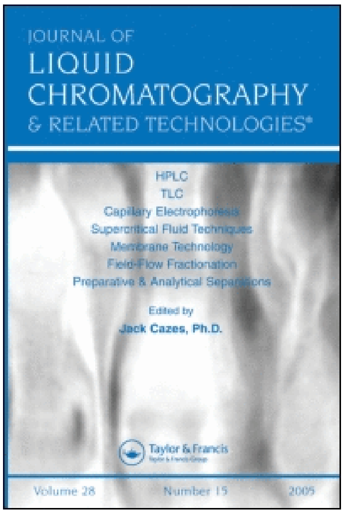

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MOLECULAR WEIGHT DISTRIBUTION OF POLYAMIDES BY GPC-VISCOMETRY. A COMPARISON BETWEEN HIGH TEMPERATURE AND LOW TEMPERATURE ELUANTS

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ABSTRACT

Synthetic polyamides (PA) owe many outstanding properties to their semicristalline morphology and to the intermolecular hydrogen bonding of the amide groups. Although the strength of the Van der Waals network confers an exceptional solvent resistance to this class of polymers, it may lead to serious difficulties in their solution characterization, such as the determination of molecular weight distribution (MWD). Over the years, a large number of dissolution schemes have been developed for the GPC characterization of PA. A recent IUPAC round-robin test on the GPC of aliphatic PAs nevertheless showed large variations in the experimental data not only between laboratories employing different methods, but also between laboratories adopting similar protocols. The purpose of the present investigation is to understand the origins of these disparities by comparing GPC-Viscometry data obtained with some frequently used eluant systems:

a) benzyl alcohol at high temperature;

b) hexafluoro-isopropanol, pure or mixed with dichloromethane, at low temperature;

c) common GPC solvents (THF, CH_2Cl_2,) after N-trifluoracetylation of the PA.

Apart from pure HFIP, all the methods tested show consistent MW results when measured in the same laboratory. Viscometry data reveal, however, that the expected linear viscosity law is obeyed only in benzyl alcohol. With the other eluants, significant departure from the Mark-Houwink relation denotes presence of non-size exclusion effects, rendering data evaluation imprecise with the Universal Calibration. The problems are particularly acute for polyamides with short methylene sequences which can only be dissolved in mixtures containing a high concentration of HFIP. To improve accuracy, it is proposed that GPC calibration for this class of polymer be performed with absolute detection (online viscometer, light scattering) or with a broad MWD standard of identical chemical composition to the analyzed sample.

INTRODUCTION

Synthetic polyamides (PA) are amongst the mostly widely used engineering thermoplastics, owing to their high strength and toughness, stiffness, abrasion resistance and retention of physical and mechanical properties over large temperature ranges. The outstanding material properties are to a large extent due to the semicristalline morphology and the cooperative intermolecular hydrogen bonding of the amide groups. Although the strength of these dipolar interactions confers an exceptional solvent resistance to PAs, it may lead to serious difficulties in the solution characterization of these polymers, such as the determination of molecular weight distribution (MWD). Because determination of MWD constitutes an essential part of material characterization, significant efforts have been devoted to the search for a suitable eluant for the GPC analysis of PAs. There are currently four approaches described in the literature:

1) High temperature GPC in strong H-bonding solvents: The first GPC analysis of PA-6 and PA-6,6 was performed in m-cresol at 135°C.(1) To avoid polymer degradation, alternative solvents such as o-chlorophenol, hexamethylphosphoramide, dimethylacetamide + LiCl and benzyl alcohol have been proposed. All of these solvents can only be used at elevated temperature, due to solubility or viscosity problems.(2) Being the least toxic of the high temperature solvents, benzyl alcohol has become as the preferred eluant.(3) To prevent poten-

tial solute interactions with the silica stationary phase, it is recommended to use crosslinked PS rather than silica columns with benzyl alcohol.(4)

2) Low temperature GPC with perfluoroalcohols on special columns: It has been known for a long time that perfluorocompounds such as pentafluorophenol, trifluoroethanol (TFE), tetrafluoropropanol (TFP) or hexafluoro-isopropanol (HFIP) have the propensity to dissolve a large number of polymeric materials which possess receptive sites for H-bonding(5) (proteins, stereoregular polyesters, aliphatic polyamides(6) and more recently polyaniline(7)). The application of HFIP to the GPC analysis of PA-6,6 and PET was first described in the 70s(8,9) and this compound is presently the preferred room temperature eluant for Nylons and polyesters. Closed loop distillation and use of narrow bore columns substantially reduces solvent consumption. Despite this progress, GPC with HFIP remains an expensive procedure due to extra investment in fluorinated solvent and special columns. Finally, it should be noted that HFIP with a pK_a of 9.3, is sufficiently acidic to react with the nitrogen in aromatic polyimides, which may result in ring opening solvolysis in some polyimide copolymers.(10)

3) Low temperature GPC in mixed solvent systems: To lower the operating temperature and minimize polymer degradation, a few authors have proposed diluting the active ingredient (m-cresol, o-chlorophenol, dichloroacetic acid) with a common GPC eluant such as toluene, dichloromethane or chloroform.(2,11,12) Amongst the different solvent combinations, it appears that mixtures based on fluorinated alcohols give the best results in terms of stability of the polymer and compatibility with the stationary phase (conventional silica or PS/DVB columns can both be used).(13,14) As in pure fluoroalcohols, a salt should be added to suppress polyelectrolyte effects.

4) Room temperature GPC of N-trifluoracetylated derivative: For analytical purposes, the chemical structures of a few semicristalline polymers such as PEEK, PES and PA have been successfully modified to allow solution characterization under ambient conditions. The procedure is limited to those compounds which do not degrade during chemical derivatization. For Nylons, N-trifluoroacetylation remains a common technique to solubilize the polymer for GPC characterization: (15,16)

$$\text{—CONH—} + (CF_3CO)_2O \rightarrow \text{—CON(COCF}_3\text{)—} + CF_3COOH \qquad (1)$$

The N-trifluoroacetylated polyamides (NTFA-PA) are soluble in many ordinary organic solvents such as acetone, methylene chloride, chloroform and tetrahydrofuran. Once prepared, the NTFA-PA solutions are unstable in presence of atmospheric humidity and should be used immediately to avoid reverse hydrolysis which converts the fluorinated polymer back into the original polyamide.

