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Qualitative and quantitative analysis of styrene and its various oligomers by liquid chromatography

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Abstract

Two polystyrenes (crystal PS 1 and choc PS 2) were tested to determine the composition of low-molecular-mass products. The RP-HPLC method shows clearly, in both polystyrenes, two oligomeric entities: higher-molecular-mass ($n>5$) and lower-molecular-mass ($n<5$). The ratio between fractions exhibits respectively the same value (1/4) in PS 1 and PS 2. However it is logical that the total oligomeric fraction in PS 1 was larger than in PS 2. In addition, the styrene level in polystyrene crystal determined by RP-HPLC coupled with gel permeation chromatography (GPC) was 2500 mg/kg. This technique exhibits a satisfactory recovery (79±5%). Styrene could not be determined in polystyrene choc. Automation of combined GPC–RP-HPLC, in the future, will permit quantification of the lower styrene levels in commercial packaging polystyrene.

Keywords: Styrene; Oligomers

1. Introduction

Polystyrene, commonly used as food packaging, can contaminate food through migration of additives, styrene and oligomers. The two latter chemicals are formed following free radical mechanisms during the processing of plastic at high temperatures. Several adverse health effects (cytotoxicity, genotoxicity and carcinogenicity) are attributed to the styrene [1–3]. Consequently, extraction techniques and analytical methods were developed to determine the monomer level in the polymeric material and the level migrating into food [4–7]. Styrene oligomers were analysed by liquid chromatography. Normal-phase LC with a selective eluent gave separations according to the number of oligomer units or to the stereoisomers of individual oligomers [8]. Analysis with the same stationary phase by isocratic elution with *n*-hexane–dichloromethane established differences in retention of oligomers that are equivalent in length but have different end groups [9]. Lai et al. [10] described an equation which incorporates the Martin and the Snyder relations between the retention factor and the degree of polymerization and the binary solvent composition to estimate the retention of oligomers on the chromatographic systems. Larmann et al. [11] used gradient elution with tetrahydrofuran–water on octadecyl-bonded phase to derive relationships which enable determination of retention parameters for high-molecular-mass oligomers in reasonable agreement with corresponding isocratic data. Styrene oligomers were also analysed on a C_{18} Bondapak

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column by gradient elution with methanol–tetrahydrofuran in combination with field desorption mass spectrometry [12]. Either UV photometric or fluorometric detection were applied, the latter being more sensitive [13].

We describe in this paper a rapid RP-HPLC method for separation and identification of the low-molecular-mass fraction of polystyrene crystal and polystyrene choc. Also, this technique was combined with gel permeation chromatography (GPC) for the quantification of styrene in polymers.

2. Experimental

2.1. Chemicals

Styrene 99% was obtained from Aldrich (St. Quentin Fallavier, France). It was kept in an amber coloured bottle at 4°C. Commercial styrene oligomer (580) is characterized by the number-average molecular mass (M_n 565) and the weight-average molecular mass (M_w 653) and the average molecular mass at the peak (M_p 580), was obtained from Waters (St. Quentin Yvelines, France). Tetrahydrofuran (THF), HPLC-grade was purchased from OSI (Elancourt, France). Acetonitrile and methanol, HPLC-grade were obtained from Prolabo (Fontenay-sous-bois, France). The plastic standard antioxidants Irganox 1076, tri-nonyl-phenyl phosphite (Tnpp) were obtained from Ciba-Geigy (Reuil Malmaison, France). The lubricant agent (mineral oil) was obtained from ESSO (Reuil Malmaison, France). Polystyrenes listed as PS 1 and PS 2 were supplied by ELF (Courbevoie, France). Only, PS 2 contains additives.

