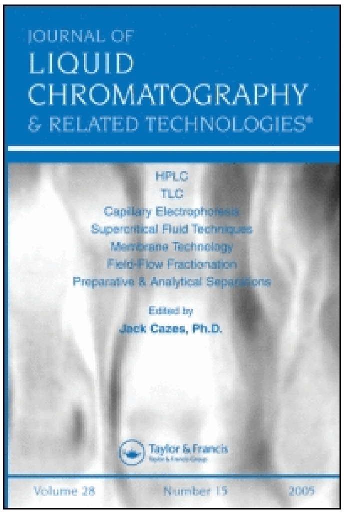

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SOLVENT EFFECT ON THE SEPARATION MECHANISM IN HPGPC OF POLYIMIDE AND POLYETHERSULFONE

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ABSTRACT

Molecular weight distributions (MWD) of polyethersulfone (PES) and various polyimides (PI) in dimethyl formamide (DMF), dimethyl acetamide (DMAc), methylene chloride ($MeCl_2$) and 0.05 M LiBr in DMF were determined using a set of Ultrastyrogel® columns of nominal porosity 10^3, 10^4, 10^5 and 10^6 Å. The resulting chromatograms were bimodal or multimodal in DMF or DMAc and thus are not useful for reliable determinations of MWD. $MeCl_2$ gave unimodal chromatograms but because of its low boiling point, this solvent is not recommended for use at or above room temperature. MWD determinations in 0.05 M LiBr in DMF also gave unimodal chromatograms and can be used for reliable MWD determinations in combination with light scattering measurements.

INTRODUCTION

High performance gel permeation chromatography (HPGPC) has become a powerful technique for determinations of molecular weight distributions of polymers [1,2]. Unlike other liquid chromatography (LC) methods for which the sizes of molecules in solution determine separation, additional separation mechanisms must be considered for HPGPC. In HPGPC, the gel material in the porous packing or stationary phase primarily determines the retention and resolution and as a result, the mobile phase is chosen primarily for sample solubility and secondarily to eliminate unwanted solute or gel effects. Dissolution and diffusion can be slow processes for large molecules and the need to maintain high column efficiency by using solvents of low viscosity is an important consideration.

Polyethersulfone and the polyimides, Matrimide 5218, XU 218, and PI 2080, are stable high temperature polymers [3]. It is important to have some knowledge of the basic structural properties of these materials such as molecular weight and molecular weight distribution. Unfortunately, as is the case for polyamides, there are only a few solvents suitable for use in high temperature measurements. They are *m*-cresol, hexafluoroisopropanol, dimethyl acetamide (DMAc), dimethyl formamide (DMF) and methylene chloride ($MeCl_2$), among others. For the present work, because of experience in the preparation of cast films of polyethersulfone/polyimide blends at moderate viscosity and at moderately high temperature, DMAc, DMF and $MeCl_2$ were chosen as solvents in the determination of molecular weight and molecular weight distribution. DMF is a commonly used solvent in HPGPC experiments [4]. It is compatible with many gel materials and many polar and apolar polymers, weak polyelectrolytes are soluble in DMF and it is inexpensive. However, results for polar polymers and polyelectrolytes in DMF are occasionally difficult to interpret [5-10].

EXPERIMENTAL

Materials

Samples of polyethersulfone (PES, 3600P, 4100P, 4800P, 5200P) were comercially available from ICI-America. The polyimides, Matrimide 5218 and XU 218HP, were obtained from Ciba-Geigy, the polyimide, PI 2080, was obtained from Dow. Polystyrene samples of narrow molecular weight distribution (M_w from 9200 to 2,950,000) were from Polymer Laboratories; a polystyrene standard, SRM-706, was from the National Bureau of Standards. All solvents (from Fisher Scientific or Aldrich) were "spectro-grade" and were used without further purification. For some measurements, LiBr (Fisher purified) was added to DMF.

HPGPC

The HPGPC apparatus consisted of a solvent delivery module 590, a universal injector U6K, a differential refractometer R410 with a temperature control oven, a set of four Ultrastyrogel® columns of porosity 10^3, 10^4, 10^5 and 10^6 Å and a data module DM 730 (Waters). All measurements were carried out at a flow rate of 1 ml/min and a temperature of 45°C (30°C when $MeCl_2$ was used). All polystyrene samples (used for calibration) and polyethersulfone and polyimide samples were dissolved overnight at a concentration of less than 2×10^{-3} g/ml; the samples were filtered through 0.5 µm Millipore filters (Millipore Corp.) before HPGPC measurements.

