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# Characterization of Polymers Using Supercritical Fluid Chromatography: Application of adsorption chromatography, size exclusion chromatography and adsorption chromatography at critical conditions

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Supercritical fluid chromatography (SFC) utilizes fluids or mixtures of fluids above their critical temperature and critical pressure which exhibit greater solvating properties with simultaneously reduced viscosities and higher diffusion coefficients compared with their liquid state; supercritical fluids, thus, offer new possibilities for characterizing polymers. The three modes of liquid chromatography are applied in the analysis of polystyrenes, using supercritical fluids (mixtures of dichloromethane with carbon dioxide) in each mode: adsorption chromatography for the separation of oligomers, size exclusion chromatography for the determination of molar mass distribution, and adsorption chromatography at critical conditions for the characterization of functionality type distribution. Advantages and disadvantages of size exclusion chromatography with fluids in their supercritical, subcritical and liquid phase are discussed with the system polystyrene in dichloromethane.

**KEY WORDS** Polymer characterization, supercritical fluid chromatography, size exclusion chromatography, chromatography at the critical point of adsorption.

## INTRODUCTION

Most of the advanced polymers and new synthetic materials are heterogeneous with regards to molar mass, chemical composition, and topology. In order to correlate material properties with polymer structures of macromers, telechelics, reactive polymers and

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copolymers new analytical methods must be developed. Moreover, new materials have to be investigated in more detail in terms of stress and degradation. New analytical techniques should also be faster or more sensitive and address problems concerning recycling of polymers and environmental issues. In this respect, supercritical fluids offer new possibilities in the characterization of polymers.

Supercritical fluid chromatography (SFC) has mostly been used by polymer chemists in the last decade in adsorption chromatography mode to determine the molar mass of oligomers and polymers, for example poly(ethylene glycols) and polysiloxanes [1]. The excellent solvating power of supercritical fluids for oligomers and additives was also used in supercritical fluid extraction (SFE) followed by chromatographic or spectroscopic analysis.

In 1977, Giddings [2] suggested and used SFC for the first time in size exclusion chromatography to separate polystyrenes in compressed 1,1-difluoroethane on silica. Because the supercritical state is characterized by lower viscosity and faster diffusion both the resolution and speed of separation would be enhanced. Jinno et al. [3] suggested dichloromethane as a mobile phase with controlled-pore glass packings at supercritical conditions for polystyrenes in the molar mass range up to 110,000 g/mol. The third mode, the separation "at critical conditions of adsorption"[4] was not realized until recently. The new experimental devices (electronically controlled restrictors) developed by Hewlett Packard enable SFC with mixed mobile phases on packed columns. Thus, it should be possible to perform all three modes of liquid chromatography of polymers with supercritical fluids, namely, supercritical fluid adsorption chromatography (SFAC), supercritical fluid adsorption chromatography at critical conditions (SFACCC), and supercritical fluid size exclusion chromatography (SFSEC). This is because interactions of a polymer molecule with a mixed supercritical fluid should be similar to those with a mixed liquid chromatography (LC) solvent. We wanted to confirm this analogy by investigating critical conditions of adsorption.

Starting points of our considerations had been Martire's unified molecular theory of chromatography and its application to supercritical fluid mobile phase in fluid-liquid-adsorption systems [5] and the thermodynamic model of Roth [6] on the retention of polymers in supercritical fluid chromatography with equations as follows,

$$\Delta G = RT \ln K_D \quad (1)$$

$$\Delta G = \Delta H - T \Delta S \quad (2)$$

$$\Delta G = \sum n_i \Delta_{ij} G_i + n_j \Delta G_j \quad (3)$$

where,

- $G$  is the free enthalpy of the polymer molecule in the adsorbent pore,
- $K_D$  is the capacity factor (distribution coefficient),
- $H$  is the interaction enthalpy of the polymer molecule with the stationary phase,
- $S$  is the entropy of the polymer molecule in the pore,
- $i$  is the structural unit of a polymer,
- $j$  is the heterogeneous group and
- $n$  is the number of groups.