2.2. Extraction of low-molecular-mass fraction by dissolution–precipitation procedure

Polymeric material (1 g) was dissolved in 100 ml of THF, during 30 min of magnetic stirring. The high-molecular-mass fraction was precipitated with 150 ml of methanol, then filtrated under vacuum through a glass fiber superimposed on two 0.45-μm, 47 mm diameter, type GF/C whatman filters (Prolabo). The extract solution obtained was evaporated to dryness by rotary evaporation at 30°C. The residue was dissolved in 1 ml of THF and a 20-μl aliquot injected into the HPLC system.

2.3. High-performance liquid chromatography

The liquid chromatograph used for analysis consisted of a pump Jasco 880 PU (Prolabo), a Waters 990 photodiode array detector, connected to a computer NEC power Mate 2 APC (Waters).

Separation was carried out using a reversed-phase column (250×4.6 mm, RP-Select B) packed with LiChrospher 5 μm (Merck, Nogent sur Marne, France).

The gradient elution consisted of the following: Phase A, THF–acetonitrile–methanol–water, (40:10:10:40, v/v); phase B, THF–acetonitrile–methanol, (40:10:10, v/v). The flow-rate was 1 ml/min. The gradient varied during 35 min as follows:

Time (min)	% Solvent A	% Solvent B
0	100	0
7	100	0
35	0	100

2.4. Gel permeation chromatography

The experiments were run on a system consisting of a Hewlett-Packard 1050 pump (Les Ulis, France), a Hewlett-Packard HP 1047 refractive index (RI) detector, a Chromjet integrator Spectra-Physics (Les Ulis, France) and three analytical Styragel columns, in series, (300×7.8 mm) HR 0.5 (50 Å), HR 1 (100 Å) and HR 4 (10 000 Å) from Waters. The flow-rate of THF was 1 ml/min.

2.5. Polystyrene

A 1.5–2.5 mg amount was weighed in a vial (100 ml) and dissolved in THF under magnetic stirring. A 20-μl aliquot of this solution was injected into the GPC system. The concentration of injected standard additives and styrene was 0.2 mg/ml.

2.6. Combined GPC–RP-HPLC

GPC separates polystyrene in high-molecular-mass (polymeric material) and low-molecular-mass (addi-

tives, oligomers, styrene) fractions. A 20-μl aliquot of the collected styrene fractionwas injected into the HPLC system to determine the monomer level in the polystyrene.

Previously, the recovery of the combined GPC–RP-HPLC method was calculated: 20 μl of styrene solution (0.06 mg/ml) was injected into the GPC system and then 20 μl of the collected styrene fraction was injected into the HPLC system.

3. Results and discussion

The analysis by RP-HPLC of the PS 1 extract leads to the chromatogram shown in Fig. 1a. The compounds detected have two maximum wavelength absorption values at around 220 and 250 nm (Fig. 1b). They correspond to the styrene oligomers because this polymer was formulated without additives. Therefore, it undergoes serious degradation. The variability of the peak areas shows clearly that oligomers are present in different proportions in the polystyrene and have different absorption levels following their molecular mass. In addition, it is apparent that the molecular mass and the polarity of styrene oligomers are the monitoring parameters of the order of elution. The correlation between Fig. 1a Fig. 1b indicates that twelve oligomers, eluted between 9 and 29 min, exhibit the same UV spectrum. This similarity is due to their analogical structure which is *n*(styrene), in fact they only differ in their degree of polymerization. Still and Peters

