Determination of the viscometric parameters for the system poly(dihexoxyphosphazene)–benzene at 25°C

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A viscometric analysis of four samples of poly(dihexoxyphosphazene), $[\mathrm{N}\overset{\cdots}{-}\mathrm{P}(\mathrm{R}_2)\text{–}]_x$ with $\mathrm{R} = \text{–O–}(\mathrm{CH}_2)_5\mathrm{CH}_3$, having very different molecular weights has been carried out using benzene as solvent. The results for intrinsic viscosity obtained at 25°C were $[\eta] = 1.61$, 1.09, 0.41 and $0.057\ \mathrm{dl\,g^{-1}}$, respectively, for samples having weight-average molecular weights, determined by light scattering, of $10^{-5}\bar{M}_{\mathrm{w}} = 22.8$, 9.17, 2.45 and $0.26\ \mathrm{g\,mol^{-1}}$. Although the samples are polydisperse, it is possible to determine the true values of the K and a coefficients appearing in the Mark–Houwink equation $[\eta] = KM^a$, by using the results obtained in a previous analysis performed on a different solvent. The values for K and a for benzene at 25°C are 2.01×10^{-5} and 0.79, respectively. The extrapolation to unperturbed conditions allows the evaluation of the characteristic ratio of dimensions as $C_n = \langle r^2 \rangle_0/nl^2 = 12.9$, in good agreement with the value of 13.2 previously obtained. This agreement validates the hypothesis used for the determination of the K and a coefficients.

(Keywords: poly(phosphazene)s; poly(dihexoxyphosphazene); intrinsic viscosity; viscometric equation; viscometric parameters)

INTRODUCTION

Poly(organophosphazene)s obtained by substitution of the chlorine atoms of the inorganic polymer poly(dichlorophosphazene) $[\mathrm{N}\overset{\cdots}{-}\mathrm{P}(\mathrm{Cl}_2)\text{–}]_x$ (PDCP) by different organic groups are a large family of polymers that has aroused a lot of interest over the last 20 years[1,2]. The reason for this interest comes from the fact that with careful selection of the organic groups attached to the inorganic chain, a large number of polymers with a wide variety of properties can be obtained. Thus, the number of polyphosphazenes synthesized to date is well over 300 and both the literature and the list of patents contain hundreds of references to studies in which the possibilities of practical applications of this kind of polymers are explored[3–7].

However, it seems strange that the number of basic studies devoted to the determination and analysis of the physico-chemical properties of these polymers in solution is relatively small[8]. Undoubtedly one of the reasons for this lag between basic and applied studies is that the practical applications seem to be more appealing than detailed analysis of basic properties such as molecular characteristics of the chains, despite the fact that the latter type of study allows a deeper understanding of the system and could facilitate a more effective search for new materials with specific properties. However, poly(phosphazene)s have some features that make it difficult to study many of their basic properties. For instance, the synthesis of the precursor PDCP produces very wide, and often multinodal, molecular weight distributions[9]. On the other hand, the fractionation of the polymers obtained after substitution of the chlorine atoms in the PCDP is difficult and not very efficient[10]. Different fractionation procedures ranging from preparative size exclusion chromatography (s.e.c.)[11] to fractional precipitation with either the standard solvent/non-solvent technique[10,12] or lowering the temperature of the polymer solutions[10], or a combination of solvent/non-solvent/centrifugation processes[13] have been tried. However, to our knowledge, all the attempts of preparing samples with narrow molecular weight distributions described in the literature so far have failed. Thus it is almost impossible to prepare monodisperse samples which are required for calibration of many experimental techniques such as viscometry or s.e.c.[8]. Therefore alternative calibration procedures that could circumvent the use of monodisperse samples are of great importance in the case of poly(phosphazene)s.

