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Journal of Chromatography B, 753 (2001) 139–149

JOURNAL OF
CHROMATOGRAPHY B

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Fractionation of functional polystyrenes, poly(ethylene oxide)s and poly(styrene)–b–poly(ethylene oxide) by liquid chromatography at the exclusion–adsorption transition point

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Abstract

The paper reports the fractionation of functional polystyrenes (PSs) and poly(ethylene oxide)s (PEOs) as well as their block copolymers, by liquid chromatography at the exclusion adsorption transition point (EATP–LC), also called ‘‘critical conditions’’ mode. In this specific elution mode (EATP–LC), the fractionation is only governed by the nature and the number of functions attached to the polymer backbone, independent of the molar mass distribution of the whole sample. Functional polystyrenes (α- and/or α,ω-alcohol-, acetal-, aldehyde- and acidic-PS) could be readily separated from non-functional polystyrenes under various chromatographic conditions. The technique also allowed the fractionation of poly(ethylene oxide)s and PS–PEO block copolymers. In the latter cases, moderately polar columns (grafted silica) and water-based polar eluents were required to obtain a satisfactory fractionation.

Keywords: Exclusion–adsorption transition point; Polystyrenes; Poly(ethylene oxide)

1. Introduction

Because of their intrinsic nature, polymers are complex materials that may exhibit simultaneously different kinds of distribution; the most common one generally examined is related to the molar mass which is determined by a size-exclusion chromatography (SEC) technique. The synthesis of functional polymers (block-, random, grafted-) copolymers and other polymer architectures, generates a series of distribution owing to the presence, in the whole sample, of polymer chains with different functionalities, chemical compositions, architectures, etc.

Consequently, a complete characterization of a polymer sample requires at least a bi-dimensional separation technique. Generally, the polymer chains are first fractionated according to their differences in molecular composition or functionality followed by a second characterization giving the molar mass distribution of the discriminated chains. This second step is usually carried out by SEC, matrix-assisted laser desoroption ionization time-of-flight (MALDI-TOF), supercritical chromatography, etc. The first fractionation step of each type of chain, according to their chemical nature, may be readily carried out by high-performance liquid chromatography (HPLC) in

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PII: S0378-4347(00)00372-8

a very specific elution mode: the exclusion–adsorption transition point (EATP) also called ‘‘critical conditions’’. This technique usually requires the use of a binary eluent with a very precise composition [1]. Theoretical approaches [2–4] as well as physical chemistry interpretation [5,6] with respect to the molecular dimensions of the eluted polymer in this specific elution mode have been previously discussed in the literature.

The specific elution mode has been mostly devoted to the fractionation of polymers with different functionalities and architectures after Belenky et al. proved the validity of the technique by thin-layer chromatography [7]. Then, Entelis et al. [8] used the technique to separate hydroxylated poly(ethylene adipate) according to the number of hydroxyl groups per chain. Fractionations according to the functionality of polybutadienes [8], polyesters [9–12], polyethers [13–22], epoxide resins [23] or oligocarbonates [24] have been widely described. The fractionation of PS–b–PtBMA (poly(terbutylmethacrylate)) block copolymers, with respect to the length of the polystyrene block, under critical conditions established for the polar block, has been further demonstrated [25,26]. The characterizations of PS–b–PMMA (poly(methylmethacrylate)) [27,28], PDMA (poly(decylmethacrylate))–b–PMMA [29,30] and PTHF (poly(tetrahydrofurane)–b–PMMA [31] block copolymers were also depicted. The concept of critical conditions was extended to the characterization of tri-block copolymers PEO–PPO (poly(propylene oxide))–PEO [32,33], to the fractionation of polymer blends [34–36] and, more recently, to the separation of PMMAs according to their tacticity [37]. Finally, the technique has also allowed the discrimination of macromolecules according to their architecture [38].

The aim of this paper is to demonstrate the potentiality of liquid chromatography (LC) EATP for the fractionation and the characterization of functional polystyrenes (PSs), poly(ethylene oxide)s (PEOs) as well as of PS–b–PEO block copolymers.

2. Experimental

2.1. Solvents

Toluene, 99.8% (Scharlau, Spain), methyl ethyl ketone (MEK), 99% (Lancaster, France), ethyl acetate (EtAc), 99.5% (Scharlau), CH_2Cl_2 stabilized with 50 ppm of amylene (Scharlau), *n*-hexane, 96% (Scharlau), methanol (MeOH), 99.97% (Scharlau), acetonitrile (ACN), 99.98% (Scharlau), 1,2-dimethoxyethane (DME), 99+% (Lancaster) were used as received. Tetrahydrofuran (THF) stabilized with 0.025% of butylated hydroxytoluene (Baker Analyzed Reagent) was distilled over calcium hydride before use. Water of Milli-Q purity served for the preparation of the eluents. Solvent mixtures were prepared by weighing; aqueous ones were degassed with ultrasound.