In SFC, as in all chromatographic methods, the capacity factor  $K_D$  is proportional to the variation of free energy  $\Delta G$ . Analogous to LC [4], three modes should exist in SFC in

order to describe interactions of a solvated polymer molecule in a pore of stationary phase. According to Equation (2) the free energy may be split into an enthalpy term and an entropy term. By varying interactions of the polymer molecule with the mixed mobile phase, different modes of elution behavior should be obtained (Figure 1).

In the case of supercritical fluid adsorption chromatography at critical conditions of polymers,  $\Delta S$  and  $\Delta H$  compensate each other using a mixed mobile phase consisting of a good fluid and a poorer one, so that  $\Delta G_i$  becomes zero. Only the different interactions of heterogeneous groups, for example end groups, with their corresponding free energy, effect retention which depends on the number of interacting heterogeneous groups  $n_j$ .

Figure 1 depicts the elution behavior of polymers in these different modes; molar mass is plotted versus elution volume. Three different dependencies are found. In a good solvent for the polymer which does not permit any interactions with the pore surfaces (SEC mode), molecules with a larger hydrodynamic volume are eluted first. At critical conditions all polymer molecules are eluted at the same elution volume independent of their molar masses. In a thermodynamically poor mobile phase molecules with higher degrees of polymerization are adsorbed in a larger extent; elution order is reversed as in SEC.

## EXPERIMENTAL

The SFC experiments were conducted on a HP-SFC G1205A (Hewlett-Packard Company, Palo Alto, CA), equipped with an autosampler and a diode array detector (1.7- $\mu$ L cell volume). The wavelength used was 254 nm; except for the experiments depicted in Figure 6,

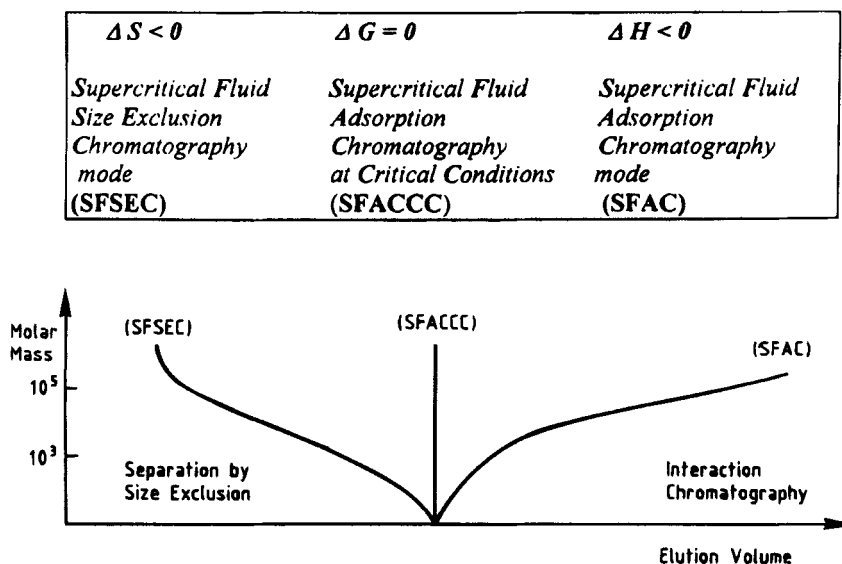


FIGURE 1 Plot of molar mass versus elution volume in terms of the three modes analogous to liquid chromatography.

the wavelength of 280 nm was used. An electronically controlled variable restrictor was part of the HP-SFC instrument, described in ref [7]. The column used for all experiments was a Hypersil 4-mm i.d.  $\times$  200 mm 5- $\mu$ m silica, 120 Å pore size (Hewlett-Packard). The flow rate of the mobile phase was 1 mL/min. The samples were dissolved in dichloromethane at a concentration of 0.1 w/w %; 0.5  $\mu$ L was injected via the rotor volume of the helium-pressure actuated switching valve.

