Polymer Bulletin 5, 603–608 (1981)

Polymer Bulletin

Separation of Styrene Oligomers by Supercritical Fluid Chromatography (SFC) Using a Modified HPLC-Instrument

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Summary

An instrument for High Performance Liquid Chromatography (HPLC) was modified by relatively simple means for working in the field of Supercritical Fluid Chromatography (SFC). By use of this modified apparatus three different gradient methods were tried with respect to their applicability for the analytical separation of oligomers. Especially by using a gradient in eluent composition or by a pressure gradient good resolution could be obtained.

Introduction

Chromatography with supercritical mobile phases is well known now for a longer period of time and has been described in a number of reports and reviews (e.g. GOUW and JENTOFT 1975; KLESPER 1978). A wide-spread use of this chromatographic technique, which can be a complement for HPLC and GC particularly in the analysis of high molecular weight compounds, has been impeded up to now by the fact that on one hand no commercially available instruments existed and that on the other hand the complete construction of a chromatograph in a user's laboratory constitutes a considerable effort.

We report therefore the modification of a commercially available HPLC-instrument for SFC-analyses. The modified instrument shows the advantage of allowing the chromatographer to do both HPLC and SFC. In addition we present as examples the separation of oligostyrenes with SFC by means of this instrument, applying gradients of temperature, pressure and composition.

Modification of the HPLC-instrument

A commercially available HPLC-instrument includes already a great number of elements which are also necessary for SFC-instrumentation, e.g., pumps for the eluents, a damping system, and flow regulation. The HPLC instrument used in our case was a Hewlett-Packard chromatograph type 1084 B, which additionally included devices for solvent purging and heating, flow measuring, programming of eluent gradients, pressure measuring, variable volume injection system, a column oven usable up to 100°C, variable wavelength UV-detector which is resistant

0170-0839/81/0005/0603/$ 01.20

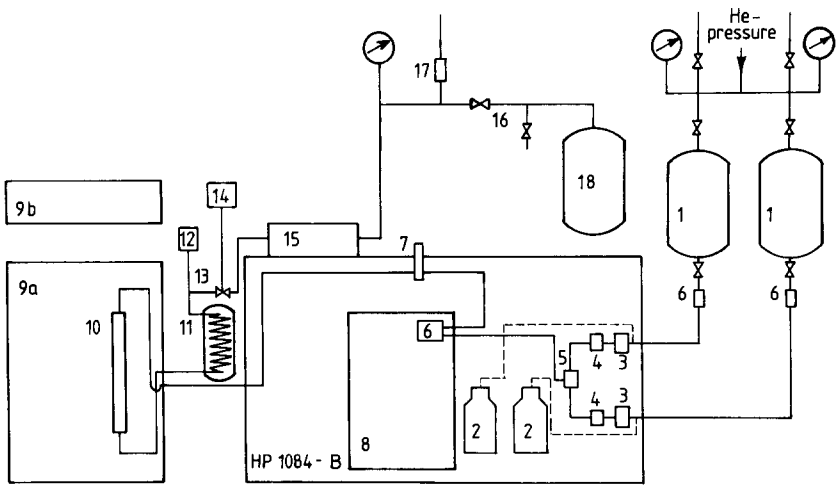

Fig. 1: SFC-apparatus (for explanation see text).

toward moderate pressures (30 bar), microprocessor control, and a calculator-plotter for data and chromatograms. By comparison of such a HPLC-system with SFC-systems described in the literature (e.g. JENTOFT and GOUW 1972, MYERS and GIDDINGS 1966, KLESPER and HARTMANN 1978) it can be seen that only some units have to be added for SFC work: pressure resistant storage containers for the low boiling mobile phases, a column oven for working at temperatures above 100°C, a valve for adjusting the pressure at the end of the chromatographic column, a pressure regulation system connected to this valve for chromatographing by pressure gradients (with time), and a pressure resistant container at the eluent outlet for working with eluents boiling below or near ambient temperature.

The modified HPLC-apparatus is shown schematically in fig. 1. The eluents boiling below 50-70°C are prepressurized in steel storage tanks (1), either by applying a He-pressure of 0,2 to 0,5 bar above ambient pressure, or by raising the temperature of the storage tank above ambient temperature using an external heating tape. In case the mobile phase posesses a sufficiently high boiling point, as for cyclohexane,it can be fed without prepressure from the glass bottles (2) provided with the HPLC instrument. The eluents are metered in the liquid state by the pumps (3) of the HP 1084 B, consecutively pass the damping system combined with a device for measuring the feed rate (4), the mixing chamber (5), a filter (6), and the variable volume injection system (7). The stream then enters the oven of the HP 1084 B (8).For SFC operation the stream is led directly out of the unheated oven to a larger external oven with forced air circulation (9a) (W.C. Heraeus, Hanau, type UT-5042 EK) which can be heated to 300°C and accomodates larger columns, if needed. In addition, the oven can be temperature programmed by a programmer (9b) (W.C. Heraeus, Hanau, type Kelvitron TPG 2,

