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Solution properties of poly[bis(piperidino)phosphazene] by size exclusion chromatography and multiangle light scattering

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Abstract

The synthesis, fractionation and characterization of poly[bis(piperidino)phosphazene] are described. Dilute solution properties of the polymer in THF at 25°C have been studied by size exclusion chromatography, using simultaneously multiangle light scattering and differential refractive index detectors. The anomalous elution behavior and the dependence of the dimensions, i.e. radius of gyration, of the polymer on the molecular weight are discussed. Coefficients for the scaling law have also been calculated. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Size exclusion chromatograhy; Multiangle laser light scattering; Poly[bis(piperidino)phosphazene]

1. Introduction

Since Allcock and Kugel [1] obtained the first poly(aminophosphazene), different alkylamino and arylamino phosphazenes have been synthesized but few of them have been successfully fractionated. For instance, Busulini et al. [2] synthesized poly(dianilinophosphazene) and several poly-[bis(phenylamino)phosphazene]s with ratios M_w/M_n ranging between 13 and 16 and bimodal distributions. The first poly(diaminophosphazene) successfully fractionated was poly [bis(*p*-methylanilino)phosphazene] with fractions having polydispersities between 1.6 and 4.1 [3]. More recent several fractions of poly(dianilinophosphazene), with polydispersity ratios ranging from 1.8 to 2.4, were obtained by Ramos-Vieira et al. [4]. The large polydispersity of the samples is the origin of large discrepancies between the different molecular weight averages which makes the study of the solution properties of these polymers difficult, especially the dependence on molecular weight of properties such as dimensions [5].

The use of coupled multi-angle laser light scattering (MALLS) and refractometric, DRI, detectors in SEC measurements [6,7], allows absolute distributions for both molecular weight and root mean square radius of gyration for polymers. Moreover, it has been recently reported that just one sample of a polydisperse polymer can be used to obtain information about the scaling law, $\langle s^2\rangle^{1/2} = QM^q$ and unperturbed dimensions of the polymer [8]. In previous works [5,9–12], we have studied several poly(alkoxy/aryloxy phosphazene)s and the on-line MALLS to SEC technique affords a better understanding of their solution properties. Thus, a natural further step is to study the behavior of a poly(diaminophosphazene) such as poly[bis(piperidino) phosphazene]. Although poly(diaminophosphazene)s are potentially interesting as hydrophilic or even water soluble polymers, their use is much less common than that of other polyphosphazenes, probably due to their anomalous solution behavior. The aim of this work is to improve our understanding of solution properties of poly(diaminophosphazenes) and gain information about the difficulties encountered in the fractionation of these polymers.

2. Experimental

2.1. Materials

Poly[bis(piperidino)phosphazene] (PDPP) was prepared by a procedure similar to that used by Allcock and Kugel [1]. Hexachlorocyclotriphosphazene (HCTP) (Fluka, 90%) was purified by recrystallyzation from hexane and polymerized in a sealed glass tube. Evacuation of the tube prior sealing was performed by the fusion–recrystallyzation method. The thermal polymerization of HCTP was carried out between 180–215°C. The polymerization was started at 180°C and the temperature was increased slowly over 12 h

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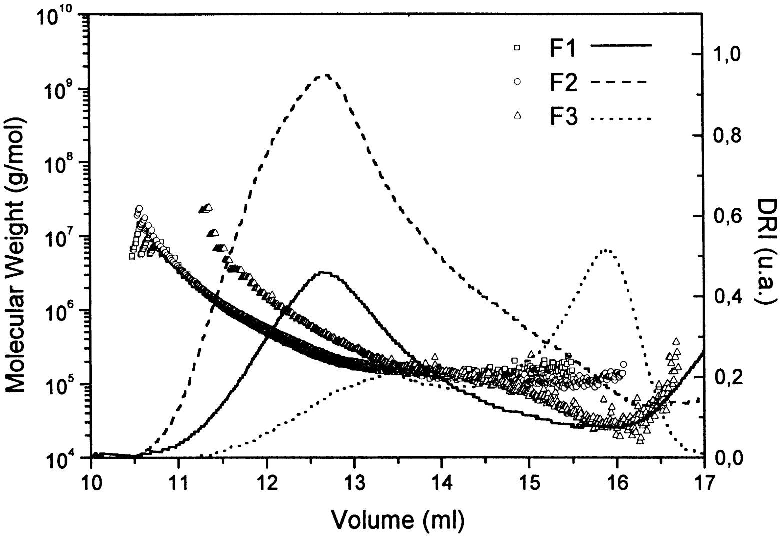