2.2. Polymer samples

PSs from PolymerExpert (France) and Cluzeau (France) ranging from 1000 to 135 000 g/mol of narrow molar mass distribution ($\overline{M}_w/\overline{M}_n < 1.1$), were dissolved in the eluent mixtures at a concentration of 0.15–0.3 wt.% before analysis. PEOs from Polymer Expert and Tosoh (Japan) ranging from 520 to 17 500 g/mol were dissolved in the eluent at a concentration of 0.5 wt.% in a bain-marie at 40–50°C before injection. The PS–b–PEO block copolymers from Polymer Expert were dissolved in the eluent at a concentration of 0.2–1 wt.% before injection.

2.3. HPLC equipment

LC–EATP experiments were performed on a HPLC system fitted with either a Varian (USA) Model 9002 pump or a Jasco (Japan) Model PU-980 pump and a Rheodyne six-port injection valve with a 20-μl sample loop. A Shimadzu SPD-6A (Japan) or a Jasco UV-975 UV spectrophotometric detector, set at 261 nm and a Varian RI-4 refractometer were used for detection. The flow-rate was 1 ml/min.

2.4. Columns

The columns were maintained at a constant temperature with a CROCO-CIL oven (Cluzeau, France). A list of the different types of columns is given in Table 1.

Table 1
Main characteristics of the adsorbents tested for the fractionation of functional PS, PEO and their related block copolymers

Column No.	Adsorbent nature	Type of silica	Dimension	Pore diameter (Å)	Particle size (μm)
1	Silica	Nucleosil	250×4.6 mm	100	5
2	Amino-silica	Nucleosil	250×4.6 mm	100	5
3	Diol-silica	Hypersil	150×4.6 mm	300	5
4	Amino-silica	Nucleosil	125×4 mm	300	7
5	Cyano-silica	Nucleosil	125×4 mm	300	7
6	Octadecyl-silica	Prontonsil	125×4 mm	300	5
7	Octadecyl-silica	Nucleosil	125×4 mm	100	7
8	Octadecyl-silica	Nucleosil	125×4 mm	300	7
9	Octadecyl-silica	Nucleosil	125×4 mm	500	7
10	Octadecyl-silica	Nucleosil	125×4 mm	1000	7

3. Results and discussion

3.1. Determination of the "critical conditions"

The fractionation and characterization of functional polystyrenes by LC–EATP require one to render "invisible" the molar mass distribution of the polystyrene sample and to separate the different chains only according to the nature and number of the functional groups they bear.

The critical composition of the eluent THF–hexane was first determined, in the case of column 1 (see Table 1), with non-functional and hydroxyl-terminated polystyrene standards. The retention times of PS standards (1000 g/mol$<\overline{M}_w<$135 000 g/mol) and ω-hydroxyl-PS standards (1500 g/mol$<\overline{M}_w<$130 000 g/mol), in THF–hexane mixtures of different compositions, are reported in Fig. 1.

As expected, Fig. 1 clearly demonstrates that the higher the hexane content, the longer the retention time of the polystyrene chains. In the case of eluents containing more than 44.2 wt.% of THF, the retention times decrease with the polystyrene molar mass in a classical exclusion mode. Conversely, for eluents with a THF content lower than 44.2 wt.%, the retention times increase with the polystyrene molar mass according to an adsorption mode. Between these two domains, for a 44.2:55.8 wt.% THF–hexane composition, the polystyrene chains are eluted at the same retention time, whatever their molar mass, in accordance with the "critical conditions" of the chromatographic system used. In addition, such a preliminary study reveals that the critical composition of the mobile phase is the same in the case of functional and non-functional polystyrene standards whatever the function (alcohol, aldehyde, acetal, acidic, etc.) attached to the polystyrene chain end.

As demonstrated in Fig. 1, the separation of functional polystyrene chains from non-functional ones, according to the nature of the functional group, requires one to be at the EATP. Indeed, in the exclusion mode (pure THF), the retention times of the non-functional and ω-hydroxyl-PS standards are nearly identical and their separation is not possible. While the retention times of functional polystyrenes are generally found to be longer than those of the corresponding non-functional polystyrene standards, in the adsorption mode (THF–hexane, 40:60 wt.% as eluent, for example), their separation is often dif-

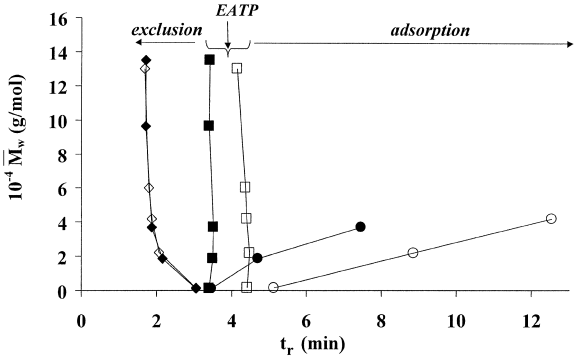

Fig. 1. Retention times of polystyrene standards (full symbols) and ω-hydroxyl polystyrenes (empty symbols) in THF–hexane mixtures of different composition (wt.%). 100:0 (♦); 44.2:55.8 (■); 40:60 (●). Adsorbent: silica (column 1) $T=25$°C, flow-rate: 1 ml/min, detection: UV ($\lambda=261$ nm).