Light Scattering

A laser light scattering photometer DLS-700 (Otsuka Electronics, Japan) was used in the static mode [11,12] at a temperature of 25°C. Solutions were prepared in volumetric flasks, by adding solvent and dissolving overnight. A set of solutions of lower concentration (1×10^{-3} to 8×10^{-3} g/ml) was prepared by diluting the stock solution. All solutions were filtered through 0.1 µm Millipore filters before use in light scattering measurements.

dn/dc Measurements

Measurements of specific refractive index, dn/dc, were carried out using a differential refractometer RM-102 (Otsuka Electronics, Japan) at a temperature of 25°C and a wavelength of 633 nm. The differential refractometer was calibrated by measuring the refractive indices of sodium chloride solutions of known concentration at four wavelengths, 436, 546, 578 and 587 nm [13]. Sample solution (usually five ranging in concentration from 2×10^{-3} to 7×10^{-3} g/ml) were filtered through 0.5 µm Millipore filters.

RESULTS AND DISCUSSION

The molecular weight distributions (MWD) of the polymer samples were calculated using calibration curves constructed using polystyrene samples with narrow MWD. The calibration curves are shown in Figure 1 for DMF and tetrahydrofuran. Figures 2,3 and 4 show HPGPC chromatograms for all samples in DMF. Average molecular weights were calculated taking into account all peaks in a multimodal chromatogram because the amount of material eluting in high molecular weight peaks was not negligible.

It has been observed that the separation yields species of more than one molecular size and that the calculated molecular weights are overestimated [4,5].

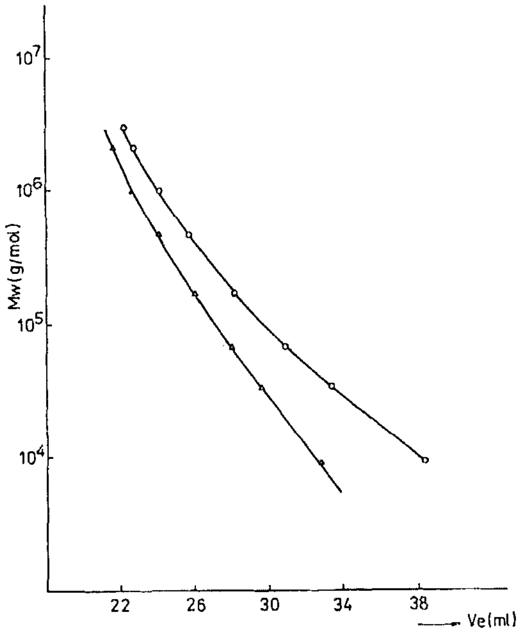

FIGURE 1 HPGPC calibration curves for the set of Ultrastyrogel ® columns used. The curves were constructed using polystyrene standards in THF at 35°C (Δ) and in DMF at 45°C (o).

These observations are characteristic of some polar polymers and polyelectrolytes in DMF [5-10]. Results for DMAc obtained in this study were similar to those for DMF. Figure 5 and the data in Table 1 show examples.

$MeCl_2$ was the third solvent used; the multimodal peaks disappeared from the resulting chromatograms and the distribution became unimodal. Sample molecular weights, calculated using the polystyrene calibration curves, decreased by an order of magnitude (Figure 6 and Table 1). However, because of its low boiling point (39°C), $MeCl_2$ is not recommended for use at temperatures close to room temperature.

Unimodal peaks were also obtained in 0.05 M LiBr solutions (Figures 7 and 8). The calculated molecular weights were lower than those obtained in DMF and DMAc (Table 2) but were still high because the polystyrene calibration curves were

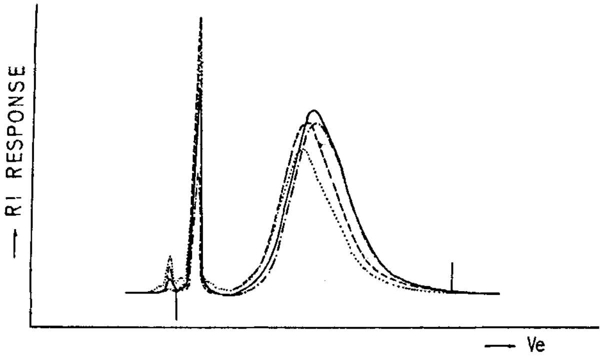

FIGURE 2 HPGPC chromatograms for PES obtained using the set of Ultrastyrogel ® columns in DMF at 45°C and a flow rate of 1 ml/min. 3600P (–·–·–·–), 4100P (———), 4800 P (------), 5200 P (·····).