Fig. 1. Logarithm of molecular weight versus elution volume for the PDPP fractions. The DRI signals are also shown.

to 215°C and this temperature was maintained until the sample did not flow. The poly(dichlorophosphazene) (PDCP) thus obtained was used without further purification.

Piperidine (Panreac, 98%, 75 ml) was dried over potassium hydroxide before use and was added dropwise to a solution of PDCP (20 g) in dry benzene (350 ml). The reaction mixture was refluxed for 48 h. Piperidine hydrochloride was filtered off, and the polymer was obtained from the filtrate by dropwise addition to a large batch of ethanol. The polymeric product was then dissolved in benzene, precipitated into methanol, and isolated by centrifuging.

The polymer was separated into eight fractions using consecutive fractional precipitations by the solvent/nonsolvent technique. A solution of the polymer in THF was cooled to 10°C and methanol added until turbidity was observed. The solution was then warmed up to 35°C and allowed to slowly cool to 10°C. The precipitated polymer was separated by centrifuging. The procedure was repeated and five consecutive fractions were obtained. Then, water was used as the nonsolvent and three more fractions were obtained.

2.2. Measurements

A Waters Associates differential refractive index detector Model 410, was used as concentration detector and a Dawn-DSP-F laser photometer from Wyatt Technology Corp. was the mass and size detector used. A Model 510 pump, a U6K injector (Waters Associates) and two columns PLgel mixed B (Polymer Laboratories) in series completed the equipment. Tetrahydrofuran (THF) freshly distilled from sodium and benzophenone, filtered through a 0.2 μm Fluoropore filter and degassed, with a 0.1% tetra-*n*-butyl ammonium bromide was used as eluent at a flow rate of 1.0 ml/min.

The Dawn photometer was calibrated with spectrometric grade toluene freshly distilled from sodium and benzophenone, the normalization of the detectors and the determination of the interdetector volume were performed with standard monodisperse polystyrenes of low molecular weight that did not show angular dependence on the light scattering signal [6]. The refractive index increment, d*n*/d*c*, in THF solution was measured with a Brice–Phoenix differential refractometer at 436 and 546 nm and extrapolated to 632 nm using Cauchy relationship. A value of $dn/dc = 0.121$ ml/g was obtained. The Dawn photometer was also used for the batch measurements. Dilute solutions in the 10^{-4}–10^{-5} g/ml range were prepared in scintillation vials. The Zimm plot afforded the second virial coefficient besides weight-average molecular weight and mean squared radius of gyration.

^{1}H NMR spectra were obtained with a GEMIN 200 MHz spectrometer using $CDCl_3$ as solvent. ^{1}H NMR δ: (ppm from TMS) = 1.41 (4H:β and 2H:γ); 3.03 (4H:α). ^{31}P NMR spectrum was obtained with a UNITY 300 MHz spectrometer. δ: 0.06 (broad singlet); −16.29 (broad singlet, 10%).

