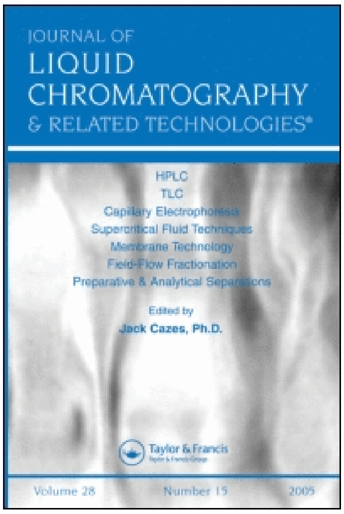

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EFFECTS OF ADDITION OF AN ELECTROLYTE ON SIZE EXCLUSION CHROMATOGRAPHY OF POLYAMIDES USING HEXAFLUORO-2-PROPANOL AS MOBILE PHASE

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ABSTRACT

Polyelectrolyte effects for polyamides and poly(methyl methacrylate)(PMMA) used as calibration standards and the suppression of these effects by the addition of sodium trifluoroacetate to the mobile phase were shown and discussed. The addition of the electrolyte helped to the disaggregation of the polymer samples by breaking down hydrogen bonding. Besides the disaggregation of the polymer samples, the addition of the electrolyte caused the change of the retention volume and peak width of PMMA. Elution of PMMA having higher molecular weight than $6x10^4$ was retarded and that having smaller one than $6x10^4$ was hastened by the addition of the electrolyte. Peak width of PMMA became also narrower in about 20%. PMMA equivalent molecular weights of polyamides were plotted against real molelcular weights of the polyamides measured by end group analysis and next equations were obtained.

$$\log M_{nylon\ 6} = -1.53402 + 1.352 \log M_{PMMA\ eq}$$
$$\log M_{nylon\ 6,6} = -4.88506 + 2.143 \log M_{PMMA\ eq}$$

INTRODUCTION

The solvent most commonly used for size exclusion chromatography (SEC) of polyamides has been m-cresol (1,2). However, m-cresol is viscous and requires the higher operating temperature over 100 °C, which has been shown to lead to the polymer degradation because of the acid catalyzed hydrolysis. Furthermore, since the differential refractive index of polyamides and m-cresol is small, the polymer concentration must be high compared to those of common systems such as a polystyrene (PS) - tetrahydrofuran system. The high concentration causes the column overloading and increases the chromatogram peak spreading.

Several combinations of solvent and stationary phase for the SEC of polyamides in which the polymer degradation was eliminated or kept to a minimum have been reported: benzylalcohol-silica gel at 100 °C (3), benzylalcohol-PS gel at 130 °C (4), o-chlorophenol-PS gel at 100 °C (5), and a mixture of m-cresol and chlorobenzene-PS gel at 43 °C (6). Fluoroalcohols are good solvents for polyamides and can dissolve polyamides at ambient temperature, thus 2,2,2-trifluoroethanol (TFE) (7-9) and hexafluoro-2-propanol (HFIP) (10,11) have been used as the mobile phases for polyamides. N-Trifluoroacetylation of polyamides leads to soluble the derivatives in, for example, dichloromethane and SEC of polyamides can also be accomplished at ambient temperature (12,13).

Although fluoroalcohols have been found to be superior solvents capable of dissolving polyamides at ambient temperature, there are two major drawbacks in the use of the solvents as an SEC solvent: the expensive price of the solvents and the insolubility of PS standards which prevents the construction of a PS calibration curve. These drawbacks were overcome by recycling use of the effluent and the indirect calibration with a poly(methyl methacrylate) (PMMA) having a broad molecular weight distribution (14). PMMA is soluble in fluoroalcohols. Besides these drawbacks, the polyelectrolyte effect of polyamides in HFIP was observed and the addition of an electrolyte to prevent this effect has been reported (10).

The use of a low-angle laser light-scattering (LALLS) detector gives the absolute molecular weight for each data point along the chromatographic peak (8,10) and the calibration with narrow-distribution standards seems to be no longer necessary. However, the use of a PMMA calibration curve to calculate molecular weihgt (MW) of polyamides is easy and simple (7). Recently, PMMA standards of narrow MW distributions are commercially available and it became possible to construct a PMMA calibration curve directly.

In this paper, HFIP was used as the mobile phase and polyelectrolyte effects of polyamides and PMMA in HFIP and the suppression of these effects by the addition of an electrolyte were discussed. MW of polyamides (nylon 6 and nylon 6,6) was calculated using a PMMA calibration curve and the conversion method from the PMMA equivalent MW to the absolute (real) MW of polyamides was proposed.

