Size-Exclusion Chromatography of Poly[bis(trifluoroethoxy)phosphazene]

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Received January 27, 1989; Revised Manuscript Received April 5, 1989

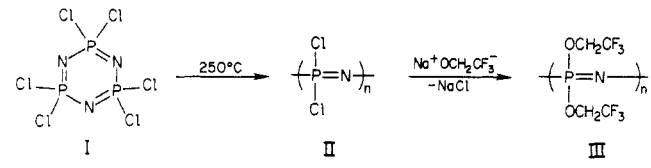
ABSTRACT: Dilute-solution properties of poly[bis(trifluoroethoxy)phosphazene] in acetone, tetrahydrofuran, and cyclohexanone in the presence of tetrabutylammonium nitrate are examined to choose optimum eluent conditions for size-exclusion chromatography. A concentration dependence on elution volume persists down to the detection limits of differential refractometry when acetone is used as eluent, which is a result of concentration-induced chain compression. A poorer solvent, such as cyclohexanone, reduces this effect and allows absolute molecular weight determination by universal calibration with on-line differential viscosity detection. Poly[bis(trifluoroethoxy)phosphazene] has a bimodal molecular weight distribution with the lower molecular weight mode possessing a different set of Mark–Houwink constants than the main, high molecular weight portion of the distribution.

Introduction

Poly[bis(trifluoroethoxy)phosphazene] is generally prepared by nucleophilic substitution of poly(dichlorophosphazene) as first described by Allcock et al. (Scheme I).[1,2] The polymer is semicrystalline at room temperature, and it undergoes a first-order transition to a mesomorphic state at $T(1)$. Several groups (ref 1–6 and references therein) have used various techniques to study this transition. Interest in the technological application of this material and polyphosphazenes in general has increased in recent years, partly because of the commercial development of synthetic processes for noncrystalline longer chain fluorinated elastomers.

Size-exclusion chromatography has been used to characterize the molecular weight distribution of the poly(dichlorophosphazene) precursor[7–9] and numerous derivatives.[3,10–15] There is general agreement among workers that the materials are high molecular weight ($M_w > 1.0 \times 10^6$) and have bimodal or multimodal molecular weight distributions with polydispersities greater than 10. The precursor is particularly difficult to characterize by size-exclusion chromatography; it requires special handling procedures and carefully dried eluent because of its susceptibility to nucleophilic attack. Several workers have alluded to the possible formation of branched structure in the precursor; however, no definitive dilute solution data verify this, and no evidence of branch sites has been reported by NMR. Of the numerous fluorinated derivatives of poly(dichlorophosphazene), only a limited number of raw size-exclusion chromatograms of noncrystalline fluorinated copolymers in dimethylformamide (DMF)[10,12] and tetrahydrofuran (THF)[14] have been presented. There is a suspicious lack of size-exclusion chromatography on the semicrystalline poly[bis(trifluoroethoxy)phosphazene], despite being one of the original derivatives made as a soluble polymer more than 20 years ago. Recently, part of the problem with solution characterization of this homopolymer was circumvented. Association in solution is eliminated and normal viscosity behavior is obtained by the addition of a small amount of an ionic species, such as tetrabutylammonium bromide, to tetrahydrofuran.[16] Neilson et al.[17] also reported that adsorption of alkyl and arylphosphazenes to polystyrene resin and glass bead packings is eliminated when quaternary ammonium salts are added to THF eluent. Unfortunately, the trifluoroethoxy derivative is nearly isorefractive with THF; thus, it requires high sample concentrations when refractive index detection is used. None of the size-exclusion separations of polyphosphazenes to date has been verified by on-line absolute molecular weight detection, such as low-angle laser light scattering (LALLS), or by differential viscometry (DV) detection and universal calibration. In part, this is because much of the work was presented before commercial LALLS and DV instruments were available.

Scheme I



The results reported here are based on poly[bis(trifluoroethoxy)phosphazene] prepared by Allcock's[1,2] original procedure. It is important to note that a small amount (<1%) of side-group cleavage can accompany this preparation (see the Experimental Section). The polymerization was carried out in the melt with only ground glass added as a catalyst.[18] This procedure is generally regarded as that which leads to the highest molecular weight poly(dichlorophosphazene). Modifications of the chlorophosphazene polymerization involving catalyst,[19] solvents,[20] and condensation of chlorinated polymers[21] have been developed, but they usually lead to lower molecular weight materials.

In this paper we examine more closely size-exclusion chromatography and dilute solution viscosity behavior in ketones and THF using both on-line LALLS and DV, and we present for the first time absolute molecular weight distributions of the poly[bis(trifluoroethoxy)phosphazene]. Our intention is to understand more clearly the effect of factors such as concentration-induced chain compression and flow rate on the calculation of accurate molecular weight distributions in poly[bis(trifluoroethoxy)phosphazene] and to introduce examples of size-exclusion chromatography using ketones as eluents—solvents that until recently were not recommended by some vendors for use with styrene–divinylbenzene-based columns.