Over the last few years we have been performing a basic study of several poly(phosphazene)s[14–16] using techniques such as viscometry, light scattering (LS) and s.e.c. to characterize the samples in order to obtain molecular magnitudes such as chain dimensions, molecular weight distributions, virial coefficients, etc. The main goal of that study is to obtain the calibration functions for both viscometry and s.e.c. which could facilitate future studies of these systems. A numerical analysis procedure that allows the combination of results from viscometry, LS and s.e.c. has been applied in order to obtain the true values of the parameters appearing in the calibration function for s.e.c. and in the Mark–Houwink viscometric equation without requiring the use of monodisperse samples.

The present work contains a viscometric study of benzene solutions of poly(dihexoxyphosphazene), $[\mathrm{N}\overset{\cdots}{-}\mathrm{P}(\mathrm{R}_2)\text{–}]_x$ with $\mathrm{R} = \text{–O–}(\mathrm{CH}_2)_5\mathrm{CH}_3$, (PDHP), in which the true values of the K and a coefficients in the

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Mark–Houwink equation for this system at 25°C are determined. Benzene is a very good solvent for PDHP and can be used for fractionation of this polymer or in routine viscometric measurement to determine molecular weights and dimensions, provided that the K and a parameters of the system are known. However benzene has the inconvenience of being almost isorefractive with PDHP and therefore it is impossible to perform LS measurements or s.e.c. using a refractive index detector. Furthermore no wavelength for which the difference in absorption between solute and solvent is large enough to allow the use of visible–u.v. detectors has been found. This situation, together with the inability to prepare monodisperse samples makes it difficult to evaluate the viscometric coefficients for this system, and, at the same time, renders their determination more important, since knowledge of the coefficients could open the door for routine studies such as those indicated above or to the use of s.e.c. with viscometric detectors.

EXPERIMENTAL

Four fractions of PDHP that had been previously studied[16] using several techniques, including viscometry with tetrahydrofuran (THF) as solvent, were used for the present work. In brief, the precursor PDCP was obtained by thermal polymerization of the cyclic trimer cyclohexachlorotriphosphazene at 245°C for 157 h. The PDHP was obtained through a nucleophilic substitution of the Cl atoms on PDCP by n-hexoxy groups. The original sample was characterized by elemental analysis, i.r. spectroscopy and ^{1}H, ^{13}C and ^{31}P n.m.r. It is important to note that the ^{31}P spectrum contains only one signal which indicates that all the P atoms in the chains are equivalent and therefore there is no branching. Fractionation of this sample by precipitation allowed the preparation of four fractions whose main characteristics are summarized in *Table 1*. The benzene used as solvent was from Panreac and was purified by distillation over sodium/benzophenone.

The experimental measurements were performed in a Schott Gerate autoviscometer equipped with a thermostatic bath regulated to 25 ± 0.1°C. The concentrations of the solutions were in the range of 0.1–1.0 g dl^{-1} and the measured flowing times were between 250 s and 490 s. Intrinsic viscosities ($[\eta]$) together with the Huggins (k_H) and Kraemer (k_K) constants were obtained by a simultaneous extrapolation of (η_{sp}/c) and $[(\log \eta_r)/c]$ to infinite dilution according to the well known Huggins[17] and Kraemer[18] equations using a least squares analysis for the evaluation of slopes and intercepts. The fitting of the experimental results is excellent for the four fractions, both extrapolations give the same intercept with differences of ~1% while the slopes fulfil the relationship $k_H - k_K = 0.5$ (within ±0.05). *Figure 1* shows the extrapolation for the second fraction. The values of the Huggins constants are in the range of 0.30–0.45 expected for a polymer–good solvent system.