3. Results and discussion

3.1. Molecular weight distributions

The use of a MALLS detector allows to calculate the weight average molecular weight and the root mean square radius of gyration $\langle s^2\rangle^{1/2}$ for each slice across a sample peak of the size exclusion chromatogram. Assuming that each slice contains molecules of a single molecular weight, or at least a very narrow distribution, the plot of *M* versus elution volume affords absolute molecular weight calibration curves for SEC. Fig. 1 shows the DRI signal for fractions 1–3 together with their corresponding molecular weight absolute calibration curves. The absolute molecular

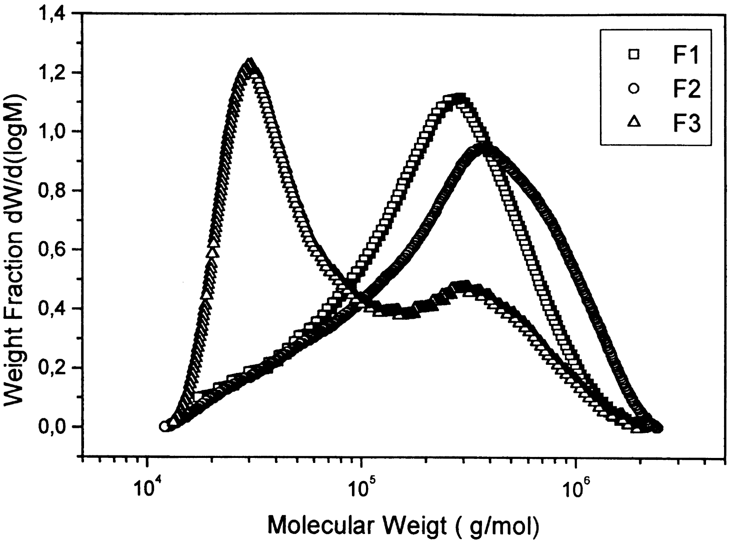

Fig. 2. Differential molecular weight distributions for the PDPP fractions.

weight distributions for the polymer fractions can be obtained from the combined measurements of molecular weight, obtained with the MALLS detector, and concentration, obtained with the DRI detector, for each elution volume [7] and are presented in Fig. 2. The mean values of molecular weights, polydispersities and corresponding standard deviations, obtained using the ASTRA software, are listed in Table 1. The fractions 1 and 2 present similar absolute molecular weight calibration curves (Fig. 1) indicating a similar composition. However, their molecular weight averages and polydispersity ratios are different. The more complex curve found for the fraction 3 and the bimodal distribution are indicative of a more heterogeneous sample. The differences are easily visualized in the molecular weight distributions (Fig. 2). The fractionation of the polymer has not been very effective. However, the SEC/MALLS technique is very precise showing slight differences between fractions.

3.2. Dimensions

Fig. 3 shows the polymer dimensions, i.e. the values of the root mean square radius of gyration, $\langle s^2\rangle^{1/2}$, calculated from the angular dependence of the intensity of the scattered light, as a function of the elution volume for the three fractions. The size of PDPP for these fractions diminish as the elution volume increase, in accordance to the SEC separation mechanism, until it reaches a point at which it starts to increase. The accuracy of the radius of gyration obtained in the region of high elution volumes (>12 ml) is lesser than that of molecular weight since the size of the polymer should be larger than $\lambda/20$ in order to notice the angular dependence of scattered light.

The increase in radius of gyration and the corresponding increase in molecular weight at high elution volumes are similar to those obtained for other polyphosphazenes [11,12], has also been encountered in other polymers and is qualitatively explained [13,14] by the existence of a small fraction of very large molecules which are retarded through the SEC columns, due to their size or molecular architecture, and elute at higher elution volumes, than those expected by a normal SEC mechanism. This fact can explain the difficulties usually found in the fractionation of these polymers.

Additional information on the polymer structure can be deduced from the study of the dependence of radius of gyration on molecular weight, usually represented as a scaling law $\langle s^2\rangle^{1/2} = QM^q$. The value of the q parameter in the scaling law may provide a hint about the shape of the polymeric chain since values of $q = 1/3$ and $q = 0.5$ are predicted for globular polymers and for random coil polymers at theta conditions, respectively, by theory [15]. For flexible chains in good solvents, q can increase up to 0.6 whereas, values of q considerably lower than 0.5 (up to ca. 0.4) have been reported for random coil polymers under theta conditions [16,17]. Fig. 4 shows the log–log plot of