Experimental Section

Poly(dichlorophosphazene) and poly[bis(trifluoroethoxy)-phosphazene] were synthesized using minor modifications of the

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original method described by Allcock et al.[1,2] Hexachlorocyclotriphosphazene (I) (>99%, Tracon Industries Corp., Melville, NY) was recrystallized and sublimed. Poly(dichlorophosphazene) (II) was prepared by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C. A total of 2 g of Pyrex glass[18] was added to 200 g of cyclic trimer, and the sealed tube was rotated 360° during polymerization.

Poly(dichlorophosphazene) (57 g, 0.49 mol) was dissolved in THF (900 mL). Sodium trifluoroethoxide was prepared in THF (500 mL) from sodium spheres (28 g, 1.2 mol) and trifluoroethanol (127 mL, 1.65 mol). The stirred polymer solution was cooled in an ice bath, and the alkoxide solution was added dropwise so that the temperature of the reaction mixture did not exceed 25 °C. The reaction was stirred for 2 h and precipitated in 200-mL aliquots into 3-L batches of water. Further purification was carried out by precipitation of 200-mL aliquots of a 10% polymer solution in acetone into 3.5-L batches of water, precipitation of 200-mL aliquots of 10% polymer acetone solution into 1.5-L batches of toluene, filtration of a 7.5% polymer solution in acetone through a Rapid-Flo brand milk filter (Filter Fabrics, Goshen, IN) followed by precipitation of 200-mL aliquots into 3.5-L batches of water, and precipitation of 200-mL aliquots of a 6.7% polymer–acetone solution into 1.5-L batches of toluene. A tough, white material was isolated (64 g, 53% yield based on chloro polymer).

The infrared spectrum was consistent with the literature[1] including a strong absorption at 1280 cm^{-1} (P=N). The proton-decoupled ^{31}P NMR spectrum was a sharp singlet at −6.4 ppm, and the ^1H NMR showed only the expected methylene peaks of the homopolymer. Elem anal. Found (calcd): N, 5.7 (5.8); C, 19.9 (19.8); H, 1.6 (1.7); P, 12.2 (12.7); F, 47.2 (46.9); Cl, <0.3 (0.0). The melting point measured by differential scanning calorimetry (DSC) was 237 °C compared to 246 °C for the true homopolymer, which indicates a small amount of side-group cleavage occurred during the synthesis of the polymer.[22,23]

Tetrahydrofuran was freshly distilled and used without an inhibitor in all studies. High-pressure liquid chromatographic grade acetone was used as received from J. T. Baker Chemical Co. Cyclohexanone (obtained from Eastman Kodak Co., *Kodak Laboratory and Research Products Catalog No. 53*) was passed through activated acidic alumina and stored over nitrogen to prevent discoloration. Eluents containing tetrabutylammonium nitrate (TBAN, obtained from Kodak) were filtered through 0.22-μm Fluoropore filters (Millipore Corp.) and stored without sparging over nitrogen. Cyclohexanone–TBAN solutions were stable for at least 1 week when used as chromatographic eluents.

Viscometry. Samples were dissolved at a concentration of 1–2 g/dL and filtered through coarse, scintered-glass filters. An Ostwald dilution capillary viscometry tube thermostated at 25 °C was charged with 7 mL of the stock solution, and a minimum of four efflux times was recorded for the stock and each dilution. Capillary diameters were chosen such that all efflux times were greater than 200 s, making kinetic energy corrections negligible. Intrinsic viscosities $[\eta]$ and Huggins constants k' were calculated by least-squares nonlinear regression analysis of the Huggins formalism.[24]

$$\eta_{sp} = [\eta]C + k'[\eta]^2C^2 \quad (1)$$

Light Scattering. Stock solutions at a concentration of 2.0 mg/mL in 0.01 M TBAN–organic solvent were dialyzed for 24 h against 500 mL of fresh 0.01 M TBAN–organic solvent using 1000 molecular weight cutoff, 35-mm-diameter Spectra/Por 6 dialysis tubes. The tubing was prepared by equilibrating with distilled water, 50:50 acetone–water, pure acetone, 50:50 acetone–organic solvent, and 0.01 M TBAN–organic solvent over a period of 3 days. The refractive indices of various concentrations of polymer solution were measured at 25 °C (40 °C for cyclohexanone solutions) with a Chromatix KMX-16 differential refractometer and the polymer refractive index increments dn/dc and solvent refractive indices n were calculated following the polynomial fitting of calibration data and calculation of slopes and intercepts by least-squares linear regression of refractive indices versus concentration (as described in ref 25).

