for polymers in theta conditions and slightly higher values, ca. 0.6, for random coil polymers in good solvents[70,71]. With the exception of the 2-naphthoxy polymer, the q exponent for the scaling law of $\langle s^2\rangle^{1/2}$ is close to or slightly larger than 0.5 which may indicate random-coil chains either close to unperturbed conditions or slightly above them. The value of $q=0.36$ found by Bravo *et al.*[24] in the case of poly[bis(2-naphthoxy)phosphazene] is attributed by the authors to the formation of intermolecular aggregates of a roughly globular shape.

It is difficult to rationalize the values of the pre-exponential factor Q for different polymers because it depends on, among other factors, the polydispersity of the samples. Thus, in the case of highly polydisperse systems, Q is very sensitive to the kind of molecular average used in the calculations. A numerical analysis that combines results of light scattering and s.e.c. measurements performed on polydisperse samples and allows for the evaluation of the scaling parameters for ideally monodisperse fractions has been proposed[72]. This procedure minimizes the effect of polydispersity, but so far, it has been employed for only one polyphosphazene.

Unperturbed dimensions

Values of the characteristic ratio of the unperturbed dimensions of these polymers reported in the literature are summarized in *Table 6* where the asterisks indicate values not given by the authors, but calculated from the data contained in their publications. The table also contains information on the number of samples used in the experimental measurements, whether or not they were previously fractionated, and their range of polydispersity ratios. The unperturbed dimensions presented in the fifth column of *Table 6* have been calculated from viscosity measurements by different methods. Following the nomenclature used by Kurata (in ref. 14), VT means that the viscosity measurements have been performed in a theta solvent so that values of $\langle r^2\rangle_0$ can be calculated

Table 6 Unperturbed dimensions of poly(organophosphazene)s

				Viscometry[a]		Light scattering[a]		
Side groups	Solvent	No. samples	$\bar{M}_w/\bar{M}_n$	$C_n=\frac{\langle r^2\rangle_0}{nl^2}$	Method	$\frac{6\langle s^2\rangle}{nl^2}$	Conditions	Ref.
Fluoroalkoxy groups								
Co. A	MIBK	7 f	7.2–23	42–64	VT	25–48	θ	47
Co. B	E2/acetone	4–15 wp, f	4–16			44	θ	49
Alkoxy or aryloxy groups								
di Ethoxy	THF	2 wp	7–27	17	VG	72		20, 22
di Hexoxy	THF	4 f	1.1–2.9	13	VG			21
di Phenoxy	THF	1 wp	4.7	20	VT	54	θ	73
bis *p*ClPh	THF	1 wp	9.7	33	VT	67	θ	73
bis *m*ClPh	Chloroform	13 f	2–11			65*		54
Ph; *p*EthylPh	THF	2 f		32	VA			55
Ph; 2,4diClPh	THF	2 f		14	VA			55
Ph; Naph	THF	2 f		6	VA			55
di Benzyloxy	Chloroform	7 f		13*	VG			53
bis Naph	THF	7 f	1.3–3.4	18	VG	103	θ	24
Amino groups								
bis *p*MeAn	THF	11 f	1.8–4.1	18	VG	50		61

[a] Values computed from data appearing in the original paper are marked with an asterisk

Abbreviations: wp, whole polymer; f, fractionated samples; Co. A: 2,2,2-trifluoroethoxy, 2,2,3,3,4,4,5,5-octafluoropentoxy; TFP: 2,2,3,3-tetrafluoropropoxy; Ph: Phenoxy; Naph: 2-naphthoxy; *p*MeAn: *p*-methylanilino

through the Flory–Fox relationship $K_\theta = \langle r^2 \rangle_0 / M)^{3/2}$. VG has been used to indicate that the dimensions were calculated using the results of viscosity in good solvents and its relationship with molecular weight extrapolated using the Kurata–Stockmayer–Fixman or an analogous equation. VA means dimensions extrapolated from values of viscosity and second virial coefficients in good solvents using the Orofino–Flory or an analogous equation.

