Size-exclusion chromatography in 1,1,1,3,3,3-hexafluoro-2-propanol

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Abstract

1,1,1,3,3,3-Hexafluoroisopropanol is re-examined as an eluent for size-exclusion chromatography (SEC) of polyesters, nylons, and other polar polymers. It is shown that anomalous SEC behavior reported in previous literature can be eliminated by adding 0.01 M tetraethylammonium nitrate to the eluent. The eluent modifier does not affect the solution viscosity or root-mean-square radii of moderately polar polymers such as polyesters and nylons, but it does decrease these quantities for more polar polymers such as poly(ethylene oxide) and poly(2-vinylpyridine). More important, this salt appears to minimize repulsive interactions with styrene–divinylbenzene column packings that have contributed to non-ideal size-exclusion behavior. As a result, conditions are established that satisfy universal calibration.   © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

1,1,1,3,3,3-Hexafluoro-2-propanol, also known as hexafluoroisopropanol (HFIP), is a common eluent for size-exclusion chromatography (SEC) of crystalline polyesters such as poly(ethylene terephthalate) (PET) and nylons. It dissolves most of these polymers at room temperature or with mild heating, and is normally modified with low concentrations of sodium trifluoroacetate (NaTFA) to suppress chromatographic artifacts such as prepeaks and early elution. HFIP dissolves a wider variety of polyesters and nylons than 2,2,2-trifluoroethanol (TFE) and has lower viscosity [1], making it more popular than the

latter for SEC despite being expensive and a severe eye irritant. Also, most polymers have large specific refractive index increments because of the low refractive index of HFIP ($n_D = 1.275$ at 25 °C), making it a particularly attractive solvent for light-scattering detection (LS).

The role of NaTFA, or other supporting electrolyte in SEC using HFIP or TFE, is vague. It appears in some applications but not in others, and explanations of its function are contradictory. For example, Provder et al. [2] did not use a supporting electrolyte in his early work with TFE for nylon analysis on Styragel columns, nor did Slagowski et al. [3] with HFIP for poly(tetramethylene terephthalate). Neither reported anomalous SEC behavior. In 1977, Drott [4,5] reported prepeaks for nylons in HFIP on porous glass and μ-Styragel columns that disappeared with sodium trifluoroacetetate (NaTFA). There was no

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dependence of nylon 6,6 chromatograms between 0.008 M and 0.01 M NaTFA, and it was suggested that the hygroscopic NaTFA immobilized water in HFIP and prevented it from acting as an ionizing solvent. Drott also stated that the 0.01 M NaTFA concentration was higher than necessary to neutralize polymer–solvent interactions, and that ''Other salts were not investigated since NaTFA proved successful in the GPC separations.''

Later work provides additional observations about NaTFA in fluorinated alcohol eluents. Schorn et al. [6] observed that HFIP without NaTFA showed less particulate spiking in light-scattering chromatograms of nylon 6 obtained on LiChrospher silica compared to chromatograms obtained with 0.005 M NaTFA. Berkowitz [7] estimated Mark–Houwink parameters for PET in HFIP by an iterative procedure using the whole polymer intrinsic viscosity, and a light-scattering molecular mass (M) at each retention volume. SEC was on DuPont silica-based columns, with no supporting electrolyte, and viscosity and light-scattering measurements were made without salt, all with no mention of prepeaks or SEC artifacts. Wang and Rivard [8] used 0.05 M LiBr instead of NaTFA in 2,2,2-TFE for nylons to supposedly break aggregates, and further suggested that blockage of the column surface active sites by LiBr also helped reduce column–solute interactions. Veith and Cohen [9] used silanized silica columns with TFE for nylon 6. They suggested that bimodal peaks observed with Styragel columns were from poor resolution caused by solvent-packing incompatibility and not by changes in the hydrodynamic volume of the nylon 6 in TFE from a polyelectrolyte effect. Deviations in Huggins Kraemer plots also were not consistent with polyelectrolyte effects. Mori calibrated with poly-(methylmethacrylate) (PMMA) in tetrahydrofuran and HFIP to produce a PET calibration curve [10] and later referred to the disintegration of nylon aggregates through osmotic diffusion of NaTFA ions and by breaking hydrogen bonding [11], similar to comments of Wang and Rivard. He reported an increase in retention volumes of high-molecular-mass PMMA standards with addition of NaTFA, and a decrease in retention volumes of the low-molecular-mass PMMA standards. Peak widths of PMMA also became more narrow, possibly a consequence of a steeper log M calibration curve. A nylon prepeak in pure HFIP did not disappear even after allowing the sample to sit 10 days, but a prepeak for PMMA disappeared by heating the sample or by allowing it to sit 10 days.