Ideally, any of the mentioned techniques should provide the same MWD for a given polymer sample. A recent IUPAC round-robin test on GPC characterization of aliphatic PAs showed nevertheless a large spread in the MW results not only between laboratories employing different methods, but also between laboratories adopting similar protocols.(17) To assess the validity of a method, it may be necessary to avoid interlaboratory variables by performing all the analyses at the same location. The purpose of the present investigation is to understand the origins of the disparity in the GPC results by carrying out a comparative study with the most popular methods selected from the preceding list:

- high temperature GPC with benzyl alcohol;
- low temperature GPC with pure HFIP and with HFIP/CH_2Cl_2 mixtures;
- room temperature GPC in THF and CH_2Cl_2 after chemical derivatization.

Practically any polyalkylamide with a number of carbons in the repeat unit ranging from 1 to 40 has been synthesized either for industrial or research purpose.(18) From this large range, we will restrict ourselves to those compounds which have achieved particular industrial importance, such as the monadic PA-12, PA-11, PA-6, PA-4, the dyadic PA-6,12, PA-6,6, PA-4,6 and the copolymer PA-6,66.

EXPERIMENTAL

Chemicals

All the chemicals are the purest grades from Aldrich or Fluka AG (Switzerland). Benzyl alcohol, even with the Puriss grade, tends to discolor on heating and should be vacuum distilled before use. Hexafluoroisopropanol was distilled over barium oxide to remove fluorhydric acid. Anhydrous dichloromethane and tetrahydrofuran were used without further purification.

Polystyrene and polymethyl methacrylate are molecular weight standards from Polymer Laboratories (Shropshire, UK). All the polyamides, except PA-4 which was a gift from Erlangen University (Germany), are additive-free grade from Aldrich Chemical Co.

Equipment

GPC analysis was performed on a Waters 150CV equipped with Styragel HR columns for low temperature and Styragel HT columns for high temperature measurements. Special TSK-Gel Alpha series columns have been selected for analyses in pure HFIP. The quantity of injected polymer was 200µL at a concentration of 2 mg/mL.

It is now well-documented that the single capillary viscometer of the 150CV may not provide the correct viscosity signal as a result of flow rate perturbations with passage of the polymer solution through the chromatographic system ("Lesec's effect"(19)). To correct for these baseline fluctuations, it is necessary to record simultaneously the flow rate and the solution viscosity as a function of elution time. This was achieved by differential viscometric detection obtained by adding a second capillary viscometer between the Baseline Optimizing Box (BOB) and the injection system.(20) For some samples, a UV-absorption detector (Kontron DAD 440) was used instead of the Differential Refractometer (DRI) to compare with the refractometer response and to improve the signal to noise ratio. Interdetector volumes were calibrated with Irganox 1035, an antioxydant from Ciba Specialty Chemicals with a MW of 642.

The density of the eluant, necessary for the calculation of polymer concentration and pump flow rate at the analysis temperature, was determined by picnometry.

The salt (sodium trifluoroacetate or tetraethyl ammonium chloride) added to the eluant to suppress polyelectrolyte effects and the solvents (HFIP, THF) are hygroscopic. It has been reported that humidity can hydrolyze the end-groups of dissolved polyamide into carboxylate ions, resulting in polymer adsorption when the eluant water content is > 0.03%.(21) To avoid this complication, the eluant was dried by passing through a column filled with an activated 3Å molecular sieve and an on-line degasser before entering the GPC pumping system.(14)

Sample Preparation

The PAs were dried in a high vacuum oven at 80°C (above T_g) for at least 48h to remove absorbed humidity. Dissolution was achieved by placing a weighed solid sample directly into a volumetric flask thermostatized to the desired temperature, with occasional stirring.

RESULTS

Results are divided into four sections corresponding to the different techniques used to dissolve the polymer.

High Temperature GPC in Benzyl Alcohol

A good correlation is found between the polymer solubility and its melting temperature (T_m). Long alkyl polyamides (PA-12, T_m = 180°C and PA-11, T_m = 190°C) were dissolved after 1 hour at 120°C whereas whereas shorter ones required higher temperatures: 140°C for PA-6,12 (T_m = 218°C), 150°C for PA-6

(T_m = 220°C) and PA 6,66 (T_m = 250°C); PA-6,6 (T_m = 262°C), PA-4,6 (T_m = 295°C) and PA-4 (T_m = 265°C) were insoluble even after 1 day at 180°C. Once dissolved, all the polymer solutions remained transparent but tend to gel (particularly PA-6,66) on cooling to ambient temperature. Nevertheless, the high viscosity of benzyl alcohol prevents GPC analysis below 130°C. Even at this temperature, the maximum usable flow rate was only 0.5 mL/min as a result of high back pressure in the Baseline Optimizing Box (BOB) of the 150CV unit, which is kept in the pump compartment at 60°C.

In their paper, Marot & Lesec reported that PS interacts with the stationary phase while PEO degrades under the analytical conditions.(4) They finally used polytetrahydrofuran standards for MW calibration. In the present investigation, we have selected PMMA standards to establish the Universal Calibration function. It has been shown that PMMA is compatible with benzyl alcohol on Styragel columns; in addition, PMMA standards are commercially available over a broader MW range than polytetrahydrofuran. Benzyl alcohol proves to be an excellent solvent for PMMA as shown by the Mark-Houwink coefficients reported in Table 1. A significant drawback when using PMMA standards is the small refractive index increment resulting in poor signal-to-noise ratio with DRI detection. The Universal calibration curve, determined with PS standards, is coincident with the curve established with PMMA standards in the high MW region. Deviations, however, become significant for MW range below 10^5 as is frequently observed in presence of non-steric exclusion effects.