Except for the analysis of the polyisoprene sample, a fused-silica capillary column SB-Biphenyl-30 (stationary phase 30% biphenyl, 70% methyl polysiloxane, 50  $\mu$ m i.d.  $\times$  10 m, 0.25  $\mu$ m film thickness) (Lee Scientific, Salt Lake City, UT) was utilized, provided with an frit restrictor. The mobile phase was pure carbon dioxide; the linear velocity through the column/restrictor was 2.2 cm/s at a pressure of 100 bar and a temperature of 125°C. The injector rotor volume was 0.2  $\mu$ L, and the injection was done in the time-split mode (0.3 s). The polyisoprene was dissolved in dichloromethane at a concentration of 2 w/w %.

Dichloromethane and toluene (purity 99.5%) were from E.Merck, Darmstadt, Germany, and the carbon dioxide 5.5 from Messer Griesheim, Krefeld, Germany. The polystyrene and polyisoprene standards were from Waters Associates, Milford, MA.

The determination of the critical point of adsorption is possible by varying the mobile phase (CO<sub>2</sub> mixed with a polar solvent) or the temperature, pressure and density of the fluid, respectively. In the SEC mode a thermodynamically good solvent is needed under supercritical conditions. By successive increase of the content of a thermodynamically poor solvent, the adsorption mode will be reached. The critical conditions are realized when the retention time of the mean peak is independent on the polymer molar mass.

In selecting a suitable stationary phase, the heterogeneous groups should have a greater retention than the monomer unit in the chain; the mean value of the pore distribution of the stationary phase has to be greater than the hydrodynamic volume of the supercritical fluid solvated polymers.

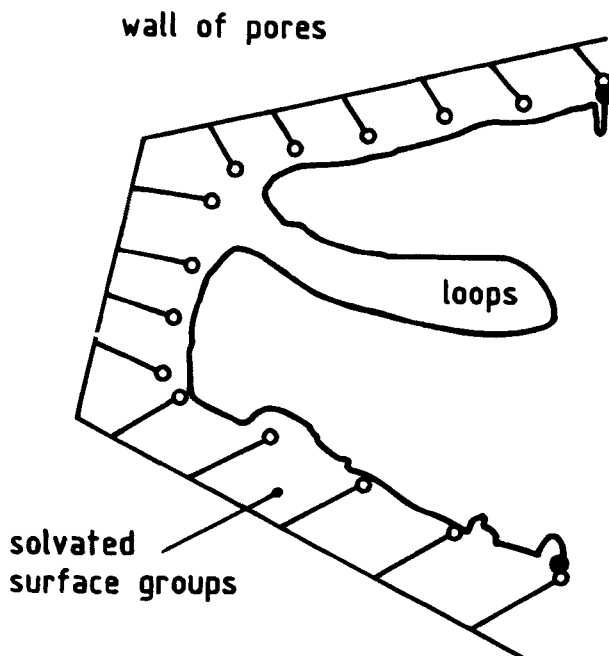
## RESULTS AND DISCUSSION

In the adsorption mode in SFC (Table I), polymer molecules must be soluble up to high molar masses; thus, in the presence of stationary phase, polymer aggregations must not occur. In this mode, all monomer basic or structural units of the polymer should contribute to retention. Occurrence of chain loops will result in broadening of chromatographic peaks, since retention will be caused exclusively by the variation of adsorption enthalpy with reduced interactions of polymer segments because of chain loops.

In Figure 2 separation of polystyrene standard 1,000 g/mol in the adsorption mode on a packed silica column is depicted. The mobile phase was 58% dichloromethane/42% carbon dioxide by volume; the fluids were drawn individually into the two pumps of the HP-SFC system and transported to the mixing chamber, then through the injector, column, detector, and restrictor; the oven temperature was held at 438 K, the column outlet pressure was kept constant at the electronically controlled restrictor with 200 bar. The short elution time combined with the high-separating efficiency using a normal HPLC column was remarkable.