Remsen [12] used HFIP to obtain SEC low-angle laser light scattering (LALLS) chromatograms of poly(vinyl butyral) without aggregates commonly seen in other solvents. NaTFA at 0.08% was used with Zorbax bimodal columns, but the effect of salt was not part of the investigation. Large second virial coefficients were reported for PMMA and poly-(vinylbutyral) in HFIP.

Jackson et al. [13] showed a decrease in the SEC distribution coefficients and a small reduction in intrinsic viscosities of nylons on styrene–divinylbenzene columns with increasing NaTFA concentration, up to 0.012 M. The SEC distribution coefficient also decreased with increasing water concentration between 0 and 0.06% while the intrinsic viscosity decreased only slightly as a function of water concentration. The suggestion was made that chromatographic adsorption occurs at >0.03% water. Additional work showed that SEC chromatograms were affected by the presence of amine and carboxylic acid end-groups in nylons [14].

Most recently, Moroni and Havard [15] used HFIP without NaTFA in the eluent, but did add it to the sample solvent. Columns were Polymer Laboratories PL HFIPgel and PLgel Mixed-C. SEC with LS and differential viscometry (DV) detection indicated that universal calibration was not obeyed for PET, poly-(ethylene oxide) (PEO), PMMA and nylon 6. No mention is made of prepeaks, although chromatograms of PET (M=63,500) have a high-molecular-mass shoulder that could be a prepeak or material that elutes near the exclusion limit of the column. This is the most extensive set of viscosity–molecular mass relationships for a variety of polymers measured by SEC–DV detection.

Several questions arise from the literature. A satisfactory explanation has not been given why some investigators report SEC 'aggregate' prepeaks in SEC using HFIP and TFE while others do not, and why NaTFA eliminates them when they are observed. Some confusion arises from trying to compare SEC in HFIP or TFE on different SEC columns, although most of the literature suggests that better results are obtained with silica or polar packings than

with styrene–divinylbenzene columns. It is puzzling, however, how some workers could obtain static light-scattering data in HFIP [7] without NaTFA if molecular aggregates were indeed present. There is little doubt that both water and NaTFA affect chromatographic retention [13], but the reasons why and the optimum concentrations of each are not obvious. In fact, it is not even obvious why NaTFA was chosen in the first place to suppress SEC anomalies in fluorinated alcohols; the choice is not discussed by Drott, who appears to be the originator of NaTFA addition to HFIP eluents. Recent data [16] indicate that potassium and ammonium trifluoroacetate increase SEC retention volumes of nylons on diol columns more than NaTFA, but probably do not provide suitable conditions for universal calibration. Likewise, SEC–viscometry–light-scattering data [15] and round-robin results on nylons [17] question whether universal calibration applies in HFIP. Considering the inconsistencies and contradictions in the literature, the common practice of converting equivalent molecular masses to absolute values using Mark–Houwink constants, and the use of viscometry detection to calculate molecular masses through the Universal Calibration curve should also be questioned.

Thus, reproducible SEC in HFIP, on conventional columns with the application of Universal Calibration, is our primary objective. This requires the elimination of SEC artifacts such as prepeaks and early elution, and an established relationship between polymer solution dimensions and SEC elution times. For this, we demonstrate the benefits of using tetraethylammonium nitrate as an eluent modifier, and provide examples of the successful application of universal calibration in HFIP on styrene–divinylbenzene columns.

2. Experimental

HFIP (Lancaster Chemical, Pelham, NH, USA) with >99% purity claimed by the manufacturer was distilled over Type 3A molecular sieve, collecting the fraction boiling at 59 °C. Major impurities identified by GC–MS included water and perfluorobutanol at concentrations less than 1%. Tetraethylammonium nitrate (TEAN) was obtained from

Acros Organics (Geel, Belgium); sodium trifluoroacetate from Sigma (St. Louis, MO, USA); sodium acetate from Aldrich (Milwaukee, WI, USA). PMMA narrow standards were obtained from Polymer Labs (Amherst, MA, USA). Poly(2-vinylpyridine) (P2VP) narrow standards, PEO narrow standards and nylon 6,6 were obtained from American Polymer Labs (Mentor, OH, USA). PET was obtained from Eastman (Kingsport, TN, USA). The nylon 6,6 [18] and PET [19] samples were characterized by us previously using SEC-light- scattering in methylene chloride–dichloroacetic acid.

