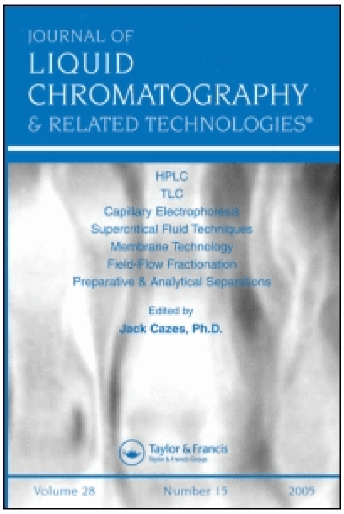

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DEGRADATION OF HIGH MOLECULAR WEIGHT POLYSTYRENES DURING THE SEC SEPARATION PROCESS, AS DEMONSTRATED BY SEC COUPLED WITH LALLS AND BY STATIC LIGHT SCATTERING

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ABSTRACT

In order to investigate the phenomenon of polymer degradation during the SEC separation process, we compared the weight-average molecular weights of a series of polystyrene (PS) samples with M_w going from $2.3\text{x}10^3$ to $1.84\text{x}10^7$, which were determined by static light scattering (LS) and by SEC-LALLS using various crosslinked PS gels.

For all the gels considered, there was a good agreement between LS and SEC-LALLS values for M_w up to $2x10^6$. For higher M_w, the values given by SEC-LALLS were lower than those given by LS; the decrease in M_w was different in various SEC columns. Since the same chromatographic equipment was used for all the SEC-LALLS measurements, we presumed that the decrease in M_w reflected the degree of shear degradation of PS molecules during their elution through the SEC columns. It depended on the origins of gels, the size of gel particles, the porosity of frits at column ends, the eluent flow rate, the usage of a pre-column filter, and of the third detector, a capillary viscometer.

INTRODUCTION

Size exclusion chromatography (SEC) is a widely used technique for determining the molecular weight (MW) averages of polymers and their molecular weight distributions (MWD), which are very important characteristics to understand the physical, rheological and mechanical properties of polymeric materials. These parameters are obtained with SEC, coupled either with a concentration detector alone (a differential refractometer or a UV spectrophotometer) or also with a molecular weight detector (a light scattering photometer).

In the former case, the columns have to be calibrated with monodisperse polymer standards, most often polystyrenes (PS) with the MW range going from 500 to $1x10^7$.[1-3] Owing to the differences in chemical nature between the samples and PS standards, the calculated MW averages are only relative values. In addition, the calibration curves of log M versus retention volume (V) are often non-linear in the region of high molecular weights (HMW). This may be a consequence of the reduced ability of gels in the SEC columns to separate large molecules effectively, or, as it was shown by some authors, it may be due to a shear degradation of HMW-PS molecules occurring during the SEC separation process.[4-14]

The degradation of some other polymers (polyisobutylene, polyethylene, polyisoprene, polymethyl methacrylate and others) during the SEC analysis was also reported.[7,11,12,15-18] With the introduction of high-performance gels with lower particle sizes, special attention should be turned to the SEC analysis of HMW polymers. Shear degradation during SEC depends on a variety of parameters: shear rate, elongation strain rate, the nature of the solvent, and the chemical nature and concentration of the polymer. Besides, the tight parts of a chromatographic system (capillary tubing, sample loops, column frits) may generate shear forces contributing to polymer degradation. Some other parameters, such as concentration effects, increased peak dispersion, and ultrafiltration of high molecular weight molecules may also contribute to decrease in MW.[11-14]

The aim of this work was to investigate the phenomenon of PS degradation during the SEC separation process on various crosslinked PS gels with tetrahydrofuran (THF) as eluent. For this purpose, size exclusion chromatography (SEC), coupled with a low-angle laser light scattering (LALLS) photometer was used because it allowed the determination of the absolute weight-average molecular weights (M_w) of PS standards. The following common experimental parameters, which could have an influence on the degree of degradation, were considered: the origins of gels (from various manufacturers), the size of gel particles, the porosity of frits at column ends, the eluent flow rate, the usage of a pre-column filter and of the third detector - a capillary viscometer. To evaluate the degradation degree of a series of PS, we compared the M_w obtained by SEC-LALLS to the M_w determined by static light scattering (LS).