TABLE I

Adsorption mode of polymers in SFC

**Mechanism**

All monomer units and heterogeneous groups are able to interact with the surface groups,  $\Delta H$  processes dominate. Intermolecular interactions of polymer segments are reduced. Retention is caused by change of adsorption enthalpy only.

**Advantages**

- More rapid analysis than in the liquid state because of better transport conditions.
- Higher resolution because of lower theoretical plate height.
- Application of capillary columns is possible.
- Multigradient elution is favorable.

Figure 3 demonstrates the high resolution of a capillary SB-Biphenyl-30 column in adsorption mode with pure carbon dioxide. A functionalized polyisoprene standard (molecular weight  $M_n$  940 g/mol) was separated using a density program with the initial density of 0.35 g/mL, increased to 0.45 g/mL in 500 s, then increased to 0.65 g/mL in 6,000 s, isothermal at 398 K. At lower degrees of polymerization, the differently functionalized end groups were separated. Assignment of peaks with regard to their functionality can be achieved by coupling SFC with NMR or MS. A quantitative determination of functionality type distribution is not yet possible because it is necessary to integrate over all degrees of polymerization.

At the critical point of adsorption (Table II), enthalpy  $\Delta H_i$  of the monomer basic unit of the polymer is compensated by entropy  $\Delta S_i$ . Only the different free enthalpies of the het-

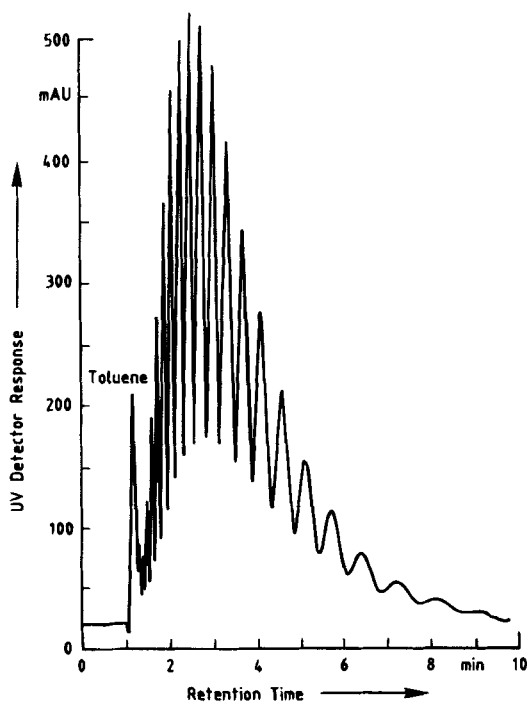


FIGURE 2 Adsorption chromatographic separation of polystyrene 1,000 g/mol in the supercritical state. Mobile phase: 58% dichloromethane/42% carbon dioxide by volume, 438 K, 200 bar.