Table 1
Averaged molecular weights, polydispersities and root mean square radii of gyration for PDPP fractions

Fraction	10^{-5} M_n (g/mol)	10^{-5} M_w (g/mol)	10^{-5} M_z (g/mol)	M_w/M_n	$\langle s^2\rangle_z^{1/2}$ (nm)
1	2.02 ± 0.09	3.7 ± 0.2	1.6 ± 0.3	1.8 ± 0.1	23 ± 3
2	2.03 ± 0.09	4.40 ± 0.09	2.1 ± 0.4	2.16 ± 0.06	25 ± 1
3	0.59 ± 0.08	2.2 ± 0.2	3.1 ± 1.0	3.8 ± 0.6	31 ± 4

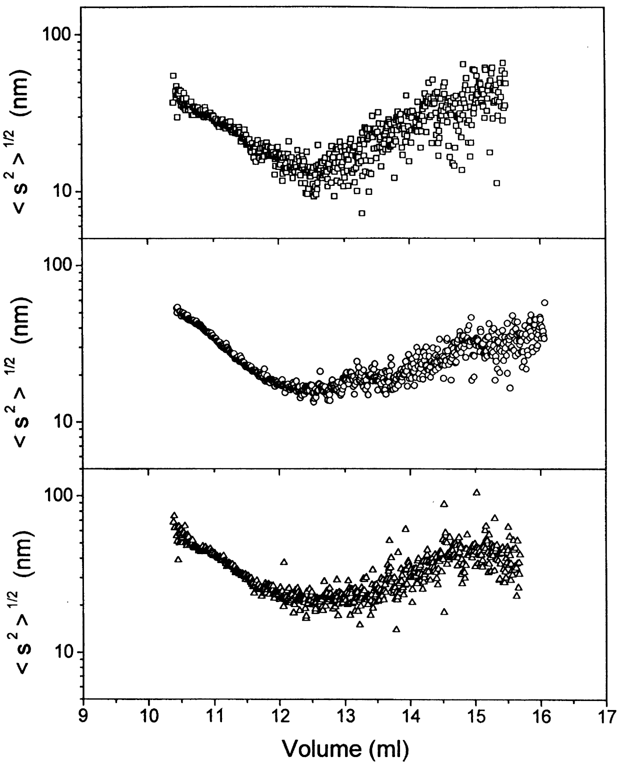

Fig. 3. Root mean squared radius of gyration versus elution volume for PDPP fractions. F1(□), F2 (○) and F3 (△).

Table 2
Concentration, weight average molecular weight and root mean square radius of gyration for three different slices of the SEC chromatogram

Slice	v_e (ml)	$10^5\ c$ (g/ml)	$10^{-6}\ M_w$ (g/mol)	$\langle s^2\rangle_z^{1/2}$ (nm)	D (nm)
1	10.817	0.36 ± 0.01	6.4 ± 0.2	40.8 ± 0.6	105 ± 1
2	11.208	1.48 ± 0.01	2.32 ± 0.03	30.0 ± 0.7	77 ± 2
3	11.667	3.38 ± 0.01	0.950 ± 0.007	20.5 ± 0.8	53 ± 2

the radius of gyration versus molecular weight, for the different slices of the fraction 2 (fraction 1 shows a similar curve and fraction 3 is not suitable due to its heterogeneity). The plot shows a pronounced curvature at low molecular weights as a consequence of the anomalous molecular weight and radius of gyration elution behavior (Figs. 1 and 3) found for PDPP and explained above. Thus, the values obtained for Q and q depend on the chosen range of molecular weights. Linear regression at high molecular weights, where the plot is linear, yields the values $q = 0.353 \pm 0.003$ and $Q = 0.162 \pm 0.007$ for the scaling law coefficients for fractions 1 and 2 of PDPP in THF. This value is close to the expected for globular aggregates [10]. In order to better interpret this result, comparison of the reciprocal scattering function, $P(\theta)^{-1}$, for particles of different shape is very convenient.