Excess Rayleigh scattering was measured for a minimum of five concentrations at an angular range of 6–7° with a Chromatix KMX-6 low-angle laser light-scattering photometer (LALLSP) by syringing approximately 5 mL of solution through the standard

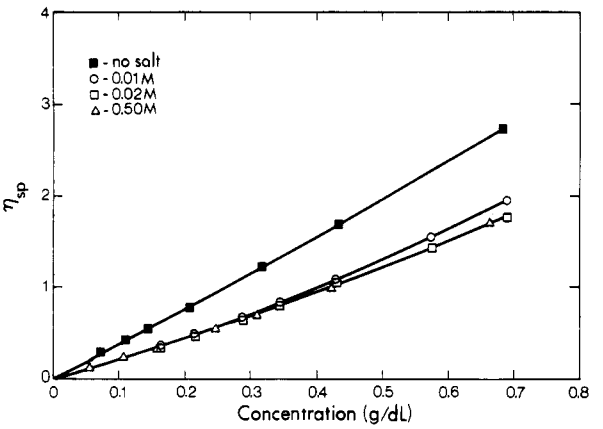

Figure 1. Effect of salt (TBAN) on the viscosity of poly[bis(trifluoroethoxy)phosphazene] in acetone at 25 °C.

15-mm-path-length static measurement cell. Molecular weights and second virial coefficients were calculated from least-squares linear regression of concentration versus $KC/R\theta$ data.

Size-Exclusion Chromatography. Two 10-μm-particle-diameter, 7.5 mm i.d. × 300 mm long, PL-gel mixed-bed columns (Polymer Laboratories, Ltd.) were connected in series after the injector and a 0.5-μm stainless steel in-line filter. Columns were received packed in THF from the manufacturer. They were converted to acetone by passing five column volumes at 0.1 mL/min, followed by 0.01 M TBAN in acetone until a stable base line was obtained. After the conversion to acetone conversion to cyclohexanone was effected in a similar fashion. Eluent was delivered by a Waters Associates 590 reciprocating piston pump. Samples were dissolved in the mobile phase without stirring or agitation and injected in a volume of 200 μL. For concentration studies, the LALLSP was connected first in series with a Waters 411 differential refractometer. A Viscotek Corp. Model 100 differential viscometer was connected in parallel with the same refractometer by a splitter tee (as described in ref 26). The differential pressure transducer was calibrated with narrow molecular weight distribution polystyrene and poly(methyl methacrylate) standards of known molecular weight whose intrinsic viscosities were measured by capillary viscometry. The columns and detectors were thermostated to 30 and 40 °C for acetone and cyclohexanone eluents, respectively. Narrow molecular weight distribution polystyrene and poly(methyl methacrylate) standards (American Polymer Laboratories), and poly(tetrahydrofurans) (Polymer Laboratories, Ltd.) were prepared in the mobile phase at concentrations of 0.1% for samples less than 900 000 Da and 0.01% for standards greater than 1 000 000.

Results and Discussion

Dilute-Solution Viscosity. The development of size-exclusion chromatographic (SEC) methods is invariably easier, and certainly the methods are more readily verified with some basic understanding of the dilute-solution properties of the sample (e.g., viscosity) and general physical properties of the solvent–solute pair (e.g., refractive index increment). This is of particular importance with poly[bis(trifluoroethoxy)phosphazene] because of the anomalous dilute-solution behavior that is reported by several workers, knowledge that the material is semicrystalline and molecular aggregates may persist in solution, and the general concern that fluorinated polymers can be difficult to separate by size-exclusion chromatography because of limited solubility and their tendency to interact with many column packings. The viscosity behavior of poly[bis(trifluoroethoxy)phosphazene] in acetone shown in Figure 1 confirms the findings of ref 16 and 17; that is, small amounts of quaternary ammonium salts reduce viscosity and anomolous behavior in pure organic solvent is to be anticipated. Each curve in Figure 1 is shown with the best nonlinear regression fit of the Huggins formalism. Although not graphically obvious, the fit to

Table I
Intrinsic Viscosity in Acetone

TBAN concn, M	$[\eta]$	k'	TBAN concn, M	$[\eta]$	k'
0	3.70	0.03	0.02	2.04	0.19
0.01	2.02	0.29	0.05	2.07	0.18

data without salt is worse than the other data sets (residuals are not random about zero); and the Huggins constant, usually a value between 0.3 and 0.5, is extraordinarily small in the absence of salt (Table I). There is no statistical difference among intrinsic viscosities of the polymer at three salt concentrations between 0.01 and 0.50 M, although Huggins constants vary considerably. Because the interpretation of Huggins constants is widely debated (e.g., see ref 27 and references therein), we offer no explanation for such variance. Tetrabutylammonium nitrate reduces the viscosity of THF and cyclohexanone solutions similarly. Some speculate that this reduction in viscosity can be attributed to breaking intermolecular interactions caused by small amounts of hydroxyl groups along the backbone. Our simple investigation neither confirms nor refutes this; however, for valid size-exclusion chromatography, we eliminate the anomaly.

