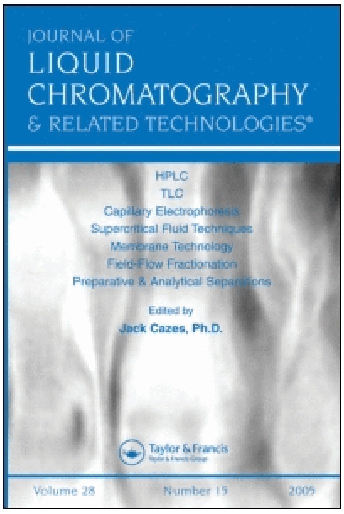

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OVERLOADING AND DEGRADATION STUDY IN GPC USING LOW ANGLE LASER LIGHT SCATTERING DETECTOR (LALLS)

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ABSTRACT

The unique macromolecular compression effect or delayed GPC elution of high M.W. material was observed using the GPC + LALLS technique for a polystyrene standard of M.W. 5.0 E5. Further overloading which resulted in nonlinear fractionation is also described. The degradation of a 4.2 E6 standard after elution was detected by LALLS with calculated M.W. of 1.0-1.1 E6 but not by GPC, as indicated by normal GPC retention time and the shape of the chromatogram. This degradation was further verified by reinjection of the collected fractions into the GPC which showed a bimodal distribution with calculated M.W. of ca. 1.0 E6 via GPC calibration and LALLS. The source of degradation was attributed to the 2 micron exit frit in the single Jordi mixed bed column. Similar degradation of 2.3 E6 standard to same M.W. of ca. 1.0 E6 was also observed. The use of these standards as GPC calibrants should not be affected by this "post column" degradation.

INTRODUCTION

There were several reports on sample concentration effects on GPC in the early 70's. Moore (1) observed the delayed elution and peak broadening in his investigation when narrow polystyrenes eluted through short but efficient columns. The unique delayed elution was attributed to the appreciable viscosity imparted by high polymers in solution. Goetze, Porter, and Johnson (2) studied the effect of changes in viscosity by varying the viscosity of the solvent in which the polymer was dissolved prior to injection but still maintaining constant polymer concentration. It was found that there was no major change in elution characteristics when the polymer sample was prepared in different solvents having different viscosities. Therefore, the delayed elution effect may be associated with the molecular weight of the high polymer. Ouano (3) studied the nonlinear fractionation process (an upshot of overloading) by comparing the chromatograms of mixtures of narrow M.W. polystyrenes with those generated by computer addition of the individual chromatograms of the components of the mixtures. Differences were seen, which were attributed to overloading. Rudin (4) introduced the concept of macromolecular compression of the dissolved polymer chains, as a result of the lack of available space for chain extension when the concentration was high. Chuang and Johnson (5) demonstrated the macromolecular coil compression effect by employing the technique of differential GPC where different concentrations of solute were added to the eluant so that the injected polymer coils would actually experience a rather viscous environment as the solute concentration in the eluant went up. The phenomenon of delayed elution associated with the compressed coil surrounded in a viscous media was clearly observed.

The objective of this work was to use a LALLS detector to study the overloading effect. In theory, GPC is a hydrodynamic separator under normal operating conditions, i.e., for the same polymer at one elution volume, there is an unique molecular weight associated with it. Should overloading occur, the M.W. values from the LALLS detector along the chromatogram would be higher than would be seen without overloading at the same elution volume because of the macromolecular compression effect which causes delayed elution. The phenomenon may be illustrated in Figure 1. Furthermore, if excessive overloading occurs, the nonlinear fractionation process described by Ouano (3) should be detected by LALLS too.

It was known that the macromolecular compression effect became more pronounced for higher M.W. materials at the same loading compared to those of lower ones. Therefore, 4.25 E6 and 5.0 E5 standards were selected for study.