The eluograms of the analyzed polyamides are plotted in Fig. 1. The relative RI sensitivity (given by the surface constant A, proportional to dn/dc) and Mark-Houwink coefficients of the analyzed polymers are reported in Table 1. Due to sign reversal in (dn/dc) with decreasing alkyl sequence length, the DRI signal for PA-6,12 is extremely weak and noisy, rendering this mode of detection unsuitable for this polymer in benzyl alcohol.

The MWD and viscosity law for two different PAs are reported in Fig. 2. It is interesting to note that, within experimental error, the Mark-Houwink coefficients are practically identical for all the PAs investigated (Fig. 2). This feature

Table 1. Relative RI Sensitivity (A) and Intrinsic Viscosity Parameters (K,a) of the Analyzed Polymers in Benzyl Alcohol at 130°C

	PA-12	PA-11	PA-6,12	PA-6	PA-6,66	PS	PMMA
A	0.50	0.35	−0.09	−1.10	−1.12	3.25	0.32
log K	−1.047	−1.022	−1.008	−0.925	−0.986	−1.734	−2.123
a(*)	0.601	0.597	0.594	0.588	0.594	0.657	0.759

(*) MWs below ~10,000 deviate from the Mark-Houwink law and are discarded from the calculation.

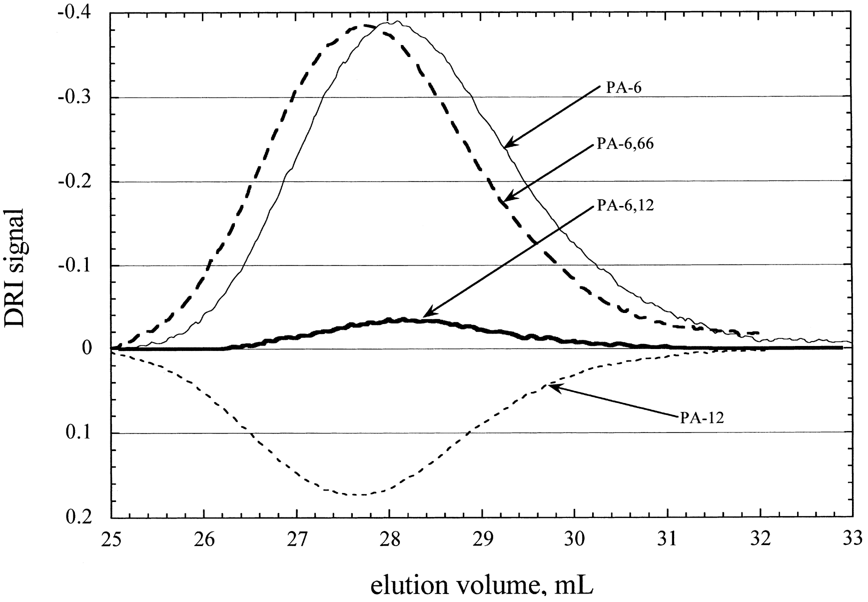

Figure 1. GPC eluograms of different PAs in benzyl alcohol at 130°C, recorded at identical polymer concentration (2 mg/mL).

simplifies the establishment of the Universal calibration curve for these polymers in benzyl alcohol. The exponent in the intrinsic viscosity law for PA-12 is slightly lower than the value of 0.66 given by Marot & Lesec,(4) but is partly compensated by a higher K constant.

In a duplicate series of measurements, 1g/L of tetraethyl ammonium chloride was added to the eluant. No change was observed in the results and it is concluded that polyelectrolyte effects are of minor importance in the polar benzyl alcohol.

Low Temperature GPC in Pure HFIP

Hexafluoro-isopropanol has a number of unique properties which make it an almost ideal solvent for the GPC analysis of PA:

- it is one of the rare compounds which can dissolve practically any aliphatic PA at room temperature
- owing to its exceptionally low refractive index (1.26), excellent RI and light scattering signals are obtained for the analyzed polymer.

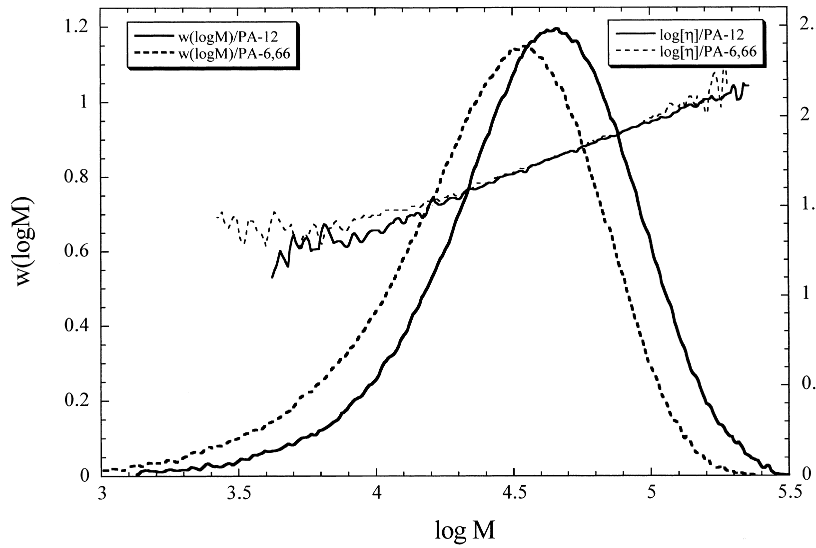

Figure 2. Molecular weight distribution and viscosity law of PA-12 (——) and PA-6,66 (- - - -) in benzyl alcohol at 130°C.

On the negative side, HFIP is acidic, highly polar and its use with conventional PS/DVB based stationary phase may result into separation difficulties, such as loss of resolution, excessive non-linearity of the calibration curve and polymer peak distortion (particularly with low porosity columns).(2,22) To minimize incompatibility problems, columns specifically designed for HFIP are now available from most major column producers. In the present investigation, we have selected the newly developed TSK-Gel Alpha columns which, according to the manufacturer, should be compatible not only with water but also with a large range of polar organic phases, including HFIP.