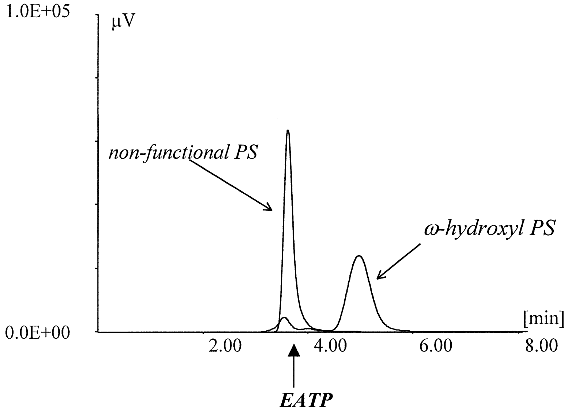

Fig. 2. Chromatograms of polystyrene standards ($\overline{M}_w = 13\,700$ g/mol) and ω-hydroxyl-PS ($\overline{M}_w = 22\,000$ g/mol) at the polystyrene EATP in THF–hexane eluent (44.2:55.8 wt.%). Adsorbent: silica (column 1) $T = 25$°C.

ficult: as an example, ω-hydroxyl-PS of $M_n = 10\,000$ g/mol and non-functional polystyrene standards of molar mass close to 30 000 g/mol are eluted at the same retention time of 6 min! At the EATP, the separation is particularly easy since any peak with a retention time of 3.5 min characterizes non-functional PS standards and any peak at 4.4 min, ω-hydroxyl-PS ones, as clearly illustrated in Fig. 2.

3.2. Fractionation of functional polystyrenes

3.2.1. PS functionalized with acetal groups

A series of functional polystyrenes have been characterized under such specific conditions. Because of the higher polarity of the function attached to the chain (acetal, aldehyde, alcohol and acidic) compared to the polystyrene skeleton, two polar adsorbents – (column 1) and silica grafted by aminopropyl groups (column 2) – have been selected to favor the fractionation in the critical conditions of polystyrene. As already undertaken in previous studies [5,6], four desorli–adsorli mixtures were tested as eluents; hexane was kept as an adsorli and toluene, CH_2Cl_2, THF and EtAc were, respectively tested as desorlis. The critical compositions of each binary eluent used were determined in the case of the two adsorbents and are reported in Table 2.

In the case of the amino-silica as an adsorbent, a desorli of higher polarity (toluene $< CH_2Cl_2 <$ THF $<$ EtAc) generally eases the elution of the ω-acetal and α,ω-acetal polystyrenes. Reversibly, the interactions between the acetal function and the adsorbent surface are favored when the desorli is not polar enough. The case of EtAc–hexane is particular due to the poor quality of the eluent with respect to polystyrene leading to the adsorption of the polystyrene chains on the adsorbent surface. The chromatographic system (eluent: CH_2Cl_2–hexane; adsorbent: amino-silica) was found to be the best system to fractionate ω-acetal and α,ω-acetal polystyrenes with suitable selectivity. The chromatograms of non-functional, ω-acetal and α,ω-acetal polystyrenes, eluted in CH_2Cl_2–hexane mobile phase of composition specified in Table 2, are presented in Fig. 3.

The α,ω-acetal-PS that bears two functional groups, interacts strongly with the adsorbent surface and is eluted at a higher retention time (7.5 min) compared to mono-acetal-PS (5 min). The elution in the critical conditions of polystyrene skeleton, allows to check that the first peak obtained at 5 min is a residual mono-acetal polystyrene.

The use of more polar adsorbent, silica instead of amino-silica, leads to an increase in the retention times of the functional PS, since the latter develops stronger interactions with the adsorbent. In the case of toluene–hexane and CH_2Cl_2–hexane as eluents, the ω-acetal and α,ω-acetal polystyrenes are irreversibly adsorbed. Moreover, in the case of THF–hexane and EtAc–hexane as eluents, the selectivity

Table 2
Critical compositions (wt.%) of eluents at the exclusion–adsorption transition point (EATP) of polystyrene: influence of the adsorbent ($T = 25$°C)

	EATP (wt.%)			
	Toluene–hexane	CH_2Cl_2–hexane	THF–hexane	EtAc–hexane
Silica	83.9:16.1	74.3:25.7	44.2:55.8	38.0:62.0
Amino-silica	81.7:18.3	63.5:36.5	56.4:43.6	50.0:50.0

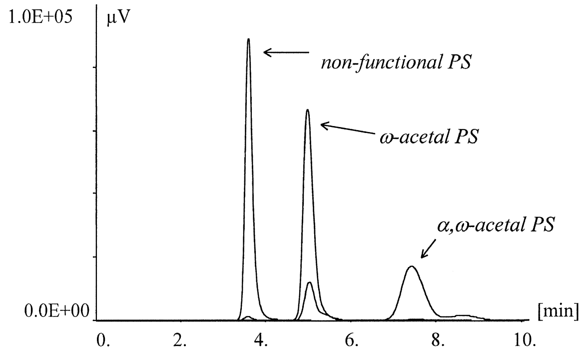

Fig. 3. Chromatograms of polystyrene standards ($\overline{M}_w = 13\,700$ g/mol), ω-acetal-PS ($\overline{M}_w = 4000$ g/mol) and α,ω-acetal-PS ($\overline{M}_w = 5100$ g/mol) at the polystyrene EATP in CH_2Cl_2–hexane (63.5:36.5 wt.%). Adsorbent: amino-silica (column 2), flow-rate of 1 ml/min, detection: UV ($\lambda = 261$ nm) or RI, $T = 25$°C.

of the whole system is very low and does not allow any fractionation.