Poly[bis(trifluoroethoxy)phosphazene] is soluble in moderately polar, hydrogen-bonding organic solvents such as ketones and THF, and it is insoluble in most other common organic solvents. Unlike the noncrystalline fluorinated copolymers studied previously,[10,12] the semicrystalline poly[bis(trifluoroethoxy)phosphazene] is insoluble in DMF–salt solutions. The viscosity behavior in three solvents, all containing 0.01 M TBAN (Figure 2 and Table II), is helpful when choosing appropriate eluents in size-exclusion chromatography. These data were obtained on the sample reported in Table I after being kept approximately 12 mo under ambient conditions. Note that the intrinsic viscosity dropped substantially with keeping. We have no evidence for formation of additional hydroxyl groups in this aged sample, as would be expected for additional hydrolysis (there were no significant differences in melting points determined by differential scanning calorimetry or ^{1}H NMR spectra of the sample before and after aging).[23] A similar drop in dilute solution viscosity after ambient keeping for 24 mo has also been observed in sample IIIA of ref 16. We suspect that this decrease in dilute-solution viscosity with keeping is related to changes in nonrandom solution conformations, which persist even in the presence of quaternary ammonium salts at concentrations required for capillary tube viscometry. This may partially explain unusual variations in Huggins constants reported in Table II and again emphasizes the complex dilute-solution behavior of this polymer. It is clear, however, from Figure 2 and the data of Table II (includes second virial coefficients obtained from static LALLS measurements) that the order of solvation, from best to worse, is THF to acetone to cyclohexanone. Tetrahydrofuran exhibits unusual dilution behavior (the Huggins constant in Table II is low), and the high viscosity in this solvent can potentially result in shear degradation in size-exclusion experiments. The refractive index increments of the polymer in THF and acetone are quite small, and large sample sizes are required when refractive

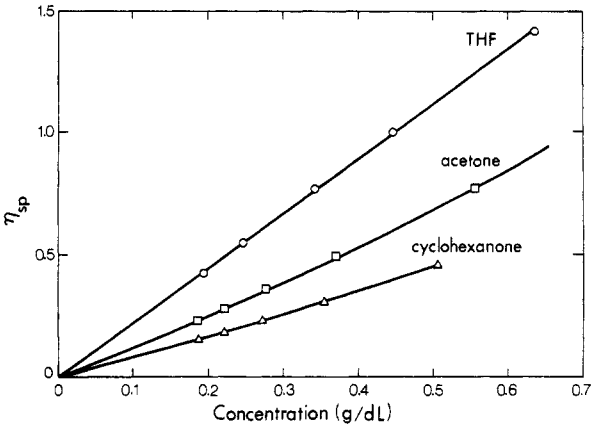

Figure 2. Viscosity of poly[bis(trifluoroethoxy)phosphazene] in organic solvent–0.01 M TBAN at 25 °C.

index detection is used in size-exclusion chromatographic experiments. [As an aside, we calculated identical values of dn/dc for polymer–salt solutions with and without dialysis in THF and cyclohexanone. Conversely, undialyzed acetone solutions result in a bulk dn/dc value of 0.003 compared to the dialyzed value of 0.019 in Table II. The resulting error in calculation of the weight-average molecular weight by light scattering using the bulk dn/dc is approximately a factor of 30. Numerous papers have been written describing the differences between bulk dn/dc values and local refractive indices of the polymer resulting from selective solvation, in this case, presumably from the TBAN. For further details refer to a standard light-scattering textbook (e.g., ref 28 and references therein).]

Optimizing Size-Exclusion Chromatography. On the basis of the above dilute-solution data, acetone and cyclohexanone with TBAN are the two best candidates for size-exclusion chromatography eluents, primarily because polymer viscosities are lower than in THF and Huggins constants are within a "normal" range. Salt concentrations greater than or equal to 0.01 M TBAN appear to eliminate most of the anomalous dilution behavior at concentrations normally used in size-exclusion chromatography (e.g., 2 mg/mL). These concentrations of polymer are approximately the same as the lowest concentrations used in capillary viscometry. Poly[bis(trifluoroethoxy)phosphazene] separated on 2–10-μm mixed-bed polystyrene–divinylbenzene resin columns using acetone–0.01 M TBAN as eluent shows a distinctly bimodal, highly polydisperse distribution (Figure 3), as was reported previously.[7-15] By increasing the sample concentration from near the workable detection limits of the refractive index detector in acetone–0.01 M TBAN, we obtain a reduction of retention volumes and a distinct broadening of the peak that can be seen quite plainly in the differential viscometry output (Figure 4). This effect is well established in SEC and is explained as a reduction of the effective hydrodynamic volume of solvated polymer coils with increasing polymer concentration.[29] The effect worsens with increasing polymer molecular weight, and considerable error can be introduced into the calculation of molecular weight averages unless suitable corrections are made. Fortunately, we observe no significant differences in raw chromatograms