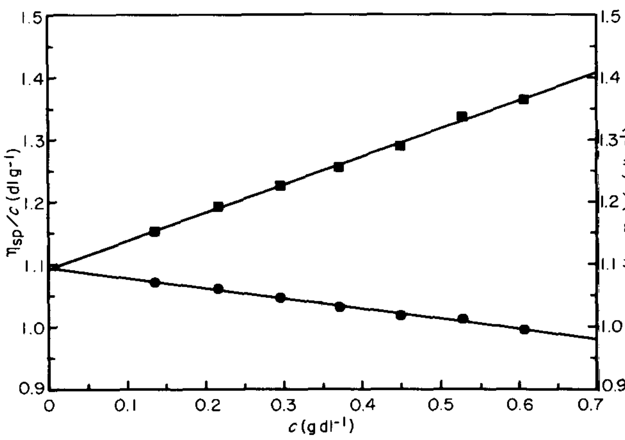

Figure 1 Huggins (■) and Kraemer (●) extrapolations for the PDHP2 fraction

Table 1 Molecular weights and viscosities (in dl g^{-1}) for the fractions of poly(dihexoxyphosphazene)

Fraction	$10^{-5}\bar{M}_w$[a]	$10^{-5}\bar{M}_v$[b]	$[\eta]$[b]	$[\eta]$[c]	$10^{-5}M_m$[d]
PDHP1	22.80	13.00	1.745	1.605	14.36
PDHP2	9.17	9.80	1.151	1.093	8.80
PDHP3	2.45	2.54	0.425	0.407	2.58
PDHP4	0.26	0.23	0.064	0.057	0.23

Experimental values determined at 25°C. Theoretical results computed from data obtained at 25°C

[a] Taken from reference 16. Measured by LS

[b] Taken from reference 16. $[\eta]$ measured in THF, $\bar{M}_v$ computed from the s.e.c. chromatogram in THF using the calibration function that provides the best fitting for the $[\eta]$ values

[c] This work. Measured in benzene

[d] This work. Computed as $M_m = ([\eta]/K)^{1/a}$

RESULTS AND DISCUSSION

Experimental values of intrinsic viscosities measured for the four fractions are shown in *Table 1* which also summarizes the molecular weights and viscosities obtained[16] for these same fractions as solutes in THF at 25°C. A comparison between the viscosities measured in benzene and THF indicates that the values are similar although they are slightly lower in the case of benzene.

It is surprising that, according to the results shown in *Table 1*, the second and third fractions have $\bar{M}_v > \bar{M}_w$. Since THF is a good solvent for PDHP, the difference between both molecular weight averages is small, but in any case, $\bar{M}_v$ should be smaller than $\bar{M}_w$. However, despite being an obvious error, the fact that $\bar{M}_v > \bar{M}_w$ in *Table 1* is irrelevant since a modification of their values of ~4% would bring about the correct relationship of $\bar{M}_v < \bar{M}_w$ and therefore it only indicates that the values of both $\bar{M}_v$ and $\bar{M}_w$ have uncertainties of at least 4% which certainly is a very conservative estimate of the experimental error in LS determinations of $\bar{M}_w$, and even more so for the calculation of $\bar{M}_v$ with any fitting procedure.

Since experimental values of $[\eta]$ for four fractions whose weight average molecular weights $\bar{M}_w$ are known, one could think of determining the coefficients for the Mark–Houwink viscometric equation $[\eta] = KM^a$ by a direct fitting of $\log[\eta]$ *versus* $\log \bar{M}_w$ which is represented by the broken line in *Figure 2* and gives $K = 3.16 \times 10^{-5}$ and $a = 0.75$. However, the experimental values show a noticeable curvature that can be attributed to the different polydispersity of the measured fractions.