EXPERIMENTAL

A Jasco TRIROTAR-V high performance liquid chromatograph (Jasco Corp., Hachioji, Tokyo 192, Japan) with a Model R-401 differential refractometer (Waters, Milford, Mass., USA) was used for the SEC measurements. Two Shodex KF-80M SEC columns (30 cm x 8 mm i.d.)(Showa Denko Co., Minato-ku, Tokyo 105, Japan) packed with PS gels for polymer separation were used and the solvent in the column (tetrahydrofuran) was displaced to HFIP at a flow rate of 0.3 ml/min. The value of the number of theoretical plates was 11000 plates/30 cm by injecting 0.05 ml of a 0.1% acetone solution at a flow rate of 0.5 ml/min. Although PS is insoluble in HFIP, i.e. HFIP is not a good solvent for PS gel, the columns filled with HFIP still kept a good efficiency.

HFIP was provided by courtesy of Central Glass Co., Ltd. (Chi yoda-ku, Tokyo 101, Japan). The solvent was reused several times after distilling the waste solvent [14]. Sodium trifluoroacetate (NaTFA) was added to HFIP at the concentration of 0.1% (w/v) and a flow rate of the mobile phase was 0.5 ml/min. PMMA standards were dissolved in the mobile phase in the concentration of 0.1% and polyamide samples were dissolved in the concentration of 0.2%. The injection volume for these solutions was 0.1 ml. SEC measurements were performed at ambient temperature.

PMMA standards in a range of MW 1950 and 1.4×10^6 were purchased from Polymer Laboratory (Shropshire, UK) through Showa Denko Co. The molecular weights and the polydispersities of the individual PMMA standards were as follows (the polydispersities were in parenthesis): 1.4×10^6 (1.07), 8.2×10^5 (1.04), 3.3×10^5 (1.11), 107000 (1.10), 60000 (1.07), 20300 (1.11), 6100 (1.11), 1950 (1.09). These standards were dissolved in the 0.1% concentration.

Polyamide samples of nylon 6 and nylon 6,6 were prepared in our laboratory by condensation polymerization with ε-caprolactam for nylon 6 and hexamethylenediamine - adipic acid salt for nylon 6,6 in a high pressure vessel at 180 °C for nylon 6 and 215 °C for nylon 6,6, respectively. The polymerization period was changed from several hours to one day (24 h) to obtain polyamides with the different MW. After polymerization, unreacted monomer and oligomers in the polyamides were removed by extracting them in hot water for 24 h. Number average MW of polyamides were obtained by end group analysis as follows. The weighted polyamides were dissolved in benzylalcohol and carboxyl groups in polyamides were titrated with base (KOH) in an alchoholic solvent, while amino groups in polyamides were titrated with acid (HCl) in an alcoholic solvent. The number average MW was calculated by using the weight of the polyamide and the amounts of KOH and HCl consumed and the results are listed in Table 1.

RESULTS and DISCUSSION

Polyelectrolyte Effects

Polyelectrolyte effects show the bimodal or multimodal elution curves of polymer samples and the effects were observed in a

TABLE 1
Number Average Molecular Weight of Polyamides Measured by End Group Analysis

Nylon 6 Sample No.	$\bar{M}_n$	Nylon 6,6 Sample No.	$\bar{M}_n$
1	1810	7	3160
2	3050	8	4520
3	4630	9	6330
4	10500	10	7460
5	11300	11	8140
6	16700	12	16700

HFIP-polyamide system (10) and were not seen in a TFE-polyamide system (8). Althoug the effects were suppressed on addition of NaTFA (10), detailed observations were not shown. Here, the examples are shown in Figure 1 for nylon 6,6. Figure 1 (a) was obtained with pure HFIP as the mobile phase and Figure 1 (b) with HFIP+0.1% NaTFA. The SEC chromatogram of nylon 6,6 obtained with pure HFIP as the mobile phase showed a small peak at V_R=13.5 ml and a large peak at V_R=19 ml. The former peak appeared at the exclusion limit of the column system and this peak disappeared when a small amount of NaTFA was added to the mobile phase (Figure 1 (b)). The first peak at V_R = 13.5 ml is considered to be aggregates or gels having large molecular sizes which cannot enter into the pore of the packing materials.