3.2.2. PS functionalized with aldehyde and acidic groups

Whatever the nature of the mobile phase, polystyrene chains functionalized by aldehyde or acidic functions are irreversibly adsorbed on modified adsorbent as silica grafted by aminopropyl groups. Such a phenomenon may be explained by the formation of stable Schiff bases after reaction between the aldehyde or acidic functions and the amine one.

In the case of silica as an adsorbent, similar behaviors as previously described with PS terminated by acetal groups are obtained. Indeed, the elution of polystyrenes bearing aldehyde or acidic functions requires the use of polar desorli such as THF or EtAc; the systems toluene–hexane or CH_2Cl_2–hexane are unable to elute such functionalized PS.

The best fractionations of ω-aldehyde-PS and α,ω-aldehyde-PS as well as ω-acidic-PS and α,ω-acidic-PS were obtained, under the critical conditions of PS, with silica as an adsorbent and EtAc–hexane as mobile phase.

As shown in Figs. 4 and 5, the retention times of polystyrene chains terminated by aldehyde or acidic functions are longer than those of PSs functionalized by acetal functions. Moreover, this separation is limited to functionalized polystyrene chains of molar mass lower than 50 000 g/mol because of the poor thermodynamic quality of the solvent with respect to the polystyrene structure. The chromatogram depicted in Fig. 4 reveals that α,ω-aldehyde-PS exhibits traces of mono-aldehyde-PS. Under the same critical conditions, mono-aldehyde-PS is also detected in the ω-acidic-PS sample as well as in the mono-acidic-PS chains with α,ω-acidic-PS sample (Fig. 4). In the latter case, the high polarity of the carboxylic groups yields strong interactions with the silica surface and leads to the formation of large peaks as well as an uncomplete recovery of the polymer sample.

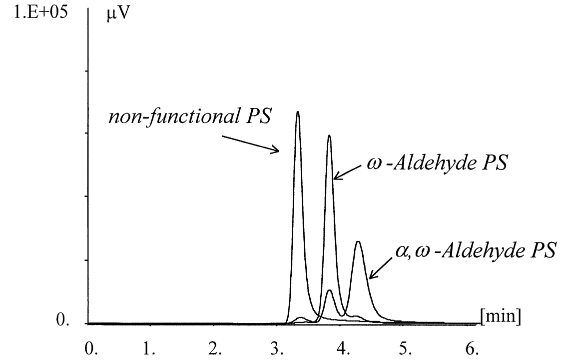

Fig. 4. Chromatograms of polystyrene standards ($\overline{M}_w = 13\,700$ g/mol), ω-aldehyde-PS ($\overline{M}_w = 4000$ g/mol) and α,ω-aldehyde-PS ($\overline{M}_w = 5000$ g/mol) at the polystyrene EATP in EtAc–hexane (38.0:62.0 wt.%). Adsorbent: silica (column 1), flow-rate of 1 ml/min, detection: UV ($\lambda = 261$ nm), $T = 25$°C.

Recently, we have shown that the temperature is a

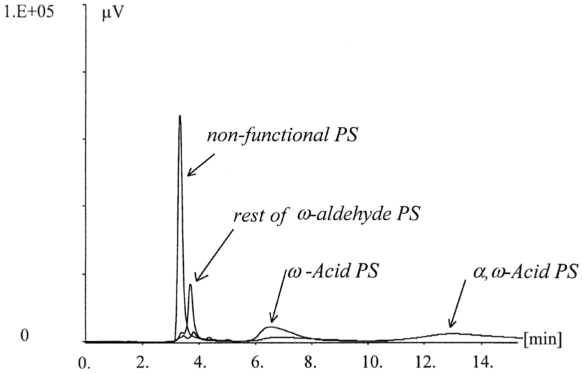

Fig. 5. Chromatograms of polystyrene standards ($\overline{M}_w = 13\,700$ g/mol), ω-acidic-PS ($\overline{M}_w = 4000$ g/mol) and α,ω-acidic-PS ($\overline{M}_w = 2000$ g/mol) at the polystyrene EATP in EtAc–hexane (38.0:62.0 wt.%). Adsorbent: silica (column 1), flow-rate of 1 ml/min, detection: UV ($\lambda = 261$ nm), $T = 25$°C.

tunable parameter to obtain the suitable critical conditions [6]. Indeed, for a given adsorbent–eluent couple, a variation of temperature may allow the transition from the exclusion mode to the adsorption one via the ‘‘critical conditions’’ without changing the composition of the eluent. Consequently, the influence of the temperature parameter for the separation of functional polystyrenes under ‘‘critical conditions’’ was also investigated. The elution of acetal-, aldehyde-, alcohol- and acidic-PSs was undertaken with THF–hexane as an eluent at two temperatures (75°C and 13°C) on the silica adsorbent (column 1). The critical compositions of the eluent THF–hexane were determined and found equal to 45:55 wt.% at 75°C and 49:51 wt.% at 13°C, respectively. The elution of ω-aldehyde- and α,ω-aldehyde-PSs under the two conditions are compared (see Fig. 6a and b).