Table II
Dilute-Solution Properties of Poly[bis(trifluoroethoxy)phosphazene] in Organic Solvents with 0.01 M TBAN

solvent	$[\eta]$	k'	M_w	A_2	dn/dc	n (solvent)
THF	2.24	ca. 0.02	$(1.48 \pm 0.13) \times 10^6$	1.0×10^{-3}	−0.023	1.405
acetone	1.17	0.30	$(1.54 \pm 0.06) \times 10^6$	5.1×10^{-4}	0.019	1.360
cyclohexanone	0.78	0.42	$(1.42 \pm 0.07) \times 10^6$	6.7×10^{-5}	−0.053	1.448

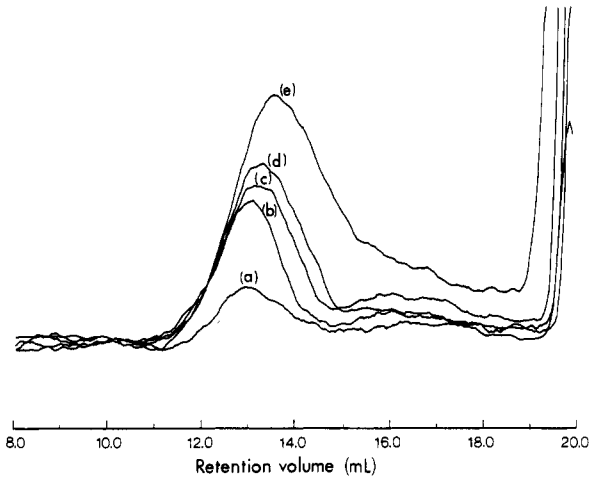

Figure 3. Raw chromatogram in acetone–0.01 M TBAN on 2-10-μm PL-gel mixed-bed columns at 30 °C, flow rate at 1.00 mL/min, refractive index detector at sensitivity 512. Concentrations (in mg/mL): (a) 1.0, (b) 2.0, (c) 3.0, (d) 4.0, (e) 5.0.

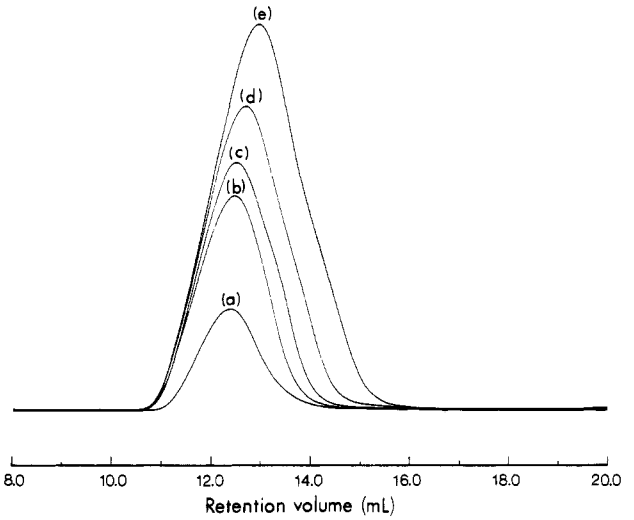

Figure 4. Differential viscometer output, same conditions and sample concentrations as in Figure 3: DV sensitivity = 100.

at a concentration of 0.3% (w/v) at flow rates between 2 and 0.3 mL/min, which indicates that shear degradation is not a significant problem.

On the basis of the large second virial coefficient and high viscosity of poly[bis(trifluoroethoxy)phosphazene] in THF, we expect a concentration dependence even worse than that in acetone. Conversely, concentration dependences decrease as the Θ state is approached. This is true in cyclohexanone. Raw chromatograms in cyclohexanone–0.01 M TBAN (Figure 5) exhibit a better signal-to-noise ratio because of the larger refractive index increment in this solvent compared to acetone, and below 0.3% (w/v) sample concentration there is no difference in computed molecular weight averages. Concentration effects are seen more clearly by LALLS detection as a second peak at longer elution volumes at concentrations greater than 0.4% (Figure 6). This example again shows that choice of a size-exclusion eluent based on dilute-solution properties (in this case, conditions approaching the Θ state) is a simple way to eliminate numerous artifacts and avoid tedious mathematical corrections.