MATERIALS AND METHODS

For this study, monodisperse polystyrenes (PS) with molecular weights going from $2.3\text{x}10^3$ to $1\text{x}84\cdot10^7$ were used (Table 1). PS were of different origins: some of them were synthesized by anionic polymerization at the Institute Charles Sadron, and others were from Waters Associates and Polymer Laboratories.

The refractive index increment of PS in THF (dn/dc=0.186 mL/g) was determined by using a Brice-Phoenix differential refractometer at the same wavelength (632.8 nm) as used with the LALLS photometer.

The LS measurements were performed with a laser light scattering photometer SEM 633 (λ=632,8 nm). Most samples for LS measurements were purified by centrifugation except for the three PS with the highest molecular weights, which were purified by filtration.

The SEC-LALLS measurements were performed on a Waters 150C chromatograph, coupled with two or three detectors in series, a home-made continuous viscometer (CVM),[19] a low-angle laser light scattering (LALLS) photometer Chromatix CMX-100, and a standard Waters differential refractometer (DR); a filter with a pore size of 2 μm was placed at the inlet of a

Table 1

Weight-Average Molecular Weights of Polystyrene Standards Determined by Static Light Scattering (LS) and by Size Exclusion Chromatography Coupled with a Low-Angle Laser Light Scattering Photometer and a Differential Refractometer (SEC-LALLS)

Polystyrene M_w (LS)	**Columns A***	**Columns B***	**Columns C***	**Columns D***	**Columns E****
$2.3\text{x}10^3$	$2.6\text{x}10^3$	$2.4\text{x}10^3$	$2.4\text{x}10^3$	$2.4\text{x}10^3$	---
$4.0\text{x}10^4$	$4.1\text{x}10^4$	$4.2\text{x}10^4$	$4.2\text{x}10^4$	$4.2\text{x}10^4$	---
$9.8\text{x}10^4$	$9.8\text{x}10^4$	$9.9\text{x}10^4$	---	$1.0\text{x}10^5$	---
$4.7\text{x}10^5$	$4.5\text{x}10^5$	$4.5\text{x}10^5$	$4.3\text{x}10^5$	$4.5\text{x}10^5$	---
$6.7\text{x}10^5$	$6.5\text{x}10^5$	$6.6\text{x}10^5$	$6.8\text{x}10^5$	$6.6\text{x}10^5$	---
$2.7\text{x}10^6$	$2.7\text{x}10^6$	$2.5\text{x}10^6$ $2.5\text{x}10^6$**	$2.3\text{x}10^6$ $2.6\text{x}10^6$**	$2.6\text{x}10^6$	---
$3.2\text{x}10^6$	---	---	---	---	$2.8\text{x}10^6$
$3.8\text{x}10^6$	$3.4\text{x}10^6$	$3.0\text{x}10^6$	---	$3.6\text{x}10^6$	---
$5.8\text{x}10^6$	$5.8\text{x}10^6$	$3.3\text{x}10^6$ $3.6\text{x}10^6$**	$2.1\text{x}10^6$ $5.1\text{x}10^6$**	$6.1\text{x}10^6$	---
$6.8\text{x}10^6$	$5.0\text{x}10^6$	$3.0\text{x}10^6$ $3.8\text{x}10^6$**	$2.3\text{x}10^6$ $4.4\text{x}10^6$**	$6.0\text{x}10^6$	$4.1\text{x}10^6$
$8.4\text{x}10^6$	---	---	---	$3.3\text{x}10^6$**	$4.5\text{x}10^6$
$1.47\text{x}10^7$	---	---	---	$2.9\text{x}10^6$**	$3.8\text{x}10^6$
$1.84\text{x}10^7$	---	---	---	---	$4.1\text{x}10^6$

---

* With a pre-column filter with a pore size of 2 μm, placed between an injector and the SEC columns.