EXPERIMENTAL

Sample Preparation for SEC

The concentrations of the two polystyrene standards were set as follows: 5.0 E5 (Pressure Chemical) 8.0, 6.4, 4.8, 3.2, 2.0, and 0.4 mg/ml, 4.25 E6 (Polymer Labs) 4.0, 3.2, 2.4, 1.6, 1.0, and 0.2 mg/ml. All solutions were filtered with a 0.2 micron

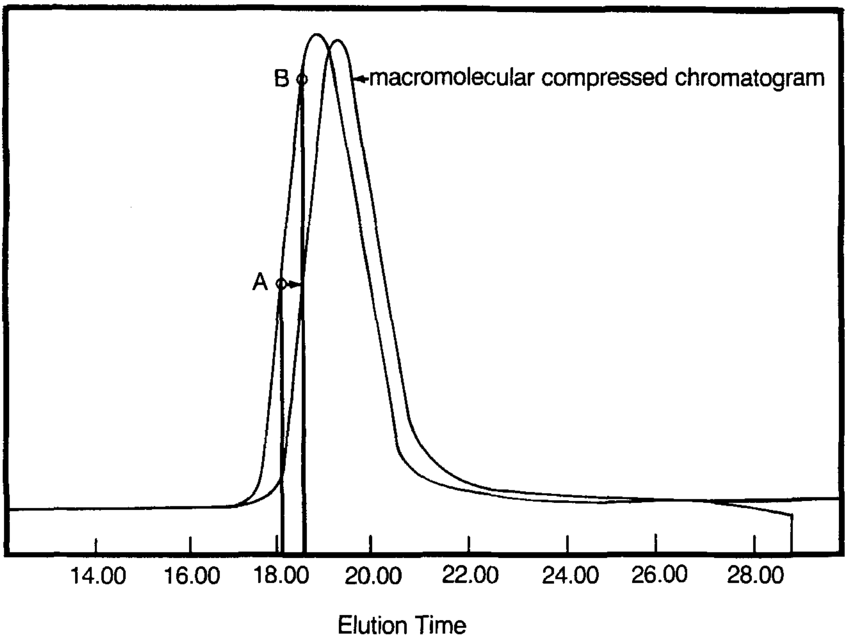

Figure 1. Delayed elution due to macromolecular compression or viscous fingering effect.

Fluoropore filter, and all injections were made at 100 microliters.

Gel Permeation Chromatography

The GPC used in this work has both concentration and LALLS detection; the former is a differential refractive index Model 1037A (Hewlett Packard) and the latter is a KMX-6 Low Angle Laser Light Scattering Photometer (LDC/Milton Roy). Data were acquired and processed with a Minc/23 computer (DEC) which used A/D interfaces and software from LDC/Milton Roy. The injector is a

Model 7125 (Rheodyne) equipped with a 200 microliter loop, and the pump is a Model 110B (Beckman) operating at 1 ml/min. Chromatography was carried out in THF using a single J-Packed mixed bed column (E3, E5 Angostrom, Jordi Associates) with the column packing specially sized for LALLS detector.

LALLS Parameters and Settings

The KMX-6 LALLS photometer was set to collect data at 6-7 forward scattering angle, using a 0.2 millimeter field stop. The specific refractive index increment for polystyrene of 0.1845 was taken from Chromatix Application Note LS 7.

RESULTS AND DISCUSSION

To check the GPC + LALLS performance, a run of NBS 706 polystyrene standard (M.W.=2.8 E5) was carried out. As can be seen in Table 1, the on-line GPC + LALLS value and GPC calculated result for NBS 706 are in good agreement with the NBS value.

The M.W. of the 4.25 E6 standard was checked with static LALLS, and it is listed along with the manufacturer's supplied value in Table 1. The value of 5.5 E6 was an average of two runs using dn/dc=0.1845, which is the dn/dc for polystyrene of M.W. 2.59 E5. In general, the dn/dc increases with increasing M.W., which may explain the higher measured M.W. value for the 5.5 E6 standard.

However, the first pass on-line LALLS values for 4.25 E6 at different loading levels were consistently lower than they should be, as also indicated in Table 1. Surprisingly, the GPC

TABLE 1

M.W. of Polystyrene Standards and Isooctyl Acrylate Control

Samples	Static LALLS	On-line LALLS	GPC
NBS 706 (2.8 E5)	2.8 E5	2.5-2.8 E5	2.8 E5
4.25 E6	5.5 E6	1.1-1.7 E6 (1st pass)	4.25 E6 (1st pass)
		0.9-1.0 E6 (2nd pass)	1.0 E6 (2nd pass)
5.0 E5	5.0 E5	5.0-5.5 E5	4.9-5.0 E5
2.3 E6	2.3 E6	0.95-1.0 E6	2.2 E6

calculated values were much higher and approached that of the static LALLS or the manufacturers. To explain the discrepancies, fractions of the repeated injections of the above standards were collected and evaporated for further GPC-LALLS analysis. The GPC results on the collected fractions gave a value close to 1.0 E6 as well as a bimodal distribution, as illustrated in Figure 2. It is therefore proposed that under the given GPC operating conditions, the 4.2 E6 standard degrades after the first elution pass as evidenced by the LALLS calculation and by LALLS chromatograms (Figure 3). It was reported in the literature (6) that column packings and frits are the primary source for degradation of high M.W. polymers. The frits used in the Jordi mixed bed column are 5-micron for entrance and 2-micron for exit,