Several factors which can affect the reliability of the C_n values must be taken into account before analysing the data in *Table 6*. First, the broad molecular-weight distributions of some of the samples presented in the table can seriously affect the different averages of dimensions or molecular weights. This is invoked by Singler *et al.*[73] for explaining the large experimental values of the dimensions obtained for poly(diphenoxyphosphazene) and poly[bis(*p*-chlorophenoxy)phosphazene] since they use unfractionated samples in their experimental measurements. However, as can be seen in the table, even fractionated samples of polyphosphazenes can have large polydispersities; thus the problem is not always surmounted using this experimental technique. The combination of fractionation of samples and numerical procedures to minimize the effect of residual polydispersities yields the best results.

The second important factor lies in the difficulties encountered by several researchers in the determination of the second virial coefficient A_2, which have been explained previously. The values of A_2 are fundamental to prove that a given polymer solvent system is at theta conditions and are also needed in the procedure of Orofino–Flory to obtain unperturbed dimensions from viscosity measurements in good solvents.

The third aspect to point out is that the values of C_n corresponding to the fluoroalkoxy copolymers are much higher than those of the other polyphosphazenes. As has been explained before, fluoroalkoxy phosphazenes present a distinct solution behaviour, probably due to some kind of intermolecular aggregates formed in the solution[44,47] which are responsible for the overestimation of the dimensions. The formation of aggregates is also supported by the analysis of the light scattering interference factor $P(\theta)$ performed by Carlson *et al.*[47] who concluded that the macromolecules are bound into supramolecular structures of roughly spherical shape either by genuine chemical bonds or by physical forces, suggesting that these structures would also be responsible for the difficulties found in the fractional precipitation of this kind of polymer which hampers the preparation of samples with narrow molecular-weight distribution. This effect can also mask the correct data interpretation and would explain why the viscometric data for these polymers cannot be fitted by a Stockmayer–Fixman extrapolation. Moreover, although the authors consider that the viscometric and light scattering measurements were performed in theta conditions because the value of the Mark–Houwink exponent is close to 0.5, the peculiar behaviour of these polymers in solution must be taken into account before deciding whether this is a secure enough proof for unperturbed conditions.

However, even taking all the precautions required by the experimental uncertainties, the dimensions obtained by viscometry are surprisingly high, with most frequent values lying in the range ca. 13–20. As for the variation in the dimensions with the kind of side group attached to the polymeric chain, it is difficult to reach any conclusion taking into account the uncertainties indicated above. Thus, for instance, Andrady and Mark[55] found large differences among the dimensions of the three polymers studied (see *Table 6*), but concluded that these differences may be due to experimental uncertainties produced by the difficulties associated with the measurement of solution properties of this kind of polymer.

The dimensions calculated by light scattering using the relation $\langle r^2 \rangle_0 = 6 \langle s^2 \rangle_0$ valid for random coils are presented in the seventh column of the table. The symbol θ has been used in those measurements which, according to the authors, were performed in theta solvents or extrapolated to unperturbed conditions. In general, the dimensions obtained by light scattering are larger than those derived from viscometric measurements. This discrepancy, together with values of the ratio $\langle s^2 \rangle_z / M_w$ which are practically independent of the molecular weight, are invoked by several authors as proof that the measured samples were linear or at least not extensively branched[49,73].

In brief, the available data do not permit conclusions to be made about the influence of the side groups on the chain dimensions although they are sufficient to show that polyphosphazenes behave as random-coil chains with large values for the dimensions. The averaged value for C_n obtained from viscometric measurements in the samples that have been extrapolated to unperturbed dimensions (values marked with either VG or VA in the table) is 16 and the value obtained by averaging all the viscometric values for all polymers except the two fluoroalkoxy copolymers is 18. These results are even more surprising taking into account that these polymers have low values of T_g. However, the coexistence of these two properties, high dimensions and low values of T_g, could be easily explained[74] by the alternance in the polymeric skeleton of pairs of P–N–P bonds possessing a remarkably high conformational freedom with N–P–N pairs that are relatively rigid. Furthermore, the variation of dimensions with side groups, if real, could be produced by modification of the conformational population arising from relatively small changes in intramolecular interactions[55,74].