Solid polyamides consist of both crystalline and amorphous parts. Polyamides have carbonyl groups and amino groups in the chain and the intermolecular hydrogen bonding by both groups is connected to the crystalline part of the polyamides. Most of the amorphous part in the solid polyamide can dissolve in pure HFIP and the crystalline part connected strongly by hydrogen bonding remaines undissolved. The addition of NaTFA to HFIP helped disintegrate the nylon agglomerates through the osmotic diffusion of NaTFA ions (8) and by breaking of the hydrogen bonding. The same phenomena were obtained for nylon 6, too.

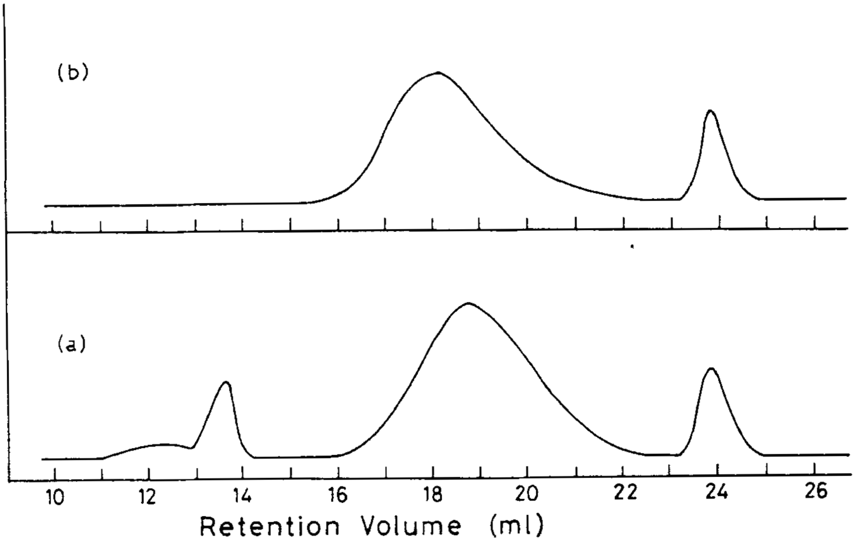

FIGURE 1. SEC chromatograms of nylon 6,6 with and without NaTFA in HFIP: concentration, 0.2%; injection volume, 0.1 ml; detector, RI; attenuation, x8; MW of nylon 6,6, 8140; mobile phase, (a) pure HFIP, (b) 0.1% (w/v) NaTFA in HFIP.

The peak appeared at V_R = 24 ml was due to the mobile phase and it appeared every time even when only HFIP was injected. The retention volume 24 ml corresponded to the sum of the interstitial volume (V_o) and the pore volume (V_i) in the column.

The aggregates of polyamides appeared at the exclusion limit of the column system didn't disappear by heating at 50 °C for 4 h or by ultrasonic treatment which was carried out in a laboratory ultrasonic cleaner (150 W - 26 kHz) for 15 min. The solutions of polyamides in pure HFIP were also left more than 10 days at ambient temperature, but the disappearance of the first samll peak was not observed. When a PMMA solution in pure HFIP prepared just 1 day before was injected into the SEC system, then the SEC chromatogram showed a small peak at the exclusion limit, but the peak disappeared by heating or by ultrasonic treatment as well as by leaving them for about 10 days (14). The addition of NaTFA to HFIP was also effective to have the peak disappeared.

The addition of NaTFA to HFIP influenced not only the disappearance of the aggregates but also the retention volume of polyamides and PMMA. The breakthrough volume and the retention volume at peak top of polyamides decreased with the addition of NaTFA(see Figure 1 (b)). The reason was estimated as follows: the portion eluted at V_R = 13.5 ml dissolved completely in NaTFA+HFIP and had somewhat higher MW than the rest which dissolved already in HFIP; the addition of NaTFA in HFIP acted to break down the remained intramolecular hydrogen bonding in the polyamides which could dissolve in pure HFIP, which caused a change in solvation and the expansion of the hydrodynamic volume of the polyamides.

Retention volumes of PMMA standards also changed with the addition of NaTFA to HFIP. Elution of PMMA having higher MW than 6×10^4 was retarded and that having smaller MW than 6×10^4 was hastened. The results are shown in Figure 2. The slope of the curve became steep by the addition of NaTFA in HFIP. Besides this change in retention volume, peak width of PMMA became narrower in about 20% by the addition of NaTFA in HFIP. The reason was also estimated as follows. Solubility parameters of HFIP and PS gel seem to be far each other, since PS cannot dissolve in HFIP. Therefore, the adsorption effect might exist in SEC of PMMA in the system of pure HFIP/PS gel. This effect results in the retardation of elution and the peak broadening and these phenomena are more significant for PMMA having lower MW. Formation of the aggregates resulted in the intermolecular hydrogen bonding expedites the elution and is more significant for PMMA having larger MW. The addition of NaTFA minimizes these effects.