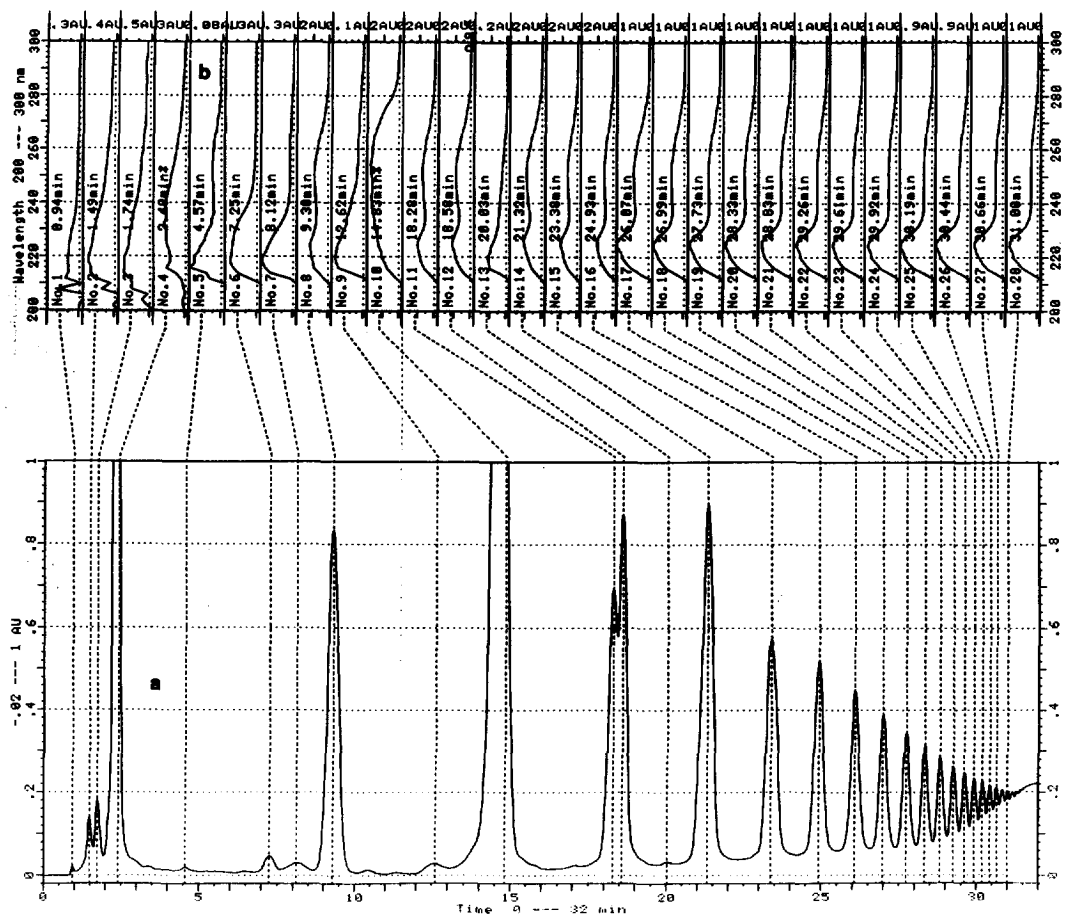


Fig. 1. Chromatographic separation of extract obtained from polystyrene crystal by dissolution–precipitation–evaporation (30°C) procedure. (a) HPLC chromatogram. (b) UV absorption (200–300 nm) of styrene oligomers.

