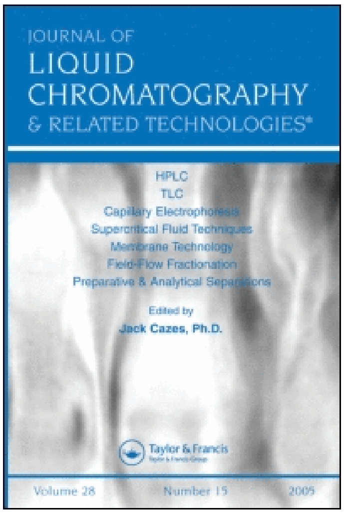

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CHARACTERIZATION OF NYLONS BY GEL PERMEATION CHROMATOGRAPHY AND LOW ANGLE LASER LIGHT SCATTERING IN 2,2,2-TRIFLUOROETHANOL

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ABSTRACT

A GPC method was developed for the analysis of several commercial nylons in trifluoroethanol + 0.05M LiBr using a styrene-divinylbenzene column custom-packed by Jordi Associates.

A broad molecular weight standard method was developed by interfacing GPC with LALLS to give the absolute molecular weight for each data point or elution volume along the chromatographic peak from a nylon sample of known molecular weight. The integrity of the interface was verified by static LALLS measurements; no loss or adsorption of solute was found in the chromatographic system.

A strong ionic effect was observed for nylon samples and the method to alleviate it was described. The molecular weights and distribution of the following nylons were determined by this method: nylon 6, nylon 4,6, and nylon 6,6. Much higher than quoted molecular weights were obtained for nylons when polymethyl methacrylates and ethylene glycols were used as standards; this necessitated the use of this broad molecular weight method for

column calibration. The ambient operating conditions offered several advantages over the conventional m-cresol solvent which required operation at higher than 100 C in order to reduce the viscosity, possessed a strong odor, and occasionally resulted in degradation of polyamides.

INTRODUCTION

Due to their high melting points and strong intermolecular interactions between amide linkages, nylons are only soluble in highly acidic solvents such as formic and sulfuric acids (1) or high boiling solvents such as m-cresol (1,2). The acidic solvents are highly viscous and tend to degrade nylons, especially in the presence of moisture (3). Fluorinated polar solvents such as 2,2,2-trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP) will also dissolve nylons at ambient temperature. The use of HFIP as a GPC solvent to characterize nylons and polymers containing hydrogen bonding sites has been reported (4). Recently, HFIP has been used to fractionate nylon 12 in preparative scale GPC (5). The use of TFE as a chromatographic solvent for polycaprolactam has been reported (6), however, there is also a report which indicates that the use of TFE had to be abandoned due to a long term solvent-gel compatibility effect (7).

Both fluorinated solvents pose certain health hazards and are expensive, especially HFIP, but they are still preferable to m-cresol or mixed solvents (e.g. 50/50 m-cresol/chlorobenzene (8)) which are commonly employed as solvent systems for GPC. The high operating temperatures (greater than 100 C) required in the use of m-cresol has been shown to degrade polyamides (8). In another case, chlorobenzene was used as a diluant to reduce the viscosity of m-cresol, thereby allowing GPC operation at ambient conditions while maintaining polyamide solubility. Any mixed solvent system may result in baseline instabilities since any slight variation in the solvent composition in either sample or reference cell will have a large effect on the response of the differential refractive index detector. Moreover, m-cresol is prone to oxidative degradation and has additional annoying low-molecular-weight impurity peaks.

ANALYSIS HISTORY

The initial GPC work with TFE was done on porous glass bead columns from DuPont. Probably due to the strong retention of solutes by porous glass after extended use of the column in various solvents, it was no longer possible to successfully elute any polymeric species with TFE.

Despite the fact that polar solvents such as TFE are not considered good swelling solvents for styrene-divinyl benzene gels, an attempt was made to convert a mixed bed column (Polymer Labs) from THF to TFE. This resulted in a column with a lower plate count which was unable to resolve polymethyl methacrylate standards (Polymer Labs) that are soluble in TFE.

A mixed bed column in THF from Jordi Associates (Bellingham, MA) was converted to TFE, resulting in a good separation of PMMA standards in spite of a 1/2" void at the column inlet, which was probably caused by the shrinkage of the gel bed in TFE. The column was subsequently sent back to Jordi Associates for repacking in acetone in the hope that the transition from the more polar acetone to TFE would result in a void-free column.

