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Revisiting molecular weight distribution of polystyrenes using adsorption high-performance thin-layer chromatography

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Keywords: polystyrenes; polystyrenes characterization; HPTLC; GPC; MWD; quantitation

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Abstract

A repeatable separation of polystyrenes according to MW, from 1920 to 520000 u.m.a, has been obtained under adsorption conditions using a method that comprises the use of Lichrospher HPTLC plates, and a controlled, isocratic elution with a 78:22 (v/v) mixture of cyclohexane (Cy)-tetrahydrofuran (THF). Likewise, UV-densitometric quantification of polystyrenes in mixtures can be achieved, by an intra-plate or an inter-plate procedure, using the corresponding polystyrene calibration curve. In the case or overlapped, unresolved peaks, an average curve of the corresponding polystyrenes can be used.

Migration of polystyrenes strongly varies with slight variations in the relative proportion of Cy and THF in the mobile phase. This allows different ranges of MW to be separated as a function of mobile phase composition. Other factors influencing repeatability have been identified.

Some reasons have been advanced to explain the current lack of activity in the research on polymer characterization by HPTLC. Old literature results concerning polystyrene separation have also been discussed in the light of modern HPTLC instrumentation.

Developed method provides similar information on Molecular Weight Distribution (MWD) to that obtained using Gel Permeation Chromatography (GPC). Advantages and limitations of HPTLC for obtaining polymer MWD have also been discussed.

1. Introduction

Polymers have been characterized for a long time using Size-Exclusion Chromatography (SEC) which is referred as to Gel Permeation Chromatography (GPC) when is carried out using organic eluants [1,2]. This liquid chromatography-based technique provides Molecular Weight Distributions (MWD) of polymers and polymer mixtures. In GPC, polymers are mostly separated by molecular exclusion, in order of decreasing MW: the first to be eluted is the highest MW.

The variety of stationary phases, the different pore size distributions, and their possible combinations makes this technique has been firmly implanted in the analysis of polymers, despite its low resolution and reproducibility [3]. For complex polymer mixtures, GPC provides curves of molecular size distribution rather than discrete, separated peaks. However, obtaining accurate information from these curves is sometimes complicated. Table 1 shows a summary of advantages and drawbacks of GPC.

In its present state of development, High-Performance Thin-Layer Chromatography (HPTLC) is a mature technique particularly well suited to the analysis of low volatile, complex mixtures [4]. Despite this, application of HPTLC to the analysis of plastics and polymers, as with petroleum, has been scarce [5]. In the field of polymers, developed HPTLC applications involve the detection, isolation and identification of additives. In contrast, very few methods have been developed or applied in the last years related to the characterization of polymers themselves [5]. We face a paradox: whilst a reliable HPTLC technology is currently available but there is almost no research activity in polymer characterization, a number of theoretical and experimental applications were proposed in the 70-90s [6-18], when TLC technology had not yet reached an adequate stage of development.

Separations of different polymers according to MW were obtained under conditions of adsorption and Size-Exclusion TLC in silica gel. This was due to the pioneering work of Belenkii et al. [9-14], and other groups [6-9,15-19]. Research also involved the development of a theoretical frame to relate polymer migration to different physico-chemical parameters of the analytical silica gel system, including determination of an exclusion-adsorption critical transition point [9,10].

From a practical approach, results were probably constrained by technology at the time. Existing sample application, development systems, and plate manufacturing and control technologies provided lower repeatabilities, and larger and less well formed peaks than those obtained using current technology. Another factor that contributed decisively to a no further use of the results was the lack of availability of scanning densitometers which have allowed detection of separated peaks, and subsequent quantification to be carried out.

Therefore it seemed interesting to examine this issue, revisiting and re-evaluating the potential of current HPTLC technology to characterize polymers.

We present in this paper an HPTLC method based on adsorption which provides information on MWD in mixtures of polystyrenes (PS), in a similar way to that obtained using GPC. A special emphasis has been stressed in repeatability of separation and quantitation by densitometry. Instead of trying to understand how the variables that influence the system work with regard to a mechanistic approach, we have preferred to directly use those variables as allowed by current technology, and look for repeatable and quantitative conditions that allow us to carry out a separation.

In a first attempt, the study of PS has several advantages. As their separation by GPC has been well studied under different conditions, we have been able to compare the effect of the technology used here, under similar or equivalent experimental conditions to those used in the past. Likewise, PS are easily soluble, are of narrow MWD and have been used for calibrating GPC chromatograms of other polymers which have broader distributions and solubility problems.

Finally, comparative pros and cons of GPC and HPTLC for MWD are also discussed.

2. Experimental

2.1. Standards and samples

Polystyrene standards (PSs) of different molecular weights from Fluka Analytical (Buchs, Switzerland), Agilent Tecnologies (Palo Alto, California), and Waters (Milford, Massachusetts) were used in this work (Table 2). They are of narrow MWD, with M_w / M_n < 1.09 where M_w is the weight-average molecular weight, and M_n the number-average molecular weight.

Mixtures of these standards were used to evaluate separation (Table 3) and quantitativity (Tables 4 and 5) of the method.

2.2. Solvents

HPLC-grade cyclohexane (Cy, 99.7 %), from Scharlab (Barcelona, Spain), and stabilisant-free tetrahydrofuran (THF, 99.9 %), from Panreac (Barcelona, Spain) were used. Prior to use in HPTLC runs, THF was eluted through an activated carbon-filled LC column (dimensions), using an iron (II) sulfate indicator, to avoid formation of peroxydes. THF was further kept under nitrogen.