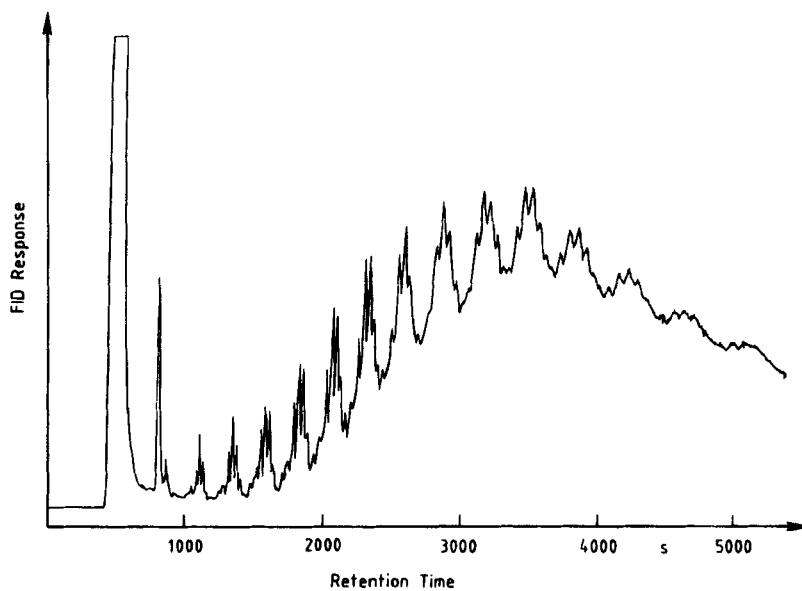
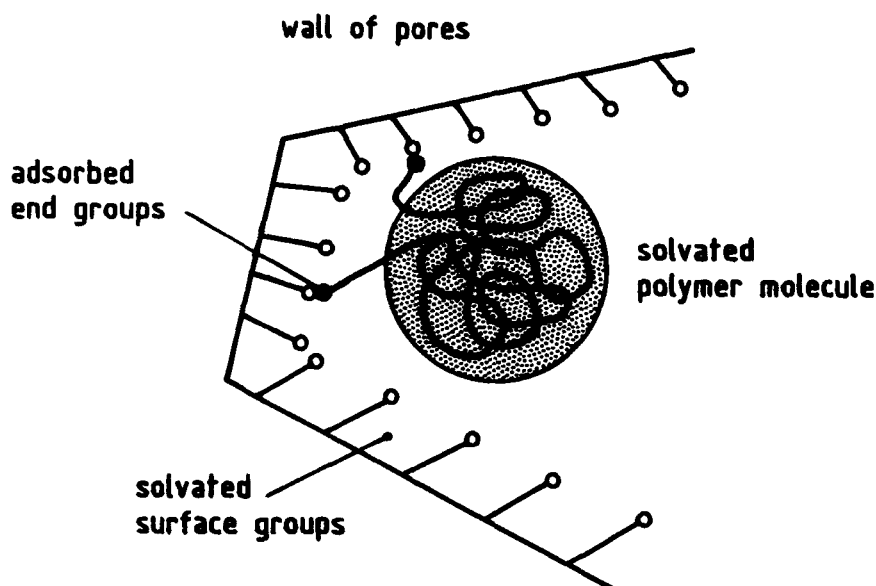


FIGURE 3 High resolution SFC of functionalized polyisoprenes in the adsorption mode. Stationary phase: SB-Biphenyl-30 capillary column; mobile phase: carbon dioxide, 398 K, density program.

TABLE II

Critical conditions of adsorption mode in SFC

**Mechanism**

Only heterogenous groups (end groups) are able to interact with surface groups; enthalpy and entropy processes ( $\Delta H$  and  $\Delta S$ ) of the monomer unit compensate each other.

The hydrodynamic volume in the mixed supercritical fluid is reduced. Intermolecular interaction of segments are stronger as in adsorption mode, entropic processes are suppressed.

Retention is caused by adsorption enthalpy of end groups only.

**Advantages**

- Critical conditions ( $\Delta H$  and  $\Delta S$  compensate each other) are realized with supercritical fluids.
- Characterization of chemical heterogeneity is possible.

erogeneous groups  $\Delta H_i$  (end groups or branching) can contribute to retention. The hydrodynamic volume of the coil is reduced under these conditions, that is, polymer molecules of higher molar masses can reach pores with equal diameter. The separation range will become larger. Entropic processes in the coil are reduced by intermolecular interactions of the segments.