EXPERIMENTAL

GPC System, Chromatographic Conditions, and Data Processing

The GPC/LALLS system consists of a Model 110A pump (Altex), mixed bed column (Jordi Associates) (1.5 ft in length), KMX-6 Low-Angle Laser Light Scattering Photometer (LDC/Milton Roy), Model 98.00 differential refractive index detector (Knauer), and a manual injector valve (Rheodyne Model 7125). The KMX-6 scattering intensity was measured with the 6-7 degree forward-scattering annulus. The instrument was operated under the following conditions: solvent, distilled TFE (Halocarbon Products Corporation, Hackensack, NJ) + 0.05M LiBr; temperature, ambient; flow rate, 1 ml/min.; concentration, 1.5 mg/ml; injection size, 200 microliters.

The chromatographic data was acquired via analog/digital Instrument Interface Modules (LDC/Milton Roy) connected in series to a Minc 11/23 (Digital Equipment Corporation) computer. Software packages for GPC/LALLS data processing (MOLWT-II) and conventional GPC calibration were from LDC/Milton Roy.

Static Light Scattering

The static weight average molecular weight was measured using a KMX-6 (LDC/Milton Roy) low angle laser light scattering photometer in TFE + 0.05M LiBr. Four solutions in the range of 4.3E-4 to 2.2E-3 gm/ml were prepared via serial dilution of a prefiltered (0.22 micron filter) stock solution. Also, a similar size filter was placed in the sample inlet line before the KMX-6 LALLS cell. The scattering data was calculated and plotted as KC/R vs. concentration; the intercept and slope of the best (visual) linear fit to the data gave the weight-average molecular weight and second virial coefficient, respectively.

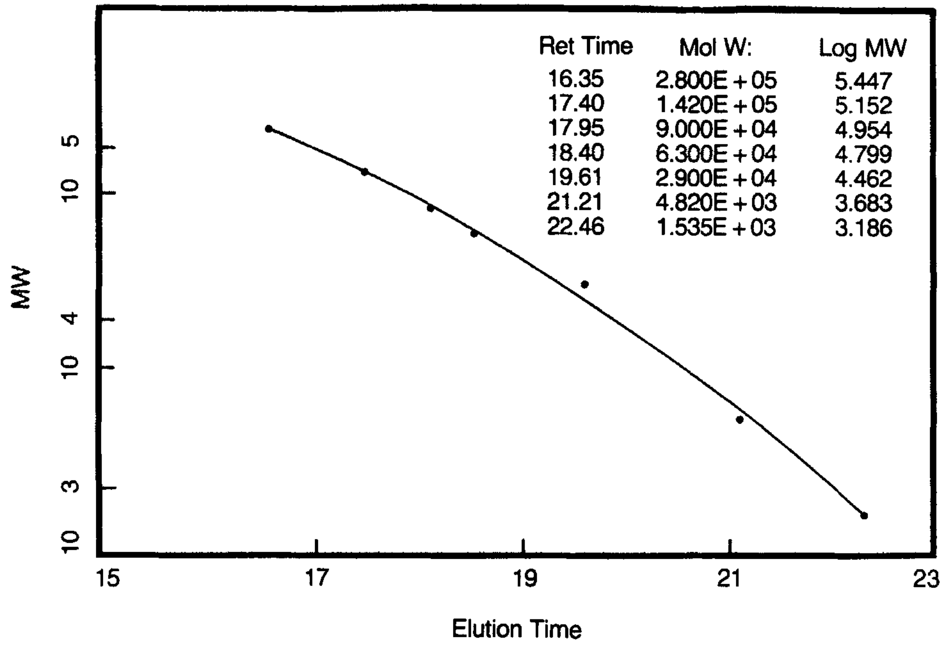
Differential Refractometry (dn/dc)

The specific refractive index increment (dn/dc) was measured via a KMX-16 Laser Differential Refractometer (LDC/Milton Roy) at ambient temperature. Generally for each sample, only one concentration ca. 5E-3 gm/ml was prepared.

RESULTS AND DISCUSSION

It is known that TFE is not a good swelling solvent for styrene-divinylbenzne gel, therefore, the mixed bed column was packed in a polar solvent such as acetone in the hope that the transition from the more polar acetone to TFE would result in a void-free column. Initially, a plate count of 12,000 for toluene was obtained for the column in THF after displacing acetone. Further work with E-caprolactam in TFE + 0.05M LiBr gave an acceptable plate count of 7000. It was found later that the acetone-repacked column operated in TFE still exhibited a 1/4" void in the inlet area which was filled with dry gel from Jordi Associates. Because polystyrene standards are insoluble in TFE, five polymethyl methacrylate standards (M.W. rom 2.8E5 to 2.9E4) along with two lower M.W. polyethylene glycol standards, were used to construct a composite calibraton curve (See Figure 1).

