Size exclusion chromatography of nylon-6

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A new size exclusion chromatography (SEC) system for nylon-6 has been developed which uses the universal calibration peak retention of narrow dispersity poly(methyl methacrylate) (PMMA) in 2,2,2-trifluoroethanol (TFEtOH). The SEC system, operated at room temperature with silanized silica columns, obviates the solvent incompatibility of TFEtOH with styrene-gel packings and gives simple and reproducible chromatograms of polyamide-6. The method provides molecular weight accuracy within ±10% without correction for dispersion. To support the universal calibration for nylon-6, it was necessary to investigate the macromolecular hydrodynamics of PMMA in TFEtOH; results are represented well by the Stockmayer–Fixman viscosity–molecular weight theory. Poly(methylmethacrylate) in TFEtOH exhibits a Mark–Houwink exponent of 0.88 and a polymer–solvent interaction parameter, χ_{12} equal to 0.38.

(Keywords: size exclusion chromatography; nylon-6)

INTRODUCTION

The same physicochemical properties that give nylon-6 its exceptional strength, toughness and solvent resistance complicates the analysis of its molecular weight distribution via size exclusion chromatography (SEC). The limited number of suitable solvents for the mobile phase in the SEC of polyamides in general has slowed the development of this analytical tool for these polymers. The current state of solvent selection for the chromatography of polyamide-6 can be divided into three main categories:

(1) high temperature solvents, e.g. *m*-cresol;

(2) common solvents (e.g. THF, CH_2Cl_2) with polyamides modified by trifluoroacetylation; and

(3) room temperature specialty solvents such as the fluorinated alcohols, e.g. 2,2,2-trifluoroethanol (TFEtOH) and hexafluoro-2-isopropanol (HFIP).

These solvents present a wide range of compatibility differences with the two major types of column packing currently used (styrene-gels and modified silicas) as well as calibration difficulties since the commonly used polystyrene standards are not soluble in the fluorinated alcohols. In this work the availability of narrow dispersity poly(methyl methacrylate) (PMMA) standards which are soluble in TFEtOH and the universal calibration concept[1] are used to develop an accurate, reproducible SEC system for determining the molecular weight distribution (MWD) of nylon-6.

High temperature solvents

Size exclusion chromatography of polyamides generally has been accomplished using *m*-cresol at temperatures of 100–130°C with μ-Styragel® columns[2–4]. Despite the elevated temperature, column dispersion resulting in broadened chromatograms was still significant and distillation of the *m*-cresol to remove water and acid contaminants did not inhibit its tendency to degrade in the chromatograph[2]. This acidity at 130°C causes transamidation and a slow degradation of the molecular weight (MW) as measured by viscosity[5] similar to known reactions with the polyesters[6]. In addition, high temperature increases the risk of oxidative degradation of the polymer as well as risk and inconvenience to the SEC operators. Despite these disadvantages, the *m*-cresol/polyamide-6 system is still in use for lack of a better solvent (see, for example, Reference 7).

Benzyl alcohol (BzOH) has not shown much promise either. Pastuska and Just used BzOH with silica columns[8] but observed strong solvent-packing (hydrogen-bonding) interactions, and Marot and Lesec had calibration problems with polystyrene (PS) standards and μ-Styragel columns at 130°C[9]. Other solvents such as hexamethylphosphoramide (HMPA) have been used in the SEC of polyamides at 105°C[10] and at 85°C[11]. In the former case, no details of molecular weight accuracy were given; in the latter case PS standards and a Q correction factor were used to determine polyamide MW but no comparison with independent MW measurements was mentioned. Goedhart *et al.*[12] had problems with frequent gelation of polyamides in HMPA, causing plugged columns and fouled tubing. These operating problems in addition to the suspected carcinogenicity[9] of HMPA are major disadvantages in its use. As with any of these high temperature solvents, the possibility of polymer degradation due to oxidation must not be overlooked.

Mixed solvent systems such as equivolume chlorobenzene and *m*-cresol[5] were tried to reduce viscosity and temperature but still showed solute adsorption effects which required the addition of benzoic acid (0.25% w/w). Other diluents to *m*-cresol such as chloroform or dichloromethane have been proposed[12] but these, like other mixed solvent systems, suffer from the main drawback of compositional changes affecting the hydrodynamic volume of the solute, the baseline stability in the refractometer and/or solvent gradients from the main flow field to the inside of the pores. These disadvantages

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along with the maintenance concerns make mixed solvents less desirable than single solvent systems.