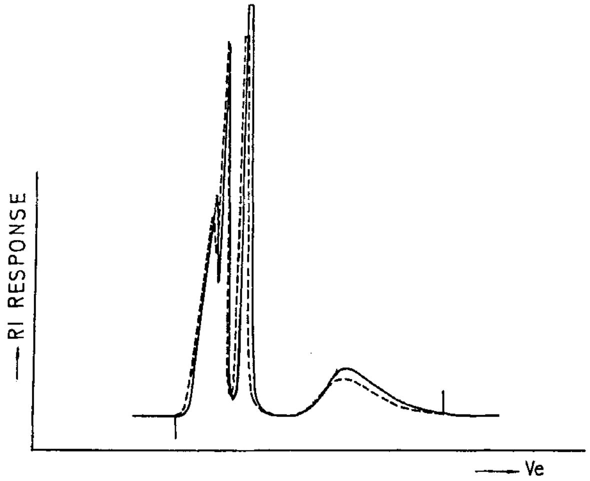

FIGURE 3 HPGPC chromatograms for PI's obtained using the set of Ultrastyrogel ® columns in DMF at 45°C and a flow rate of 1 ml/min. Matrimid 5218 (——), XU 218 (------).

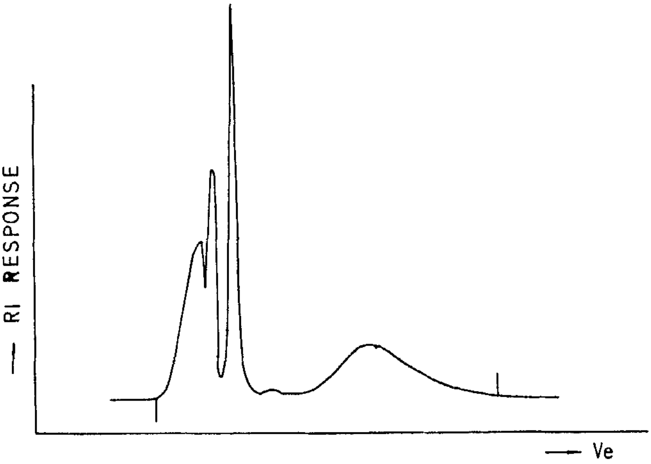

FIGURE 4 HPGPC chromatogram for PI 2080 obtained using the set of Ultrastyrogel ® columns in DMF at 45°C and a flow rate of 1 ml/min.

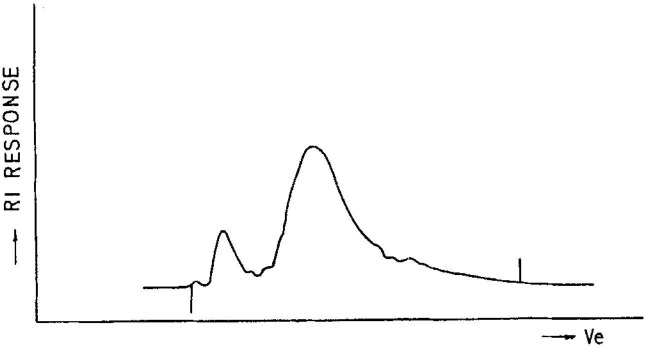

FIGURE 5 HPGPC chromatogram for PES 4100P obtained using the set of Ultrastyrogel ® columns in DMAc at 45°C and a flow rate of 1 ml/min.

TABLE 1

Weight Average, M_w, and Number Average, M_n, Molecular Weights for Polyethersulfone and Polyimides Derived from MWD Data Obtained Using Various Solvents

	M_w g/mol x 10^3	M_n g/mol x 10^3	M_w g/mol x 10^3	M_n g/mol x 10^3	M_w g/mol x 10^3	M_n g/mol x 10^3
Sample	DMF		DMAc		$MeCl_2$	
PES 3600	379.7	78.3			47.7	26.9
PES 4100P	551.1	86.8	280.6	23.6		
PES 4800P	723.6	100.8				
PES 5200P	1310.2	117.4				
PI 2080	7163.0	121.3				
Matrimid 5218	7336.3	408.8				
XU 218 HP	8710.0	533.7				

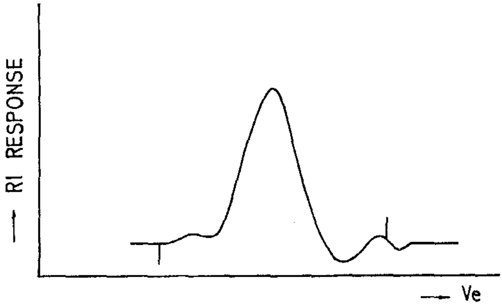

FIGURE 6 HPGPC chromatogram for PES 3600P obtained using the set of Ultrastyrogel ® columns in $MeCl_2$ at 45°C and a flow rate of 1 ml/min.