2.3. Planar Chromatography experiments.

2.3.1. Plates.

High-performance silica gel HPTLC plates and Lichrospher plates, on glass, 10 x 20 cm; 3-10 µm particle size; 60 Å pore size; 0.2 mm thick layer, F_{254}), from Merck (Darmstadt, Germany) were used.

Before sample application, plates were developed (90 mm) with THF using a conventional, vertical tank, and subsequently activated 30 min at 105 ºC using the Camag TLC Plate Heater III (Camag, Müttenz, Switzerland).

2.3.2. Sample application.

Samples were freshly prepared before each HPTLC run. They were dissolved in a 1:1 v/v mixture of Cy and THF. They were applied onto the plate using the Automatic TLC Sampler 4 (ATS4) from Camag, as 4 mm bands. Typically, up to 31 samples were applied on the same plate with a distance of 2 mm between tracks. Two tracks were always kept free of sample application: a solvent blank run, and a blank run.

The first application position was 10 mm (x coordinate), and the distance from lower edge of plate was 10 mm (y coordinate)

Typical sample load and application volumes were between 0.1-1.2 µg and 0.1-1.2 µL, respectively.

2.3.3. Chromatographic development.

An Automatic Multiple Development (AMD2) system (Camag, Müttenz, Switzerland) was used for chromatographic development using a one-step, isocratic elution with Cy:THF (78:22, v:v). The total migration distance (m.d.) was 80 mm.

The mobile phase was prepared and the plate introduced into a vacuum-tight chamber. Chromatography was monitored, and the run stopped when the selected developing distance was reached. The remaining solvent was withdrawn from the chamber by vacuum, and the plate was completely dried.

Repeatability of AMD2 was ± 0.45 mm.

Retention properties of polystyrenes are given as m.d., in mm, or R_f (polystyrene migration distance / solvent front migration distance).

2.3.4. UV Scanning densitometry.

A TLC Scanner 3 (Camag, Müttenz, Switzerland) was used in UV mode (190 nm). Camag WinCats software was used for controlling ATS4, AMD2 and TLC Scanner 3, and also for data acquisition and treatment.

3. Results

3.1. Separation of polystyrenes according to their MW

A repeatable separation of polystyrenes from 1920 to 520000 u.m.a has been obtained by the described HPTLC method using Lichrospher plates, elution with Cy:THF 78:22 v/v, and other conditions described in Experimental. Figure 1A shows superposed HPTLC chromatograms of studied PS, injected as individual standards under the above conditions.

Migration of polystyrenes strongly varies with slight variations in the relative proportion of cyclohexane and THF in the mobile phase. This allows different ranges of MW to be separated as a function of mobile phase composition. Therefore, PS from 1920 to 17300 have been separated by elution with Cy:THF 90:10 v/v; and from 1920 to 52100 using Cy:THF 85:15 v/v. A further increase of relative proportion of THF to 30% favoured PS standard migration but did not improve separation. When THF reached 50 %, PS standards were eluted with the solvent front.

Figure 1B shows the corresponding log M_w vs R_f curve which relates elution properties of a given polymer with its MW for the different mobile phases used.

This curve gives similar information that those obtained from GPC in HPLC mode.

3.2. Repeatability of separation

Repeatability has been studied for the elution conditions that gave the wide range of separation for PS standards: Cy:THF 78:22 v/v.

R_f and m.d. values for each PS, individually injected using the procedure described in Experimental, are given in Table 2 together with repeatability parameters. Standard deviation (σ_{std}), variability of R_f and of migration distance (± mm) for a given confidence interval, *C.I.* (95%) are also given in this Table, where

$$C.I. = X_m \pm t\, \sigma_{std}\, n^{-0.5}$$

where X_m is the migration distance average, t is the Student distribution, and n is the number of measurements. They have been obtained by applicating three replicates in different plates and different days. Results show that the procedure has an adequate repeatability.

The lower the MW, the higher the R_f (or the longer the polymer m.d. with regard to the application point, R_f=0). Therefore, separation is governed by adsorption.

In order to evaluate whether a matrix effect may exist, R_f of each polymer in mixtures was compared to those obtained as individual pure standard. As shown in Table 3, Variations in R_f (ΔR_f) are within the experimental interval of variability for C.I. 95%. Therefore, matrix effects can be excluded. In this context, Figures 2 and 3 shows the HPTLC chromatograms corresponding to the separation of polystyrenes in the studied mixtures using Cy:THF 78:22 v/v elution system.

Repeatability has been tested for a time after the study by random analyses of mixtures of PS. The results obtained are found mostly within the variability interval provided by the given confidence interval.

3.3. Detection, calibration and quantitative analysis

UV signal provided at 190 nm is adequate for PS detection. In general, responses (expressed as Area counts per mass unit) decrease as MW increases. Thus, for example, response for PS 524000 is half that of PS 1920.

The possibility of doing quantitative analyses was assessed by using samples that include mixtures of two to five polystyrenes, which have known compositions (Table 4). Proposed mixtures include polystyrenes in different MW ranges. HPTLC chromatograms of mixtures in which PS are baseline-resolved (Figure 2) or unresolved (Figure 3) are shown. Their quantitative results are given in Tables 4 and 5, respectively.