The SEC system consisted of a Waters (Milford, MA, USA) M590 pump, Hewlett-Packard (Agilent, Avondale, PA, USA) 79855A autosampler, Kratos Spectroflow (Perkin-Elmer, Shelton, CT, USA) 757 UV absorbance detector, Precision Detectors (Franklin, MA, USA) PD2020 LS detector, Viscotek (Porter, TX, USA) H502A DV detector, and a Waters 410 differential refractive index (DRI) detector. The DV and DRI detectors were thermostated at 40.0 °C, and the UV and LS detectors were operated at ambient conditions. The detectors were connected in the order UV, LS, DV and DRI. Columns were either two Polymer Labs 250 mm×4.6 mm HFIPGel or one Polymer Labs 300 mm×7.5 mm PLGel mixed-C, thermostated at 45.0 °C. The nominal eluent flow-rate was 0.3 ml/min for the HFIPGel columns and 0.4 ml/min for the PLGel Mixed-C column. Samples were injected in a volume of 50 µl. Narrow standards were injected at concentrations between 3.0 mg/ml (lowest molecular mass standards) and 0.02 mg/ml (highest molecular mass standards). High-molecular-mass PEO and P2VP standards are sparingly soluble and require mild heating and shaking in the eluent for several hours. PET and nylon sample concentrations were 1.0 mg/ml. Flow rate corrections were made using the retention volume of a negative system peak in the DRI chromatogram. Specific refractive index increments dn/dc (PMMA)=0.191 and dn/dc (PET)=0.257 were used for light-scattering, calculated by extrapolating from values given by Berkowitz [7] to 800 nm. The specific refractive index of nylon 6,6 dn/dc=0.240 was measured from the area under the DRI chromatogram using PET as a reference material of known dn/dc.

Precaution: HFIP should be used only by ex-

perienced operators trained in the safe handling and chromatographic application of a severe eye irritant. A designated fume hood that prevents exposure to vapors, a full face shield, and protective gloves and clothing are strongly recommended. Refer to Materials Safety Data Sheets for further information.

3. Results

A comparison of narrow standard calibration curves on two HFIPGel columns using 0.00735 M NaTFA and 0.01 M TEAN are shown in Fig. 1. These columns are made of styrene–divinylbenzene resins by a method that creates a distribution of pore sizes within each packing particle, and are recommended for HFIP chromatography. Excessive particulate spiking was observed in light-scattering chromatograms with NaTFA, similar to the observations of Schorn et al. [6] on silica columns, while few spikes were observed with TEAN. Retention volumes of all standards are less for NaTFA eluent than for the TEAN eluent, and the shapes of PEO and P2VP calibration curves using NaTFA are nonlinear with several high-molecular-mass standards eluting near the column exclusion limit. Similar results were obtained for a single PLGel mixed-C column, which is also made from styrene–divinylbenzene, but contains a mixture of particles with different pore sizes. Both columns were used by Moroni and Havard [15] with pure HFIP as the

eluent and NaTFA in the sample solvent. They obtained calibration curves similar to ours in HFIP with 0.00735 M NaTFA.

The shapes of the NaTFA calibration curves in Fig. 1 usually indicate polymer conformation changes such as a polyelectrolyte effect, aggregation or ion exclusion from the porous media. The common solution for all cases is to increase the concentration of salt. This is not possible with NaTFA, which dissolves at concentrations of 0.00735 M only with continuous stirring for several hours. Sodium acetate is more soluble in HFIP, readily permitting solution concentrations up to 0.1 M. We observed no differences in retention times or peak shapes of narrow standards, PET and nylon 6,6 with 0.00735 M NaTFA and 0.00735 M sodium acetate, but obtained a considerable reduction of particulate spikes in light-scattering chromatograms with the more soluble sodium acetate. Figs. 2–4 indicate that increasing sodium acetate concentration from 0.05 M to 0.1 M increases retention times, but not to the extent of TEAN, particularly for PEO and P2VP.