Figure 4 depicts the chromatograms of two polystyrene standards and toluene at the critical conditions for polystyrene. The mobile phase was a mixture of 79% dichloromethane and 21% carbon dioxide by volume. The retention times proved to be independent of the molar masses of polystyrenes. Figure 5 shows the chromatograms of the polystyrene precursor ( $M_w$  2,000 g/mol) and the functionalized polystyrenes ( $M_w$  65,000 g/mol), synthesized by reaction of the living polystyrene precursor with a trifunctional 2,4,6-chloro-1,3,5-triazine.<sup>8</sup> The length of arms corresponds to the size of the initial



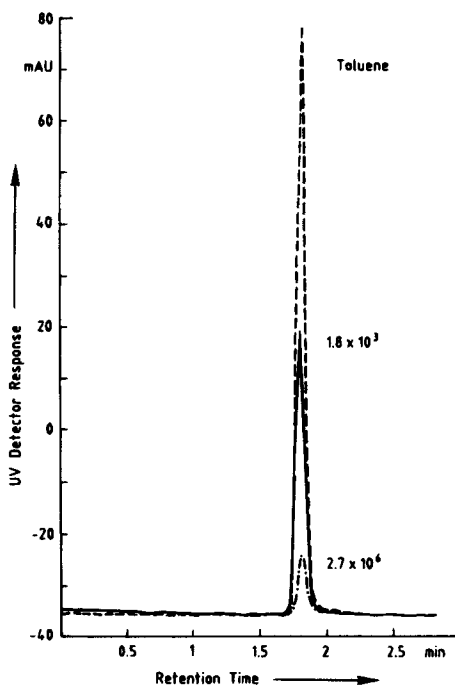


FIGURE 4 SFC at critical conditions of adsorption of polystyrene standards  $2.7 \times 10^6$ ,  $1.8 \times 10^3$  g/mol, and toluene. Mobile phase: 79% dichloromethane/21% carbon dioxide (by volume), 473 K, 200 bar.

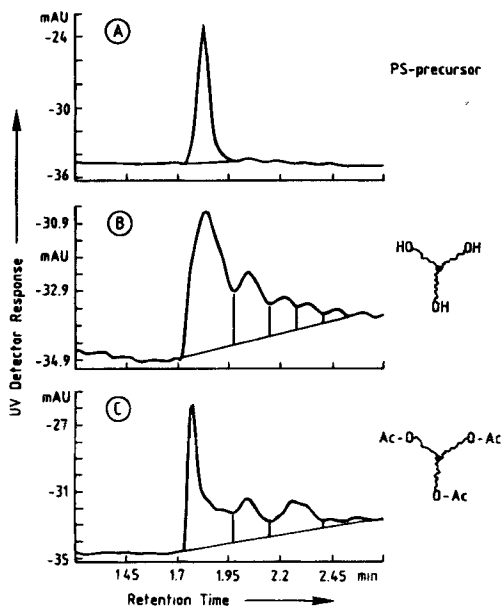


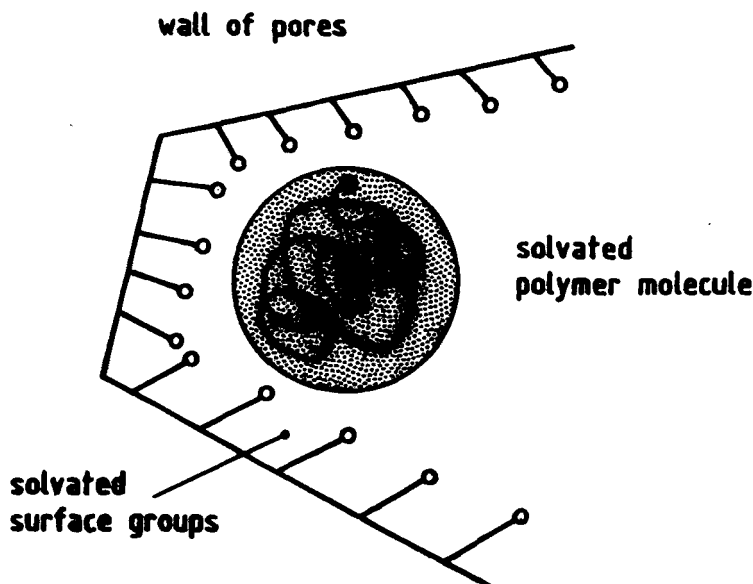
FIGURE 5 Separation of polystyrene precursor (A), OH-terminated three-armed polystyrene (B), and acetyl-terminated three-armed polystyrene (C) at critical conditions of adsorption in SFC. Mobile phase: 79% dichloromethane/21% carbon dioxide (by volume), 473 K, 200 bar.