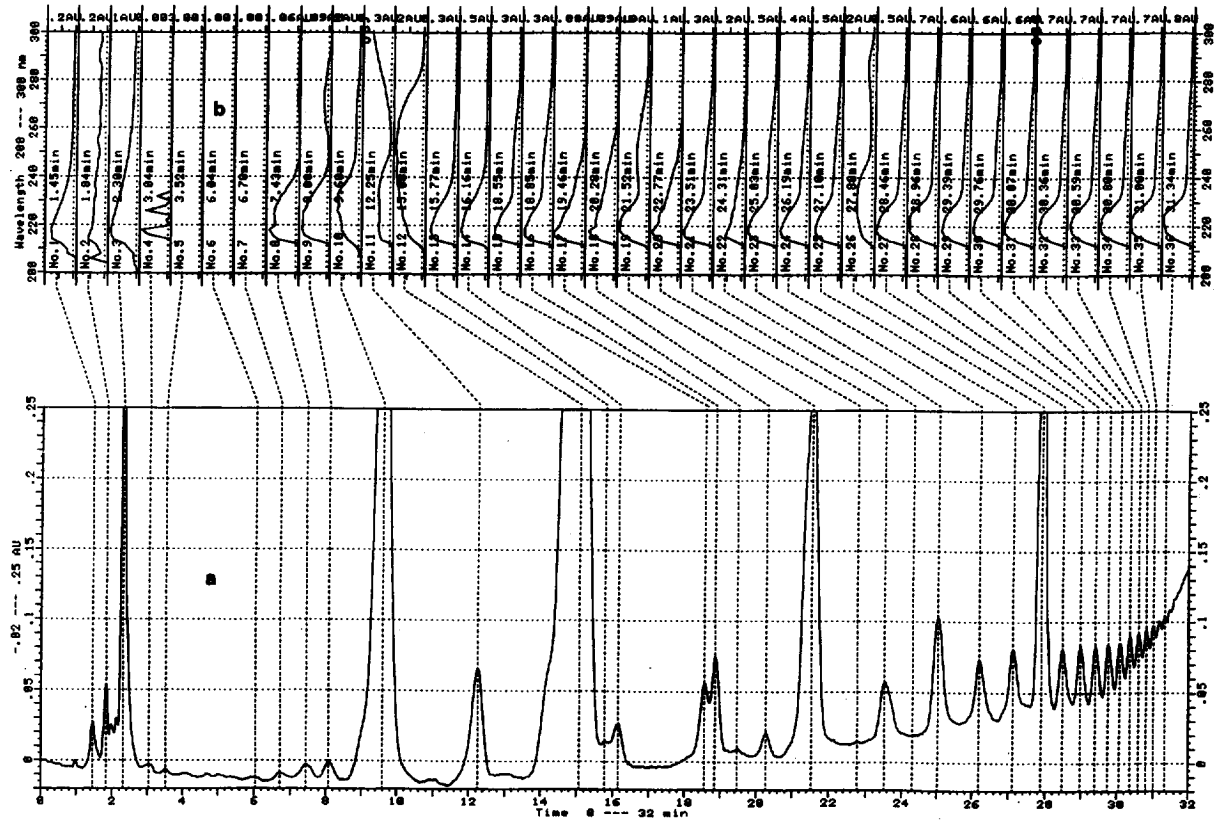


Fig. 2. Chromatographic separation of extract obtained from polystyrene choc by dissolution–precipitation–evaporation (30°C) procedure. (a) HPLC chromatogram. (b) UV absorption (200–300 nm) of styrene oligomers and additives.

[14] reported that pyrolysis of polystyrene at 400°C involves formation of monomer, dimer, trimer and possibly heptamer. In our work we enumerated some oligomers common to the PS 1 and PS 2 (Figs. 1a and 2a). However their absorption intensity is higher in PS 1 than in PS 2. This difference is due to the presence of additives which partially inhibit the mechanism of degradation. In view of this, additives lead practically to a dry residue of PS 2 which is heavier than PS 1, Table 1. Martin's Law [15] could be used to evaluate the degree of polymerization in isocratic elution but not in quaternary gradient elution. In addition, the RP-HPLC analysis of oligomer standard (580) shows six chromatographic peaks with different areas (Fig. 3). Among them, one main chromatographic peak eluted at 25 min, absorbs at two maxima wavelengths (225, 264 nm) and presents the higher area. Thus, we consider that this peak (product 1) exhibits the molecular mass equal to 580, and has the following molecular structure:

Table 1
Residual mass of polystyrenes crystal and choc

Degree of polymerization	Polystyrene crystal PS 1		Polystyrene choc	
	Total area	Relative % of oligomers	Total area	Relative % of oligomers
$n \leq 5$	1.5	79	0.2	80
$n > 5$	0.4	21	0.05	20