Back-calculation on one of the PMMA standards indicated excellent agreement with the supplier's value (MW=63,245, D=1.19 vs. MW=63,000 and D=1.19 (Polymer Labs)). The elution volume of these standards remained fairly constant with or without LiBr in the eluant, however, dramatic differences were observed for the nylon samples as shown in Figure 2. Without LiBr, the chromatographic peak was very broad suggesting that nylon molecules may be interacting with the column packing under these conditions. There have been some reports of a polyelectrolyte effect with polar eluants such as water (9,10,11) and DMF (12,13). For nylons, the bimodal phenomenon typical of the polyelectrolyte effect was observed with hexafluoroisopropanol (HFIP) although it was not seen in our case. In HFIP, the effect was suppressed on addition of sodium trifluoroacetate (4). In TFE, the addition of LiBr helped disintegrate the nylon agglomerates through the osmotic diffusion of LiBr ions into the giant nylon molecules possibly formed and held together by intermolecular hydrogen bonding. Blockage of the column surface active sites by LiBr ions also helped reduce column-solute



Ret Time	Mol W:	Log MW
16.35	2.800E+05	5.447
17.40	1.420E+05	5.152
17.95	9.000E+04	4.954
18.40	6.300E+04	4.799
19.61	2.900E+04	4.462
21.21	4.820E+03	3.683
22.46	1.535E+03	3.186

Figure 1. Calibration curve of Jordi mixed bed column. The five high M.W. standards are polymethylmethacrylate and the two low standards are polyethylene glycols.

interactions. A Gaussian shaped symmetrical peak was obtained with the addition of 0.05M LiBr as shown in Figure 2. PMMA and PEG did not exhibit the same effect since they are less polar than the nylons. Nylon dissolution also appeared to be greatly enhanced by LiBr. It has been observed that during sample preparation, a clear solution was obtained by dissolving nylon pellets in TFE containing 0.05M LiBr overnight whereas in the absence of LiBr there were still some insoluble particles under the same conditions (plus additional gentle heating for 1 hr).

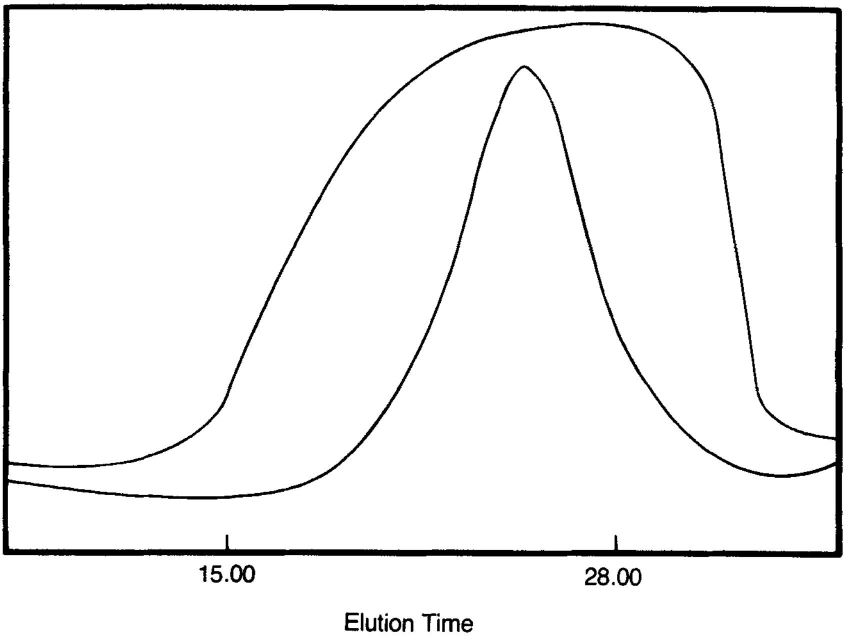


Figure 2. Chromatograms of Allied 820F nylon 6 in TFE + 0.05 M LiBr (narrow) and Du Pont Zytel 120, nylon 6, 6 in TFE only (broad).

The molecular weight averages of a variety of nylons have been determined including nylon 6, nylon 4,6, and nylon 6,6. Nylon 4,6 is the nylon with the reported high modulus, high melting temperature (295 C vs. 260 C for nylon 6,6 and 220 C for nylon 6), high crystallization rate, and high crystallinity (14,15,16). Insolubility and partial solubility in TFE + 0.05M LiBr precluded the analysis of nylon 6,10, nylon 6,12, nylon 11 and nylon 12. Examination of the data indicates that the greater the length of hydrocarbon chain between amide linkages, the lower the overall solubility. Recently published work to the contrary (17), dissolving these nylons in TFE/CHCl3 (30/70) with or without LiBr did not result in a true solution. An attempt to use the mixed solvent system in our GPC proved fruitless due to problems with baseline stability.

Based on the composite calibration of PMMA and PEG, it was found that the calculated weight average of 7.8E4 for Allied Capron N6 grade 8207F and 2.1E5 for nylon 4,6 was much higher than the reported literature values (15,17). This is attributed to the use of two types of standards below M.W. 20,000 as well as conceivably greatly different Mark-Houwink constants among PMMA, PEG, and nylons. It was concluded that this calibration method cannot be utilized for nylons.