Absolute Molecular Weight Distributions in Cyclohexanone. The intrinsic viscosity of each eluting slice of a poly[bis(trifluoroethoxy)phosphazene] chromatogram can be calculated from the concentration obtained from the refractive index detector and the specific viscosity η_{sp}

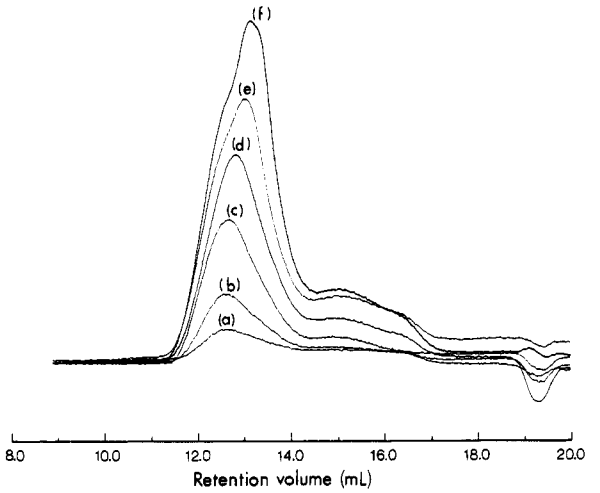

Figure 5. Raw chromatogram in cyclohexanone–0.01 M TBAN on 2-10-μm PL-gel mixed-bed columns at 40 °C, flow rate at 1.00 mL/min, refractive index detector at sensitivity 256. Concentrations (in mg/mL): (a) 0.50, (b) 1.0, (c) 2.0, (d) 3.0, (e) 4.0, (f) 5.0.

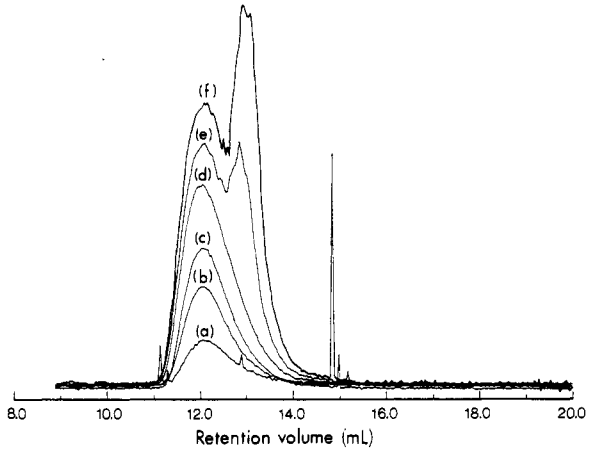

Figure 6. LALLSP output for same conditions and sample concentrations as in Figure 5.

that is measured by differential pressure in matched capillaries in the DV detector simply as

$$[\eta] = \lim_{C \to 0} \eta_{sp}/C \tag{2}$$

assuming that concentrations across the chromatogram are sufficiently low as to approximate the value of $[\eta]$ equal to the value extrapolated to zero concentration. Absolute molecular weights are calculated by generation of a universal calibration curve where the relevant parameter is hydrodynamic volume, and use of the product $M_1[\eta]_1$ for a series of narrow molecular weight distribution standards allows calculation of the molecular weight of unknown polymer 2 from the equivalency

$$M_1[\eta]_1 = M_2[\eta]_2 \tag{3}$$

The relationship between molecular weight and viscosity is usually described by the empirical Mark–Houwink relationship

$$[\eta] = KM^a \tag{4}$$

where K and a are constants that depend on the polymer, quality of solvent, and temperature. Generally, a ranges between 0.5 at Θ conditions and 0.75 for polymer in a good solvent.

A universal calibration plot generated for narrow molecular weight distribution polystyrenes, poly(methyl methacrylates), and poly(tetrahydrofurans) (Figure 7) in

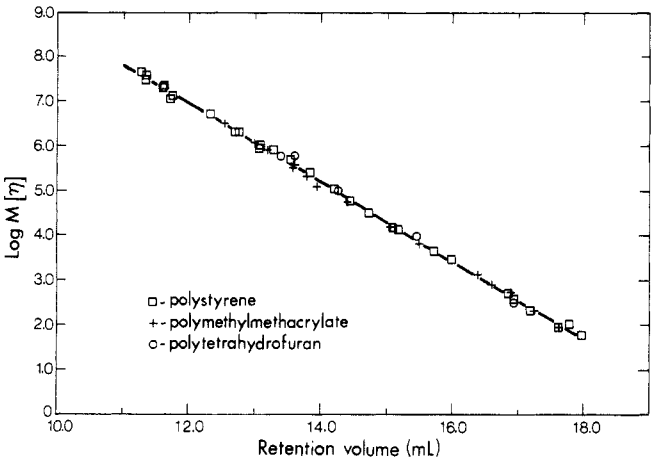

Figure 7. Universal calibration in cyclohexanone–0.01 M TBAN. Same conditions as in Figures 5 and 6; sample concentrations given in the Experimental Section.