SUMMARY

As has been stated throughout this paper, the dilute solution characterization of polyphosphazenes presents many difficulties, some of which may have played an important role in the discrepancies among the results published to date. However, several considerations can be made in order to facilitate and improve this characterization.

First, the nature of the samples plays a fundamental role since, depending on the conditions of the synthesis, the samples can be linear or branched and therefore produce widely different behaviour in solution.

Another problem is the great polydispersity of the synthesized samples, which together with the difficulties in the fractionation, produces very broad fractions even after extremely careful fractionations. Thus it is convenient to use numerical analyses as encountered in the literature in order to improve the results for parameters obtained by calibration procedures.

With respect to the different experimental techniques

used in the dilute solution measurements, it must be pointed out that the anomalous behaviour in s.e.c. is easily eliminated by adding quaternary ammonium salts to the eluent as has been reported. Viscometry presents normal behaviour except for poly(organophosphazene)s containing fluorine atoms in the side groups. However, difficulties are encountered in studying the unperturbed dimensions by light scattering, since this technique seems to overestimate them. Thus it is important to compare the results obtained by light scattering with those obtained by viscometry, which seems to give consistent values.

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REFERENCES

1 Stokes, N. S. *Am. Chem. J.* 1897, **19**, 782
2 Allcock, H. R. and Kugel, R. L. *J. Am. Chem. Soc.* 1965, **87**, 4216
3 Allcock, H. R., Kugel, R. L. and Valan, K. J. *Inorg. Chem.* 1966, **5**, 1709
4 Allcock, H. R. *Makromol. Chem., Suppl. 4*, 1981, **19**, 3
5 Hagnauer, G. L. *J. Macromol. Sci., Chem.* 1981, **16**, 385
6 Kireev, V. V., Mitropol'skaya, G. I. and Zinovich, Z. K. *Russ. Chem. Rev.* 1982, **51**, 149
7 Tur, D. R. and Vinogradova, S. V. *Polym. Sci. USSR* 1982, **24**, 2572
8 Vinogradova, S. V., Tur, D. R. and Minosyants, I. I. *Russ. Chem. Rev.* 1984, **53**, 49
9 Allcock, H. R. *Chem. Eng. News* 1985, **63**, 22
10 Allcock, H. R. in 'Inorganic and Organometallic Polymers' (Eds. M. Zeldin, K. J. Wynne and H. R. Allcock), ACS Symp. Ser. No. 360, American Chemical Society, 1988, Ch. 19
11 Neilson, R. H. and Wisian-Neilson, P. *Chem. Rev.* 1988, **88**, 541
12 Potin, Ph. and De Jaeger, R. *Eur. Polym. J.* 1991, **27**, 341
13 Allcock, H. R., Connolly, M. S., Sisko, J. T. and Al-Shali, S. *Macromolecules* 1988, **21**, 339
14 Brandrup, J. and Immergut, E. H. (Eds.) 'Polymer Handbook', 2nd Edn, Wiley, New York, 1989