It is worth noting that the fractionation of ω-aldehyde- and α,ω-aldehyde-PSs can be readily obtained whatever the experimental conditions. Nevertheless, the selectivity of the whole system seems to be constant independently of the elution temperature since the retention time of each functional polystyrenes is nearly identical under the two experimental conditions tested. Therefore, in the specific case of ω-aldehyde- and α,ω-aldehyde-PS elution, the conditions depicted in Fig. 4 with EtAc–hexane as an eluent will be preferred because of the better separation between each population.

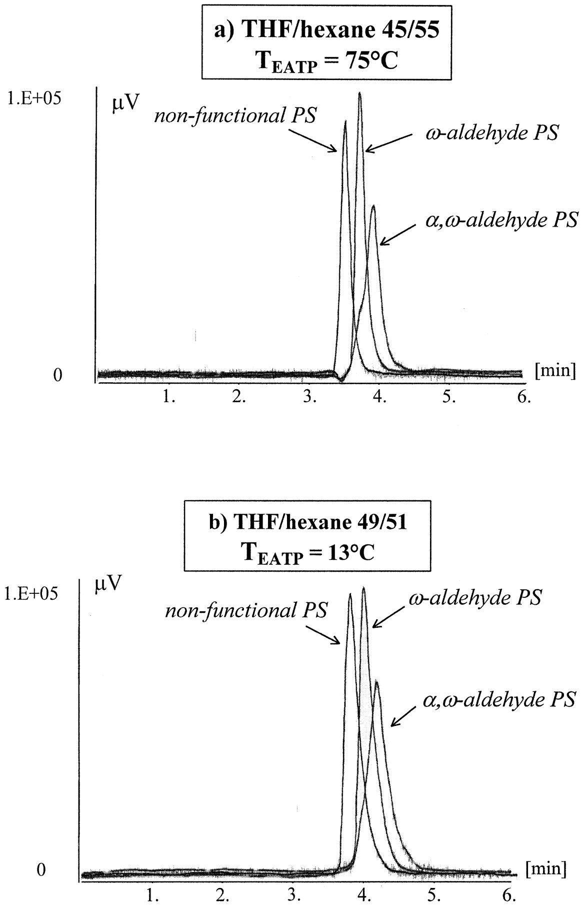

Fig. 6. Chromatograms of polystyrene standards ($\overline{M}_w = 13\,700$ g/mol, blue curve), ω-aldehyde-PS ($\overline{M}_w = 4000$ g/mol) and α,ω-aldehyde-PS ($\overline{M}_w = 5000$ g/mol) at the polystyrene EATP in THF–hexane eluent (49:51 wt.%) at 13°C (a) and (45:55 wt.%) at 75°C (b). Adsorbent: silica (column 1), $T = 25$°C.

3.3. Fractionation of functional poly(ethylene oxide)s

The separation of α,ω-hydroxyl- and α-hydroxyl-, ω-diphenyl-PEOs with respect to the nature of the terminal groups, under the critical conditions of PEO, requires to examine, first, various adsorbent–eluent couples, allowing the determination of the critical conditions of PEO.

The research of the PEO ‘‘critical conditions’’ was undertaken with different adsorbents of variable polarity: silica, grafted silica with diol, aminopropyl, cyanopropyl or octadecyl groups. In each case, the choice of the eluent was restricted by the detection of PEO units which exhibit a high value of refractive index ($n_D \approx 1.45$) and a UV absorbency at low wavelength ($\lambda = 261$ nm). Another drawback linked to PEO structure is its low solubility in a majority of solvents and more particularly its ability to aggregate.

With polar adsorbents (silica and diol-silica, columns 1 and 2, respectively), PEO interacts strongly with the surfaces and is irreversibly adsorbed. The use of very polar eluents such as MEK, MeOH, ACN or water is not sufficient to avoid the adsorption phenomenon. Acidification of the eluent may improve the elution of PEO but the EATP could never be attained. Besides, the acidification of the eluent was limited by the instability of silica under pH equal to 3.

With less polar adsorbents (amino-silica and cyano-silica, columns 4 and 5, respectively), the PEO–adsorbent interactions are less important. In this case, polar eluents such as water–MeOH, ACN–water and DME–water allow the transition from the exclusion mode to the adsorption one. The terminal group must interact sufficiently with the adsorbent surface to ease the separation of the functional PEO. When less polar desorli such as THF, MEK or CH_2Cl_2 are used, a strong adsorption of the PEO chains on the adsorbent is observed.

With non-polar adsorbents (octadecyl-silica, column 8), the critical conditions of PEO could be obtained with the ACN–water and MeOH–water eluents but not with DME–water.

To summarize, this study shows that the EATP of PEO can be reached only with moderately polar or non-polar adsorbents as well as with polar eluents based on water. Table 3 gives the eight adsorbent–eluent couples tested and the corresponding critical compositions of PEO.