There is no appreciable dependence of PMMA, PEO, P2VP, PET or nylon 6,6 retention on TEAN concentrations between 0.01 M and 0.1 M. Chromatograms are shown for PET in Figs. 5 and 6. This example is presented because of a 'prepeak' that is most obvious in the light-scattering chromatograms in Fig. 6 because of the sensitivity of this detector to highest molecular mass molecules. Comparison with
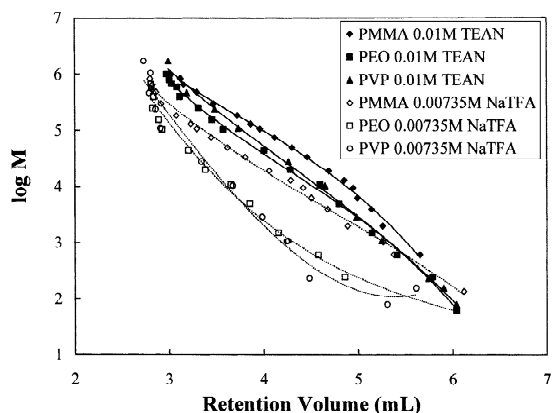
Fig. 1. Narrow standard molecular mass calibration curves, two 250 mm×4.6 mm HFIPGel columns.
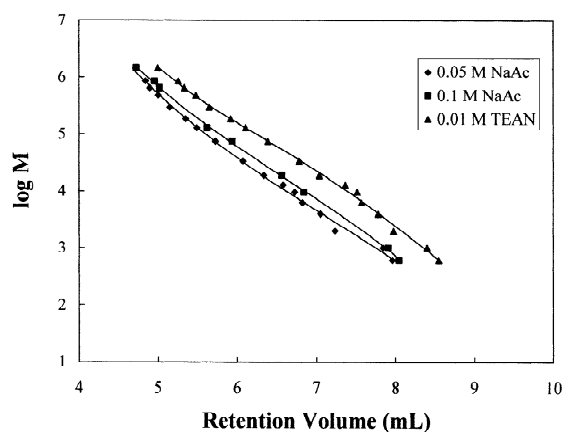
Fig. 2. PMMA narrow standard molecular mass calibration curves, one PLGel 300 mm×7.5 mm Mixed-C column. NaAc is sodium acetate.
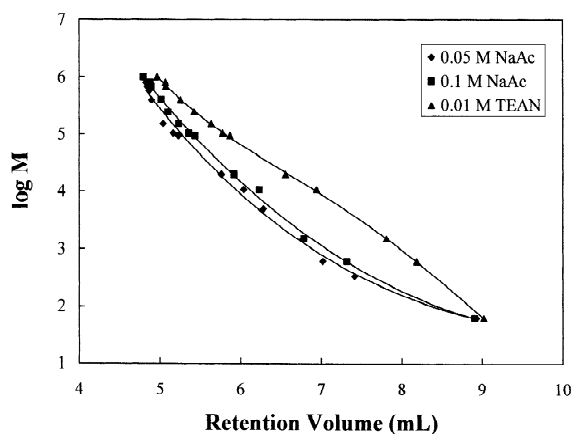
Fig. 3. PEO narrow standard molecular mass calibration curves, one PLGel 300 mm×7.5 mm Mixed-C column.

the calibration curves in Fig. 1 indicates that this 'prepeak' appears in a region near the column exclusion limit, and is probably totally excluded polymer rather than aggregates. Changing to the PLGel mixed-C column, which has a higher column exclusion limit (Fig. 7), reduces but does not completely eliminate the excluded fraction.

Molecular mass calibration curves for PMMA, PET and nylon 6,6 shown in Fig. 8 indicate that these polymers have different size and mass relationships in HFIP with TEAN. Universal calibration curves are shown in Fig. 9. Apart from small deviations at very high and very low molecular
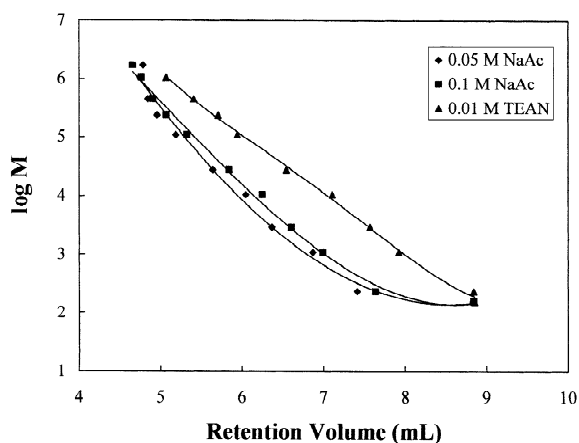

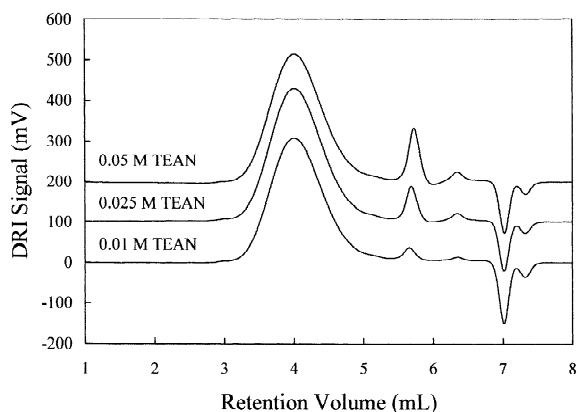Fig. 4. P2VP narrow standard molecular mass calibration curves, one PLGel 300 mm×7.5 mm Mixed-C column.

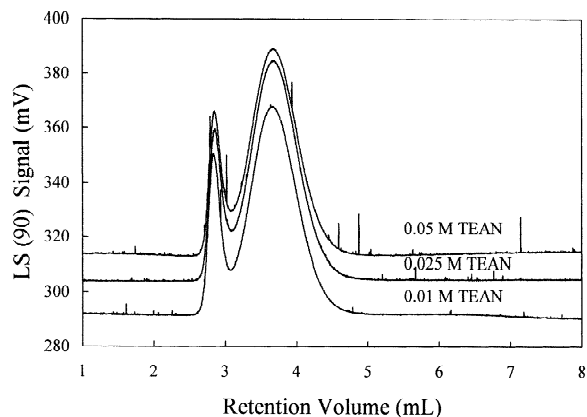Fig. 5. PET DRI chromatograms for different concentrations of TEAN, two 250 mm×4.6 mm HFIPGel columns.