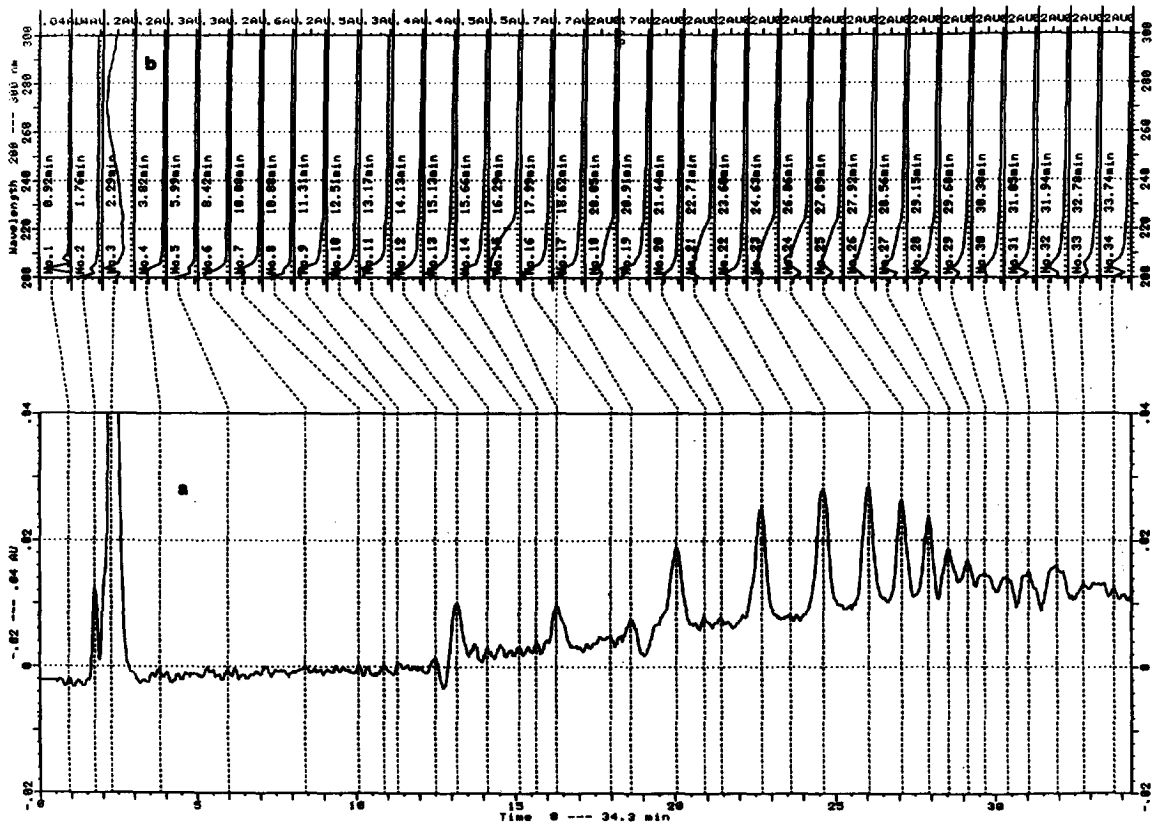
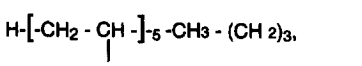
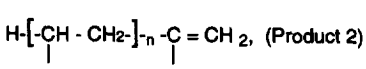


Fig. 3. Chromatographic separation of the pentamer standard (580). (a) HPLC chromatogram. (b) UV absorption (200–300 nm).