Common solvents with acetylated polyamide-6

An alternative method to the use of polar, high temperature solvents is to acetylate the amide group with trifluoroacetic anhydride, which destroys the crystallinity of the polyamide and facilitates dissolution in common solvents. This technique was developed originally by Schuttenberg and Schulz[13,14] and later extended by Biagini *et al.*[15] and Weisskopf[16,17]. All investigators of *N*-trifluoroacetylated polyamides claim nearly quantitative conversion with no polymer degradation as determined by infrared, viscometry and titration. However, Biagini *et al.*[15] cite significant differences in the MWD of polyamide-6 depending upon the degree of acetylation. Also, if the modified polyamide absorbs moisture via contact with a high humidity environment or wet solvents, hydrolysis occurs leading to an incorrect MWD via SEC. This necessitates rigorous drying of solvents and exclusion of atmospheric moisture from the polymer.

In some cases, the acetylated polyamides did not seem to follow the universal calibration (UC) concept, e.g. PS standards in $CHCl_3$[15]. Weisskopf[17] achieved better *MW* accuracy from broad dispersity acetylated polyamides standardized by light scattering and osmometry via the method of Weiss and Cohn-Ginsberg[18]. Here, the experimental chromatogram is fitted to the Schulz–Zimm[19,20] distribution, and peak retention volume is equated to the known $\bar{M}_w$ of the broad standard[21]. Weisskopf attributes the decrease in accuracy of the universal calibration to polar interactions of the $-COCF_3$ side groups and consequently uses his 'effective' calibration curve from the polydisperse samples. However, it is generally accepted that calibration with broad standards is useful only when the polydispersity of the sample approximates that of the standards due to the 'effective' nature of the calibration[22].

Fluorinated alcohols

The fluoroalcohols are attractive SEC solvents because of their ability to dissolve most polyamides at room temperature, their low to moderate viscosity and good spectral properties (low ultraviolet cutoff and low refractive index increment). Costa and Russo[23] have discussed several fluoroalcohols including trifluoroethanol, HFIP and 2,2,3,4,4,4-hexafluorobutanol (HFB) as potential solvents for polyamides. The HFB was synthesized and characterized with nylon-6 with respect to the Mark–Houwink constants, which show it to be a good solvent ($K' = 4.2 \times 10^{-4}$ dl g^{-1}, $a = 0.76$). It has a lower volatility than the other two fluoroalcohols, but no data as a SEC solvent were presented.

Hexafluoroisopropanol has been used as a SEC solvent[12,24] but required the addition of sodium trifluoroacetate to obtain a unimodal, Gaussian shaped peak for nylon-6,6. Without this salt, the chromatogram was bimodal, which was attributed by Drott[24] to the polyelectrolyte effect. This phenomenon occurs in low pK_a solutions where protonation of the amide nitrogen yields polymeric ammonium ions, causing intramolecular repulsion and expansion of the chain. The additive salt increases the ionic strength of the solution, electrically balancing the charged chain by replenishing the anions near the backbone. These additional ions suppress and counteract the osmotic forces which drive counterions away from the charged chain. This results in a return to normal chain conformation, which leads to predictable and reproducible fractionation and elimination of the bimodality.

However, HFIP is expensive (>US$1000 per litre), which necessitates solvent reclamation, and it should not be used with μ-Styragel because it does not swell the polystyrene-gel packing sufficiently, as evidenced by a column efficiency of only 1400 plates/(4)-column set[24]. The high cost of this solvent and poor performance with μ-Styragel columns are the main reasons why we consider TFEtOH a better SEC mobile phase for polyamide-6.

Since it was recognized early on that PMMA is soluble in TFEtOH, Provder *et al.*[25] developed a hydrodynamic volume calibration technique based on broad dispersity PMMA. This involved a series of transformations from PS standards in THF to broad MWD PMMA in TFEtOH based on the concept of equivalent hydrodynamic volumes (PS/THF to PMMA/THF to PMMA/TFEtOH). This procedure required clarification[26] because of its complexity, the need for more than one set of (K', a) values to describe the hydrodynamics of the various PMMA fractions and the fact that TFEtOH was used with Styragel columns, which results in false peaks and broadened chromatograms as reported by Dudley[2].

Matzner *et al.*[27] also used μ-Styragel columns (10^5–250 Å*) with TFEtOH but reported no 'false-peak' chromatograms. They did not show any calibration and their results via light scattering in TFEtOH for the molecular weights of both hydrolytic and anionic nylon-6 did not agree with their chromatogram peak retention volumes. Matzner's single peak chromatograms contradict Dudley's work and results obtained in our laboratory where multimodal, false peaks are seen for nylon-6 with μ-Styragel columns (10^4, 10^3, 500 Å) in TFEtOH.