15 Sennett, M. S., Hagnauer, G. L., Singler, R. E. and Davies, G. *Macromolecules* 1986, **19**, 959
16 Ganapathiappan, S., Dhathathreyan, K. S. and Krishnamurthy, S. S. *Macromolecules* 1987, **20**, 1501
17 Potts, M. K., Hagnauer, G. L., Sennett, M. S. and Davies, G. *Macromolecules* 1989, **22**, 4235
18 Mujumdar, A. N., Young, S. G., Merker, R. L. R. and Magill, J. H. *Macromolecules* 1990, **23**, 14
19 Klein, J. A., Bell, A. T. and Soong, D. S. *Macromolecules* 1987, **20**, 782
20 Bravo, J., Tarazona, M. P., Roig, A. and Saiz, E. *An. Quim.* 1991, **87**, 27
21 Bravo, J., Tarazona, M. P. and Saiz, E. *Macromolecules* 1991, **24**, 4089
22 Tarazona, M. P., Bravo, J., Rodrigo, M. M. and Saiz, E. *Polym. Bull.* 1991, **26**, 465
23 Bravo, J., Tarazona, M. P. and Saiz, E. *Polym. Commun.* 1992, **33**, 3312
24 Bravo, J., Tarazona, M. P. and Saiz, E. *Macromolecules* 1992, **25**, 5625
25 Allcock, H. R., Gardner, J. E. and Smeltz, K. M. *Macromolecules* 1975, **8**, 36
26 Sennett, M. S. Sagamore Army Mater. Res. Conf. Proc. 1985, 32nd Elastomers Rubber Technol., 1987, p. 297
27 Tur, D. R., Korshak, V. V., Vinogradova, S. V., Pavlova, S. A., Timofeeva, G. I., Goguadze, Ts. A. and Alikhanova, N. O. *Dokl. Akad. Nauk SSSR, Ser. Khim.* 1986, **291**, 364
28 Sennett, M. S., Hagnauer, G. L., Singler, R. E. and Davies, G. *Macromolecules* 1986, **19**, 959
29 Lee, D., Ford, J. R., Fytas, G., Chu, B. and Hagnauer, G. L. *Macromolecules* 1986, **19**, 1586
30 Knoesel, R., Parrod, J. and Benoit, H. *C. R. Acad. Sci.* 1960, **251**, 2944
31 Hagnauer, G. L. 'Size Exclusion Chromatography', ACS Symp. Ser. No. 138, American Chemical Society, Washington DC, 1980, p. 239
32 Hagnauer, G. L. and Koulouris, T. N. *Chromatogr. Sci.* 1981, **19**, 99
33 Hagnauer, G. L. and Singler, R. E. *Org. Coat. Plast. Chem.* 1979, **41**, 88
34 Ferrar, W. T., Marshall, A. S. and Whitefield, J. *Macromolecules* 1987, **20**, 317
35 Gabler, D. G. and Haw, J. F. *Macromolecules* 1991, **24**, 4218
36 Allcock, H. R., Mang, M. N., Dembek, A. A. and Wynne, K. J. *Macromolecules* 1989, **22**, 4179
37 Allcock, H. R. and Chang, J. Y. *Macromolecules* 1991, **24**, 993
38 Allcock, H. R. and Kim, C. *Macromolecules* 1991, **24**, 2841
39 Patat, F. and Kollinsky, F. *Makromol. Chem.* 1951, **6**, 292
40 Chu, B. and Lee, D. *Macromolecules* 1986, **19**, 1592
41 Kireyev, V. V., Bittirova, F. A., Mitropol'skaya, G. I., Mikitayev, A. K., Papkov, V. S. and Il'ina, M. N. *Polym. Sci. USSR* 1984, **26**, 156
42 Rose, S. H. *J. Polym. Sci., Polym. Lett. Ed.* 1968, **6**, 837
43 Neilson, R. H., Hani, R., Wisian-Neilson, P., Meister, J. S., Roy, A. K. and Hagnauer, G. L. *Macromolecules* 1987, **20**, 910