** Without a pre-column filter.

LALLS photometer to prevent spikes from micro particles possibly present in the eluent. The mobile phase was THF with flow rates going from 0.4 to 2.3 mL/min at 25°C; a flow rate of 1.0 mL/min was used regularly. The concentrations of PS samples in THF varied with MW, and for HMW-PS with MW over 10^6 the latter was 3 - $1\text{x}10^{-3}$ g/mL; the injection volume was 100 μL. THF was distilled over sodium wire and filtered over a Millipore filter FGLP with pore size 0.2 μm. Five sets of SEC columns with the crosslinked PS gel of various manufacturers were used; details are described in Table 2. All the columns were tested for the possible adsorption of HMW-PS on gel particles

Table 2

Characteristics of SEC Columns

Columns	Manu-facturer	Set of Columns	Particle Size, μm	Porosity of Column Frits, μm
A*	I	10^6, 10^5, 10^4, 10^3	35-45	10
B*	I	10^6, 10^5, 10^4, 10^3	≈10	2
C*	I	10^6, 10^5, 10^4, 10^3	<10	5
D*	II	10^6, 10^5, 10^4, 10^3	8	3
E	III	10^6, 10^5, 10^4, 10^3, $5x10^2$	10	5

---

* A filter with a pore size of 2μm was placed between an injector and the SEC columns. I - Waters Assoc.; II - Showa Denko; III - Polymer Laboratories. **A** - Styragel; **B** - μ-Styragel; **C** - Ultrastyragel; **D** - Shodex (A-800 series); **E** - Plgel.

by comparing the injected amounts and corresponding areas under DR curves of HMW-PS and PS with low M_w (123,000), which did not degrade during the SEC separation. Differences were of the order of experimental error and did not exceed ±3%.

RESULTS AND DISCUSSION

Since laboratories running the routine SEC characterization of polymers have been usually employing sets of columns covering a broad range of MW, the sets chosen for the present study consisted of four or five columns in series with comparable exclusion limits and MW working range. The columns differed in gel particle size and in the porosity of frits at the column ends, the biggest being for columns *A* (Table 2); they appeared first on the market and are very rarely used for routine SEC analyses at the present time.

According to gel particle size and to frit pore size, columns *C* and *E* could be classified in one group (10 μm, 5 μm), and columns *B* in the other (10 μm, 2 μm). Columns *D* differed from the previous ones, both in gel particle size and in frit pore size (8 μm, 3 μm). Besides, the sets of columns *A*, *B*, *C*, and *D* were used with a pre-column filter with pore size 2 μm.

