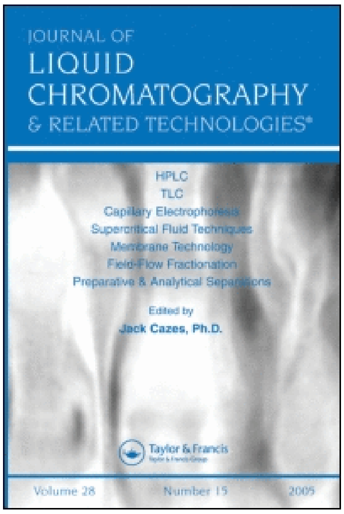

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

A Study of Mechanical Degradation of Polymer in High Performance GPC

Ye Mei-ling[a]; Shi Liang-he[a]
[a] Institute of Chemistry Academia Sinica, Beijing, People's Republic of China

To cite this Article Mei-ling, Ye and Liang-he, Shi(1982) 'A Study of Mechanical Degradation of Polymer in High Performance GPC', Journal of Liquid Chromatography & Related Technologies, 5: 7, 1259 — 1267
To link to this Article: DOI: 10.1080/01483918208067585
URL: http://dx.doi.org/10.1080/01483918208067585

JOURNAL OF LIQUID CHROMATOGRAPHY, 5(7), 1259-1267 (1982)

A STUDY OF MECHANICAL DEGRADATION OF POLYMER IN HIGH PERFORMANCE GPC [*]

Ye Mei-Ling and Shi Liang-He
Institute of Chemistry
Academia Sinica
Beijing, People's Republic of China

ABSTRACT

Four narrow distribution polystyrene samples ($M = 2.7 \times 10^6$, 6×10^6, 6.5×10^6, 7×10^6) were dissolved in tetrahydrofuran and the solutions were passed through a Shodex A-80M column at a concentration of approximately 1×10^{-3} g/ml, injection volume of 500 microliters, and a flow rate of 2 ml/min (i.e., maximun flow rate allowable for this column). Molecular weights of eluants were then determined by viscosity and laser light scattering methods; concentrations were determined by ultra- violet spectrophotometry. From the results of analysis of the eluate, it was shown that no significant degradation was detectable for all four samples in this colulmn which was packed with a cross-linked polystyrene gel. When a silica gel (irregular shaped) column was used, under same operating conditions, only sample PS-4, with a molecular weight of $M = 7 \times 10^6$ underwent degradation up to 15%. High pressure exerted on the column is believed to be the main cause of the degradation.

---

[*] Presented at the GPC Symposium, Chinese Chemical Society, Guilin, People's Republic of China, June 2-6, 1981.

INTRODUCTION

When a polymer solution passes through a GPC column at high pressure, the high molecular weight portion of the sample may be degraded by shearing stress. The degradation of polystyrene ($M = 10^7$) and polyisobutylene ($M = 10^6$) in conventional GPC has already been reported{1,2} . The degradation is expected to be more serious in high performance and high temperature GPC. Degradation was observed for polystyrene ($M = 4 \times 10^6$) in 1,2,4-trichlorobenzene at 135 °C and for PE ($M = 7.5 \times 10^5$) in the same solvent and temperature, even at low flow rate{3} . As a result of degradation in the high molecular weight portion of the sample, errors are introduced both to the calibration curve and to the calculated average molecular weight for high molecular weight samples. Therefore it is worth while to look deeper into the problem of degradation of high-molecular weight polymer after passing through a GPC column. GPC chromatographers are very much concerned about the question of what is the upper limit of molecular weight of polymer that will not undergo degradation in high performance GPC at room temperature. Since polystyrene is widely used as standard sample to calibrate GPC columns, our study initially involved this polymer.

EXPERIMENTAL

1. Instruments:

Two sets of columns were used in a Waters Associates Model ALC/GPC 244 instrument. The first set was a Shodex A-80M column (inner diameter = 0.8 cm, theoretical plates = 18000 plates / 50 cm). The second set was a silica gel (irregular shape) column (inner diameter = 0.8 cm, 50 cm in length theoretical plates = 16000 plates / 50 cm). This prepared porous silica gel was supplied by Jilin Institute of Chemical Industry.

2. Samples

PS-1 M = 2.7×10^6 (Waters standard sample)

PS-2 (Polysciences, Inc.)
$\bar{Mw} = 6 \times 10^6$ (measured by LALLS in our laboratory)

PS-3 (Jilin Institute of Chemical Industry)

PS-4 (PS polymerized at room temperature and fractionated twice)

3. Eluent: Tetrahydrofuran (THF)

4. Detection method for molecular weight and concentration:

The experimental procedure was carried out as follows: A sample was collected as it eluted from the chromatographic column. Its MW was determined and compared with the value obtained for a "blank" that was not passed through the GPC column. The concentration of eluate was determined with a UV Spectrophotometer (Specord UV-VIS): Molecular weights of the samples were determined with a laser low angle light scattering photometer (Chromatix KMX-6). Due to the extremely low concentration of the eluate, the experimenatal error in the light scattering measurement was rather large. Intrinsic viscosities were also measured to supplement the light scattering data. Any changes in intrinsic viscosities were taken as a measure of the degradation. The low concentration (ca $3 - 8 \times 10^{-5}$ g/ml) of sample in the eluate from GPC column necessitated a proper choice of viscometer. Two viscosimeters with quite long efflux times (to = 27'18"8 for THF at 25 °C) were selected and an effluent time difference, Δt , between polymer solution and pure solvent of more than 10 seconds could be obtained. In such a way, the intrinsic viscosities $\{\eta\}$ of dilute solutions were determined with good reproducibilities.