In the work reported here, the aforementioned complications of calibration in TFEtOH have been obviated by using narrow MWD PMMA standards with the universal calibration to develop a new, simple and reproducible SEC system for nylon-6. The solution hydrodynamics of the PMMA fraction in TFEtOH at 30°C have been measured and are used to construct the nylon-6 calibration using literature values for the Mark–Houwink parameters of hydrolytic nylon-6 in TFEtOH. When combined with silanized silica columns, which eliminate the false, multimodal peaks and which show much better resolution than Styragel in TFEtOH, simple and reproducible analysis of nylon-6 with molecular weight accuracy, within 10% (i.e. <10% error) is achieved.

EXPERIMENTAL

Size exclusion chromatography

The nylon-6 HPSEC system is a home-made unit consisting of the following equipment: Altec 100A dual action positive displacement metering pump; (2) DuPont Zorbax® bimodal (60, 1000 Å) silanized silica columns; Waters Lambda Max 480 variable wavelength UV spectrophotometer; Waters R401 differential refractometer; and Rheodyne injector, model no. 7125.

The mobile phase is 2,2,2-trifluoroethanol (Aldrich, gold label 99+%) operated at a flow rate of 1.0 ml min^{-1} at room temperature. Injection volume is 100 μl with concentrations 0.3–0.4% w/v. Solvent was dried over

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* 1 Å = 10^{-10} m

molecular sieves to remove traces of moisture and then degassed and filtered through 0.5 μm filters. This gave good reproducibility and baseline stability.

Narrow MWD PMMA standards were purchased from the Pressure Chemical Co, ($M \geqslant 27\,\mathrm{kg\,mol^{-1}}$) and Polymer Standards Service, West Germany (low molecular weights, $M = 9$ and $17\,\mathrm{kg\,mol^{-1}}$). Polymer polydispersity varied from 1.06 to 1.15 as reported by the manufacturer (from supplementary data of $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_v$ from standard techniques as well as chromatograms supplied by Polymer Standards Service). Peak retention volumes were used and correlated with the reported peak molecular weight, M_p, which always fell between $\bar{M}_n$ and $\bar{M}_w$. The chromatography system has a theoretical plate count of 13 000 and chromatograms were integrated by in-house software.

Viscometry

The Mark–Houwink parameters for PMMA standards in TFEtOH were determined in a Ubbelohde No. 1 viscometer immersed in an oil bath maintained at $30 \pm 0.1°\mathrm{C}$. With dilute solutions, the kinetic energy correction (second term) in the Newtonian fluid mechanics analysis was neglected and the ratio of flow times ($t > 100\,\mathrm{s}$) was used to calculate the relative viscosity. A check for excessive wall shear rates was performed by calculating the β parameter, which shows positive deviation from unity for shear thinning conditions[28]. Its low value, as shown in the following equation for $M = 60\,\mathrm{kg\,mol^{-1}}$, implies first Newtonian regime, confirming the accuracy of flow time ratios:

$$\beta = \frac{100[\eta]M\eta_0|\gamma_w|}{RT} = 1.5 \times 10^{-3} \qquad (1)$$

where $[\eta]$ = intrinsic viscosity, η_0 = solvent viscosity, M = molecular weight, γ_w = wall shear rate ($\mathrm{s^{-1}}$), T = temperature (K) and the factor of 100 converts the CGS units to $\mathrm{dl\,g^{-1}}$.

Four PMMA fractions ranging in nominal molecular weight from 525 to $27\,\mathrm{kg\,mol^{-1}}$ were prepared at concentrations of $\approx 0.8\,\mathrm{g\,dl^{-1}}$ and slowly filtered through 0.5 μm filters. The polymer concentration after filtration was rechecked. A minimum of three timings were recorded for each concentration followed by successive dilution with filtered solvent to extend the measurements towards infinite dilution. Intrinsic viscosity was determined by least squares regression of both the inherent and the reduced viscosities as a function of concentration for each fraction. Agreement of the intercepts for each regression was within ±0.5–1.0%.

The Mark–Houwink parameters for nylon-6 in TFEtOH are available from several sources in the literature[29,30,31] and are shown in *Table 1*. The agreement between the K' and a values from the first two sources is good considering the known variability of molecular architecture in hydrolytic polyamides as a function of polymerization temperature and concentration of chain regulator as well as the varying extents of polymer fractionation and monomer extraction. The last sample obviously differs from the first two due to the lower molecular weight range, which causes a shift towards the 'free draining' molecule and a Mark–Houwink exponent of 1.0–1.1. The molecular weights used in our work are in the range $18–40\,\mathrm{kg\,mol^{-1}}$ and the best agreement of SEC molecular weight with other independent measurements (such as end group analysis or viscosity) is obtained with the K', a values from Mattiussi *et al.*[30].