equipped with a Pt-100 temperature sensor). The stream which is supercritical within the oven passes through the separation column (10) and is liquefied again outside the oven in a water cooled heat exchanger. The pressure at the column end is monitored by an electric pressure transducer (12) (Siemens, Teleperm Messumformer D, type M 56 441), while the pressure upstream of the column is measured by the pressure transducer of the HP 1084-B itself. Regulation of the pressure at the column end is by a needle metering valve (13), which, for creating a pressure gradient is slowly turned by adapting the potentiometer axis of a "cut-a-curve" time programmer (14) (Zeitplangeber, Siemens, type M-122-A9) to the stem of the valve (13). The eluate is then returned to the HP 1084 B, i.e. to its variable wavelength UV-detector. Consecutively, an external metering valve (16) allows to raise the pressure in the detector to a level which prevents formation of gas in the stream. For keeping a constant pressure level and for protection of the detector, an adjustable, spring actuated safety valve is provided (17). The eluent is finally collected in a pressure resistent metal container as a liquid under its own vapor pressure.

Modification of the original HPLC instrument thus is only carried out by adding external devices, leaving the HP 1084 B itself unchanged.

Applications

As it has been described earlier, n-pentane is a suitable eluent in the separation of oligostyrenes by SFC (KLESPER and HARTMANN 1978). Therefore n-pentane (purum; Fluka, Neu Ulm) was also used in this study. As a second eluent for working with eluent gradients, cyclohexane (distilled over Na) was selected.

a) Chromatography with a temperature gradient: Fig. 2 shows two chromatograms of an oligostyrene sample with M_n=520 g/mol (Knauer, Oberursel).The upper has been recorded isothermally at 250°C, the lower by applying a negative temperature gradient; the temperature was lowered to a point which is a few degrees above the critical temperature of n-pentane (196,6°C). Comparison between the two chromatograms shows, that the retention times are lowered (esp. for the later eluted peaks) by lowering the temperature. This is because the lower temperature brings about a higher density of the supercritical phase. This effect on elution time is opposite to that in GC, where a positive gradient leads to lowered retention times.

b) Chromatography with a pressure gradient: Pressure gradient chromatography is particularly useful in SFC; separations of oligomer mixtures by SFC have been performed in most cases by applying pressure gradients. This can be seen again by working with the apparatus described above, as demonstrated in Fig. 3: an oligostyrene sample with M_n=2200 g/mol (Pressure Chemical Co., Pittsburgh, USA) could be separated in a relatively short time (2,5 h) with good resolution.

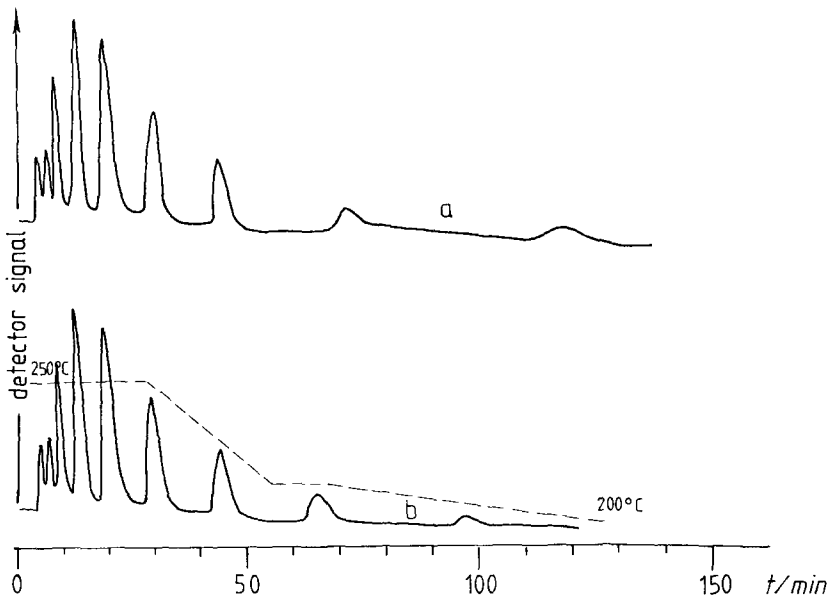

Fig. 2: Chromatograms of PS 600; a) without temperature gradient, T=250°C (pressure: 59 bar), b) with temperature gradient (pressure: 58 bar). Eluent: n-pentane; sample: 50 µl of 34 mg PS 600 in 1,3 ml n-hexane; column: Si 100-10 µ, 20 cm, internal diameter 4,6 mm (manufacturer Hewlett-Packard); detector: UV, 254 nm, flow rate: 0,5 ml/min; —— detector signal; ----- temperature