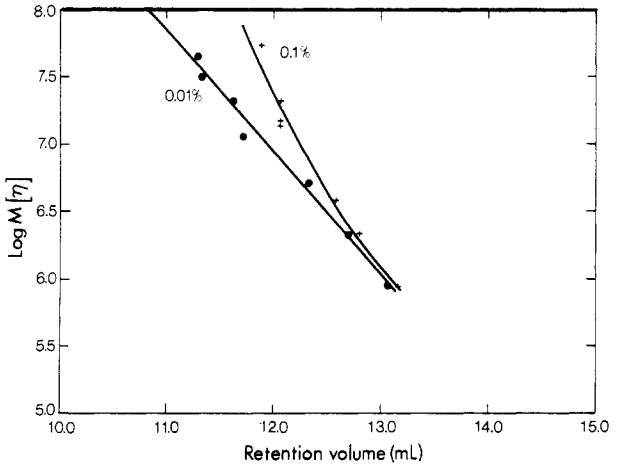

Figure 8. Effect of standard concentration on universal calibration plot for high molecular weight polystyrenes (MW between 900 000 and 6 300 000). Same conditions as in Figures 4 and 5.

Table III
Mark–Houwink Coefficients Cyclohexanone–0.01 M TBAN (40 °C)

standard	a	K
polystyrene	0.643	0.000 302
poly(methyl methacrylate)	0.603	0.000 366
poly(tetrahydrofuran)	0.676	0.000 416

cyclohexanone–0.01 M TBAN at 40 °C exhibits excellent linearity for molecular weights ranging between 6 300 000 and 1470 Da. Superposition of the three polymers is evidence that the universal calibration principle applies. We chose 10-μm-particle-diameter mixed-bed columns rather than commercially available 5-μm packings because of the larger linear range, lower back pressure, and presumably lower shear field in the former. We understand that 10-μm particles also respond better to solvent changeovers, and to date we have not tried conversions to ketones with smaller particle-diameter materials. Mark–Houwink constants for the three standards are given in Table III. Only five poly(tetrahydrofuran) standards were examined, and the reliability of Mark–Houwink constants derived from so few standards is considerably less than those for polystyrene and poly(methyl methacrylate). In addition, since polystyrene standards above 900 000 are sensitive to concentration, as shown in Figure 8, it is essential to keep concentrations of standards near a minimum detectable concentration to reduce such effects.

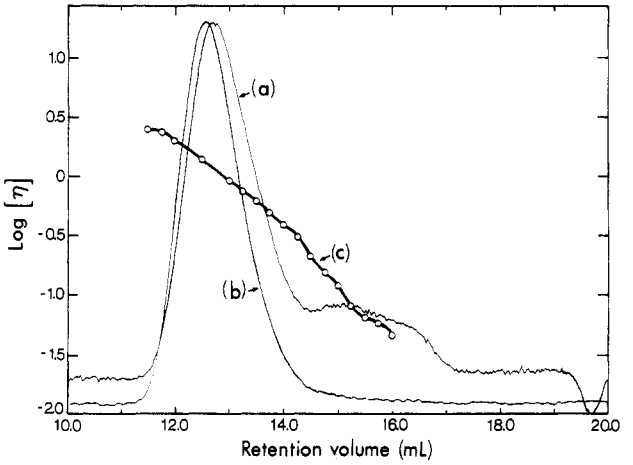

Figure 9. (a) Refractive index output, (b) differential viscometer output, and (c) intrinsic viscosity of poly[bis(trifluoroethoxy)-phosphazene].

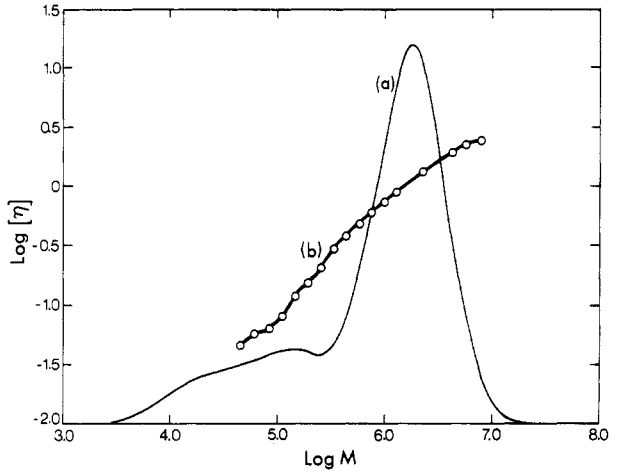

Figure 10. Molecular weight distribution of (a) poly[bis(trifluoroethoxy)phosphazene] and (b) corresponding Mark–Houwink plot.