Different calibration procedures have been tested for each polymer:

- intra-plate calibration : the corresponding polystyrene standards (n=5 per polymer) have been applied on the same plate that the corresponding problem mixtures
- inter-plate calibration: points from intra-plate calibration have been accumulated for each polymer to additional 5 points obtained from different plates. In total, n=10 per polymer

Therefore two calibration curves per polymer have been obtained, and polystyrenes have been analyzed in the mixtures using their corresponding curves.

Some of the proposed mixtures show polystyrenes with close MW values, which show unresolved peaks (Figure 3). As in the case of GPC-chromatograms, HPTLC chromatograms of complex polystyrene mixtures and mixtures containing polymers with close MW do not usually show discrete peaks but rather curves of MW-distribution, with peaks which are not resolved to baseline. In these cases, two procedures of quantification have been tried here:

- resolving the overlapped peaks by a valley-to-baseline integration (dashed lines in Figure 3), using for quantitative analysis the corresponding calibration curve of each polymer (○ in curves in Figure 3)
- integrating the whole area of the overlapped peaks, and using an average calibration curve (continuous line in curves of Figure 3) which come from the accumulation of the points corresponding to the curves of each polymer.

A similar approach was also used in the case of mixture 7 (Figure 2). Although in this case there are no overlapped peaks, the peak at 10 mm covers in fact two peaks corresponding to PS-215000 and PS-524000 which have been integrated as a single peak. Therefore an average calibration curve has been used with calibration points coming from both polymers.

Tables 4 and 5 gives the normalized results of quantitative analyses using the above-mentioned calibration procedures compared to the known weight percentages of the polymers in each mixture. Results indicate that a quantitative approach is possible. Results show that both intra- (n=5) and inter-plate (n=10) procedures can be used. This suggests that an accumulation of calibration points from different plates may even improve quantitative results. The calibration approach for unresolved peaks which uses an average calibration curve from a joint integration of the overlapped peaks (Table 5) provides percentages close to reference values although it shows a tendency to underestimate low-MW and overestimate high-MW polystyrenes. The higher deviation with regard to known weight percentages has been found in mixture 7 which contains the higher-MW polystyrenes.

4. Discussion

4.1. Issues related to the described method

We have confirmed that little differences in the composition of mobile phase provide important differences in polystyrene migration. This was pointed out elsewhere [15]. In our opinion, this influence, although important, may have been overestimated in the literature. It was reported, for example, that a difference of 1 % in ketone, in a ternary Cy-benzene-acetone eluant, provided important changes in migration [10]. Some of results obtained in the past which concerns variations in elution conditions might be due to an inadequate repeatability of runs derived from existing technology rather than to small differences in composition.

Both factors may have contributed to discredit results in the past.

Anyway, with the current state of HPTLC technology it seems possible to control the different steps of chromatographic process and obtain repeatable methods. According to our results, experimental conditions must be strictly followed so that migration of the polymers are within the variability of the method.

The key points to obtain a repeatable method have been: the use of Lichrosphere HPTLC-plates; the use of freshly-prepared samples; and the need of a controlled elution.

The use of Lichrospher plates has been crucial for method repeatability. Their use provided better peaks, and had a clear impact on the inter-plate repeatability of the experiment probably due to the shape of particles, and pore and particle size distribution. Under the described conditions, Lichrospher plates provide separation by adsorption and not by exclusion.

We were unable to obtain a repeatable method for PS using conventional HPLC silica gel plates. In five runs, migration distances were out of the variability interval. Likewise, we noticed in some runs exclusion effects from a given polystyrene MW (Figure 4). Previous works showed that the adsorption mechanism is overlapped by the size-exclusion mechanism for PS [8,15].

Samples must be freshly prepared and should not be stored in the freezer.

Elution should be carefully controlled. Separation in conventional, vertical tank was studied before the use of AMD. Although some separation was obtained, peaks were wide and the baseline, deficient. It was also noticed that the saturation of the vertical tank had no effect on PS migration, unlike what was suggested elsewhere [19].

An adequate separation has been obtained using AMD. It provides a better baseline and narrower peaks than those obtained from a conventional tank. Likewise, AMD allows a tighter control of the elution conditions, with controlled drying and vacuum steps. Probably, other automatic chambers, simpler and cheaper than AMD and not necessarily based on multiple development, may be used to obtain repeatable and well-formed peaks [4]. In principle, AMD was selected because of the possibility of using elution gradient. However, it was not possible to separate PS according to their molecular weight using a Cy-THF gradient.

On the other hand, adsorption has been favoured against exclusion. Plate heating prior to chromatographic development was done to reduce moisture and increase the active groups in the adsorption of silica gel surface.

The possibility of separating PS up to 500000 using Cy-containing binary mixtures was pointed out elsewhere using silica gel with pore diameter of 110 Å or higher [19]. In this study we have used silica gel with 60 Å pore diameter which is the most common pore size in commercially available silica gel plates.

Separations of polystyrenes up to 1800000 with Cy-toluene-methyl ethyl ketone mixtures were also reported elsewhere [12], using silica gel with 500 Å pore diameter. However, we were unable to reproduce this separation using a 60 Å sorbent.

Results suggest that quantitative analysis of mixtures of polystyrenes by HPTLC is possible and open the door to a reliable polymer caracterization using HPTLC. Calibration can be done either in the same plate or by accumulation of calibration points from different plates.