It is worth noting that MeOH plays a different role according to the polarity of the adsorbent. It behaves as an adsorli with polar adsorbents and as a desorli in the reverse phase. Indeed, in the normal phase, the elution phenomena are governed by the PEO–adsorbent interactions while in the reversed phase, the PEO chains are shared between the hydrophobic surface of the adsorbent and the aqueous eluent.

The chromatograms of α-hydroxyl-, ω-diphenyl- and α,ω-hydroxyl-PEOs under different ‘‘critical conditions’’ of elution are presented in Fig. 7a and b.

Table 3

Critical compositions (wt.%) of eluents at the exclusion–adsorption transition point (EATP) of poly(ethyleneoxide): influence of the adsorbent ($T=25$°C)

Adsorbent type	Desorli–adsorli at the EATP (wt.%)
Amino-silica	Water–MeOH (14.0:86.0) ACN–water (31.8:68.2) DME–water (18.5:81.5)
Cyano-silica	Water–MeOH (15.0:85.0) ACN–water (28.1:71.9) DME–water (21.5:78.5)
Octadecyl-silica	MeOH–water (85.0:15.0) ACN–water (36.7:63.3)

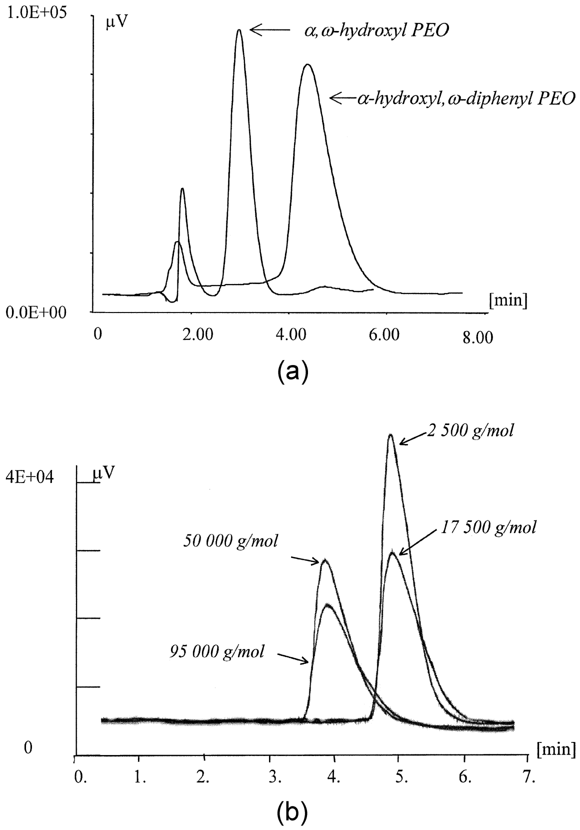

Fig. 7. Chromatograms of α-hydroxyl, ω-diphenyl PEO (250 g/mol$\leq \bar{M}_w <$17 500 g/mol) and α,ω-hydroxyl PEO (24 000 g/mol$< \bar{M}_w <$95 000 g/mol) at the poly(ethylene oxide) EATP in various eluents. ACN–water or DME–water for a series of adsorbents: (a) cyano-silica (column 5), (b) octadecyl-silica (column 8). Flow-rate of 1 ml/min, detection: refractometry, $T=$ 25°C.

The validity of the ‘‘critical conditions’’ concept is illustrated in Fig. 7b in the case of ACN–water as an eluent and octadecyl-silica as an adsorbent. Indeed, two α,ω-hydroxyl-PEO of different molar masses (50 000 g/mol and 95 000 g/mol) are eluted at the same retention time (4 min) while α-hydroxyl-, ω-diphenyl-PEO appears after 5.5 min of elution whatever the molar mass (2500 g/mol and 17 500 g/mol). This proves that the nature of the functional groups is the only parameter coming into play in the separation process.

Whatever the nature of the adsorbent, the MeOH–water eluent does not allow the separation of the functional PEO. The substitution of MeOH for less polar desorli as ACN and DME allows stronger interactions between the phenyl or hydroxyl end groups with the various adsorbents tested (amino-silica, cyano-silica and octadecyl-silica) and improves the selectivity of the whole chromatographic system.

In the normal phase, the phenomenon is emphasized by a decrease in the polarity of the adsorbent surface and the separation of the two functional PEO is eased with the cyano-silica adsorbent. Finally, the best separation of α,ω-hydroxyl-PEO and α-hydroxyl-, ω-diphenyl-PEO under the PEO ''critical conditions'' is obtained with the DME–water eluent and the adsorbent cyano-silica as well as with ACN–water as an eluent and ocatadecyl-silica as an adsorbent (Fig. 7a and b).

3.4. Copolymers poly(styrene)–b–poly(ethylene oxide)s

The possibility to elute functional polystyrenes and poly(ethylene oxide)s in the corresponding ''critical conditions'', led us to examine the fractionation of poly(styrene)–b–poly(ethyleneoxide) block copolymers under similar experimental conditions.

A series of PS–b–PEO copolymers of different composition was analyzed (see Table 4).