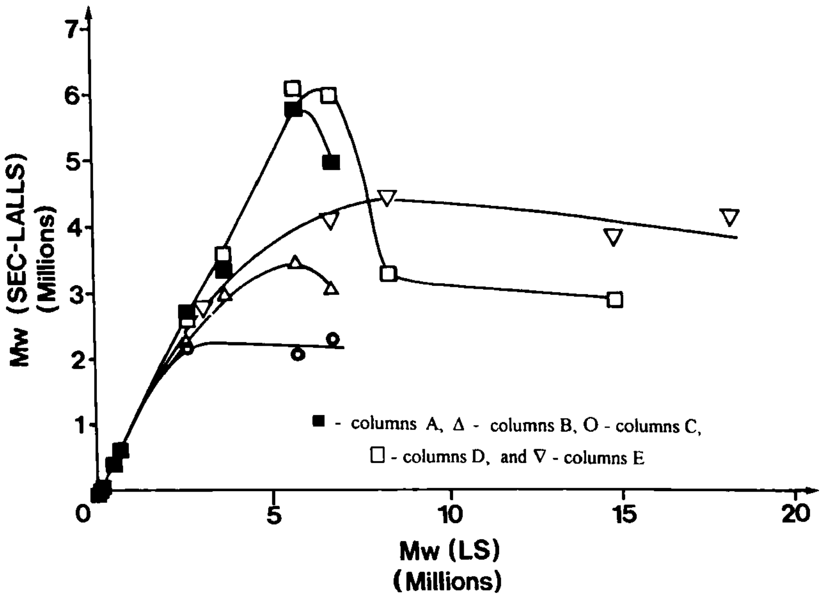

Figure 1. Correlation between the weight-average molecular weights of polystyrene standards determined by LS and SEC-LALLS in THF, 1mL/min; ■ - columns A, Δ - columns B, ○ - columns C, □ - columns D, and ∇ - columns E.

The M_w values of PS standards obtained by LS and SEC-LALLS with various sets of columns are listed in Table 1. We can see that, for PS with M_w up to $2x10^6$, agreement between the two M_w values is very good irrespective of the type of column. Differences become evident especially for PS with M_w over $2x10^6$, where the type of column plays an important role.

The correlation between $M_{w,LS}$ and $M_{w,SEC\text{-}LALLS}$ on different sets of columns are presented in Figure 1, while the decrease in M_w in the MW region of over $6.7x10^5$ is shown in Figure 2. The decrease in M_w is given as the percent ratio of the two M_w values, of $M_{w,SEC\text{-}LALLS}$ (after SEC separation) to $M_{w,LS}$ (without SEC separation).

On all types of columns, no degradation has been observed below M_w = $2x10^6$, even in the presence of a pre-column filter. Above this value, and with a pre-column filter, it proceeds more rapidly on columns *C* (for M_w = $6.8x10^6$, $M_{w,SEC\text{-}LALLS}$ is 34% of $M_{w,LS}$) than on columns *B*. Without a pre-column filter, the degradation is stronger on columns *B* with a low frit pore size (2 μm) and comparable for columns *C* and *E* with the same frit pore size (5 μm).

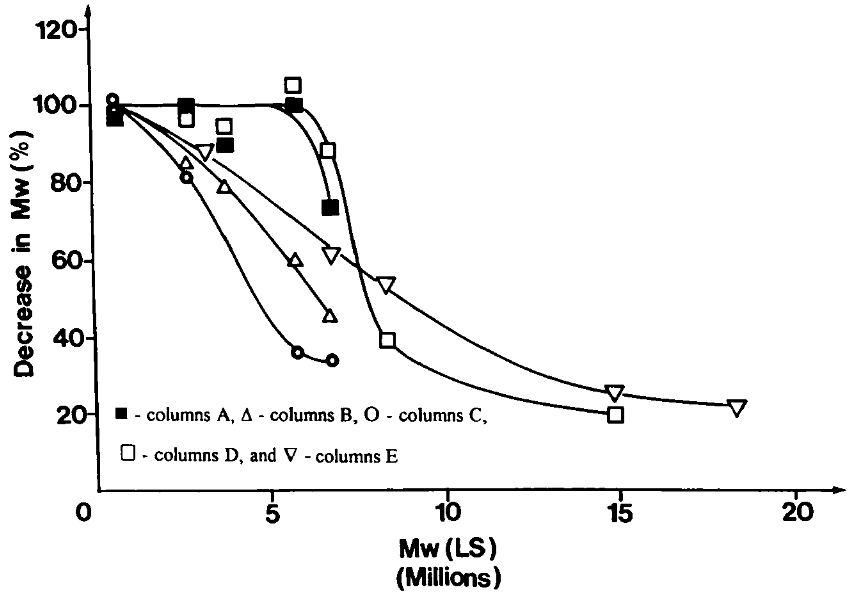

Figure 2. Decrease in M_w of polystyrene standards during the SEC separation process in THF, 1mL/min; ■ - columns A, Δ - columns B, ○ - columns C, □ - columns D, and ∇ - columns E.