Polystyrene MWD derived from GPC chromatograms are usually interpreted in comparative or semiquantitative terms, for a comparative evaluation of production or operation parameters. This information can be also provided by HPTLC chromatograms.

4.2. HPTLC as a potential technique for MWD of polymers

In general, advantages of HPTLC are derived from the inherent ones of a planar technique with regard to those of HPLC (column technique) which can be summarized as follows [4]:

- the whole sample is scanned. This provides a complete, quantitative analysis
- rapid, flexible analysis with low solvent consumption
- analysis in parallel; samples and standards can be run on the same plate under the same conditions
- non-destructive analysis. The plate is an storage device that can be re-scanned or re-developed under different conditions

While these advantages are important, the main ones in our case are its rapidity (several minutes for sample application, 15 min elution, scanning in seconds) and high sample throughput (30 samples per plate under the described conditions). Likewise, there is no need for detector stabilization, and the complete process is flexible and semi-automatized.

Several labels have been unfairly branded to HPTLC. HPTLC has become, in its present state of development, a repeatable technique which provides adequate separation and quantitative analysis when calibration is properly performed. Likewise, the availability of a commercial TLC-MS interphase and the possibility of performing mass spectra on the plate surface (MALDI, DART, etc. [20]) can open the door to a further development of hyphenation with other techniques.

However, HPTLC has limitations with regard to the obtention of polymers MWD. The potential use of silica gel by exclusion is limited because practically only one pore size distribution is commercialized.

In the context of adsorption, results show that different ranges of MW can be separated by using different elution sequences. The application of the developed HPTLC method to polymers other than PS should be done by using other stationary phases. In the past, a study on PS separation using reversed-phase HPTLC was reported [18]. However, we were unable to reproduce the described separation. Other works should be revisited using the modern HPTLC technology. Likewise, other recently developed stationary phases should also be tested.

5. Conclusions

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Captions for Figures

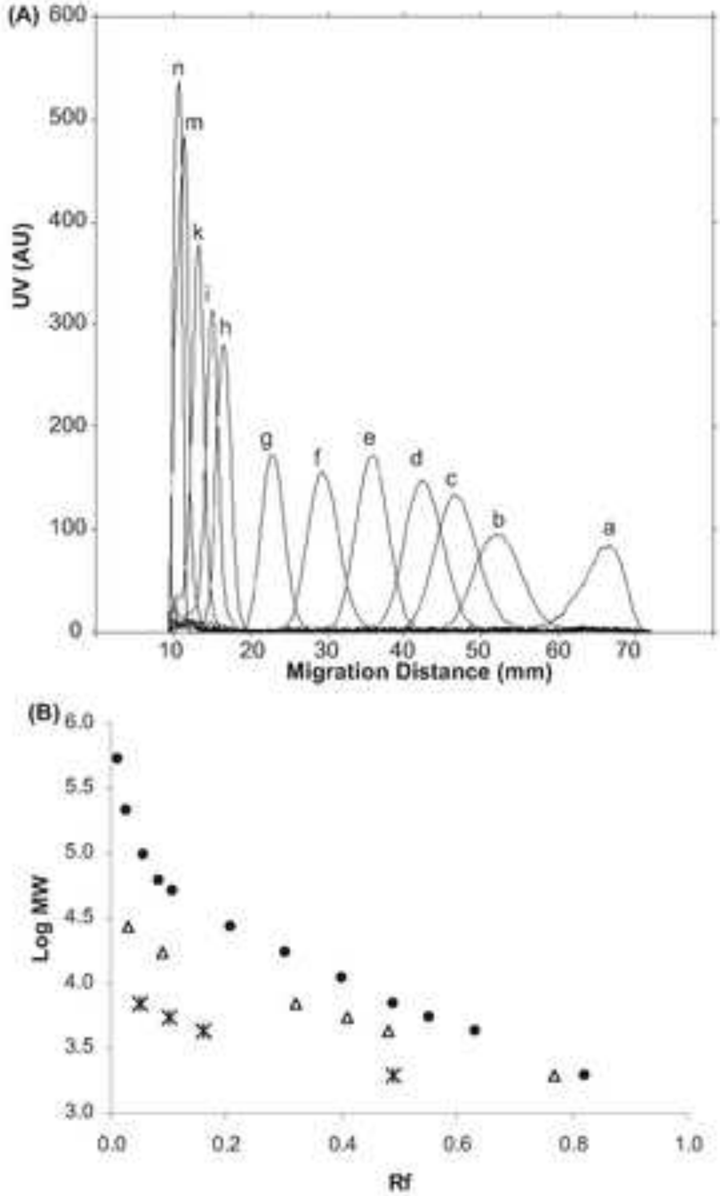
Figure 1.- HPTLC-UV chromatograms **(A)** of PS, injected as pure standards: PS-1920 (a), PS-4330 (b), PS-5460 (c), PS-6890 (d), PS-10850 (e), PS-17300 (f), PS-27500 (g), PS-52100 (h), PS-62300 (i), PS-96000 (k), PS-215000 (m), PS-524000 (n). (Lichrospher plates; 78:22 v/v Cy:THF as mobile phase; see other conditions in Experimental).