(Product 1),

Whereas Daoust [7] and Still and Peters [14] reported that polystyrene degradation leads to two types of primary radicals which induce, after intramolecular transfer of labile hydrogen, dimer and trimer. Their structure is the following:



(Product 2)

The pentamer, if it were formed in the polystyrene, would have the structure proposed by Doust [7] and Still and Peters [14] (product 2). However, this pentamer could not present the same UV spectrum and time retention in our RP-HPLC conditions as the standard oligomer (product 1). Effectively, the pentamer exhibiting a chemical structure like product 1 has a calculated Rekker hydrophobic constant [16] equal to 15.2, larger than the one of the pentamer like product 2 (13.4). So, it proved that oligomers exhibiting a degree of polymerization less than 5 were eluted in less than 25 min whereas oligomers

Table 2
High-molecular-mass oligomers ($n>5$) and low-molecular-mass oligomers ($n<5$) in polystyrenes PS 1 and PS 2

Polymers	Residue extracted (mg/g)	σ ($n=3$) (mg/g)	R.S.D. (%)
Polystyrene crystal (PS 1)	38	2	5.3
Polystyrene choc (PS 2)	56	1.2	2.2

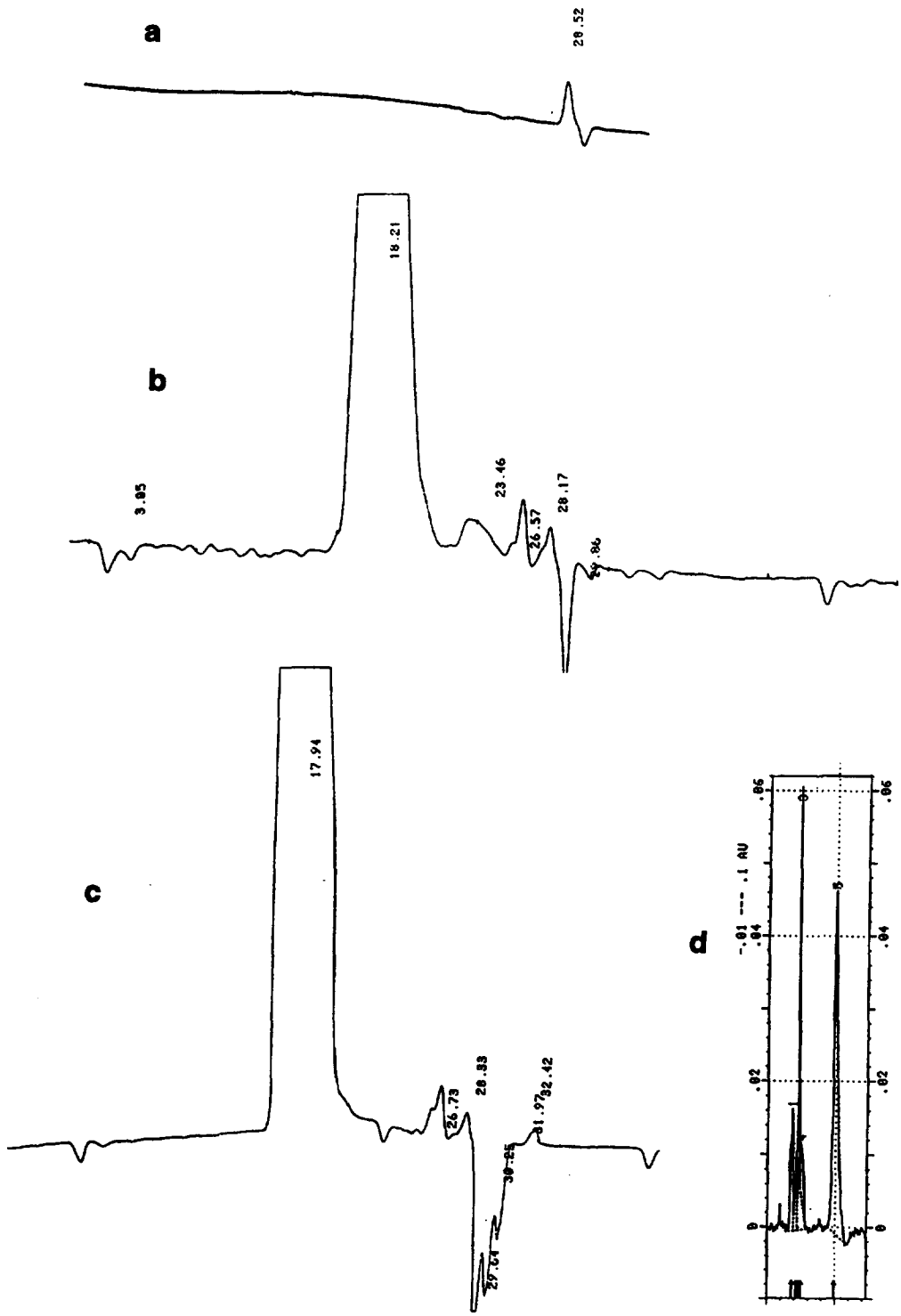


Fig. 4. GPC chromatograms. (a) Solvent THF. (b) Polystyrene choc. (c) polystyrene crystal. (d) Chromatogram of isolated styrene fraction obtained from combined GPC–RP-HPLC.

eluted after 25 min, have a degree of polymerization greater than 5.

A relative amount of each oligomer was determined in the polymers PS 1 and PS 2 using the ratio between corresponding areas and total oligomer areas. For this, we consider only peaks having an absorbance at 250 nm, the co-eluted compounds were not considered in this calculation such as the product eluted at 28 min (Fig. 2a) and exhibiting a maximum absorption at 280 nm. It was identified as a phenolic antioxidant (Irganox 1076). Table 2 illustrates the typical peaks and their relative proportion in PS 1 and PS 2. The ratio between oligomeric fraction $n>5$ and the oligomeric fraction $n<5$ is the same in two polymers and equal to (1/4). Only, the RP-HPLC chromatogram of PS 1 (Fig. 1a) exhibits a small peak attributed to styrene (t_r=4.6 min) by comparison with the standard. In our work GPC was used to isolate