Fig. 6. PET 90 degree LS chromatograms for different concentrations of TEAN, two 250 mm×4.6 mm HFIPGel columns.

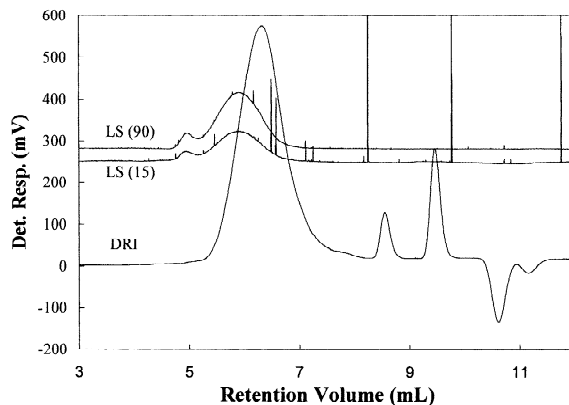

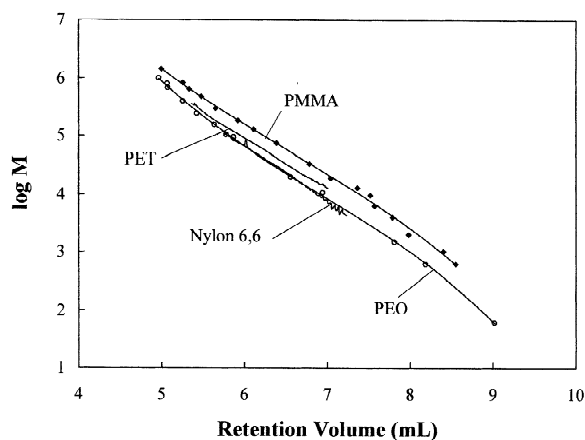Fig. 7. PET DRI, 15 degree and 90 degree LS chromatograms, one PLGel 300 mm×7.5 Mixed-C column.

Fig. 8. Molecular mass calibration curves for PMMA and PEO narrow standards and PET and nylon 6,6 measured by LS detection, one PLGel 300 mm×7.5 mm Mixed-C column.

Fig. 10. Mark–Houwink plot using M_w measured by LS detection and $[\eta]$ from viscometry detection.

masses, the superposition of the curves is acceptable, considering the uncertainty introduced by the small total column volume of a single SEC column. Mark–Houwink constants estimated from the linear portions of data in Fig. 10 are tabulated in Table 1. Universal Calibration curves constructed using intrinsic viscosities calculated from literature values of Mark–Houwink constants K and a given in Table 1 are shown in Fig. 11. The superposition of PET, nylon 6,6 and PMMA curves (Fig. 11) is obtained
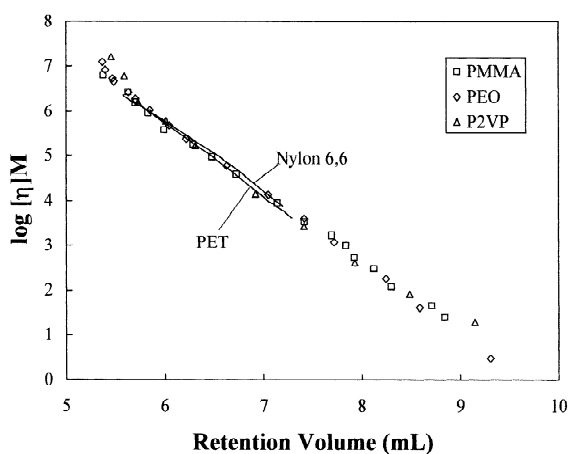
for K and a constants taken from multiple literature references (given in Table 1), all measured in pure HFIP. The data indicate that the intrinsic viscosity, and therefore the hydrodynamic radii, of these polymers is independent of the type or amount of salt. PEO is an exception using the constants of Moroni and Havard [15], falling off the other universal calibration curves.