GPC Experiment:

Since degradation occurs most readily at high concentration and high flow rate, a high concentration of 1 - 2 x 10^{-3} g/ml and a high flow rate of 2 ml/min were used for both the Shodex A-80M and silica gel columns.

RESULTS AND DISCUSSION

(1) Four polystyrene samples (M = 2.7 x 10^6 - 7 x 10^6) were injected into a Shodex A-80M column at a concentration of approximately 1 x 10^{-3} g/ml, injection volume of 500 microliters and a flow rate of 2 ml/min, (pressure gauge indicating 300 psi). All of the fractions were collected in one bottle and analyzed by the viscosity method. The determinations were repeated several times. The results are listed in Table 1. Under identical operating conditions, solutions of two

TABLE 1. [η] of polystyrene samples prior to and after passage through a Shouex A-80M column

sample No.	sample conditions		$C\times10^5$ g/ml	η_r	[η]	[η]	$[\eta]-[\eta]^1$	$\frac{[\eta]=[\eta]^1}{[\eta]}$ %
1	PS-1							
	$M=2.7\times10^6$	prior	4.9239	1.024	487.4			
	2^{ml}/min 300psl	after	5.25	1.025		476.2	11.2	2.3
2	PS-2	prior	7.3903	1.065	852.5			
	$Mw=6\times10^6$	after	7.03	1.063		867.7	-15.2	-1.8
	2^{ml}/min 300psl	after	6.62	1.061		865.1	-12.6	-1.5
3	PS-3	prior	5.2181	1.048	919.9			
		after	4.22	1.039		925.1	- 5.2	-0.6
	2^{ml}/min 300psl	after	5.65	1.054		955	-35.1	-3.8
4	PS-4	prior	7.818	1.079	984.9			
		after	3.20	1.032		1000	-15.1	-1.5
	2^{ml}/min 300psl	after	7.95	1.081		994	- 9.1	-0.9

TABLE 2. $[\eta]$ of polystyrene samples prior to and after passage through a silica gel column

sample No.	sample condition		$C \times 10^5$ g/ml	η_r	$[\eta]$	$[\eta]$	$[\eta]-[\eta]^1$	$\frac{[\eta]-[\eta]^1}{[\eta]}$ %
1	PS-2	prior	5.4964	1.047	855.1			
	$M_w=6\times10^6$	after	5.71	1.048		840.6	14.5	1.7
	2' ml/min	after	5.26	1.045		855.5	-0.4	-0.05
	1500 psl	after	5.72	1.049		856.6	-1.5	-0.18
2	PS-4	prior	5.0667	1.050	986.8			
		after	5.26	1.044		836	150.8	15.3
	2' ml/min	after	5.23	1.045		837.5	149.3	15.1
	1500 psl	after	5.21	1.044		844.5	142.3	14.4
	1 ml/min	after	5.25	1.047		897	89.8	9.1
	800 psl	after	5.24	1.047		896	90.8	9.2

polystyrene samples (M = 6 x 10^6 , 7 x 10^6) were passed through the silica gel column (pressure gauge indicating 1500 psi). The viscosities of the fractions were determined similarly. Results are given in Table 2.

(2) It is obvious from Table 1 that all four samples passing through the Shodex A-80M column were not degradated at all. On the silica gel column, the situation was quite different. Sample PS 4 underwent degradation to a extent of approximately 15%, (see Table 2). Flow rate and injection concentration on the two columns were the same. The only difference was pressure on the two columns. The pressure on the silica column was much higher than that of Shodex A-80M column. We believe that column pressure is vital to the occurrence of shear degradation.

(3) The data of Table 1 and Table 2 show that the degradation of PS-THF system is not so serious in the high performance GPC column at room temperature as we first thought. Our data pointed to the fact that mechanical degradation is negligible when PS samples with molecular weights up to 6 x 10^6 are used as standard samples for column calibration.

REFERENCES

1. E.L. Slagowski, L.J. Fetters and D.Mcintyre, Macromolecules, 7, 394 (1974).

2. C. Huber and K.H. Lederer, Polym. Letters, 18, 535 (1980).

3. J.G. Rooney, G. Ver Strate, Polymer Preprints, 21, 196 (1980)