Hexafluoro-isopropanol is relatively viscous at room temperature and GPC analysis was carried out at 40°C, at a reduced flow rate of 0.5 mL/min. Polystyrene is insoluble in HFIP and calibration was performed with PMMA standards. To prevent polyelectrolyte effects, sodium trifluoracetate was added to HFIP at a concentration of 0.05 M. This relatively high quantity of ion-pairing agent is dictated by a recent study which showed that $-NH_2$ polymer end-groups may interfere with the separation mechanism if the salt concentration is below the cited level.(23)

The Mark-Houwink coefficients determined for PMMA, $K = 1.08 \cdot 10^{-2}$ and $a = 0.761$, are in good agreement with results obtained by other groups under similar experimental conditions.(22) The viscosity law for the analyzed PAs are perfectly linear (Fig. 3). However, the corresponding Mark-Houwink exponents,

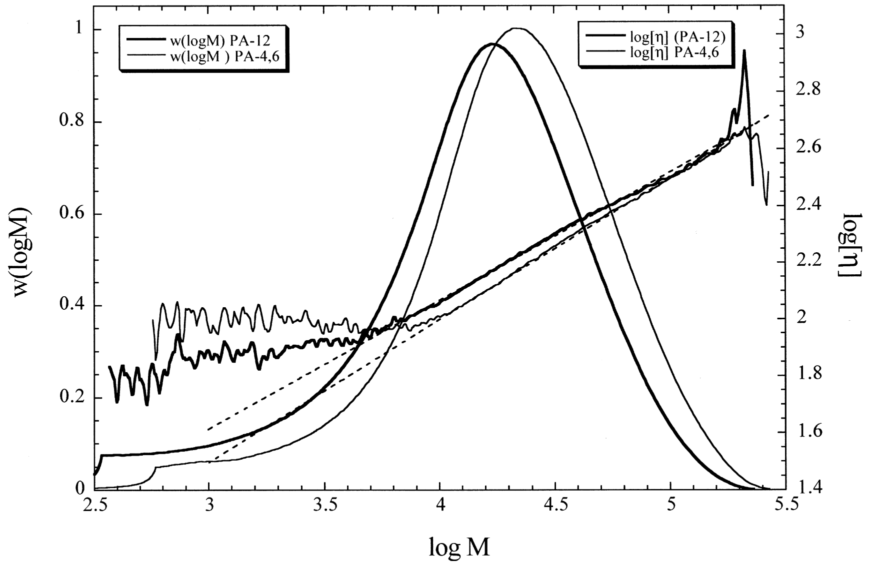

Figure 3. MWD (left scale) and intrinsic viscosity plot (right scale) for PA-12 (——) and PA-4,6 (—–) in HFIP + 0.05M NaTFA at 40°C (columns TSK-Gel Alpha 3000/4000/5000). Dotted lines are Mark-Houwink fits to the viscosity laws.

which vary from 0.46 for PA-12 to 0.51 for PA-4,6, are much smaller than values previouly reported with fractionated polymer:(24)

[η] (PA-6,6/ hexafluoropropanol, 25°C) = $1.98 \cdot 10^{-3}$ $M^{0.63}$

[η] (PA-6,6/tetrafluoropropanol, 25°C) = $1.14 \cdot 10^{-3}$ $M^{0.66}$

The GPC tracings reveal significant tailing which tends to indicate presence of adsorption effects (Fig. 3). However, the most serious problem encountered is the large discrepancy in the MWD obtained in HFIP in comparison to data obtained in benzyl alcohol (Fig. 4) and in the other dissolution media using the Universal Calibration concept (Cf. section: “Comparison of MWD”).

We are in communication with the column manufacturer to try to interpret the sources of this deviation (too high salt concentration, impurities in HFIP, polymer degradation, incompatibility with the stationary phase etc.). Because the problem is still unsettled, we will not discuss results obtained in pure HFIP any further.

Low Temperature GPC in HFIP/CH_2Cl_2 Mixtures

In many instances, mixtures should constitute a better alternative than single-component solvents in polymer dissolution. Pure HFIP and TFE, for instance,

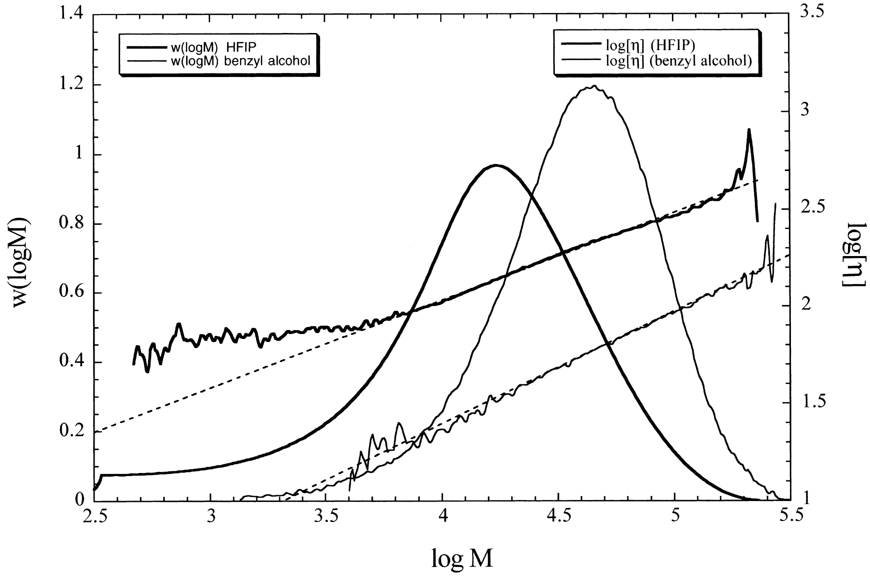

Figure 4. MWD (left scale) and intrinsic viscosity plot (right scale) for PA-12 in HFIP at 40°C (——) and in benzyl alcohol at 130°C (——). Dotted lines are Mark-Houwink fits to the viscosity laws.