The root-mean-square radii (R_g) estimated from the ratio of 15 degree and 90 degree excess Raleigh factors, assuming a random coil particle scattering function [20,21], for several narrow standards as a function of molecular mass (conformation plots) are plotted in Figs. 12–14. The measurable size range of the 800 nm light source is limited to polymer

Fig. 9. Universal Calibration curves using M_w from LS detection and $[\eta]$ from viscometry detection. One PLGel 300 mm×7.5 mm Mixed-C column.
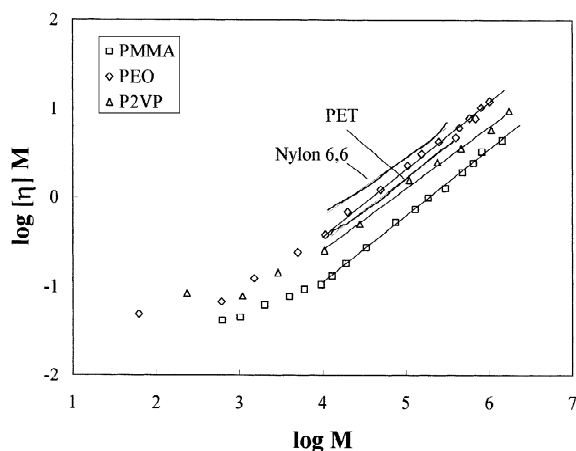
Table 1
Mark–Houwink Constants in HFIP

Sample	HFIP–0.01 M TEAN (this work[a])		HFIP (literature)		Ref.
	$K \times 10^3$	a	$K \times 10^3$	a	
PMMA	0.115	0.746	0.06	0.80	[15]
PEO	0.525	0.722	0.51	0.92	[15]
P2VP	0.438	0.692			
PET	0.411	0.721	0.13	0.83	[15]
			0.52	0.695	[7]
nylon 6,6	1.236	0.673	1.98	0.63	[34]

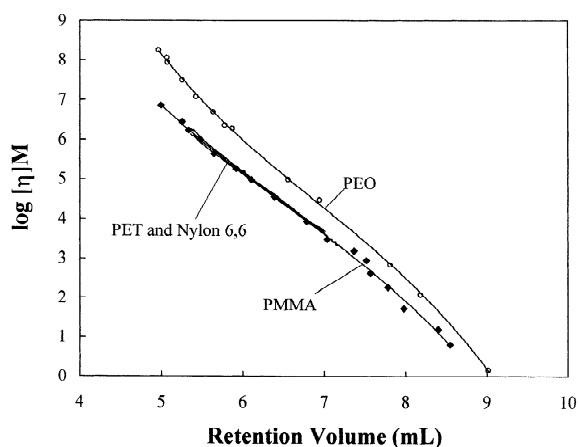[a] K and a values for molecular masses greater than 10 000.

Fig. 11. Universal calibration curves for PMMA, PEO, P2VP narrow standards, PET and nylon 6,6 measured by LS detection; one PLGel 300 mm×7.5 mm Mixed-C column, HFIP containing 0.01 M TEAN. Viscosity values were calculated from literature K and a values of Table 1.

molecules approximately $R_g > 20$ nm, and the quality of data in HFIP containing NaTFA is poor because of excessive particulate spiking. Slopes of the plots are close to the theoretical prediction of 0.58 for a linear random coil polymer, although the number of data points limits the accuracy of slope measurements. More important, there are only small differences in PMMA radii with various types and concentrations of salts. Also included in Fig. 12 are R_g values for PMMA in pure HFIP estimated from the
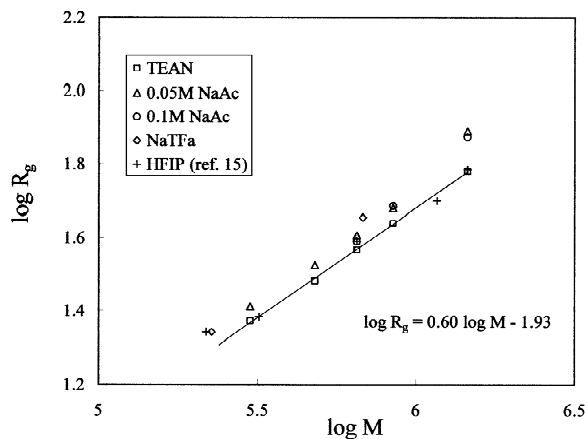

Fig. 13. PEO conformation plot.

data of Moroni and Havard [15]. In contrast, radii of PEO (Fig. 13) and P2VP (Fig. 14) are smallest in TEAN and decrease with increasing NaTFA and sodium acetate concentration.

4. Discussion

The use of NaTFA as a supporting electrolyte in the solution characterization of nylons began as long ago as 1959 with Beachell and Carlson [22] who observed that the salt eliminated an increase in specific viscosity with decreasing nylon concentration in 2,2,3,3-tetrafluoropropanol. They attributed

Fig. 12. PMMA conformation plot.