The observations are quite different for the sets of columns *A* and *D*, where degradation starts only at very high M_w, around $6x10^6$, and increases with increasing M_w: in the case of the set of columns *D*, for $M_w = 8.4x10^6$, $M_{w,SEC-LALLS}$ is 39% of $M_{w,LS}$, and for $M_w = 1.47x10^7$, $M_{w,SEC-LALLS}$ is 20% of $M_{w,LS}$.

This high critical M_w for columns *D* is rather unexpected since they have the smallest particle size among all the columns used (8 µm) and a small frit pore size (3 µm). On the contrary, a high critical M_w could be anticipated for columns *A*,[4,7] since they have the biggest particle and frit pore size (35-45 µm, 10 µm).

Our findings agree well with the data reported in the literature. Some data were obtained by SEC-LALLS[8,10,11] and some of them by SEC with common PS calibration and/or by viscometric or LS measurements of PS samples before and after the SEC separation.[4,6,7] The critical M_w for the PS degradation on the columns of type *A* was estimated to be $1x10^7$,[4,7] and on the columns of type *B* lower than $8x10^6$.[7] However, these results were obtained on

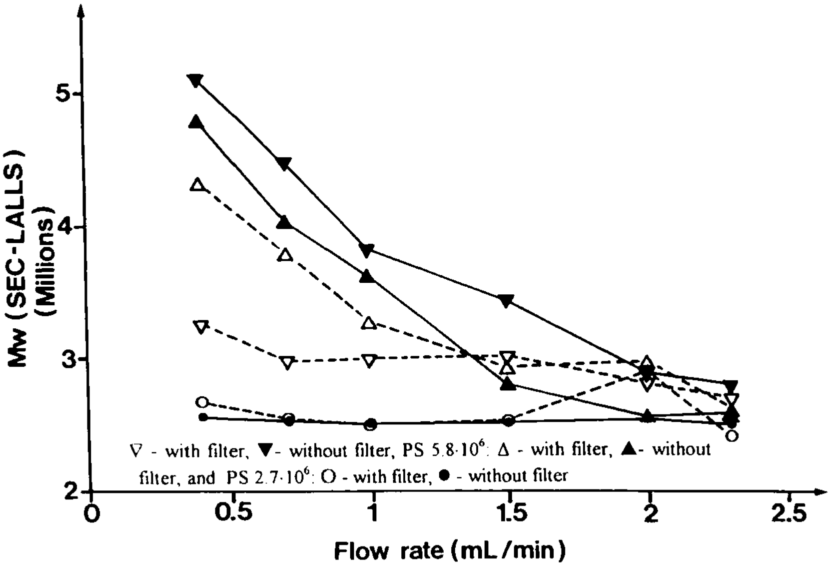

Figure 3. M_w (SEC-LALLS) of polystyrene standards as a function of flow rate, columns *B*; PS 6.8·10^6: ∇ - with filter, ▼- without filter, PS 5.8·10^6: Δ - with filter, ▲- without filter, and PS 2.7·10^6: ○ - with filter, ● - without filter.

5- or 7-column sets covering a high MW working range (from 5×10^4 to 5×10^6) and without using a pre-column filter. Our critical M_w for the PS degradation on columns *D* (6×10^6) can be only compared to the similar value obtained on a mixed bed column from the same manufacturer.[6]

Regarding the columns of type *E*, V. V. Guryanova et al.[10] observed on the series of columns 10^4, 10^5 and 10^6 Å in chloroform no degradation of PS 3.3×10^6, but a severe degradation of PS 6.6×10^6; the decrease in M_w was much higher than in our case in THF ($M_{w,SEC\text{-}LALLS}$ in $CHCl_3$ is only 27% of $M_{w,LALLS}$) and did not change after reducing the flow rate from 1.0 mL/min to 0.2 mL/min. The findings of McIntyre et al.[7] may explain this discrepancy in the degradation degree of PS 6.6×10^6: they have shown that in a non-swelling solvent for the packing the degradation is enhanced because of the lower pore diameters of gel particles.