Table 1 Summary of Mark–Houwink constants for nylon-6–TFEtOH at 25°C

M-H parameters				
$10^4K'$ ($\mathrm{dl\,g^{-1}}$)	a	Type nylon-6/T_{pzn} (°C)/$10^{-3}MW^a$	Technique^b	Ref.
4.58	0.742	H/NA/20–100	IV	29
5.36	0.75	H/180–280/13–100	IV, LS	30
0.97	1.0	H/230/1–4	EG	31

[a] H, hydrolytic nylon-6; T_{pzn} polymerization temperature; MW, molecular weight range ($\mathrm{kg\,mol^{-1}}$); NA, not available
[b] Independent technique of measuring MW: LS, light scattering; IV, intrinsic viscosity; EG, end group analysis

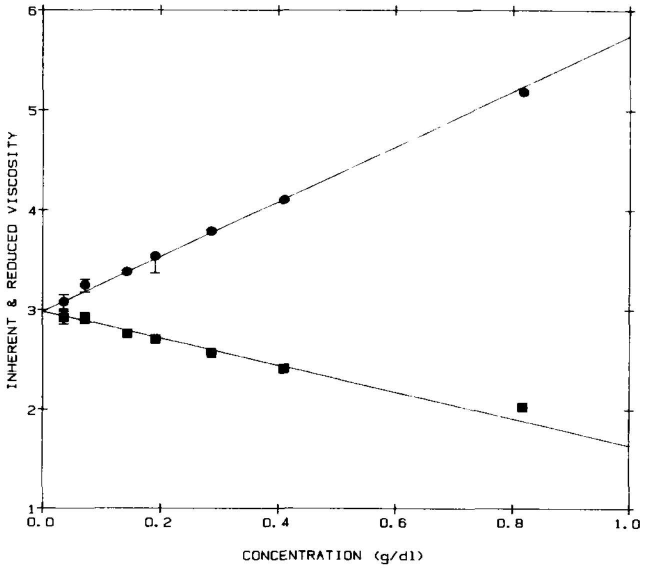

Figure 1 Intrinsic viscosity determination for one of the PMMA standards in TFEtOH at 30°C; $M = 525\,\mathrm{kg\,mol^{-1}}$. ●, reduced viscosity, $k' = 0.31$; ■, inherent viscosity, $k'' = -0.15$; $[\eta] = 2.98\,\mathrm{dl\,g^{-1}}$

Table 2 Intrinsic viscosity–molecular weight data for PMMA–TFEtOH at 30°C

		Slope constants	
Molecular weight ($\mathrm{kg\,mol^{-1}}$)	$[\eta]$ ($\mathrm{dl\,g^{-1}}$)	Huggins (k')	Kraemer ($-k''$)
27.0	0.228	0.48	0.06
63.0	0.422	0.42	0.10
179.0	1.135	0.42	0.11
525.0	2.980	0.31	0.15

RESULTS AND DISCUSSION

Viscometry

The inherent viscosity ($\ln \eta_r/c$) and reduced viscosity (η_{sp}/c) were plotted *versus* concentration for each PMMA fraction; *Figure 1* shows the plot for $M = 525\,\mathrm{kg\,mol^{-1}}$. The other three plots were similar and all four intrinsic viscosities are detailed in *Table 2*. The difference between the Huggins'[32] and Kraemer[33] constants in each of the trials is very close to the expected value of 0.50 (ref. 34), as shown in *Table 2*.

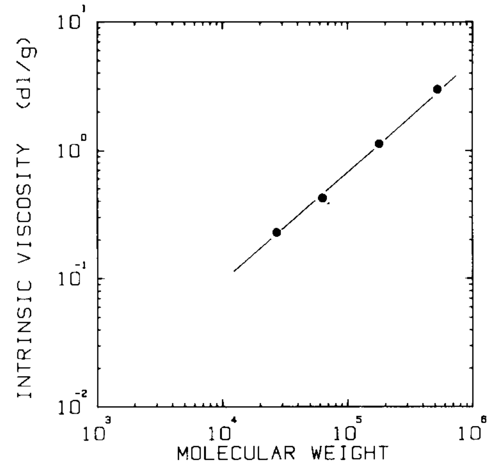

Figure 2 Mark–Houwink plot for the $[\eta]$ of PMMA in TFEtOH at 30°C as a function of molecular weight. The intercept and the slope give the constants K' and a, respectively: $K' = 2.81 \times 10^{-5}$; $a = 0.88 \pm 0.03$; $(r = 0.999)$

The Mark–Houwink parameters for PMMA in TFEtOH are determined by the relation

$$[\eta] = K'M^a \qquad (2)$$

as shown in the log–log plot of *Figure 2*. The Mark–Houwink parameters from the slope and the intercept are $K' = 2.81 \times 10^{-5}\,\mathrm{dl\,g^{-1}}$ and $a = 0.88 \pm 0.03$.