The characterization principle of diblock copolymer is to render ''invisible'' the molar mass distribution of one block – elution at the EATP for this block – and to separate the diblock copolymer only according to the molar mass of the second block. This requires a precise choice of an adsorbent–eluent couple, which must be suited to each of the two blocks. In this particular case, the choice of the chromatographic system is difficult because of the opposite chemical nature of the two blocks. Indeed, an adsorbent with a polar surface will lead to an irreversible adsorption of the PEO block. In addition, the choice of a desorli–adsorli binary mixture as an eluent allowing the three elution modes (exclusion, adsorption and ''critical conditions'' modes) is rather difficult because of the solubility differences between the PS and the PEO blocks, in a given solvent. Finally and after many attempts, the retained system is a non-polar adsorbent – grafted silica by octadecyl groups – and THF–water as an eluent. Under these conditions, the copolymers PS–b–PEO were characterized according to the length of the PEO block in the critical conditions of polystyrene.

The research of the critical conditions for PS as well as the characterization of the various copolymers were undertaken with a series of C_{18}-silica of different natures (Nucleosil or Prontosil, columns 6 and 8, respectively) and porosity (100, 300, 500 and 1000 Å, columns 7–10). The critical compositions of the eluents obtained with the different systems tested are given in Table 5. As already discussed [5,6], such critical compositions vary slightly with the type and the porosity of the adsorbent.

The elution of two block copolymers PS–PEO only differing by the length of the polystyrene block is shown in Fig. 8.

As can be seen, their retention time is identical

Table 4
Composition of the tested PS–PEO block copolymers

$\overline{M}_w$ PS[a] (g/mol)	$\overline{M}_w$ PEO[b] (g/mol)
2700	250
12 500	5600
12 500	8700
12 500	11 000
22 000	10 900
1500	10 000
1500	20 000
1500	30 000
22 000	52 000

[a] Defined by SEC with THF as mobile phase and polystyrene calibration.

[b] Calculated from ^{1}H-nuclear magnetic resonance (NMR).

Table 5
Critical compositions (wt.%) of THF–water at the exclusion–adsorption transition point (EATP) of polystyrene with octadecyl-silica as an adsorbent: influence of the chemical nature and the porosity of the adsorbent (T=25°C)

Silica nature	Pore diameter (Å)	THF–water at the EATP (wt.%)
Nucleosil	100	87.1:12.9
	300	87.4:12.6
	500	87.0:13.0
	1000	86.4:13.6
Prontosil	300	87.7:12.3

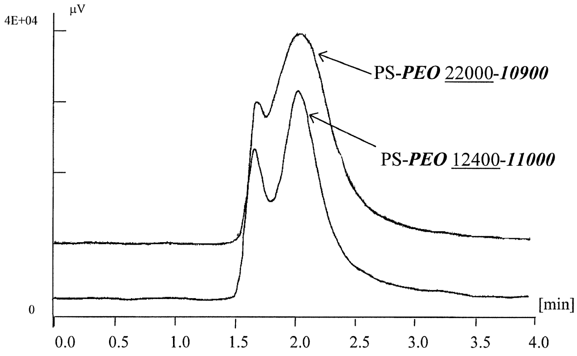

Fig. 8. Chromatograms of PS–b–PEO block copolymers at the polystyrene EATP. Mobile phase: THF–water (87.0:13.0 wt.%), adsorbent: octadecyl-silica (column 9) of porosity 500 Å, $T=25$°C, detection: UV ($\lambda=261$ nm), concentration of the solutes in the eluent: 0.2% (wt.%), flow-rate: 1 ml/min.

confirming that elution occurs in the critical conditions with respect to polystyrene. The presence of a second peak at a lower retention time is explained later.

The retention time of the PS–b–PEO block copolymers, eluted with THF–water as an eluent, under the "critical conditions" of polystyrene, with C_{18}-silica of different nature and porosity as adsorbents are plotted in Fig. 9.

As can be observed, the chemical nature of the adsorbent used (columns 6 and 8) as well as the pore size (columns 7–10) have a strong influence on the elution mode of the block copolymers PS–b–PEO.

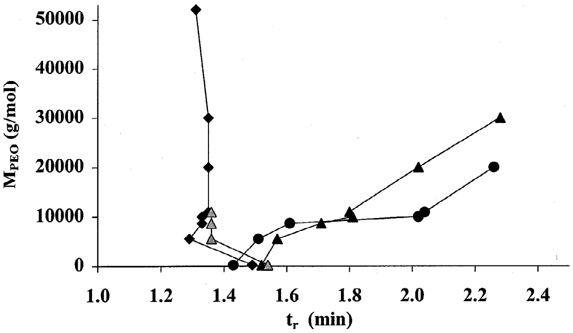

Fig. 9. Retention times of PS–b–PEO, as a function of the PEO length, at the polystyrene EATP in the case of octadecyl-silica columns of different types (Nucleosil, black symbols and Prontosil, gray symbols) and porosity: 100 Å (♦); 300 Å (▲,△); 500 Å (●). Mobile phase: THF–water, $T=25$°C, flow-rate of 1 ml/min, detection: refractometry.