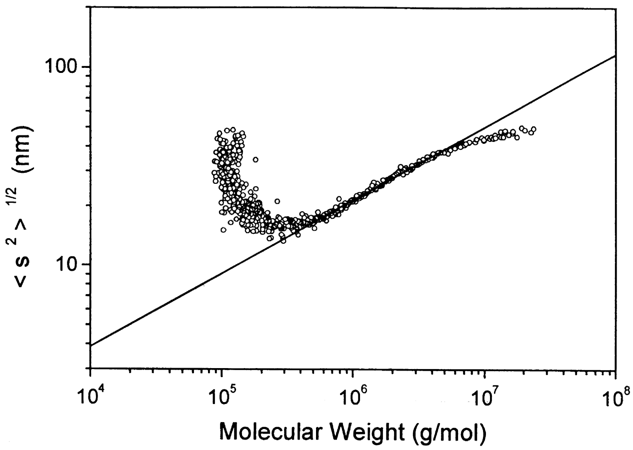

Fig. 4. Log–log plot of root mean squared radius of gyration versus molecular weight for fraction 2

The reciprocal scattering function, $P(\theta)^{-1}$, can be written as [17]:

$$\lim_{\theta\to 0} P(\theta)^{-1} = 1 + \frac{h^2\langle s^2\rangle}{3} = 1 + \frac{16\pi^2}{3\lambda^2}\langle s^2\rangle \sin^2\left(\frac{\theta}{2}\right) \qquad (1)$$

where h represents the scattering vector magnitude, related to the scattering angle, θ, and wavelength of light, λ. This expression in the small h-limit, is independent of the particle shape and thus, it enables the radius of gyration to be determined from the initial slope of the reciprocal scattering function with $\sin^2(\theta/2)$.

On the other hand, the scattering function, $P(\theta)$, for spheres of diameter D can be calculated as [17]:

$$P(\theta) = \left[\frac{3}{u^3}(\sin u - u\cos u)\right]^2 \qquad (2)$$

$$\text{where } u = \frac{2\pi}{\lambda} D \sin\left(\frac{\theta}{2}\right)$$

The diameter, D, can be easily obtained from the value of $\langle s^2\rangle$ using the geometrical relationship for spheres $\langle s^2\rangle = 3D^2/20$.

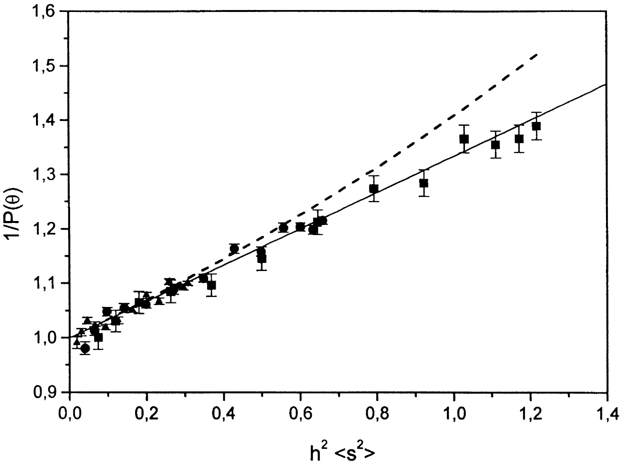

Fig. 5. $P(\theta)^{-1}$ as a function of $h^2\langle s^2\rangle$. Experimental data: slice 1 (■); slice 2 (●); and slice 3 (▲). Solid line: calculated by Eq. (1). Dotted line: calculated by the sphere model.