Universal calibration

The universal calibration, introduced by Benoit *et al.*[1] is based on separation by the macromolecular hydrodynamic radius (or volume) in size exclusion chromatography. At a given retention volume, V_R, the hydrodynamic size of a PMMA molecule and a nylon-6 molecule is the same and since this size is proportional to the product of molecular weight and intrinsic viscosity[35,36]

$$[\eta]_1 M_1 = [\eta]_2 M_2, \qquad V_R = \text{const.} \qquad (3)$$

where subscripts 1 and 2 refer to PMMA and nylon-6, respectively. Substituting the Mark–Houwink expressions (Equation (2)) for the intrinsic viscosities of both polymers and the peak molecular weight as a function of retention volume for PMMA (obtained from the PMMA calibration using the standards) into equation (3) yields the relation of nylon-6 *MW* as a function of retention volume:

$$M_2 = D_1 \exp(-D_2 V_R) \qquad (4)$$

where

$$D_1 = (K'_1/K'_2)^{1/(1+a_2)} D_1'^{(1+a_1)/(1+a_2)} = 5.4006 \times 10^9$$

and

$$D_2 = D_2'^{(1+a_1)/(1+a_2)} = 1.4602$$

The parameters D'_1 and D'_2 are the intercept and absolute value of the slope of the PMMA calibration curve. This method gave a very linear calibration curve (regression coefficient = 0.999) from $2\,\mathrm{kg\,mol^{-1}}$ to $250\,\mathrm{kg\,mol^{-1}}$ nylon-6 molecular weight.

Size exclusion chromatography

Two different types of nylon-6 were analysed: commercial hydrolytic nylon-6, Allied Chemical's Capron, which contains carboxyl and amine end groups; and Monsanto's RIM (reaction injection moulded) nylon-6 containing an acetyllactam (initiator) moiety and a terminal lactam ring. Chromatograms of these are shown in *Figure 3*, uncorrected for any dispersive behaviour.

To check the accuracy of the calculated nylon-6 molecular weights, independent *MW* determinations via end-group analysis and intrinsic viscosity were performed on Allied's hydrolytic nylon-6. The end group analysis gave an average (three trials), $\bar{M}_n$ of $20.2 \pm 0.36\,\mathrm{kg\,mol^{-1}}$, compared with $21.7\,\mathrm{kg\,mol^{-1}}$ via the SEC. The inherent and reduced viscosities were measured in the Ubbelohde No. 1 viscometer mentioned previously at 30°C and used to determine the intrinsic viscosity of Allied nylon-6 in TFEtOH as shown in *Figure 4*. From this, the viscosity average molecular weight, $\bar{M}_v$, was calculated to be $40.3\,\mathrm{kg\,mol^{-1}}$ using the (K', a) values of Mattiussi *et al.*, as compared with the SEC $\bar{M}_v$ of $37.0\,\mathrm{kg\,mol^{-1}}$. These results are accurate to within $\pm 10\%$ using the SEC system described here and offer, in our view, the best combination of simplicity and accuracy of any system available in the literature for the determination of nylon-6 molecular weight.

To illustrate the inaccuracies that can develop when μ-Styragel columns are used with TFEtOH, anionic nylon-6 synthesized in our laboratory was chromatographed on both 10^3, 10^4 Å μ-Styragel and DuPont ZSM Zorbax columns with TFEtOH at room temperature and a flow rate of $1.0\,\mathrm{ml\,min^{-1}}$. *Figure 5*, solid curve, shows the molecular weight distribution of the anionic nylon-6 as eluted from the Zorbax columns (the normal columns used in this work), which gives $\bar{M}_w = 47.3\,\mathrm{kg\,mol^{-1}}$ and $\bar{M}_n = 21.8\,\mathrm{kg\,mol^{-1}}$. In contrast, the same sample chromatographed with μ-Styragel columns produced the dashed curve of *Figure 5*, which shows the incorrect bimodal peak with highly inaccurate molecular weights due to an abnormal *MW* distribution. This result agrees with the comments of Dudley[2] and demonstrates that μ-Styragel should not be used with TFEtOH because of insufficient swelling of the styrene-gel packing, which can minimize operational pore volume and cause channelling leading to artificially high molecular weights and poor column performance.