As was indicated above, it was not possible to carry out s.e.c. for PDHP using benzene as eluent and therefore $\bar{M}_v$ cannot be determined in this solvent. However the values of $\bar{M}_v$ in THF had been determined previously[16] at the same temperature and are summarized in *Table*

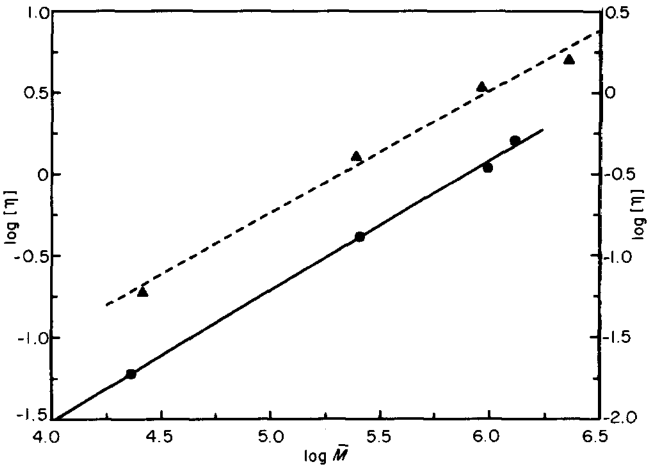

Figure 2 Fitting of log[η] *versus* log $\bar{M}$ data. Values of [η] measured in benzene at 25°C: (– – –) $\bar{M}_w$ measured by LS; (——) $\bar{M}_v$ computed for THF solutions at 25°C

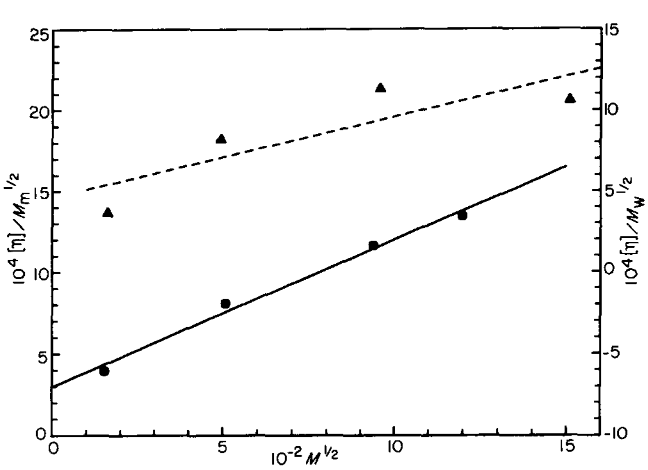

Figure 3 Stockmayer–Fixman extrapolation to unperturbed conditions: (– – –) using values of $\bar{M}_w$; (——) with $\bar{M}_m = ([\eta]/K)^{1/a}$

1. Since both benzene and THF are good solvents for PDHP and the values of [η] measured in these two solvents are similar (cf. columns four and five in *Table 1*), it seems reasonable to assume that $\bar{M}_v$ should be very similar in both solvents. Thus the fitting of log [η] *versus* log $\bar{M}_v$ could be performed with [η] measured in benzene and $\bar{M}_v$ calculated for THF. This fitting is represented by the solid line in *Figure 2* and gives $K = 2.01 \times 10^{-5}$ and $a = 0.79$.

The difference in the quality of the two fittings shown in *Figure 2* corroborates the hypothesis used to compute the viscometric parameters. Nevertheless, it is possible to perform a more quantitative verification by extrapolating the results to unperturbed conditions using the Stockmayer–Fixman equation[19].

$$\frac{[\eta]}{M^{1/2}} = K_\Theta + AM^{1/2} \tag{1}$$

where A contains Flory's universal constant Φ and a function of the interaction parameters for the solute–solvent pair and therefore depends on the polymer–solvent–temperature system but does not change with the molecular weight of the sample. The intercept gives the unperturbed value of the Mark–Houwink constant K_Θ which should not depend on the solvent used to perform the measurements of [η] and therefore a value close to $K_\Theta = 3.08 \times 10^{-4}$ previously determined[16] in THF at 25°C should be obtained.