As shown in Fig. 9, the elution of PS–b–PEO block copolymers follows different modes according to the nature of the grafted C_{18}-silica [Nucleosil type (black triangles) or Prontosil type (gray triangles)]. Indeed, with the Prontosil type, the copolymers are eluted according to an exclusion mode while with the Nucleosil type, they are separated in an adsorption mode.

To support the calibration curve with respect to the PEO block length presented in Fig. 9, the chromatograms of three PS–PEO block copolymers (2700:250; 12 500:8700; 1500:20 000 g/mol) eluted with THF–water are given in Fig. 10.

In the case of a column of 100 Å porosity, the copolymers with a PEO block lower than 5600 g/mol are separated in an exclusion mode. Above this molar mass threshold, the elution time of the copolymers remains constant and equal to the total volume of the column (V_i+V_p) (limit of exclusion). In the case of adsorbents with higher porosity ($D=300$ Å and 500 Å), the copolymers are fractionated according to the PEO block length in an adsorption mode. In these conditions, it is possible to separate the PS–PEO block copolymers according to the length of the PEO block provided that its molar mass does not exceed 50 000 g/mol. Indeed, above this PEO molar mass, the copolymer is irreversibly adsorbed. A similar phenomenon (irreversible adsorption) was also observed with columns of higher porosity ($D=1000$ Å).

As can be observed in Fig. 10, some of the given chromatograms exhibit two peaks in the case of the elution of block copolymers with a PEO block when $\overline{M}_n$ is higher than 10^4 g/mol. A fractionation of these two peaks was carried out on a semi-preparative scale and showed that the first peak obtained at the total volume of the column (V_i+V_p), was a residual PEO homopolymer.

4. Conclusion

In conclusion, the present study shows that the fractionation and characterization of functional polystyrenes and poly(ethylene oxide)s could be achieved at the exclusion–adsorption transition point of the

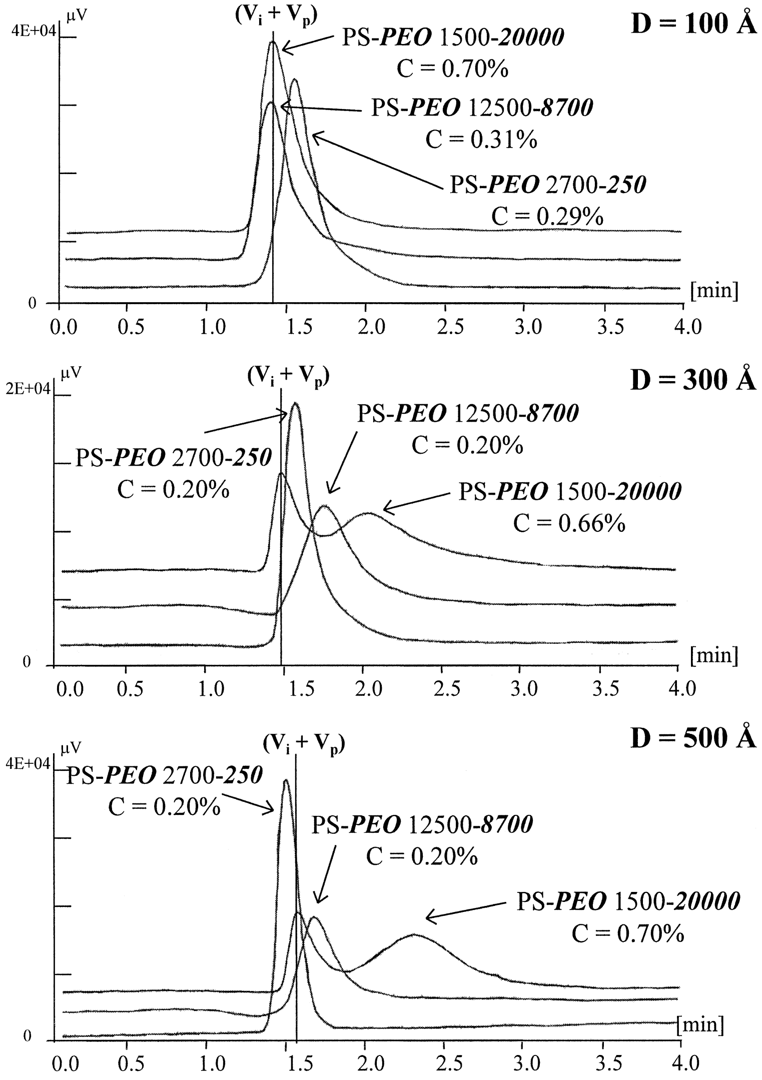

Fig. 10. Chromatograms of PS–PEO copolymers at the polystyrene EATP in THF–water. Influence of octadecyl-silica adsorbent porosity (*D*, pore diameter), $T=25°C$, *C*: concentration of the solute in the eluent (wt.%), flow-rate: 1 ml/min, detection: refractometry. ($V_i + V_p$): total volume of the column, defined by the elution of pure THF.

related polymer skeleton with very good efficiency. This technique was also found suitable to separate PS–PEO block copolymers provided that the PEO length does not exceed $5 \cdot 10^4$ g/mol. The latter observation will lead us to study the preparation of new adsorbents to obtain the fractionation and characterization of polymers. Results will be reported in forthcoming papers.

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