The SEC results in *Figure 3* also indicate that the polydispersity of Monsanto's RIM nylon-6 (anionically synthesized) is comparable to that of Allied's hydrolytically produced nylon-6, both with $\bar{M}_w/\bar{M}_n \approx 1.8$. The applicability of the same SEC accuracy achieved with the hydrolytic nylon-6 to anionically synthesized nylon-6 can be substantiated by Tuzar *et al.*[37], who showed that the (K', a) parameters for the two types of nylon-6 are the

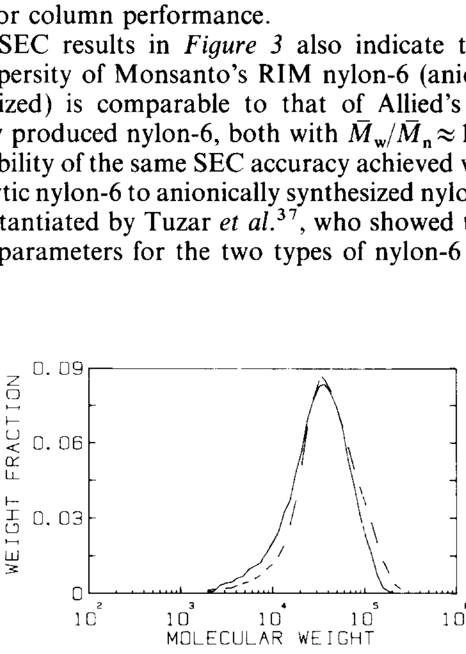

Figure 3 The actual uncorrected chromatograms of Allied Capron nylon-6 (——) and Monsanto's RIM nylon-6 (– – –) at 25°C and $Q = 1.0\,\mathrm{ml\,min^{-1}}$. Molecular weight averages ($\mathrm{kg\,mol^{-1}}$) as calculated from the SEC: ——, $M_w = 39.2$; $M_n = 21.7$; $M_v = 37.0$; – – –, $M_w = 49.0$; $M_n = 26.7$, $M_v = 46.0$

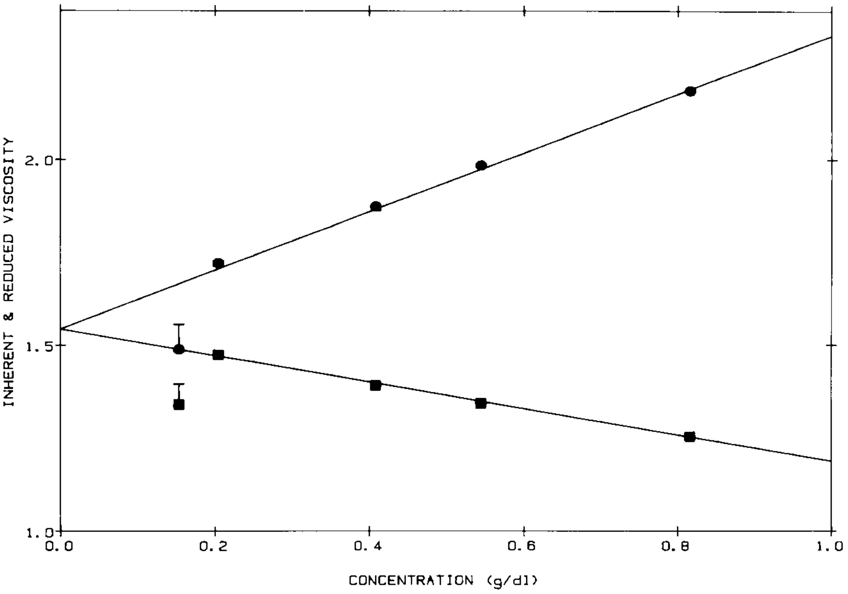

Figure 4 Determination of intrinsic viscosity of Allied Capron nylon-6 in TFEtOH at 30°C. ●, reduced viscosity, $k'=0.33$; ■, inherent viscosity, $k''=-0.15$; $[\eta]=1.525\,\mathrm{dl\,g^{-1}}$

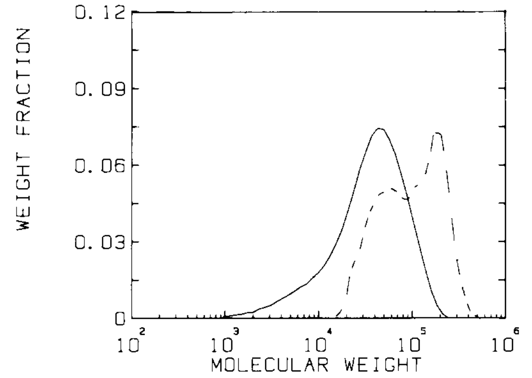

Figure 5 Comparison of nylon-6 anionically synthesized at 170°C as chromatographed in TFEtOH on silanized DuPont Zorbax columns (——) and 10^3, 10^4 Å μ-Styragel columns (- - -) $T=25°C$; $Q=1.0\,\mathrm{ml\,min^{-1}}$. Molecular weight averages ($\mathrm{kg\,mol^{-1}}$): ——, $M_w=46.9$: $M_n=19.7$; - - -, $M_w=119.3$; $M_n=69.8$

same in tetrafluoropropanol (TFP). Thus, if moderate synthesis temperatures are used to keep the anionic nylon-6 essentially linear, the two types of nylon-6 seem to be indistinguishable and to adopt essentially the same conformation in solution.