To check the M.W. of several commercial nylons, static LALLS experiments using the KMX-6 photometer in TFE + 0.05M LiBr in conjunction with the dn/dc value from the KMX-16 measurement gave absolute weight average M.W. data (see Table 1). For Allied 8207F, the M.W. of 44,800 was obtained in this lab from static LALLS as compared to the value of 42,500 (17) from the intrinsic viscosity measurement in m-cresol using the appropriate Mark-Houwink constants (K=5.26E-4, a=0.745).

In the calculation of M.W. from either static or on-line LALLS work, a potential source of error lies in the value of either the concentration (static) or the exact mass injected (on-line). Any loss of sample from prefiltration or column

TABLE 1

Molecular Weights of Some Commercial Nylons

Sample	(a) Mw	(b) Mw	(c) Mw	(d) Mw	(e) dn/dc
Allied Capron 8207F, Nylon 6	7.8	4.5	4.2	4.2	0.209
Zytel 120 Nylon 6,6	6.4	5.1	-	-	0.214
Vydyne 2006-4 Nylon 6,6	8.5	4.4	3.8	-	-
DSM LAB Nylon 4,6	21	5.2	5.1	4.9	0.215

Note: Molecular weights = Mw x E4

(a) GPC based on PMMA+PEG as calibration standards
(b) Static LALLS
(c) LALLS/GPC
(d) GPC based on calibration generated by LALLS/GPC
(e) Specific refractive index increment

adsorption may severely affect the results. To ensure the mass balance in our chromatographic system, detector response was measured at four different concentrations, and the resulting linear plot passing through the origin indicated full mass recovery.

Figure 3 shows the SEC/LALLS chromatograms for Allied's 8207F nylon 6. Note that the LALLS detector still exhibited good response at the given molecular weight range and returned to the original baseline which provided further evidence of the lack of

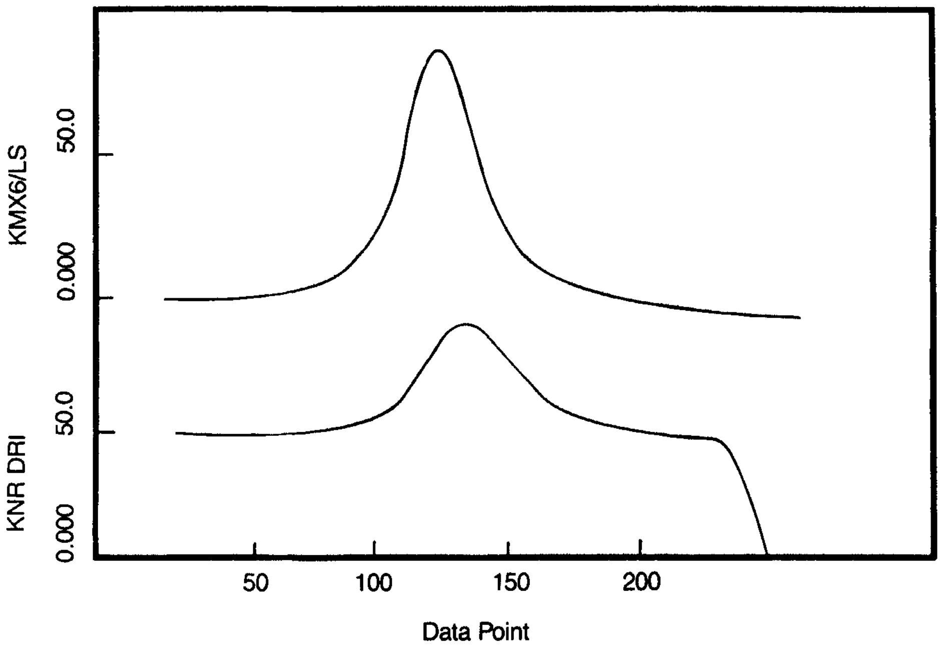


Figure 3. GPC and LALLS chromatograms of Allied 8207 F nylon 6.

solute adsorption. Based on the printout of the MOLWT II program from Chromatix, the M.W. vs. elution volume converted from data points under the chromatographic peak was plotted as the GPC calibration curve for this particular type of nylon. Subsequent GPC calculations using the aforementioned calibration on the same sample during a repetitive analysis indicated fairly good agreement between on-line LALLS and static LALLS for several nylons as seen in Table 1.

CONCLUSION

A GPC/LALLS method was successfully developed for varous nylons employing a custom-packed mixed bed column operating in TFE + 0.05M LiBr. The styrene-divinylbenzene column has maintained its performance during an eight month period. The addition of LiBr played an important role in sample dissolution, disaggregation, and elution.

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