are highly polar and may not be the best dissolution medium for several polyesters and polyamides. In search for a better solvent, it was found that dissolution of aliphatic PAs was enhanced in fluoroalcohol/ chloroalkane mixtures in comparison to the pure solvents.(25) Mixing TFE or HFIP with either $CHCl_3$ or CH_2Cl_2 caused a large decrease in solution temperature (up to 8K) accompanied by notable volume expansion (~1.2% after thermal equilibration). These thermodynamic excess properties were qualitatively explained as arising from repulsive forces between fluoroalcohol and chloroalkane molecules. The presence of PA reduces such antagonistic contacts, thus favoring polymer dissolution. Although application of mixed eluants to GPC characterization was proposed long ago to take advantage of the desirable properties of both solvent systems, its use raises fundamental concerns about the possible consequences of preferential solvation of the stationary phase and the polymer by one of the eluant component. Such effects may complicate correct interpretation of the experimental results.(26,27)

Both HFIP/$CHCl_3$ and HFIP/CH_2Cl_2 have been used with equal success in the GPC analysis of PET.(11,14,28-30) In the present investigation, we opted for HFIP/CH_2Cl_2 because it is more stable and less toxic than HFIP/$CHCl_3$. On the negative side, HFIP/CH_2Cl_2 forms a 30:70 v.v % azeotrope at 30°C, thus limiting its use to around room temperature. It is worth noting that HFIP/$CHCl_3$ does not form an azeotrope whereas TFE/$CHCl_3$ possesses a lower azeotrope at 55°C.

Solubility of PAs in HFIP/CH_2Cl_2

The repeat unit of aliphatic PA incorporates an hydrophobic alkyl portion and a polar amide group. This bimodal nature is reflected in the dissolution behaviour which depends on the length of -CH_2- sequence as has been noted with benzyl alcohol. The solubility of some typical PAs was determined by cloud point measurement at 20° and 30°C in HFIP/CH_2Cl_2 mixtures. These data are useful to assess the minimum amount of HFIP necessary for GPC analysis. Under the prevalent analytical conditions (30°C, 2 mg polymer/mL), PAs with the longest methylene sequences (PA-12, PA-11, PA-6,12) require eluant with less than 5% v.v. of HFIP whereas those with shorter alkyl groups necessitate an increasing proportion of HFIP (10% for PA-6, PA-6,6, PA-6,66; up to 25% for PA-4 and PA-4,6).

Universal Calibration in HFIP/CH_2Cl_2

The eluants were prepared by mixing the desired amount of HFIP to anhydrous CH_2Cl_2 (the quoted composition refer to the initial volumes of solvents). Tetraethyl ammonium chloride was added at a concentration of 1 g/L to suppress electrolytic effects. Disregarding MWs below 10^4, the following Mark-Houwink relations have been obtained for the system PS/(HFIP/CH_2Cl_2) at 30°C ([η] in units of mL/g):

0% HFIP $[\eta]_{PS} = 1.272 \cdot 10^{-2}\ M^{0.715}$
5% HFIP $[\eta]_{PS} = 1.277 \cdot 10^{-2}\ M^{0.712}$
10% HFIP $[\eta]_{PS} = 1.317 \cdot 10^{-2}\ M^{0.705}$
20% HFIP $[\eta]_{PS} = 1.673 \cdot 10^{-2}\ M^{0.678}$

HFIP is a non-solvent for PS, a characteristic which is reflected in the decrease in polymer intrinsic viscosity with the percentage of fluoroalcohol. The shrinkage of the polymer coils increases the retention volume without affecting the Universal calibration curves up to 10% HFIP. At higher HFIP cocentration, however, the shift in the Universal calibration becomes noticeable, particularly at the low MW end.(14) This may indicate either non-steric effects and/or change in pore dimensions as a result of interactions between the mixed eluant and the stationary phase.

GPC Results

Practically any aliphatic polyamide tested can be dissolved in HFIP/CH_2Cl_2 with appropriate fluoroalcohol concentration. However, as will be detailed in the "Comparison of MWD" section, mixtures with >10% HFIP cannot reliably be used as a GPC eluant due to non-steric interactions. A typical MWD for a PA-6,12 sample obtained with the mixed eluant technique is shown in Fig. 5.

N-Trifluoroacetylation

Chemical derivatization was accomplished at room temperature with a 0.5 M trifluoroacetic anhydride solution in dichloromethane. About 8 mg of polymer was weighted in a 4 mL glass vial fitted with a rubber septum and a magnetic stirrer. After purging with dry Argon, a 3-fold excess of trifluoroacetic anhydride solution was added with a syringe under gentle stirring. As with the other dissolution techniques, it was observed that long alkyl polyamides (PA-12 and PA-11) were completly dissolved after only ~1 hour whereas PA-4 and PA-4,6 require more than 10 hours. After 24 hours of reaction, the N-trifluoroacetylated polymer (NTFA-PA) was recovered by vacuum evaporation and redissolved with the GPC

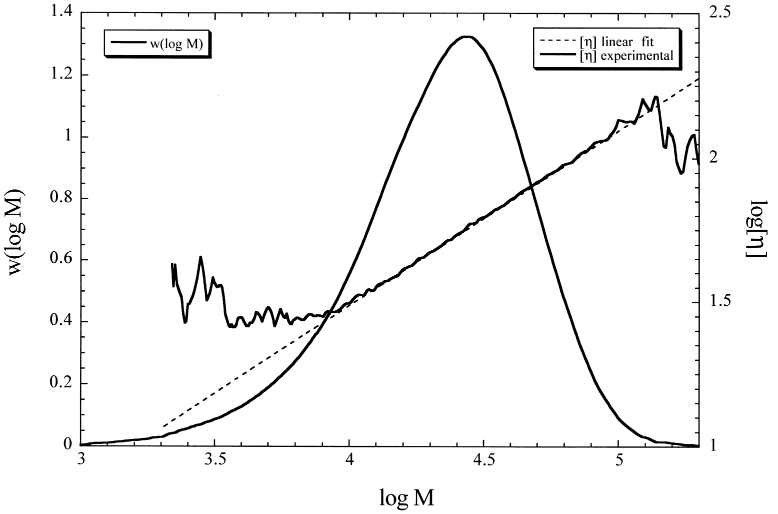

Figure 5. Molecular weight (left scale) and Mark-Houwink plot (right scale) for PA-6,12 in 5:95 v.v. HFIP/CH_2Cl_2 mixture. Dotted line is the Mark-Houwink fit to the viscosity law.

eluant (CH_2Cl_2 or THF). Once prepared, the NTFA-PA solutions are unstable in presence of atmospheric humidity and should be used immediately to avoid hydrolysis which converts the trifluoroacetyl groups back into the original amides.(31)

Although both DRI and UV-absorption could be used for detection, the latter provides a much better S/N ratio since trifluoroacetylated polyamides have a rather small dn/dc but an intense absorption band at 240 nm in THF and CH_2Cl_2 (this absorption is actually so strong that detector saturation has to be avoided by measuring at a wavelength slightly off the peak maximum, 260 nm, for instance).