the high-molecular-mass from the low-molecular-mass fraction. Analysis of the standard additives showed that mineral oil and antioxidants were eluted at the same time (23.4 min) but styrene was eluted at 29.5 min. The GPC chromatograms of PS 1 and PS 2 are illustrated in Fig. 4b and 4c). The PS 1 chromatogram exhibits a styrene peak eluted at 29.5 min and unknown compounds retained on the column for 30 and 32 min are degradation products or synthesis residues. To determine the level of styrene, GPC is not an ideal method because of the lack of specificity. Numerous publications report that some polystyrenes contain other low and volatile chemicals such as toluene, ethylbenzene and cumene [4,6,7] which were estimated at 400 mg/kg in a polystyrene formulated with an UV stabilizer and mineral oil [7] and could be co-eluted, in GPC, with styrene. So, to determine the monomer level, the option of combining GPC with RP-HPLC is available. The RP-HPLC chromatogram of the styrene fraction isolated by GPC is illustrated in Fig. 4d). Initially, the styrene linearity on RP-HPLC, between peak areas and concentration was determined and then the method was validated in terms of linearity, repeatability and limit of detection. In addition, the recovery of the combined GPC–RP-HPLC method is nearly 80%. The styrene level of PS1 is 2500 mg/kg (Table 3). The oligomeric fraction is significantly reduced in PS 2 so the combined GPC–RP-HPLC method was difficult to carry out.

Table 3
Determination of the amount of styrene in polystyrene crystal

Linearity range (mg/ml)	0.0014–0.135
Equation of calibration	$4.7928 \cdot 10^{-3} + 2.2665x$
Correlation coefficient	0.999
R.S.D. (%)	4.5
Recovery of method extraction (%)	79
R.S.D. (%)	5.22
Amount PS 1 (mg/kg, n=3)	2500
Amount PS 2	n.d.

n.d.=not determined.

4. Conclusion

A manually combined GPC–RP-HPLC method is very easy to use for polystyrene which contains non-negligible styrene levels. This technique assures a total extraction of styrene and presents analytical advantages (rapidity, specificity and satisfactory recovery). Therefore we intend, in the future, to automate the process by using several Rheodyne valves.

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