Fig. 14. P2VP conformation plot.

the result to a polyelectrolyte effect. A reason was not given for the choice of NaTFA, but it was likely because the low refractive index of NaTFA 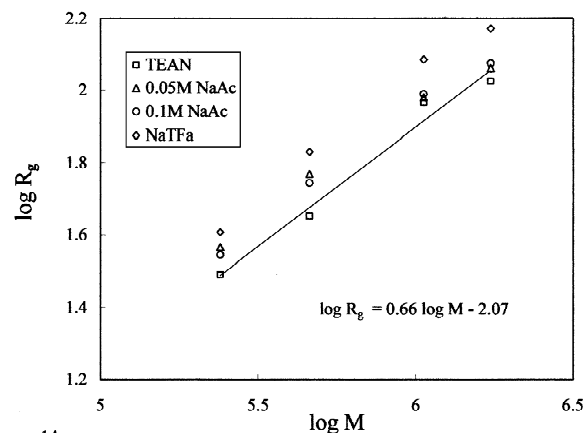made it better suited for light-scattering experiments in the low-refractive-index fluorinated alcohol. Saunders [23] later claimed that the role of NaTFA was to immobilize water molecules in 2,2,3,3-tetrafluoro-propanol rather than to act as an electrostatic screen for nylon 6,6 because there was no observable dependence of viscosity on salt concentration and NMR indicated that the alcohol proton was readily exchangeable. We suspect that Drott's original choice of NaTFA as an eluent modifier for SEC in HFIP was influenced by these early light-scattering and viscosity studies in tetrafluoropropanol because his explanation of the function of NaTFA in eliminating SEC prepeaks was essentially the water immobilization argument given by Saunders. Thereafter, the addition of NaTFA to HFIP apparently became a precautionary step in most SEC applications using fluorinated alcohol eluents.

However, it has not been shown if polymers indeed undergo conformational changes in HFIP with addition of NaTFA or if aggregates exist in the solvent. Successful light-scattering and viscosity experiments have been conducted in pure HFIP on nylon 11 [24] and PET [7], and photon correlation spectroscopy showed that NaTFA has no affect on the hydrodynamic radius of PET in HFIP [25]. These polymers do, however, exhibit SEC prepeaks, which have sometimes been attributed to aggregates, although none of the static dilute solution characterization supports aggregation or conformational changes with addition of salt. Consistent with these results, our R_g data indicate that PMMA does not change size appreciably with addition of any of the salts examined. The root-mean-square radii of PET and nylon samples in this work are too small for us to measure accurately by light-scattering at 800 nm, but the intrinsic viscosity data of Moroni and Havard [15] in pure HFIP and the results of Jackson et al. [13] at various concentrations of NaTFA indicate only small decreases in hydrodynamic radii of PET and nylons with increasing salt concentration. On the other hand, PEO and P2VP are highly expanded in HFIP with NaTFA and sodium acetate, presumably because of hindered polymer backbone rotations that result from strong hydrogen bonding of HFIP to the ether oxygen of PEO and aromatic amine nitrogen of

P2VP. The considerable reductions in R_g upon addition of TEAN suggest that the salt disrupts this hydrogen bonding to some extent, resulting in a less rigid and extended polymer coil.

HFIP is a solvent of surprisingly high ionizing power and low nucleophility [26]. It extensively solvates anions, poorly solvates cations and does not easily autoprotolyze [27]. With $pK_a = 9.3$ in water [28], it is possibly capable of protonating certain polyanilines [29], but is too weak an acid to proto-nate most esters, amides, ethers, or even P2VP. It chemisorbs to silica surfaces without dissociation, with the possible formation of small amounts of alkoxy species [30]. Given these properties and the results observed with TEAN, some previous SEC observations may be put in perspective.

The lack of dependence of retention on TEAN concentration argues against an appreciable polyelec-trolyte effect causing early elution of the polymers examined in pure HFIP or HFIP with NaTFA. Increasing salt concentration normally reduces poly-electrolyte sizes and increases SEC elution times. Apart from the possible dissociation of carboxylic acid end-groups or protonation of amine end-groups on some nylons, formal charges should not develop on any of the polymers examined. Also, the extent of early elution is too large to be accounted for by only changes in the radii of polymers with various amounts and types of salts. Similar observations were made with polyacrylonitrile in N,N-dimethyl-formamide (DMF) [31], to which LiBr is commonly added to suppress prepeaks and early elution. In the case of DMF, it was proposed that the peculiar SEC behavior was at least partially caused by the exist-ence of 'substances' in the column packing [32], implying some form of ion-exclusion or repulsion. A similar argument is justified for a repulsive inter-action between some polymers and styrene–di-vinylbenzene packing surfaces in HFIP.