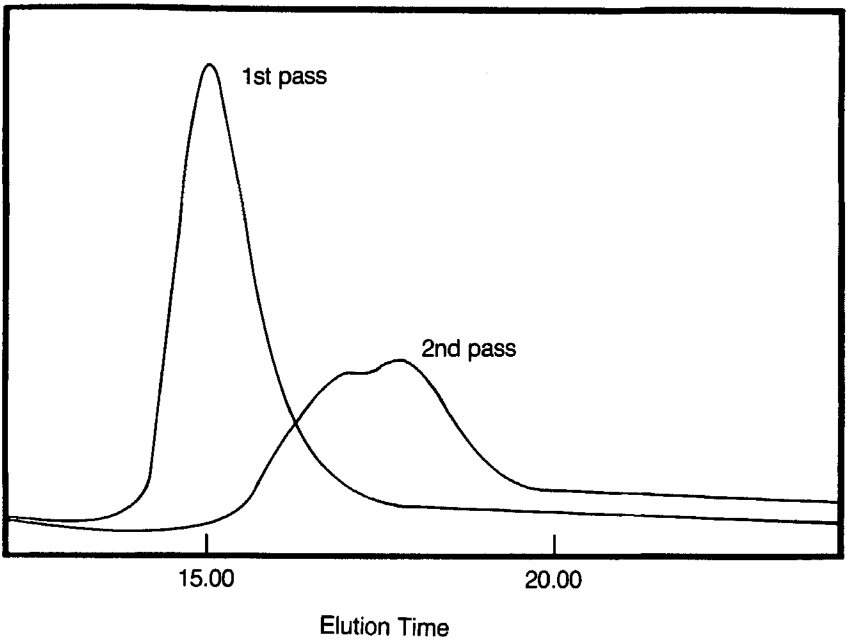

Figure 2. Chromatograms of refractive index detector for 4.25 E6 polysyrene standard in the first and second elution pass.

respectively. It is suspected that the exit frit causes the degradation which may also explain the inability for GPC to detect the degradation in the first pass. Therefore, the degraded molecules exiting from the column still follow the elution order as if they are not degraded because they do not have a chance to reseparate from one another according to normal GPC exclusion mechanism. Reinjection gives the molecules a chance to separate throughout the column packing thereby showing a bimodal chromatogram. The degradation to nearly the same 1.0

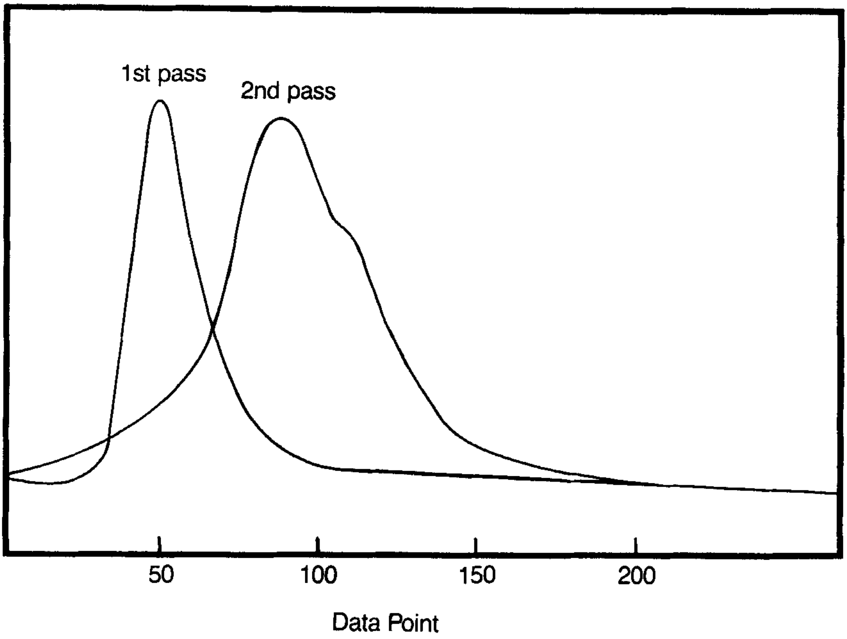

Figure 3. Chromatograms of LALLS detector for E6 polystyrene standard in the first and the second elution pass.