44 Mourey, T. H., Miller, S. M., Ferrar, W. T. and Molaire, T. R. *Macromolecules* 1989, **22**, 4286
45 Allen, G., Lewis, C. J. and Todd, S. M. *Polymer* 1970, **11**, 44
46 Tate, D. P. *J. Polym. Sci., Polym. Symp.* 1974, **48**, 33
47 Carlson, D. W., O'Rourke, E., Valaitis, J. K. and Alternau, A. G. *J. Polym. Sci., Polym. Chem. Ed.* 1976, **14**, 1379
48 Penton, H. R. *Polym. Prepr. Am. Chem. Soc.* 1987, **28** (1), 439
49 Hagnauer, G. L. and Schneider, N. S. *J. Polym. Sci., Part A2* 1972, **10**, 699
50 Ferrar, W. T., Marshall, A. S., Flood, E. C., Goppert, K. E. and Myers, D. Y. *Polym. Prepr. Am. Chem. Soc.* 1987, **28**, 444
51 Tur, D. R., Korshak, V. V., Vinogradova, S. V., Timofeeva, G. I., Goguadze, C. A., Alichanova, N. O., Tarasov, A. I. and Dubrovickij, V. I. 'PolyKondensations-prozesse '85', Sofia Bulg. Akad. Wiss. 1986, 152
52 Tur, D. R., Vinogradova, S. V., Korshak, V. V., Janout, V., Cefelin, P. and Borisov, G. *Acta Polym.* 1988, **39**, 424
53 Sulkowski, W., Kireev, V. V., Zinovic, Z. K. and Davtjan, A. G. *Polimery (Warsaw)* 1989, **34**, 207
54 Hagnauer, G. L. and LaLiberte, B. R. *J. Polym. Sci., Polym. Phys. Ed.* 1976, **14**, 367
55 Andrady, A. L. and Mark, J. E. *Eur. Polym. J.* 1981, **17**, 323
56 Allcock, H. R. and Kugel, R. L. *Inorg. Chem.* 1966, **5**, 1716
57 Allcock, H. R., Cook, N. J. and Mack, D. P. *Inorg. Chem.* 1972, **11**, 2584
58 Allcock, H. R. *Angew. Chem., Int. Ed. Engl.* 1977, **16**, 147
59 Busulini, L., Osellame, M., Lora, S. and Pezzin, G. *Makromol. Chem.* 1977, **17**, 277
60 White, J. E., Singler, R. E. and Leone, S. A. *J. Polym. Sci., Polym. Chem. Ed.* 1975, **13**, 2531
61 Pezzin, G., Lora, S. and Busulini, L. *Polym. Bull.* 1981, **5**, 543
62 Allcock, H. R., Desorcie, J. L. and Harris, P. J. *J. Am. Chem. Soc.* 1983, **105**, 2814
63 Allcock, H. R., Desorcie, J. L. and Rutt, J. S. *Organometallics* 1988, **7**, 612
64 Wisian-Neilson, P. and Neilson, R. H. *J. Am. Chem. Soc.* 1980, **102**, 2848
65 Neilson, R. H. and Wisian-Neilson, P. *J. Macromol. Sci. Chem.* 1981, **16**, 425
66 Allcock, H. R., Moore, G. Y. and Cook, W. J. *Macromolecules* 1974, **7**, 571
67 Krigbaum, W. L. and Flory, P. J. *J. Am. Chem. Soc.* 1953, **75**, 1775
68 Fuyita, H. and Norisuye, T. *Macromolecules* 1985, **18**, 1637
69 Yamaka, H. *Macromolecules* 1992, **25**, 1912
70 De Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, NY, 1979
71 Rey, A., Freire, J. J., Bishop, M. and Clarke, H. R. *Macromolecules* 1992, **25**, 1311
72 Tarazona, M. P., Bravo, J. and Saiz, E. *Polym. Bull.* 1992, **26**, 465
73 Singler, R. E., Hagnauer, G. L., Schneider, N. S., Laliberte, E. R., Sacher, E. R. and Matton, R. W. *J. Polym. Sci., Polym. Chem. Ed.* 1974, **12**, 433
74 Saiz, E. *J. Polym. Sci., Polym. Phys. Ed.* 1987, **25**, 1565