Log M_w vs R_f calibration curves **(B)** for the above polystyrenes under different elution conditions using Cy:THF proportions (v/v): 78:22 (●), 85:15 (Δ), 90:10 (ж)

Figure 2.- HPTLC-UV chromatograms of PS mixtures with baseline resolved peaks: mixture 1 (**A**), mixture 5 (***B***), mixture 7 (**C**), mixture 3 with detail of calibration curve for each peak, using replicate samples (**D**). Composition of mixtures are given in Table 4. (Lichrospher plates; 78:22 v/v Cy:THF as mobile phase). Equations: inter-plate PS-17300 (∆): y= 17246 x + 766.4 (r^2= 0.9667); PS-4330 (○): y= 23118.5 x + 762.3 (r^2= 0.9971)

Figure 3.- HPTLC-UV chromatograms of PS mixtures with details of averaged calibration curves for unresolved peaks: mixture 2 (**A**), mixture 4 (**B**), mixture 6 (**C**). Composition of mixtures are given in Table 4. (Lichrospher plates; 78:22 v/v Cy:THF as mobile phase). Example of equations for (A): inter-plate PS-6890 (ж): y= 21936 x + 995.8 (r^2= 0.9799); PS-4330 (□): y= 23118.5 x + 762.3 (r^2= 0.9971). Average curve (-): y= 22527 x + 879.1 (r^2= 0.9878)