Calculation of MW of Polyamides

SEC chromatograms of several polyamide samples (nylon 6 and nylon 6,6) were determined and examples are shwon in Figure 3. Gaussian shaped symmetrical peaks were obtained. PMMA equivalent

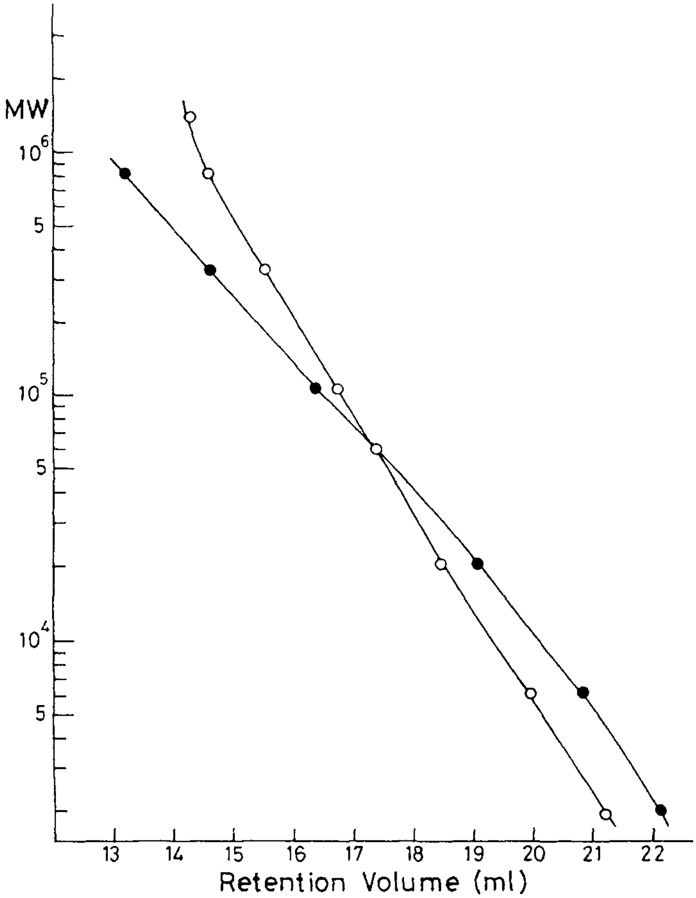

FIGURE 2. Calibration curves of log M vs V_R for PMMA: mobile phase, (o) 0.1% NaTFA in HFIP, (●) pure HFIP.

MW averages of polyamide samples were calculated by using a PMMA calibration curve(Figure 2) and the results are listed in Table 2.

Naturally the PMMA equivalent MW averages of polyamides were not consistent with those obtained by end group analysis (compare Tables 1 and 2). In order to obtain good agreement between both values, any correction must be taken into the PMMA equivalent MW

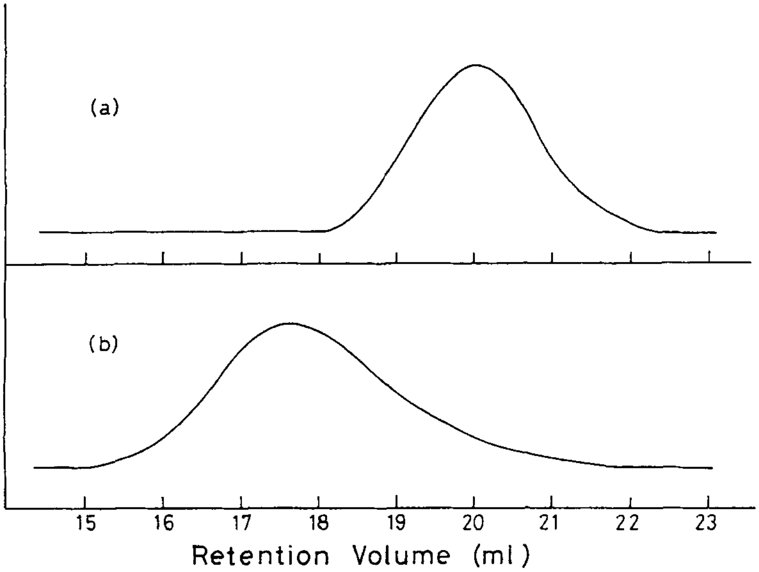

FIGURE 3. SEC chromatograms of nylon 6 and nylon 6,6: (a) nylon 6, MW=1810; (b) nylpon 6,6, MW=16700.

averages. The term number average conversion factor f_n is designated as (14)

$$f_n = \frac{\bar{M}_n \text{ obtained by end group analysis}}{\text{PMMA equivalent } \bar{M}_n} \qquad (1)$$

PMMA equivalent MW averages can be converted to real polyamide MW averages by multiplying f_n to PMMA equivalent MW averages. The values of f_n are listed in Table 2. The conversion factors are not constant and the values increased with increasing MW.