Although the polyelectrolyte effect has been demonstrated in 2,2,3,3-tetrafluoropropanol[38], its presence in TFEtOH has not been confirmed. Matzner *et al.*[27] performed light scattering in TFEtOH without observation of this effect and Mattiussi *et al.*[30] attributed the larger unperturbed dimension of nylon-6 in TFEtOH than in HCOOH or *m*-cresol to strong polymer–solvent (1–2) interactions rather than the polyelectrolyte effect (see the Appendix for a further discussion of nylon-6 hydrodynamics in TFEtOH). Our observations substantiate these viewpoints as well. The acidity of TFEtOH is simply not sufficient to protonate the amide group substantially, causing widespread polarization and expansion of the polyamide chain; the K_a of TFEtOH is $O(\sim 10^{-13})^{27}$, compared with K_a of strong acids such as HCOOH or H_2SO_4 of $O(\sim 10^{-2}$–$10^{-5})$. In addition, the deviation from linearity of the reduced viscosity at low concentrations in the presence of the polyelectrolyte effect is positive[38] (i.e. η_{sp}/c increases with decreasing concentration), whereas our observed nonlinear effect with Allied nylon-6 is negative, as seen in *Figure 4* below concentrations of $\sim 0.2\,\mathrm{g\,dl^{-1}}$. This implies that the bimodality of the nylon-6 in TFEtOH with μ-Styragel columns is caused simply by the poor resolution due to the solvent-packing incompatibility and not by a change in the true hydrodynamic volume of the polyamide-6 in TFEtOH due to the polyelectrolyte effect.

CONCLUSIONS

A new, accurate and simple SEC system has been developed for the analysis of the MWD of nylon-6 based on proven and accepted principles of polymeric hydrodynamics. The method combines the utility of silanized silica columns and the solubility of PMMA standards in TFEtOH mobile phase to yield molecular weight accuracy within 10% via the universal calibration. Although the molecular weight accuracy was proven with hydrolytic nylon-6, the system will give accurate molecular weight values of anionic nylon-6 as well, provided the polymer is essentially linear (synthesized at moderate polymerization temperatures). The system is easy to operate, calibrate and maintain and offers the best combination of advantages over any other current SEC system for nylon-6.

The hydrodynamics of PMMA in TFEtOH have been determined (see Appendix) via viscosity relationships which show a much more compact conformation for PMMA than for nylon-6 in TFEtOH for equivalent molecular weights. The universal calibration has satisfactorily related the sizes of the two polymers in solution to give a very linear calibration over two and a half decades of nylon-6 molecular weight. This calibration gives accurate molecular weights without the need for the dispersive corrections which are necessary for other systems used in the SEC of polyamides. It is this advantage that makes this SEC system particularly useful for both routine analyses and on-line molecular weight analysis during synthesis.

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APPENDIX

In the course of calculating the hydrodynamic volume of PMMA for the universal calibration, the solution thermodynamics of PMMA and nylon-6 in TFEtOH were investigated with respect to several existing theories.

Solution thermodynamics

PMMA–TFEtOH. The Flory[39] expression for intrinsic viscosity

$$[\eta] = KM^{1/2}\alpha_\eta^3 \tag{5}$$

where

$$K = \Phi_0(\overline{r_0^2}/M)^{3/2} \tag{6}$$

M is the molecular weight and α_η the viscosity expansion factor, is valid for all random coil macromolecules of molecular weight $\gtrsim 10\,\mathrm{kg\,mol^{-1}}$. The constant K contains the product of the unperturbed root-mean-square (r.m.s.) end-to-end distance divided by the molecular weight, $(\overline{r_0^2}/M)^{3/2}$ and a universal constant, $\Phi_0 \approx 2.5 \times 10^{21}$ (Reference 40). From this relationship, Flory *et al.*[41] predicted the polymer–solvent interaction parameter, χ_{12}, and unperturbed dimension $(\overline{r_0^2}/M)^{1/2}$ from $[\eta]$–M data as shown in the following equation:

$$\frac{[\eta]^{2/3}}{M^{1/3}} = 2C_m(1-2\chi_{12})K^{5/3}\frac{M}{[\eta]} + K^{2/3} \tag{7}$$