Although not capable of protonating polar groups in the polymers studied here, HFIP strongly hydro-gen bonds with these functional groups, increasing the dipole moment of HFIP molecules that solvate the polymer. These strongly bonded and oriented solvent molecules limit chain rotation and create extended chain conformations, resulting in high solution viscosities and large radii of gyration. HFIP is a non-solvent for polystyrene, and the solvent molecules will orient with the hexafluoro-portion of

the HFIP molecules in preferential contact with the polystyrene surface, creating a strong, oriented dipole on the packing surface. We suspect that the orientation of solvent molecules on the packing surface and along the polymer chain create dipole–dipole repulsions that are strong enough to cause early SEC elution. TEAN likely disrupts the oriented dipole solvent layer at the packing surface both by participation in hydrogen bonding with HFIP and by competing for packing surface sites. It can be envisioned as a dynamic surface modifier that wets the styrene–divinylbenzene packing. Sodium acetate and sodium trifluoroacetate are apparently less effective dynamic modifiers. Polar end-groups such as amine and carboxylic acid on nylons, likely increase repulsive forces. Regardless of the exact mechanism, TEAN appears to provide conditions of true size separation, while NaTFA and sodium acetate do not.

Much of the reported 'prepeak' behavior of nylons and polyesters is likely from portions of samples that are completely excluded from the pore space. Totally excluded material is easily mistaken for 'aggregates', when it is a normal consequence of molecules that are repulsively excluded from pores. As NaTFA or sodium acetate are added, polymer retention shifts to longer times because of a reduction in repulsion from the pore space, and material near the exclusion limit such as Figs. 5 and 6 become less prominent. Veith [9] alluded to this for TFE, and it is consistent with Mori and Nishimura [11] observations that the prepeaks for nylon did not disappear after allowing solutions to sit for a week. However, Mori and Nishimura also reported prepeaks for PMMA, which disappeared with aging of the sample solution. PMMA prepeaks have never been reported for this amorphous polymer and aggregates are much more difficult to rationalize. We suspect that the SEC artifacts are difficult to reproduce and depend greatly on the sample, column materials and the quality of solvent.

There is no evidence in our work to suggest that water affects elution times in HFIP–0.01 M TEAN. We have taken no special precautions to eliminate water from the eluent other than to distill the solvent over molecular sieves and to continuously sparge the eluent with helium. The hygroscopic quaternary ammonium salt is used as received from the manufacturer. Periodic GC–MS assay of the solvent indicates that water content varies between 0.01% and 0.03%, but we observe no changes in retention volumes or peak shapes, as reported by Jackson et al. for HFIP with NaTFA [13]. In fact, we have deliberately injected samples that contain approximately 3% water in the sample solvent, and see no effects on retention. We also have observed no evidence for elevated levels of trifluoroacetic acid in HFIP after repeated distillation of solvent containing TEAN, as observed in distillates of HFIP containing NaTFA [33].

In this study, the PLgel mixed-C is preferred to HFIPGel because of a higher exclusion limit and a shallower molecular mass calibration curve (greater total column volume). Two columns can be used for larger total column volume and improved resolution at flow-rates of 0.5 ml/min; however, the high viscosity of HFIP creates high column backpressures, and larger particle diameter columns may be an alternative provided the amounts of materials with different pore sizes can be properly matched in HFIP to prevent discontinuities and breaks in calibration curves that are often observed in polar solvents that poorly swell styrene–divinylbenzene columns.

Our experience, and the observations of Schorn et al. [6] indicate that NaTFA probably contributes to particulate spiking in light-scattering chromatograms. NaTFA is marginally soluble in HFIP and it appears that even at 0.00735 M, undissolved salt particles are present.

The superposition of Universal Calibration curves in HFIP/0.01 M TEAN is reasonably convincing evidence that this eluent provides true size separations of the polymers examined. The fact that Mark–Houwink constants measured in pure HFIP and in HFIP–0.01 M TEAN result in the same Universal Calibration behavior suggest that there are only small conformational changes in PMMA, PET and nylon 6,6 upon addition of salt, and that TEAN primarily eliminates unwanted interaction with the column packing. The same unwanted repulsion is also eliminated for PEO and P2VP, but both polymers also undergo significant reductions in size with addition of TEAN, which effectively brings these polymers into the separable size range of conventional SEC columns.

We qualify that our results are for styrene–divinylbenzene columns, which are the most durable and popular columns for SEC in organic solvents.

The literature suggests that fewer anomalies are observed on polar columns, and some of these packings may not require the addition of salt to eliminate early elution. TEAN may be also beneficial for SEC on these columns because it causes significant reductions in the size and viscosity of polar polymers such as PEO and P2VP, which can reduce the effects of SEC elution on sample concentration.

5. Conclusions

Tetraethylammonium nitrate effectively eliminates early SEC elution of polymers in HFIP from styrene–divinylbenzene columns. The modifier does not significantly affect the size or viscosity of nylons, PET and PMMA but does cause macro-molecular contraction of polar polymers such as PEO and P2VP. Together, the data suggest that TEAN disrupts repulsive interactions between polymer molecules and the column packing surface and affects the solvation of very polar polymers by HFIP, although further studies are needed to better elucidate the interactions of solvent, modifier, polymer and packing surface sites. More important, the salt eliminates artifacts in multidetector SEC that have previously prevented use of Universal Calibration in HFIP.

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