E6 M.W. was also observed for 2.3 E6 standard. In spite of the degradation seen with high M.W. standards, they still can be used for GPC column calibration since they elute in much the same manner as if they are not degraded in the first pass.

Figure 4 shows the LALLS M.W. vs. elution volume for 5.0 E5 at different levels of loading. The loading of 0.04 mg would be the normal amount used in our lab. As can be seen in Figure 4, the macromolecular compression effect started to appear at increasing loadings. In other words, the higher LALLS molecular

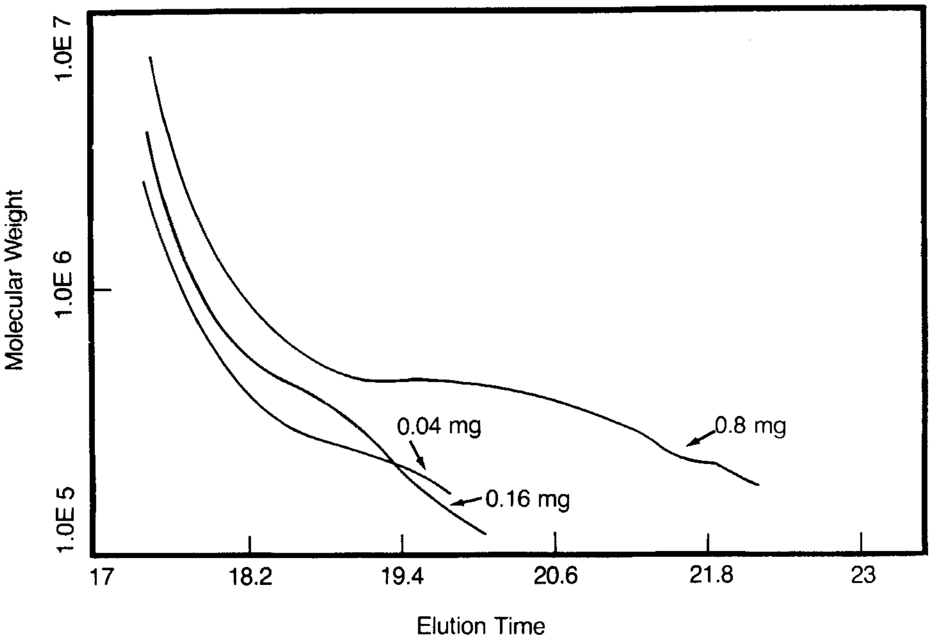

Figure 4. LALLS M.W. of 5.0 E5 standard VS. elution volume at various levels of loadings.

weights at higher loadings (0.16 mg and 0.8 mg) at any given elution volume are the manifestation of the macromolecular compression effect.

At the 0.16 mg loading, the column still maintained a linear fractionation mechanism, i.e., a monotonic decrease in M.W. as elution volume increases, although complexed with the compressing effect. However, the compression effect should be avoided in the branching determination of certain materials since comparison has to be made to a linear standard at each elution volume and therefore the correct M.W. ought to be measured in order to obtain meaningful results. Otherwise, linear molecules may be misidentified as branched ones because of overloading.

As the loading level was increased, the nonlinear fractionation process took place. Nonlinear fractionation may be defined as nonmonotonic decrease of M.W. with increasing elution volume. This was seen in Figure 4 at the 0.8 mg loading level where beginning at around 19.0 ml elution volume, a slight rise in M.W. was noted as retention volume increased. This behavior may be explained as follows. When the pores available for the separation of comparable size molecules were filled up by the large number of incoming molecules, the "excess" molecules eluted through a non-size exclusion process traveling faster than those experiencing exclusion, thus resulting in the described phenomenon.

SUMMARY

1. A macromolecular compression effect and nonlinear fractionation were clearly observed via LALLS detection with GPC separation using 5.0 E5 polystyrene standard.
2. Degradation of a 4.25 E6 standard to lower M.W. under the given operation conditions on the first elution pass was detected by LALLS but not by GPC; reinjection of the collected fractions into the same column corroborated the hypothesis of degradation. Effect of frit size on degradation should be

checked more carefully for the GPC method development of ultrahigh M.W. polyethylene (M.W. between 2 to 7 million).

3. Because of degradation and overloading, great caution must be exercised in using LALLS to determine polymer branching in certain materials in order to obtain meaningful results.

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