The broken line in *Figure 3* shows a representation of equation (1) using the values of $\bar{M}_w$. The fitting is very poor and gives $K_\Theta = 4.63 \times 10^{-4}$ which differs by >50% from the value obtained in THF. The solid line shows the same extrapolation using the molecular weights M_m defined as $M_m = ([\eta]/K)^{1/a}$ where K and a are the viscometric coefficients for the PDHP–benzene system. Thus the M_m values represent the molecular weights of ideally monodisperse samples having the same [η] values measured for the actual fractions. The values of M_m are summarized in *Table 1*. As *Figure 3* shows, the fitting is noticeably improved and provides a value of $K_\Theta = 2.98 \times 10^{-4}$ differing by ~3% from the result obtained in THF.

The characteristic ratio of unperturbed dimensions can be computed as:

$$C_n = \frac{\langle r^2\rangle_0}{nl^2} = \frac{M_r\langle r^2\rangle_0}{2Ml^2} = \frac{M_r K_\Theta^{2/3}}{2l^2\Phi^{2/3}} \tag{2}$$

where n is the number of bonds in the chain skeleton, l is the bond length ($l = 0.152$ nm for P–N bonds), M_r is the molecular weight of the repeating unit ($M_r = 247.3$ for PDHP) and Φ is Flory's universal constant ($\Phi = 2.5$ with l in nm and [η] in dl g^{-1}). Using the value $K_\Theta = 2.98 \times 10^{-4}$ the result $C_n = 12.9$ is obtained which differs by ~2% from the result $C_n = 13.2$ previously determined from measurements performed in THF.

The expansion coefficient of the chain α can be computed from the experimental viscosities and those extrapolated to unperturbed conditions as:

$$\alpha^3 = \left[\frac{\langle r^2\rangle}{\langle r^2\rangle_0}\right]^{3/2} = \frac{[\eta]}{[\eta]_\Theta} = \frac{[\eta]}{K_\Theta M^{1/2}} = 1 + K_\alpha M^{1/2} \tag{3}$$

where the last part is obtained by solving equation (1) for $[\eta]/M^{1/2}$ and representing the ratio A/K_Θ by K_α which indicates the variation of α^3 with increasing molecular weight. The fitting of data to equation (3) is shown in *Figure 4* and gives $K_\alpha = 3.02 \times 10^{-3}$ which is very high, as expected in a good solvent with the Mark–Houwink parameter very close to $a = 0.8$. With this value of K_α one obtains $\alpha^2 = 2.36$ for the fraction of highest molecular weight among those studied here, therefore this fraction has a value of $\langle r^2\rangle$ in benzene

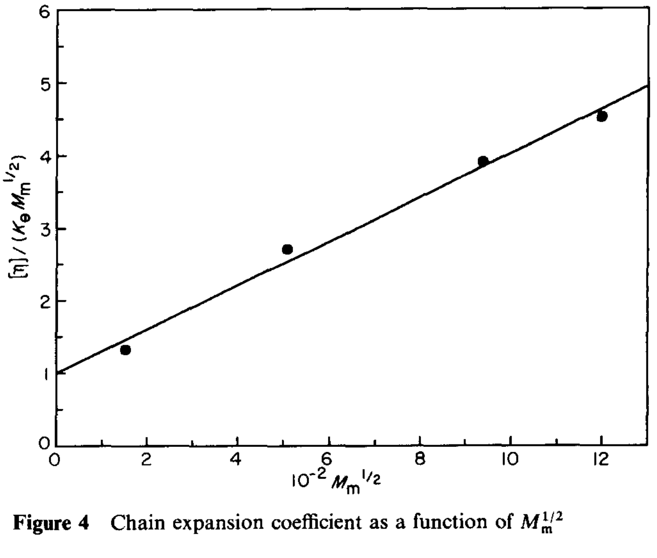

Figure 4 Chain expansion coefficient as a function of $M_m^{1/2}$

solution which is more than twice the value in the unperturbed state.

Thus the present work determines the viscometric parameters for the PDHP–benzene system at 25°C using a procedure which is much better than a straight fitting of viscosity data *versus* molecular weights obtained for instance by LS. It is foreseeable that a similar procedure could be used for many other systems for which monodisperse samples could not be easily obtained.

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