Results of GPC-Viscometry depend on the exact weight of injected polymer. With the molar mass increase after N-trifluoroacetylation, a conversion factor should be applied to recover the MW of the original polyamide. This procedure, however is dependent on the degree of N-trifluoroacetylation which may not reach 100%, particularly for Nylons with short alkyl sequence.(32) To avoid this incertitude, MWD was calculated from the initial weight of the polymer *before* derivatization.

It has been reported that GPC separation of NTFA-PA does not follow the Universal Calibration in dichloromethane,(33) whereas better agreement was obtained in tetrahydrofuran.(16) For the purpose of comparison, we have analyzed NTFA-PA in both solvent systems. Results show that at least w ith Styragel HR columns, identical MWD is obtained regardless of the dissolution medium (Fig. 6).

Comparison of Molecular Weight Distributions

Obviously, obtaining the correct MWD information is the ultimate goal in any GPC characterization. To appraise the source of variations conveyed by different experimental conditions, we have superimposed in Figs. 7 through 9 the MWDs obtained with the described methods for three representative PA samples. The corresponding average MWs and viscometry data are summarized in Tables 2 to 4. As mentioned in the section "Low Temperature GPC in Pure HFIP," results obtained in pure HFIP are not included in this comparison.

Reasonable agreement are obtained between the MWDs determined from different GPC techniques. Closer inspection reveals, however, systematic variations of the viscometric law with the method employed:

a) samples analyzed in benzyl alcohol give a perfectly linear Mark-Houwink plot;

b) in HFIP/CH_2Cl_2 mixtures, a linear log[η]–log M relationship is obtained for PA-12 and PA-6,12 (Figs. 7 & 8), but a slight curvature is observed for PA-6 (Fig. 9);

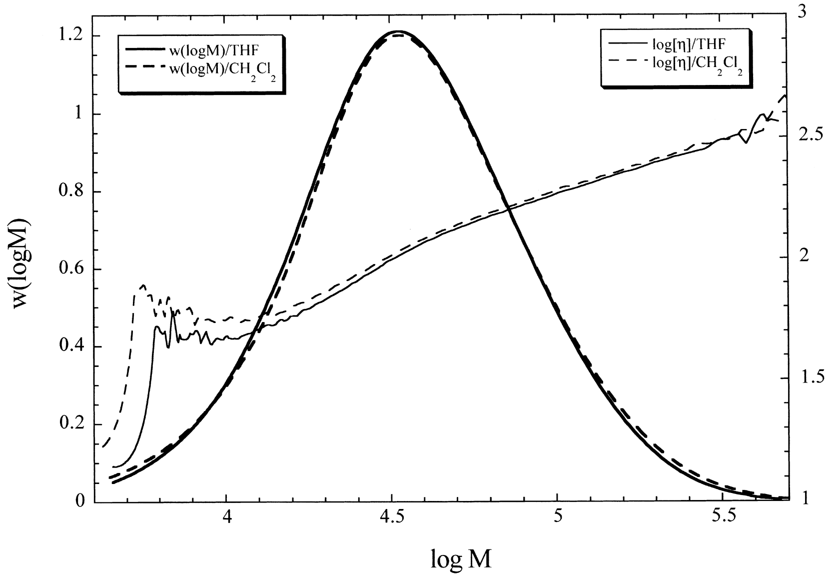

Figure 6. MWD (left scale) and intrinsic viscosity plot (right scale) for NTFA-PA12 analyzed in THF at 40°C (——) and in CH_2Cl_2 at 30°C (- - -). Values on the abscisse refer to the MW of the <u>original</u> PA (Cf. text for details).

Table 2. GIPC-Viscometry Results for PA-12

	PA-12 (Benzyl Alcohol)		PA-12 (5%HFIP/CH_2Cl_2)		NTFA-PA12(*)	
	PMMA Calibration	Universal Calibration	PS Calibration	Universal Calibration	PS Calibration	Universal Calibration
M_n	41960	24770	48000	20370	60310	25810
M_w	74990	49970	98240	46880	110440	49450
M_p	69340	46240	94110	44180	96280	41650
M_z	111030	79460	155260	80830	182080	93370
M_w/M_n	1.79	2.02	2.05	2.30	1.83	1.92
[η] (ml/g)	—	54.67	—	102.74	—	122.80
Log K	—	−1.047	—	−0.7228	—	−0.4349
a (MH)	—	0.601	—	0.592	—	0.545

(*) MW data for NTFA-PA referred to the values of the original polymer.

Table 3. GPC-Viscometry Results for PA-6,12

	Benzyl Alcohol		5%HFIP/CH_2Cl_2		NTFA-PA (*)	
	PMMA Calibration	Universal Calibration	PS Calibration	Universal Calibration	PS Calibration	Universal Calibration
M_n	33870	19570	32490	15620	37870	18260
M_w	50490	32710	53290	28130	68070	32340
M_p	48500	30320	54650	28480	65370	31200
M_z	66840	45500	76800	42460	104620	53370
M_w/M_n	1.49	1.67	1.64	1.80	1.80	1.77
[η] (ml/g)	—	42.55	—	59.78	—	81.47
Log K	—	−1.008	—	−0.9036	—	−0.9228
a (MH)	—	0.594	—	0.608	—	0.634

(*) MW data for NTFA-PA referred to the values of the original polymer.

c) all trifluoracetylated polymers show a pronounced curvature in the viscosity, regardless of the dissolution medium. Interestingly enough, this curvature seems always to appear in the region of $M \cong 30000$ ($\log M \cong 4.5$).