precursor. Separation of hydroxyl- as well as acetyl-terminated polystyrenes could be achieved. The main peak indicates the polystyrene precursor, whereas the following peaks are caused respectively by the hydroxyl-, and acetyl end groups of the polystyrene molecules with increasing number of arms. The assignment of peaks have not been determined, but could by matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS).

In size exclusion mode, the whole polymer molecule is solvated by the fluid in such a way that no interactions with the pore walls are possible (Table III). The coil is expanded so that no interactions of the segments are permitted. Exclusively entropy is responsible for separation. The separation range of stationary phase is smaller than with the two other modes because of expanded coils.

TABLE III

Size exclusion mode of polymers in SFC



### **Mechanism**

Monomer units and end groups do not interact with the stationary phase.

The coil is expanded, interaction between polymer segments allow the entropic processes in the polymer coil to occur.

Retention is caused by change of entropy.

### **Advantages**

- More rapid analysis than in the liquid state because of better diffusion conditions and lower viscosities at the higher separation temperatures
- Higher resolution and exclusion limit.
- Lower theoretical plate heights.
- Suitable for micro SEC and process control.

Figure 6 demonstrates size exclusion chromatography of a standard mixture of polystyrenes ( $2.7 \times 10^6$ ,  $35 \times 10^3$ , and  $1.8 \times 10^3$  g/mol) and toluene, respectively under supercritical conditions utilizing pure dichloromethane. The separation range of the silica column is broad and resolution is more pronounced in the higher molar mass range. Peak shapes are good. Further investigations are necessary to understand these effects completely.

Chromatograms performed in the supercritical state at 518 K, in the subcritical state at 413 K, and in the liquid state at 308 K, depicted in Figure 7, show that the highest elution velocity with equal resolution can be achieved in the supercritical state. The flow rate of the mobile phase dichloromethane is the highest under supercritical conditions because of its low density in this state.

Figure 8 shows the calibration curves of polystyrenes in dichloromethane with different temperatures but isobaric conditions. The calibration curves shift with regard to elution volumes, because with higher temperatures more rapid elution takes place due to the lower viscosities of the fluids. Retention is changed considerably because of higher values of free volume of the solvated polymer molecules. Under the thermodynamic conditions used, no thermochemical change of silica could be observed. Further experiments are necessary in order to optimize the resolution in the whole molar mass range by variation of pressure, temperature and density of mobile phases.

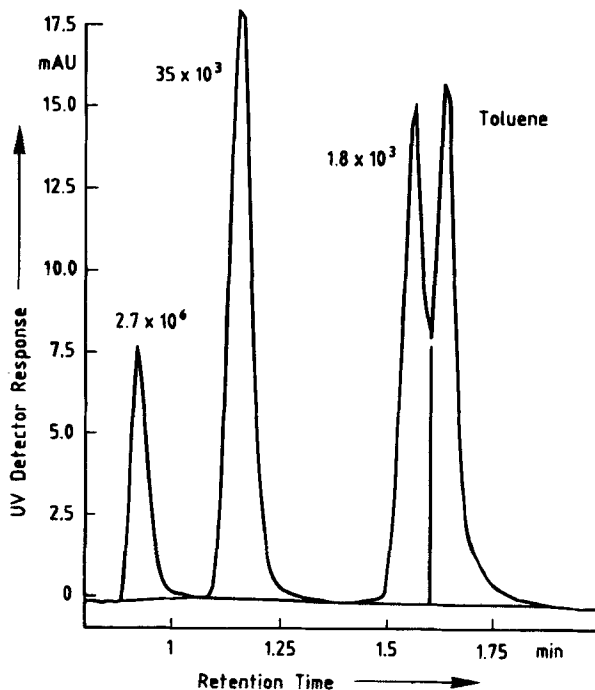


FIGURE 6 SEC of polystyrene standards in supercritical dichloromethane at 518 K, 150 bar.