We have also examined the effects of flow rate on PS degradation. For this purpose, three HMW-PS and the sets of columns *B* and *C* were selected; results are summarized in Tables 3 and 4 and shown in Figures 3 and 4.

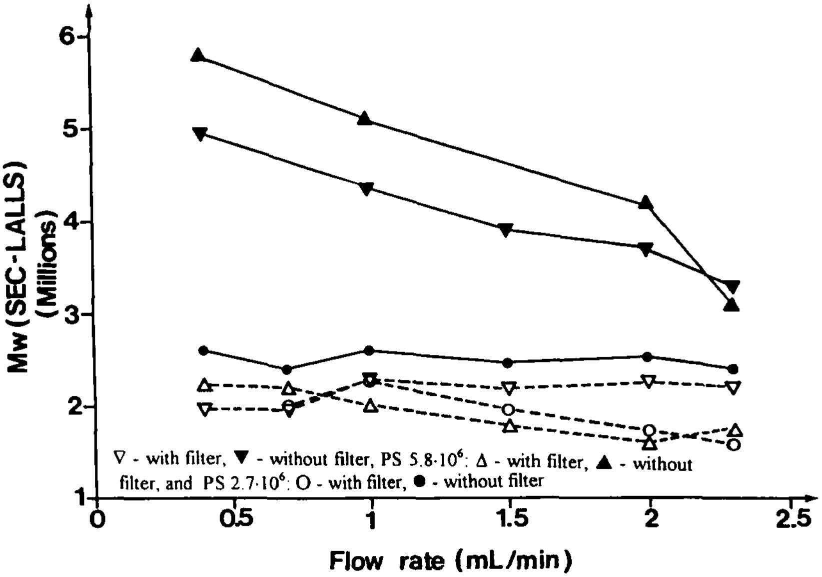

Figure 4. M_w (SEC-LALLS) of polystyrene standards as a function of flow rate, columns *C*; PS 6.8·10⁶: ∇ - with filter, ▼ - without filter, PS 5.8·10⁶: Δ - with filter, ▲ - without filter, and PS 2.7·10⁶: ○ - with filter, ● - without filter.

Table 3

Weight-Average Molecular Weights of Three Polystyrene Standards Determined by SEC-LALLS as a Function of Flow Rate*

Flow Rate	----- 10^{-6} x M_w (SEC-LALLS) -----					
	PS 2.7x10⁶		PS 5.8x10⁶		PS 6.8x10⁶	
mL/min	Without	With	Without	With	Without	With
0.4	2.56	2.67	4.79	4.32	5.10	3.25
0.7	2.52	2.54	4.04	3.79	4.47	2.97
1.0	2.51	2.49	3.62	3.27	3.82	2.98
1.5	2.51	2.53	2.80	2.92	3.43	3.00
2.0	2.54	2.90	2.56	2.97	2.88	2.80
2.3	2.50	2.42	2.60	2.62	2.79	2.70

---

* Columns B, with or without a pre-column filter (2μm).

Table 4

Weight Average Molecular Weights of Three Polystyrene Standards Determined by SEC-LALLS as a Function of Flow Rate*

Flow Rate mL/min	**----- 10^{-6} x M_w (SEC-LALLS) -----**					
	PS $2.7x10^6$		**PS $5.8x10^6$**		**PS $6.8x10^6$**	
	Without	**With**	**Without**	**With**	**Without**	**With**
0.4	2.60	---	5.8	2.23	4.95	1.96
0.7	2.40	2.00	---	2.19	---	1.95
1.0	2.60	2.26	5.1	2.10	4.35	2.28
1.5	2.46	1.96	---	1.78	3.90	2.18
2.0	2.53	1.73	4.2	1.60	3.7	2.25
2.3	2.40	1.58	3.1	1.76	3.3	2.20

---

* Columns C, with or without a pre-column filter (2 μm).