Long chain branching can occur for some PAs synthesized by anionic polymerization, but rarely for polycondensation polymers used in the current investigation. The most plausible explanation for the observed curved viscosity law is the presence of non size-exclusion effects under defavorable experimental conditions.

Table 4. GPC-Viscometry Results for PA-6

	Benzyl Alcohol		10%HFIP/CH_2Cl_2		NTFA-PA (*)	
	PMMA Calibration	Universal Calibration	PS Calibration	Universal Calibration	PS Calibration	Universal Calibration
M_n	37190	21050	42090	21020	45780	22590
M_w	70010	47300	72330	41300	81870	42820
M_p	65180	42680	76360	42800	74930	38120
M_z	103010	73400	100340	63150	128520	74610
M_w/M_n	1.88	2.25	1.72	1.96	1.79	1.90
[η] (ml/g)	—	51.78	—	72.75	—	86.30
Log K	—	−0.9255	—	−0.4255	—	−0.8759
a (MH)	—	0.588	—	0.502	—	0.614

(*) MW data for NTFA-PA referred to the values of the original polymer.

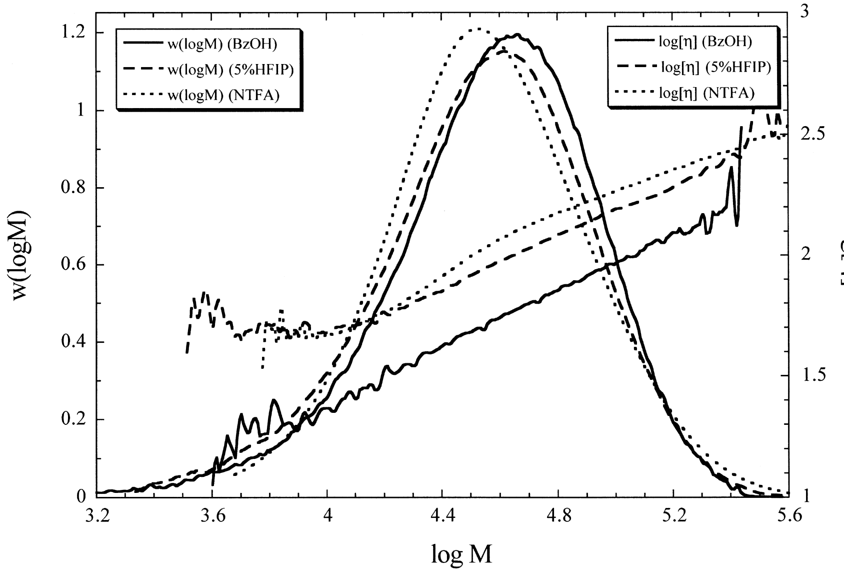

Figure 7. MWD (left scale) and intrinsic viscosity plot (right scale) for PA-12 in benzyl alcohol at 130°C (——), in HFIP/CH_2Cl_2 at 30°C (- - -), from the N-trifluoracetylated polymer in THF at 40°C (·····).

In mixed eluants with HFIP, the presence of highly polar fluoroalcohol may cause hydrophobic interactions with the apolar stationary phase, resulting into a non-linear viscosity law. To assess the role of HFIP in this abnormal viscosity behaviour, GPC analysis has been performed at varying percentage of fluoroalcohol. The results, reported in Fig. 10, clearly indicate that departure from the Mark-Houwink law increases with the HFIP content. As a result of this deviation, the calculated MWD tends to become narrower and shift to lower MW at high HFIP concentration.

With N-trifluoroacetylated polymers, adsorption of partially hydrolyzed or incompletely derivatized polymer may result in a non-linear viscosity law. This last hypothesis seems to be supported by some of our preliminary investigations which indicate that the degree of N-trifluoroacetylation of aliphatic PAs decreases with increasing MW and shortening of the alkyl sequence.(32)

CONCLUSIONS

The present study has allowed us to evaluate the merits and weaknesses of different GPC techniques currently employed in the MWD characterization of PAs.

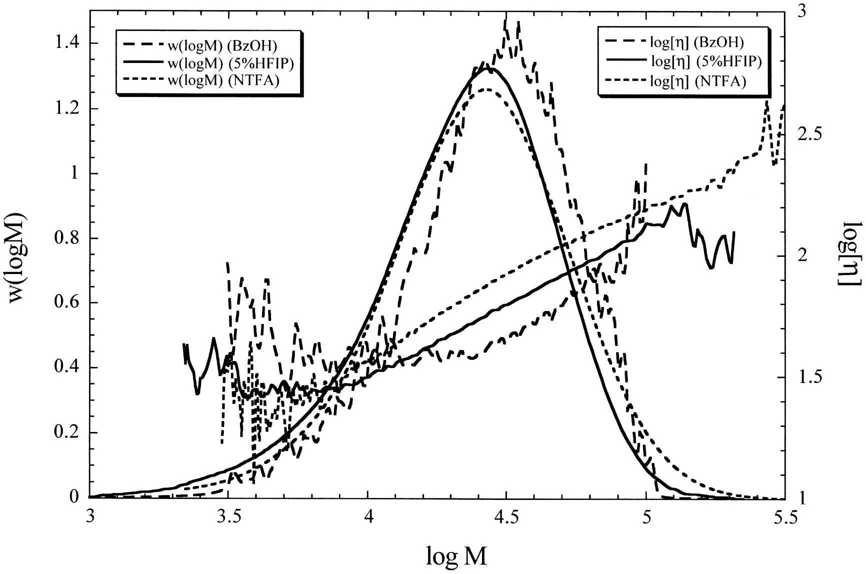

Figure 8. MWD (left scale) and intrinsic viscosity plot (right scale) for PA-6,12 in benzyl alcohol at 130°C (——), in HFIP/CH_2Cl_2 at 30°C (- - -), from the N-trifluoroacetylated polymer in THF at 40°C (·····). The DRI signal in benzyl alcohol is particularly noisy due to the low dn/dc in this solvent.