If the conversion factor is to be constant over the entire range of MW, then a linear relationship must stand up between a PMMA equivalent MW and a real polyamide MW. In most cases, however, there is a linear relationship of log MW between two polymers(15). Therefore, instead of the conversion factor method, the other method must be considered in order to convert a PMMA

TABLE 2
PMMA Equivalent Molecular Weight Averages of Polyamide Samples and Conversion Factors

Nylon 6 Sample No.	PMMA equivalent MW $\bar{M}_n$	$\bar{M}_w$	f_n	Nylon 6,6 Sample No.	PMMA equivalent MW $\bar{M}_n$	$\bar{M}_w$	f_n
1	3430	5420	0.528	7	7790	18860	0.406
	3290		0.550		8500		0.372
	3760		0.481		8150		0.388
2	5000	7840	0.610	8	9310	20700	0.485
	5160		0.591		9660		0.468
	4900		0.622		9370		0.482
3	7460	14530	0.621	9	10810	26060	0.586
	7280		0.636		12660		0.500
	7430		0.623		12100		0.523
4	13000	25800	0.808	10	13150	32100	0.567
	12250		0.857		12620		0.591
	12800		0.820		11930		0.625
5	13850	26850	0.816	11	12940	26800	0.629
	13300		0.850		13200		0.617
	14200		0.796		12400		0.656
6	17200	36200	0.971	12	17650	50100	0.946
	18000		0.928		16750		0.997
	17900		0.933		16240		1.028

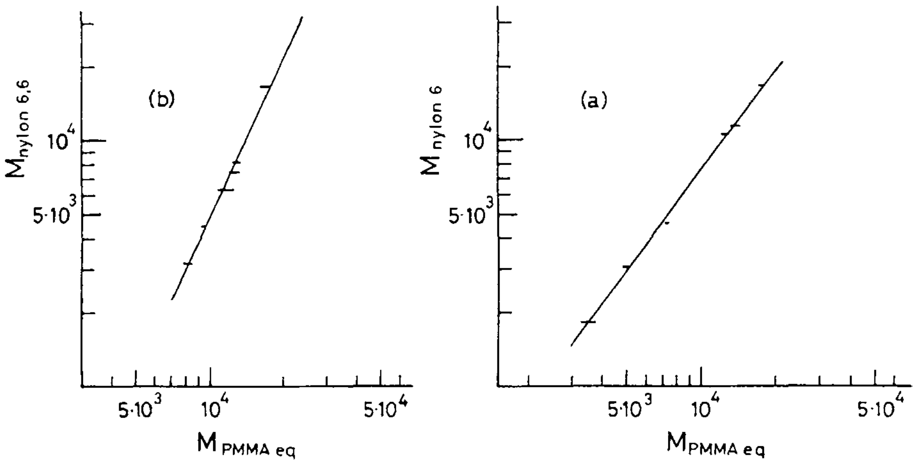

FIGURE 4. Relationship between PMMA equivalent MW and real polyamide MW: (a) nylon 6, (b) nylon 6,6.

equivalent MW to a real polyamide MW. Figure 4 shows the plot of log PMMA equivalent MW and log real polyamide MW. The horizontal line segments used as the data points in Figure 4 means confidence intervals for repeated three determinations. There is a linear relationship between them. From these plots, next equations were calculated.

$$M_{\text{nylon } 6} = 0.02924\, M_{\text{PMMA eq}}^{1.352} \quad (2)$$

$$M_{\text{nylon } 6,6} = 1.3027\text{x}10^{-5}\, M_{\text{PMMA eq}}^{2.143} \quad (3)$$

where $M_{\text{nylon } 6}$ and $M_{\text{nylon } 6,6}$ are a real polyamide MW for nylon 6 and nylon 6,6 and $M_{\text{PMMA eq}}$ is a PMMA equivalent MW for polyamide. The absolute (real) MW of polyamides can be obtained by calculating PMMA PMMA equivalent MW first and by inserting them into these equations.

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