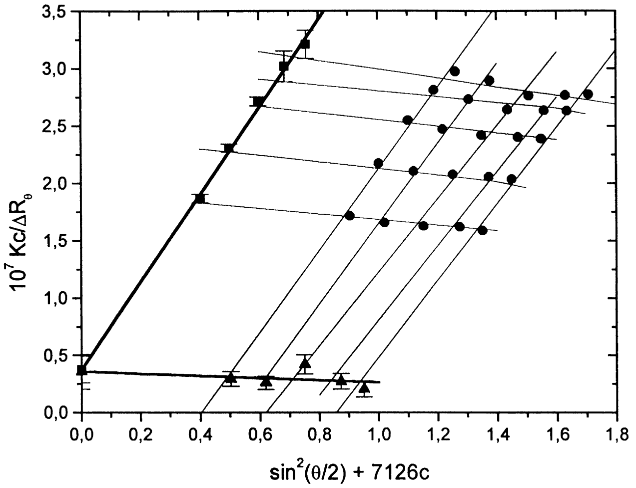

Fig. 6. Zimm plot of the fraction 2 of PDPP.

The reciprocal scattering function, $P(\theta)^{-1}$, can be obtained from the measured light-scattering data for each slice of the chromatogram as:

$$P(\theta)^{-1} = \frac{\Delta R_{\theta=0}}{\Delta R_\theta} = \frac{Kc/\Delta R_\theta}{Kc/\Delta R_{\theta=0}} = \frac{Kc}{\Delta R_\theta} M_W \tag{3}$$

where K is the optical constant for the system, c the concentration of PDPP in the slice and ΔR_θ the Rayleigh's ratio for angle θ. The values of concentration, weight average molecular weight, root mean square radius of gyration and its corresponding diameter, obtained for three slices of the chromatogram at different elution volumes are listed in Table 2.

Fig. 5 presents the experimental values, with their error bars, of $P(\theta)^{-1}$ as a function of $h^2\langle s^2\rangle$ for the above three slices together with the line (solid) that fits them according to Eq. (1). The dotted line represents the curve that fits the calculated values of $P(\theta)^{-1}$ according to the sphere model (Eq. (2)). As it is expected [18] and can be easily seen in Fig. 5, information about the shape of the polymer can only be achieved for high values of $h^2\langle s^2\rangle$, i.e. if the molecular weight and angle of observation are sufficiently large. Thus, the differences between experimental $P(\theta)^{-1}$ and the theoretical sphere model values of the scattering function are only evident for the slice 1. This behavior suggest that the conformation of the chain is close to a flexible chain in a very poor solvent, i.e. under theta conditions and that the collapse of the chain to a globular state has not been reached.

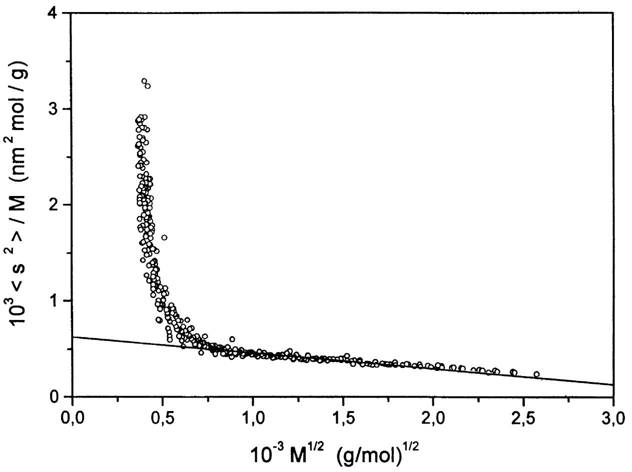

Fig. 7. Dependence of experimental values of the ratio radius of gyration and molecular weight on molecular weight. The solid line shows the extrapolation to unperturbed dimensions.