Once again, the difference in performance of the two types of columns is quite evident. Without a pre-column filter, $M_{w,SEC\text{-}LALLS}$ of PS $6.8x10^6$ and PS $5.8x10^6$ decrease continuously with increased flow rate for both sets of columns, but, for columns *C*, the M_w values of PS $6.8x10^6$ are lower than those of PS $5.8x10^6$, which indicates a stronger degradation of PS chains higher than $6.0x10^6$. With a pre-column filter, the degradation is stronger on columns *C* and practically does not change with flow rate.

On columns *B*, the same observation is valid for PS $6.8x10^6$, while M_w of PS $5.8x10^6$ gradually decreases with the flow rate up to 1.5 mL/min. For PS $2.7x10^6$, the increase in flow rate and the use of a pre-column filter do not affect M_w on columns *B*, while on the *C* columns, M_w is lower with a pre-column filter.

The change in flow rate is related to the shear rate in columns and, at higher flow rates, it contributes to the stronger degradation of HMW polymers, which is also demonstrated by our results. Moreover, the influence of a pre-column filter on PS degradation is surprisingly great for MW over $3x10^6$, which indicates a noticeable contribution of the pre-column filter to the increase in shear rate.

Finally, we examined how the capillary viscometer (CVM) affected the degradation of HMW-PS with M_w over $8.4x10^6$ using the set of columns *E* (Table 5). Owing to viscometer design (capillary and coil diameter),

Table 5

Weight-Average Molecular Weights of Three Polystyrene Standards Determined by LS, SEC-LALLS, and SEC-CVM, LALLS*

Polystyrene	10^{-6} x M_w	
M_w (LS)	**SEC-LALLS**	**SEC-CVM, LALLS**
$8.4 x 10^6$	4.5	3.1
$1.47 x 10^7$	3.8	2.6
$1.84 x 10^7$	4.1	4.3

---

* Columns E without a pre-column filter

degradation might be expected for polymers with very high MW.[20] Actually, when we used SEC coupled with the additional third detector (CVM), the degradation degrees of PS $8.4 x 10^6$ and PS $1.47 x 10^7$ were higher as compared to SEC-LALLS measurements. For PS $1.84 x 10^7$ with the highest M_w, the degradation degree did not increase after coupling SEC with the third detector. It appears that the degradation was already very strong when only two detectors were used ($M_{w,SEC-LALLS}$ is approx. 20% of $M_{w,LS}$), and, for this reason, the effect of the third one could not be observed.

CONCLUSIONS

The phenomenon of high molecular weight PS degradation during the SEC separation process was studied on various SEC columns with the crosslinked PS gel packings. The weight-average molecular weights (M_w) for a series of monodisperse PS in THF were first determined by static light scattering (LS) and then, after the SEC separation, by SEC-LALLS. Critical M_w and degradation degree depended primarily on the gel origin; however, they were also influenced by the size of gel particles, by the porosity of column frits, and by common experimental parameters: the eluent flow rate, the use of a pre-column filter and of the capillary viscometer.

The authors did not intend to distinguish between "good" or "bad" SEC columns; they simply wanted to demonstrate the performance of several types of SEC columns in the high molecular weight region. They also wished to direct the attention of polymer analysts to the fact that, in order to obtain accurate molecular weight averages by SEC, it is of utmost importance to consider the possible degradation of high molecular weight polymer standards and samples on the chosen sets of columns, and to take into account the experimental parameters used for the particular SEC analysis.

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