where

$$C_m = \left[\frac{3}{(2\pi)^{1/2}}\right]^3 \frac{v_2^2}{N_A V_1}\left(\frac{\overline{r_0^2}}{M}\right)^{-3/2} \tag{8}$$

with v_2 the specific volume of the polymer, V_1 the molar volume of the solvent and N_A Avogadro's number, 6.023×10^{23}. However, the $[\eta]$–M data for PMMA–TFEtOH do not follow the mathematical form of the Flory–Fox–Schaefgen Equation (7). The fit is poor, with a regression coefficient of 0.88, and yields a negative intercept, which is physically unrealistic. This result may arise if the unperturbed dimension depends significantly on short-range polymer–solvent interactions, which has been observed for polar solvent–polymer systems such as hexene-1-polysulphone in methyl ethyl ketone/isopropanol mixtures[42]. This polar theta-solvent mixture

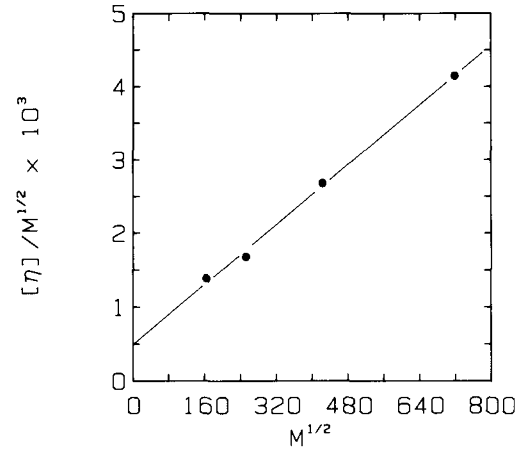

Figure 6 Use of the Stockmayer–Fixman theory to represent the $[\eta]$–M relationship of PMMA–TFEtOH. The slope is proportional to the polymer–solvent interaction parameter χ_{12}, which equals 0.38, and the intercept gives the unperturbed dimension, $(\overline{r_0^2}/M)^{1/2} = 0.595$ Å $(\text{g mol}^{-1})^{-1/2}$; $(r = 0.998)$

decreases the 'unperturbed' dimension by 20–25% compared to less polar, n-hexylchloride, also a θ solvent.

An alternative viscosity theory that better represents polymer hydrodynamics in good solvents is that of Stockmayer and Fixman[43]:

$$[\eta] = KM^{1/2} + 0.51\Phi_0 BM \qquad (9)$$

where $B = v_2^2(1 - 2\chi_{12})/V_1 N_A$ with the other nomenclature as previously defined. The data for the PMMA–TFEtOH system are plotted in accordance with the Stockmayer–Fixman (S–F) theory in *Figure 6*. Good linear regression is obtained and the unperturbed chain end dimension, $(\overline{r_0^2}/M)^{1/2}$ is equal to 0.595 Å $(\text{g mol}^{-1})^{-1/2}$, in excellent agreement with Kriste's[44] and Fox's[45] identical value of 0.61 Å $(\text{g mol}^{-1})^{-1/2}$ for PMMA in 50/50 v/v butanone/propanol at 22.5°C, a θ-solvent as reported by the former and an average of various θ-solvents ranging in θ-temperatures from 30 to 70°C in the case of the latter investigator. From the slope of our plot the polymer–solvent interaction parameter is calculated to be 0.38.

Nylon-6–TFEtOH

The intrinsic viscosity–molecular weight data of Mattiussi *et al.*[30] for nylon-6–TFEtOH give a slightly larger unperturbed dimension at 25°C in TFEtOH of $(\overline{r_0^2}/M)^{1/2} = 1.108$ Å $(\text{g mol}^{-1})^{-1/2}$ compared with 0.971 Å $(\text{g mol}^{-1})^{-1/2}$ in 85% formic acid. This expansion of the unperturbed dimension from the S–F theory has also been observed for nylon-6 in other fluorinated alcohols: $(\overline{r_0^2}/M)^{1/2} = 1.09$ Å $(\text{g mol}^{-1})^{-1/2}$ at 25°C in Perfluoroalcohol P-1 (a commercial tradename), which is close to tetrafluoropropanol in material properties[46]. This contrasts with the random-coil unperturbed dimensions of nylon-6 in HCOOH[30], *m*-cresol[47] or TFP–H_2O–LiCl[48], which are all equivalent and approximately 25% smaller than $(\overline{r_0^2}/M)^{1/2}$ in the two fluoroalcohols. This 'stiffening effect' plus the fact that TFEtOH is a better solvent for nylon-6 ($\chi_{12} = 0.09$, Reference 30) than for PMMA ($\chi_{12} = 0.38$, this work) explains why the hydrodynamic volume of nylon-6 is much greater than PMMA in TFEtOH for equivalent molecular weight.