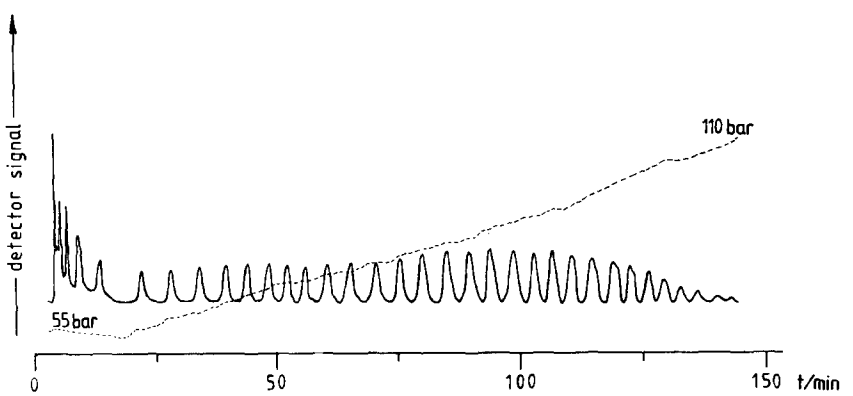

Fig. 3: Chromatogram of PS 2200 with pressure gradient. Eluent: n-pentane; sample: 50 µl of 80 mg PS 2200 in 1,4 ml cyclohexane; column: Si 100-10 µ, 20 cm, internal diameter 4,6 mm (manufacturer Hewlett-Packard); detector: UV, 254 nm; oven temperature: 240°C, flow rate: 1ml/min
——— detector signal; ---- pressure
The chromatogram is baseline-corrected for baseline shifts caused by pressure changes.

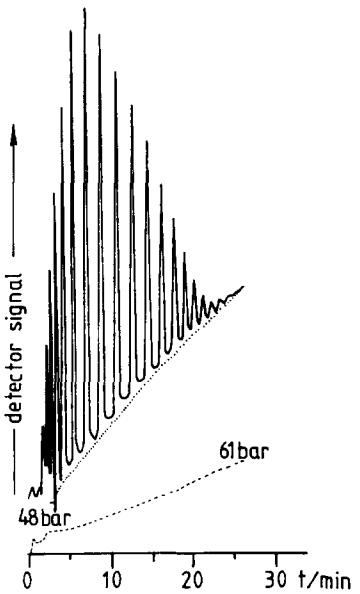

Fig. 4: Chromatogram of PS 800 with eluent composition gradient. Eluents: n-pentane/cyclohexane; sample: 50 µl of 50 mg PS 800 in 1,4 ml n-hexane; column: 25 cm, internal diameter 4,6 mm, packed with LiChrosorb Si100, 7 µm (Merck, West-Germany); detector: UV, 262 nm; oven temperature: 250°C, flow rate: 1 ml/min; cyclohexane gradient: 5 to 30 % cyclohexane from 0 to 30 min; —— detector signal, ····· baseline; ----- pressure

c) Chromatography with an eluent composition gradient: This type of gradient is very often useful in HPLC. The chromatogram shown in Fig. 4 makes evident that eluent composition gradients can also be of advantage in SFC. A pentane/cyclohexane eluent mixture with an increase in cyclohexane content from 5 % to 30 % within 30 min resolved the 19 oligomers of an oligostyrene sample with $\bar{M}_n$=810 g/mol (Pressure Chemical Co.). The baseline drift of the chromatogram is due to the higher UV-absorption of cyclohexane and can be reproduced by a run without injection of oligostyrene. The column end pressure was not regulated during the runs but allowed to increase according to the increase in viscosity with the composition gradient. Since composition gradients have to our knowledge not been applied so far to SFC, further work will be reported (SCHMITZ and KLESPER 1981).

Gradient chromatography with supercritical fluids as mobile phases appears to be suitable for the analysis of oligomers; the apparative expenditure can be reduced by use of a commercial HPLC apparatus as the base instrument. Chromatographic columns can be the same as used in HPLC. Compared with previous SFC results (KLESPER 1978) analysis times could be

shortened to a great extent.

Acknowlegements

We wish to thank Mr. B. Lorenschat for his aid in experimental work and the Arbeitsgemeinschaft Industrieller Forschungsvereinigungen (AIF) for financial support.

References

GOUW, T.H. and JENTOFT, R.E.: Adv. Chromatogr. 13, 1 (1975)

JENTOFT, R.E. and GOUW, T.H.: Anal. Chem. 44, 681 (1972)

KLESPER, E. and HARTMANN, W.: Eur. Polym. J. 14, 77 (1978)

KLESPER, E.: Angew. Chem. 90, 785 (1978); Angew. Chem., Int. Ed. Engl. 17, 738 (1978)

MYERS, M.N. and GIDDINGS, J.C.: Sep. Sci. 1, 761 (1966)

SCHMITZ, F.P. and KLESPER, E.: in preparation

Received September 26, accepted October 3, 1981