Figure 4.- HPTLC chromatograms showing mixed adsorption / exclusion effects on elution of PS, applied as pure standards: PS-1920 (a), PS-4330 (b), PS-5460 (c), PS-6890 (d), PS-10850 (e), PS-17300 (f), PS-27500 (g), PS-52100 (h), PS-62300 (i), PS-96000 (k), PS-215000 (m), PS-524000 (n), PS-1056000 (o), PS-2522000 (p). Conditions: silica gel HPTLC plates; 76:24 v/v Cy:THF as mobile phase; see other conditions in Experimental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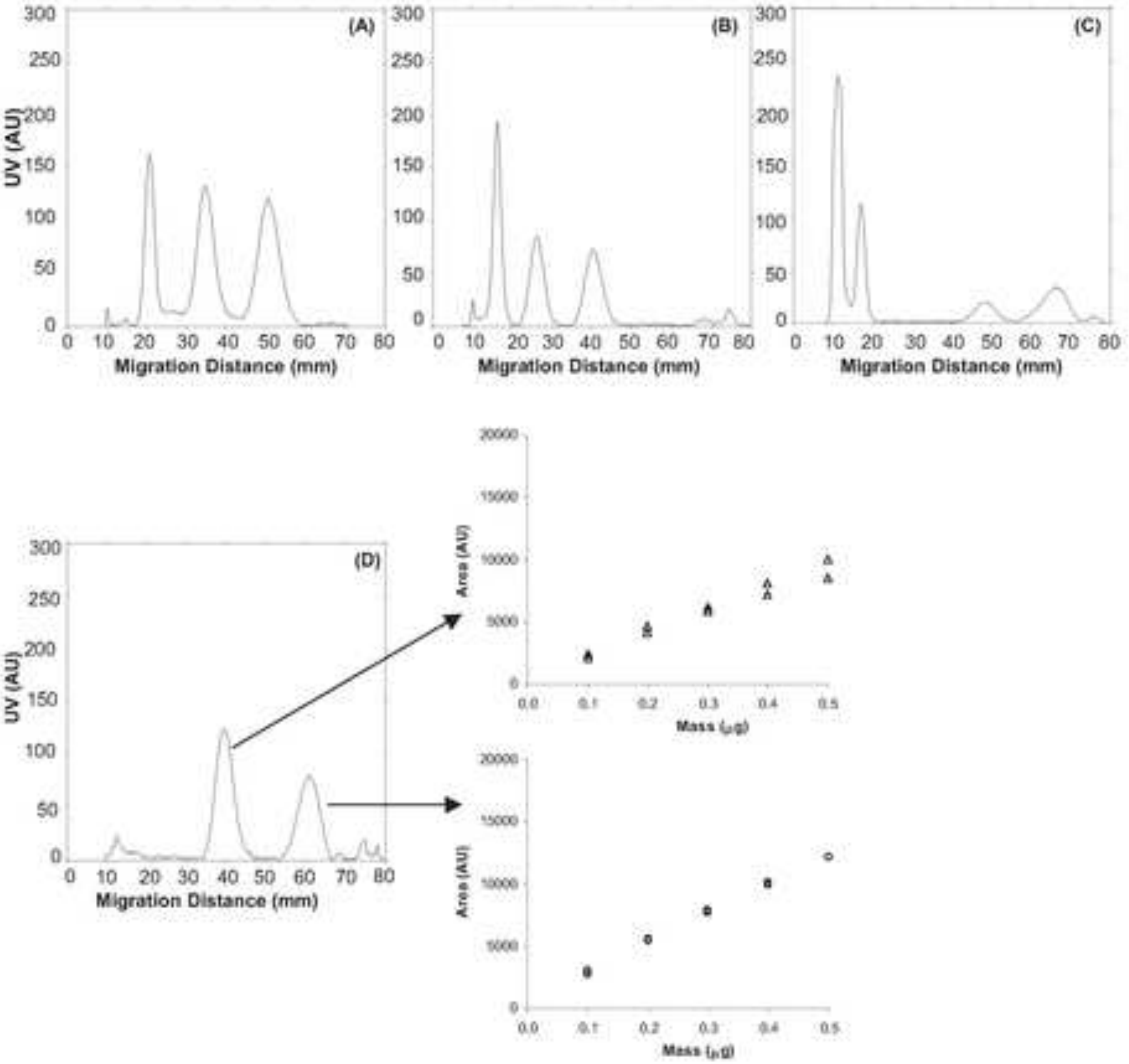
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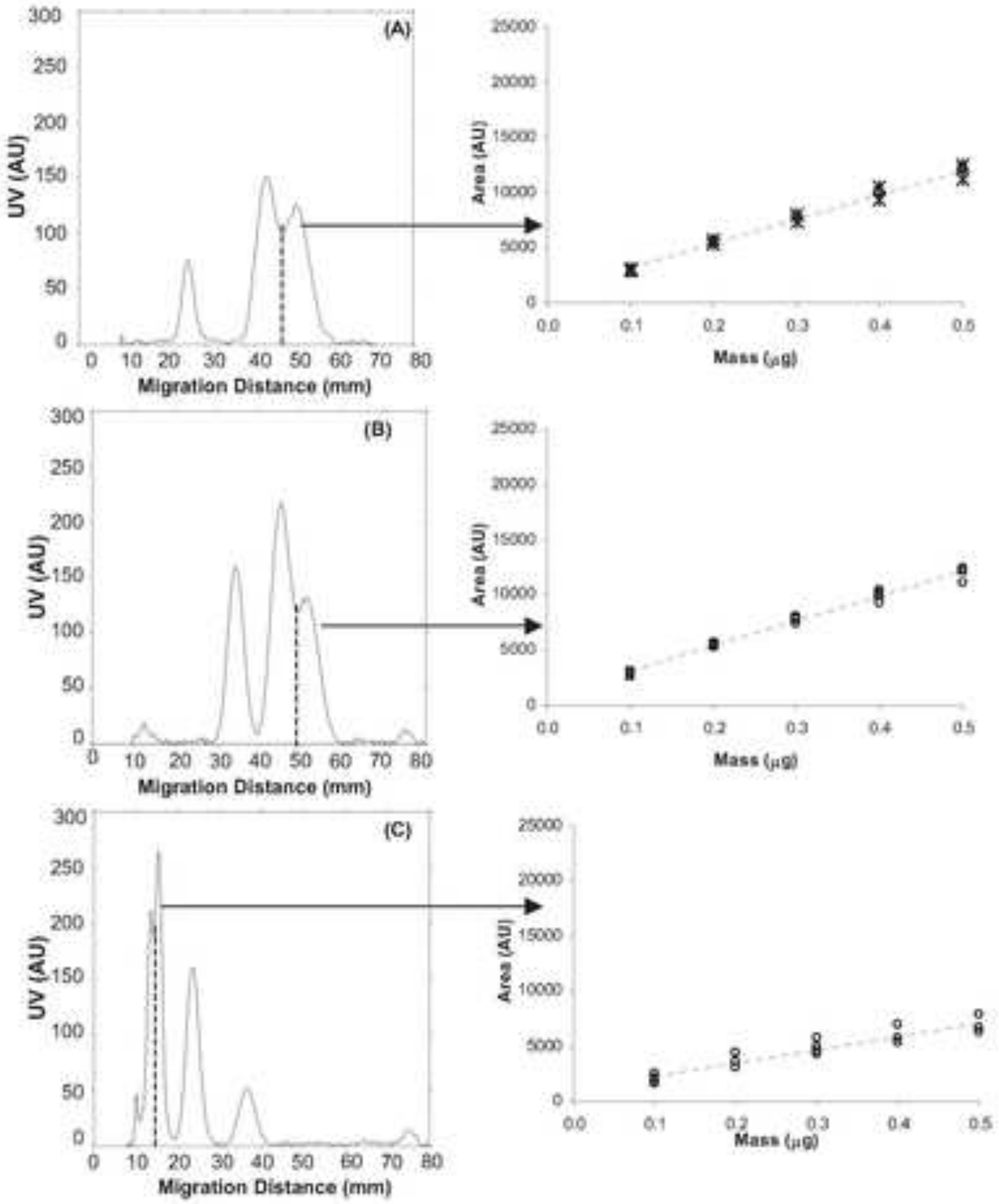
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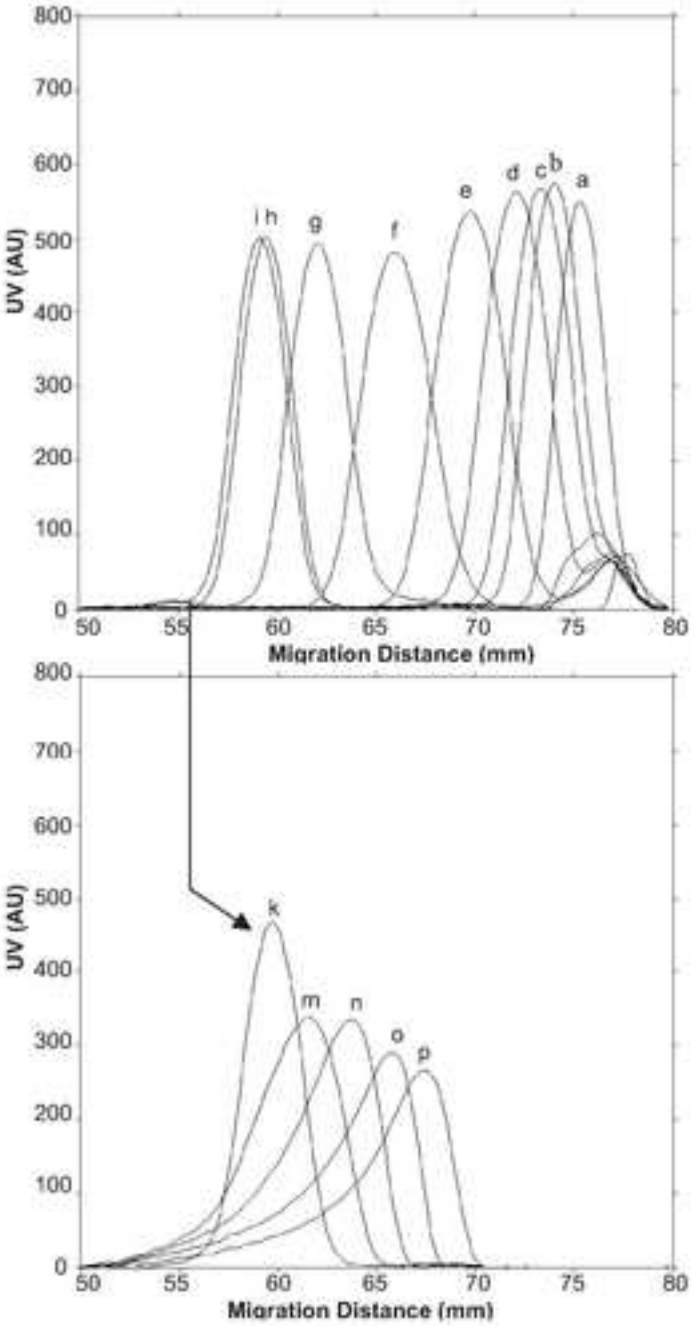
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Figure for the Graphical Abstract