One disadvantage of the coupled SEC–MALL measurements is that the second virial coefficient, A_2, cannot be determined. Thus, off-line light scattering measurements were performed in order to both, compare the results of molecular weights and radius of gyration obtained in the on-line measurements and to gain information of the thermodynamic characteristics of the solution from the A_2 value. Fig. 6 presents the Zimm plot of fraction 2. The value of A_2, obtained from the slope of the extrapolation at zero concentration is $-(3.4 \pm 4)\ 10^{-5}$ mol ml/g^2. The negative value of A_2 confirms the idea expressed in the previous paragraph about the polymer being under θ conditions. However, the values of M_w and $\langle s^2\rangle^{1/2}$ obtained are $(2.6 \pm 0.2)\ 10^7$ g/mol and 195 ± 9 nm, respectively, much larger than the values obtained in SEC. This can be due to the fact that the solution contains in addition to individual molecules also supermolecular structures that cannot be removed from the solution by filtration. This structures can be branched or crosslinked particles and would be the reason of the small broad singlet that appear in ^{31}P NMR. Due to their high molecular weight, they increase considerably the weight average molecular weight and radius of gyration in the batch measurements. Moreover, they can be retained and degraded during flow through the SEC column, and they are responsible of the anomalous behavior. The advantage of the SEC–MALLS technique is that it is possible to differentiate the molecularly dissolved PDPP, the first part of the chromatogram, which has a normal behavior, from the abnormal structures, eluted at higher volumes. Thus, the unperturbed dimensions of the polymer can be calculated as explained below.

3.3. Unperturbed dimensions

Further evidence about the contraction behavior of the PDPP/system is seen on examining the dependence of the chain expansion factor on molecular weight. The perturbed and unperturbed mean square radius of gyration are related through the chain expansion factor, α:

$$\langle s^2\rangle = \alpha^2 \langle s^2\rangle_0 \tag{4}$$

and according to the two parameters theory [19]:

$$\alpha^2 = (1 + 1.276z - 2.082\, z^2 + \dots) \tag{5}$$

where z is a parameter proportional to $M^{1/2}$ and to the excluded volume interaction energy of

$$\frac{\langle s^2\rangle}{M} = \frac{\langle s^2\rangle_0}{M}(1 + AM^{1/2} + B\,M + \dots) \qquad (6)$$

the polymer system, β which is negative if the system is under theta conditions [20].

Thus, the values of $\langle s^2\rangle/M$ versus $M^{1/2}$ should fit a polynomial: with $\langle s^2\rangle_0/M$ as the independent term. Fig. 7 shows the experimental values of $\langle s^2\rangle/M$ versus $M^{1/2}$ for PDPP in THF. As explained above, there is a fraction of very large molecules that are retarded through the SEC columns, causing the anomalous behavior of the scaling law at high elution volumes. Thus, only experimental points at low elution volumes are taken into account for the linear extrapolation, represented by the solid line in the figure. A value of $\langle s^2\rangle_0/M = (6.29 \pm 0.07)10^{-4}$ nm^2 mol g^{-1} is obtained. The negative slope exhibited by the extrapolation is a straight consequence of the under-θ conditions of the system, i.e.: the value of α should decrease below unity and the ratio $\langle s^2\rangle/M$ will increase with decreasing M.

$$C_N = \frac{\langle r^2\rangle_0}{Nl^2} = \frac{6M_0}{2l^2}\frac{\langle s^2\rangle_0}{M} \qquad (7)$$

The characteristic ratio C_N can be calculated from the extrapolated value of $\langle s^2\rangle_0/M$ as: where N is the number of skeletal bonds, M_0 is the molecular weight of the repeating unit which contains two bonds P–N of length $l = 0.157$ nm, and $\langle r^2\rangle_0$ the unperturbed value of the mean square end to end distance, which for flexible chains is $\langle r^2\rangle_0 = 6\langle s^2\rangle_0$. The calculated value of C_N is 16 which is in very good agreement with values obtained for other polyphosphazenes [3–5].

4. Conclusions

Some conclusions concerning the solution behavior of PDPP may be drawn. The polymer in THF is under θ conditions, as it is confirmed by both, the scaling law obtained by SEC–MALLS and the Zimm plot determined through batch light scattering measurements. Supramolecular structures or aggregates coexist with molecularly dispersed polymers causing the batch measured weight average molecular weight and mean squared radius of gyration to increase. These aggregates are retained through the SEC columns and are responsible for the anomalous behavior. The SEC–MALLS technique allows us to differentiate the molecularly dissolved PDPP and thus to calculate the unperturbed dimensions of the polymer.

Acknowledgements

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