Notwithstanding the difficulties associated with high temperature GPC, the use of non-toxic benzyl alcohol seems to provide the most reliable results for polyamides that can be dissolved and give a good signal in this solvent (PA-12, PA-11, PA-6 and PA-6,66). The C—H bond of the methylene group vicinal to nitrogen in polyalkylamides is sensitive to temperatures above 200°C.(34) Therefore, the possibility of thermal degradation should be considered if the dissolution temperature has to be increased beyond this temperature.

Owing to their ability to form strong H-bonding, fluoroalcohols, and in particular HFIP, are capable of dissolving a variety of semicristalline polar polymers (PA, PET, POM, PEEK, PANI) at room temperature. The use of pure HFIP as a GPC eluant remains, however, an expensive enterprise. In addition, significant adsorption effects were encountered even with columns specially designed for this solvent, rendering the Universal Calibration inoperative.

A mixed eluant based on HFIP is a sensible alternative to pure HFIP for some aliphatic PAs. The degree of incompatibility between the eluant and the stationary phase increases with the percentage of HFIP and the mixed solvent tech-

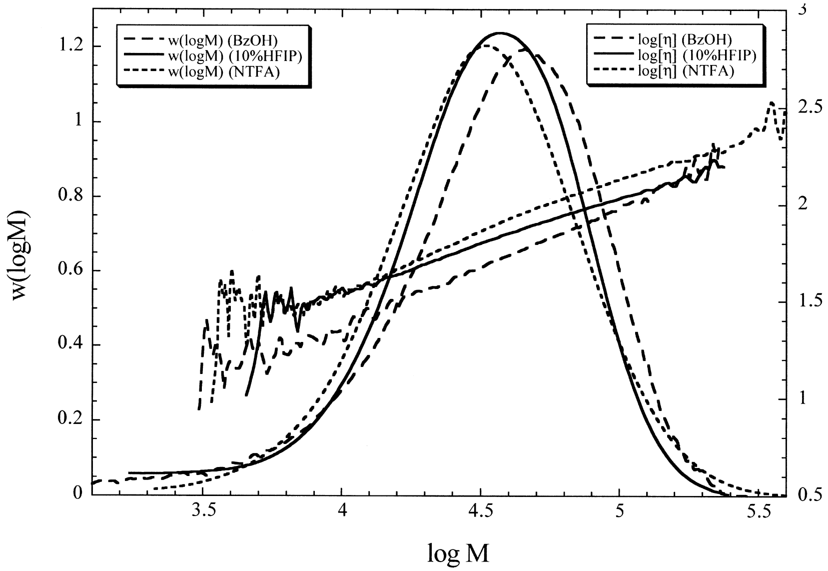

Figure 9. MWD (left scale) and intrinsic viscosity plot (right scale) for PA-6 in benzyl alcohol at 130°C (——), in HFIP/CH_2Cl_2 at 30°C (- - -), from the N-trifluoracetylated polymer in THF at 40°C (·····).

nique should be applied only to polymers which can be dissolved with a minimum amount of HFIP such as PA-12, PA-11, PA-6,10, PA-6,12. For polyamides with short methylene sequences (PA-6,6, PA-4,6 and PA-4), the high concentration of HFIP (15-25 % vv) required for its dissolution may interfere with the size-exclusion separation mechanism, in addition to the possibility of preferential solvation. The most conspicuous outcome of these effects is a curved viscosity law which can be already detected at 5% HFIP with some high MW samples ($>10^5$).

N-trifluoracetylation is a simple and inexpensive technique to dissolve polyamide. However, GPC characterization of the derivatized product is highly dependent on the presence of unsubstituted amide groups and results should be carefully evaluated for possible artefacts.

As a final conclusion, one may state that, in spite of numerous investigations, GPC analysis of PAs remains a difficult endeavour in comparison with other amorphous thermoplastics that can be readily dissolved in common solvents at low temperature. To improve MW accuracy, calibration for this class of polymer should be performed with absolute detection (on-line viscometer, light

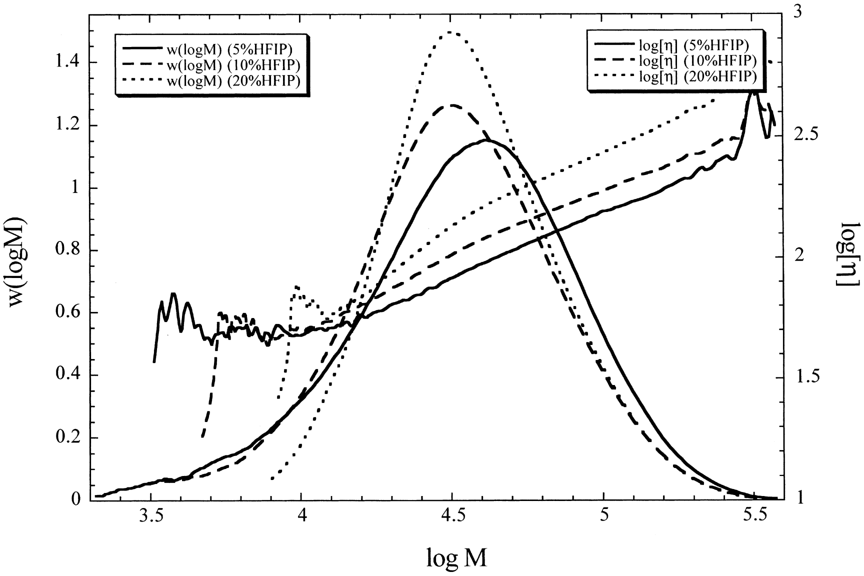

Figure 10. MWD and intrinsic viscosity plot of PA-12 in HFIP/CH_2Cl_2.

scattering) or at least with a broad MWD standard of identical chemical composition to the analyzed sample.

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