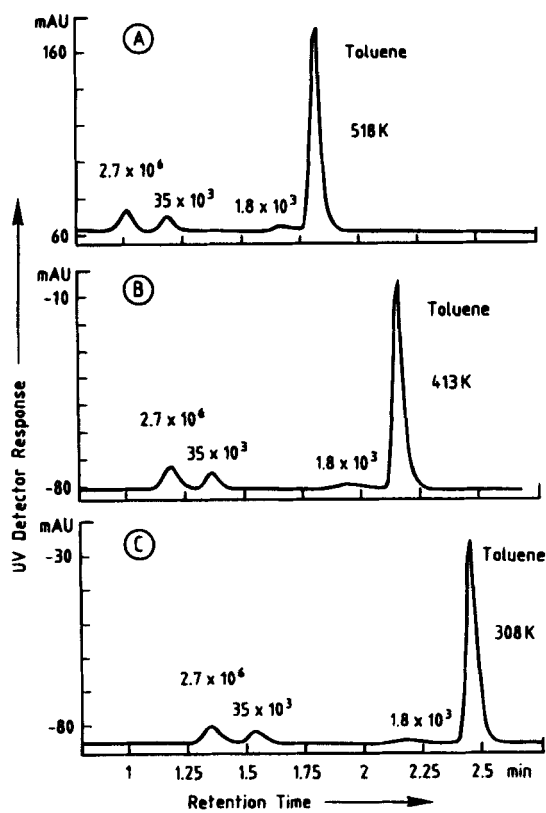


FIGURE 7 SEC of polystyrene standards with dichloromethane in the supercritical (A), subcritical (B), and liquid state (C).

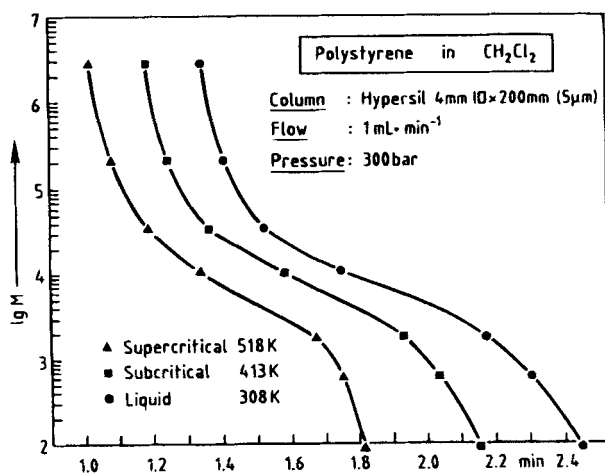


FIGURE 8 Calibration curves in different states of mobile phase.

## CONCLUSIONS

The principle of entropy-enthalpy compensation in liquid adsorption chromatography at critical conditions was applied for the first time in SFC. At critical conditions the separation and analysis of end-group functionalized macromers, telechelics, cycles and branched polymers appears to be possible.

SEC separations up to high molar mass can be carried out with supercritical mobile phases using electronically controlled restrictors; in frit restrictors polymers may precipitate, and clogging of the restrictor may occur. SEC in supercritical fluids allows more rapid separation with higher resolution. Micro methods using capillary columns may be possible permitting rapid process control during the production of polymers.

Supercritical fluids offer new possibilities in polymer characterization of multidimensional chromatographic techniques. SFC may be preferred for preparative investigations and coupling with Fourier-transform infrared spectroscopy and mass spectrometry.

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