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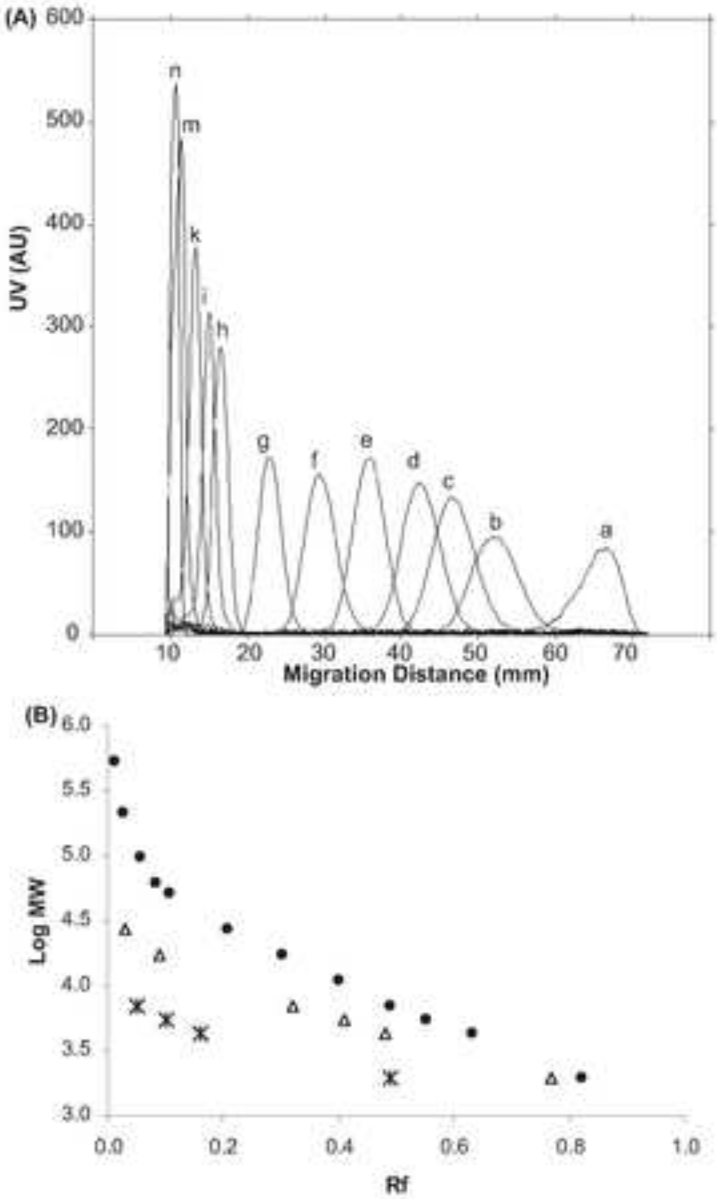

Table 1.- Advantages and drawbacks of GPC

Advantages	Drawbacks
- Diversity of columns (phase, distributions of pore size, connections between columns)	- Low resolution. Distribution curves rather than discrete peaks are obtained
- Coupling to mass selective detectors (viscosity, LALLS, etc.)	- Low inter-lab reproducibility [3]
- Application to a wide range of polymers	- Difficulty in obtaining accurate data from chromatograms (artefacts in connections between columns and between detectors, problems associated to particular detectors such as differential refractometry, etc).
- Possibility of working at temperature	- Adsorption phenomena