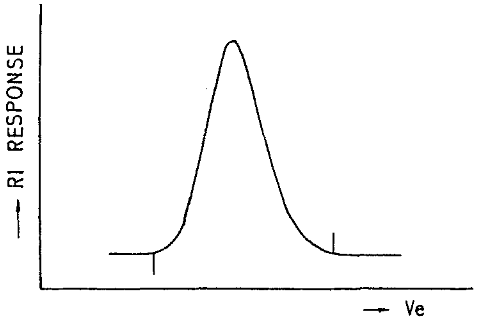

FIGURE 7 HPGPC chromatogram for PES 3600P obtained using the set of Ultrastyrogel ® columns in DMF containing 0.05 M LiBr at 45°C and a flow rate of 1 ml/min.

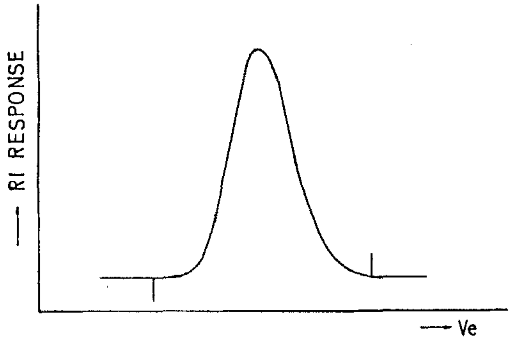

FIGURE 8 HPGPC chromatogram for PI XU 218 HP obtained using the set of Ultrastyrogel ® columns in DMF containing 0.05 M LiBr at 45°C and a flow rate of 1 ml/min.

TABLE 2

Weight Average, M_w, and Number Average, M_n, Molecular Weights for PES and PI Derived from MWD Determinations in DMF Containing 0.05 M LiBr

Sample	M_w (g/mol) x 10^3	M_n (g/mol) x 10^3
PES 3600P	210.1	153.0
PES 4100P	203.1	148.2
PES 4800P	235.6	169.2
PES 5200P	264.9	189.6
PI 2080	182.0	108.4
Matrimid 5218	278.4	195.0
XU 218 HP	293.4	201.3

TABLE 3

Weight Average Molecular Weights, M_w, for PES and PI in DMF Derived from Light Scattering Data

Sample	M_w (g/mol) x 10^3	dn/dc (ml/g)
PES 3600P	31.0	0.188
PES 4100P	34.0	0.188
PES 4800P	40.0	0.188
PES 5200P	45.0	0.188
PI 2080	31.5	0.208
Matrimid 5218	59.0	0.189
XU 218 HP	69.0	0.194

used. The anomalous behavior of the solution properties of polymers in solvents such as DMF and DMAc is reflected by the fact that in these solvents, there is no consistent relationship between molecular weight and viscosity.

Light scattering (LS) measurements were used to supplement the molecular weight data obtained for polyethersulfone and polyimides by HPGPC; LS measurements followed the determination of specific refractive indices (dn/dc). A calibration constant for the RM-102 differential refractometer at a wavelength of 633 nm was determined from the refractive indices of sodium chloride solutions determined at several wavelengths. The data were then extrapolated to 633 nm using the linear portion of the Couchy formula which approximately describes the relation between the refractive index and the wavelength [14]. To check this procedure, the dn/dc for polystyrene SRM-706 was measured in several commonly used solvents and the results were compared to established values. (The dn/dc in THF was 0.186 ml/g and in toluene was 0.107 ml/g.)

Table 3 shows light scattering data obtained in an appropriate concentration range [12] together with dn/dc values. It is clear from these data that even though unimodal chromatograms were obtained from HPGPC measurements in 0.05 M LiBr in DMF and polystyrene calibration curves were used, the calculated molecular weights of the PES and PI samples are greatly overestimated. However, using molecular weights determined by light scattering and polydispersity factors obtained from HPGPC measurements, it is possible to calculate a molecular weight distribution for each sample by fitting a calibration coefficient until the best agreement between the moleculasr weights determined by light scattering and HPGPC is obtained.

FTIR studies of PES and PI [15] showed no structural anomalies; the appearance of peaks in the high molecular weight region may be explained by intermolecular association due to dipole-dipole interactions or to hydrogen bonding. Both types of interactions are favored in these aprotic solvents.

CONCLUSION

The determination of the molecular weight distribution of polyethersulfone and polyimides by HPGPC in DMF and DMAc is not a reliable procedure because multimodal chromatograms are obtained. The use of methylene chloride is not recommended for HPGPC at room temperature even though unimodal chromatograms were obtained. However, the use of 0.05 M LiBr as the mobile phase also gave unimodal chromatograms probable because of diminished aggregation of solute. In combination with light scattering measurements reliable molecular weight distribution data can be obtained using the LiBr solvent system.

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