A typical raw chromatogram of poly[bis(trifluoroethoxy)phosphazene] with its accompanying viscosity versus retention volume curve is given in Figure 9. The viscosities at identical retention volumes from four chromatograms were averaged to generate curve b in Figure 9. The intrinsic viscosity decreases nearly linearly with retention volume across the main mode of the distribution, but it then drops distinctly near the low molecular weight region of the chromatogram. The limited sensitivity of the differential viscometer at low molecular weights limits the range over which the viscosity is plotted in Figure 9. The absolute molecular weight distribution (Figure 10) has a weight-average molecular weight of 1 490 000 compared to 1 420 000 obtained by static LALLS, and the intrinsic viscosity obtained by summing across the differential viscometer and refractive index traces is within 5% of the value obtained by capillary viscometry. This is within the error of both experiments.

Structural Heterogeneity. The Mark–Houwink plot superimposed on the molecular weight distribution in Figure 10 illustrates that the Mark–Houwink coefficients are changing across the distribution (a result of a structurally heterogenous sample) and that any computational methods employing a single set of Mark–Houwink parameters are subject to error. From these data we can only hypothesize that the heterogeneity is either caused by a difference in branching (e.g., the low molecular weight fraction is branched more than the high molecular weight

portion), there is a chemical difference between the two modes, or there is a chromatographic problem such as adsorption to the column packing. However, the latter is inconsistent with a decrease in viscosity (we anticipate high molecular weight polymer to adsorb preferentially), and it is highly unlikely that molecular weights obtained by universal calibration will agree with an independent light-scattering experiment if adsorption were occurring.

A change in Mark–Houwink constants at the low end of the molecular weight distribution was not reported by Hagnauer and LaLiberte[11] in their semipreparative size-exclusion fractionation of a bimodal poly[bis(*m*-chlorophenoxy)phosphazene] prepared from poly(dichlorophosphazene). We suspect that their lowest molecular weight fraction was far too broad ($M_w/M_n = 7.8$) to observe changes in the viscosity–molecular weight relationship. The authors of ref 11 clearly state that the high polydispersities and limited molecular weight range of their fractions "hamper interpretation and could be masking some of the effects of branching on dilute solution properties". We do not believe that our data in any way contradict the findings of ref 11; rather, it demonstrates that on-line viscosity detection resolves subtle differences at the low molecular weight end of the distribution better than semipreparative collection of fractions.

A final comment about the choice of DV versus LALLS on-line detection is appropriate. After examining both, we find the viscometry detection preferable in this application for at least two reasons: (1) it has far greater sensitivity, particularly in the low molecular weight region, than LALLS (primarily because of the low refractive index increments of the polymer in the solvents examined); and (2) we experienced plugging of in-line 0.22-μm Teflon filters that are commonly used before the LALLS cell. This was caused by the polyphosphazene samples, and it worsened as sample concentrations increased. We suspect that the fluorinated homopolymers bind to the Teflon surface. We frequently obtained weight-average molecular weights by SEC-LALLS that were as much as 28% lower than values obtained by the static LALLS experiment, indicating possible loss of sample before the LALLS cell.

Recommendations and Conclusions

The results presented are for a single class of polyphosphazene derivatives. From this, however, we can make recommendations that may be useful to workers interested in size-exclusion chromatography of other high molecular weight phosphazene derivatives. These recommendations apply to size-exclusion using light-scattering and viscosity detectors as well as to the simpler and more common practice of determining equivalent molecular weight distributions via use of narrow standard calibrants: (1) an eluent should be chosen that eliminates association. Examination of dilute solution viscosity behavior is a simple method of screening potential solvents. (2) The concentration of high molecular weight narrow standard calibrants must be kept as low as possible. (3) Many polyphosphazenes made by the original method of Allcock contain high molecular weight fractions, and artifacts in size-exclusion chromatograms caused by concentration effects should be anticipated. Distortions can be minimized by any of several common techniques (e.g., see ref 30), including choice of a poor solvent that still permits elution of the polymer without adsorption and minimizes sample concentrations. The latter can typically be accomplished by increasing the detector signal (e.g., choose a solvent that gives a large value of dn/dc for refractive index detection). (4) Polyphosphazenes synthesized by this method are structurally heterogeneous across the molecular weight distributions. Regardless of the form and source of this heterogeneity, workers should be cautious in applying any of the common methods of converting equivalent molecular weight distributions to absolute distributions through use of a single set of Mark–Houwink parameters.

Registry No. TBAN, 1941-27-1; tetrahydrofuran, 109-99-9; acetone, 67-64-1; cyclohexanone, 108-94-1.

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