Table 2.- Molecular Weight averages of standards, migration values (R_f, m.d.)[a] and repeatability parameters

Polystyrene (PS)	Mw[b] (g mol^{-1})	Mn[c] (g mol^{-1})	Mw/Mn[e]	R_f	R_f variability (±)	m.d. (mm)	m.d. variability (±mm)
PS-1920	1920	1770	1.08	0.82	0.3	67.6	1.6
PS-4330	4330	4160	1.04	0.63	0.6	54.1	4.1
PS-5460	5460	5301	1.03	0.55	0.6	48.9	4.1
PS-6890	6890	6720	1.03	0.49	0.5	44.5	3.6
PS-10850	10850	10637	1.02	0.40	0.5	37.8	3.7
PS-17300	17300	16900	1.03	0.30	0.6	31.2	3.7
PS-27500	27500	26600	1.04	0.21	0.5	24.4	3.6
PS-52100	52100	50750	1.03	0.11	0.4	17.6	2.7
PS-62300	62300	60600	1.03	0.08	0.3	15.8	1.8
PS-96000	96000	92000	1.04	0.06	0.2	13.9	1.4
PS-215000	215000	203000	1.06	0.03	0.2	11.9	1.0
PS-524000	524000	502000	1.04	0.01	0.1	10.9	0.5
PS-1056000	1056000 (Mp[d])		1.03	0.01	0.1	10.7	0.5
PS-2522000	2522000	2437000	1.03	0.01	0.1	10.7	0.6

[a] using Cy:THF (78:22, v:v), other conditions in experimental, [b] $Mw = \frac{\sum_i W_i}{\sum_i M_i}$, [c] $Mn = \frac{\sum_i W_i}{\sum_i \frac{W_i}{M_i}}$

[d] Mp is the molecular weight corresponding to that of the maximum of the GPC chromatographic peak (provided by the manufacturer), [e] polydispersity

Table 3.- Composition of studied PS mixtures and migration data of standards using the elution sequence Cy:THF (78:22, v:v)

Mixture	Mw (g mol^{-1})	R_f		ΔR_f
		In mixture	As pure standard	
Mixture 1	PS-5460	0.58	0.55	0.03
	PS-17300	0.35	0.30	0.05
	PS-52100	0.15	0.11	0.04
Mixture 2	PS-4330	0.58	0.63	0.05
	PS-6890	0.35	0.49	0.14
	PS-27500	0.15	0.21	0.06
Mixture 3	PS-4330	0.64	0.63	0.01
	PS-17300	0.38	0.30	0.08
Mixture 4	PS-4330	0.59	0.63	0.04
	PS-6890	0.51	0.49	0.02
	PS-17300	0.35	0.30	0.05
Mixture 5	PS-10850	0.42	0.40	0.02
	PS-27500	0.22	0.21	0.01
	PS-62300	0.09	0.08	0.01
Mixture 6	PS-10850	0.37	0.40	0.03
	PS-27500	0.19	0.21	0.02
	PS-62300	0.08	0.08	0.00
	PS-96000	0.05	0.06	0.01
Mixture 7	PS-1920	0.80	0.82	0.02
	PS-5460	0.55	0.55	0.00
	PS-52100	0.10	0.11	0.01
	PS-215000	0.02	0.03	0.01
	PS-524000		0.01	0.01

Table 4.- HPTLC-based quantitative analysis of baseline-resolved PS mixtures using intra-plate and inter-plate calibration procedures

Mixture	Mw (g mol^{-1})	wt %	wt % by HPTLC method	
			Intra-plate calibration[a]	Inter-plate calibration[a]
Mixture 1	PS-5460	37.4	n.m.[b]	36.2
	PS-17300	32.8		35.4
	PS-52100	29.8		28.4
Mixture 3	PS-4330	43.8	36.4	34.6
	PS-17300	56.2	63.6	65.4
Mixture 5	PS-10850	28.6	24.8	23.3
	PS-27500	30.8	31.4	30.6
	PS-62300	40.6	43.8	46.1
Mixture 7	PS-1920	21.2	15.2	16.2
	PS-5460	10.3	6.4	6.7
	PS-52100	28.0	26.1	24.8
	PS-215000 PS-524000	40.5	52.3[c]	52.3[c]

[a] Normalized results

[b] Not measured

[c] Integration was performed as a single peak. Calibration using an average curve from both polymer’s points (see text)

Table 5.- HPTLC-based quantitative analysis of baseline-unresolved PS mixtures

			wt % by HPTLC method		
Mixture	Mw (g mol^{-1})	wt %	Intra-plate calibration[a]	Inter-plate calibration[a]	Inter-plate calibration using average curve[b]
Mixture 2	PS-4330	39.8	n.m. [c]	37.1	81.8
	PS-6890	44.5		43.9	
	PS-27500	15.7		19.0	18.2
Mixture 4	PS-4330	26.3	24.9	23.8	68.2
	PS-6890	44.0	43.1	43.6	
	PS-17300	29.7	32.0	32.6	31.8
Mixture 6	PS-10850	10.6	9.4	8.2	7.6
	PS-27500	38.2	39.1	37.8	35.1
	PS-62300	34.8	35.1	35.8	57.3
	PS-96000	16.4	16.4	18.2	

[a] Normalized results

[b] Whole integration of overlapped peaks was used. Calibration was performed using an average curve (see text)

[c] Not measured