The high dissolving power of supercritical fluids for some polymers and the high efficiencies of capillary columns make supercritical fluid chromatography (SFC) particularly suitable for analyses of oligomeric and polymeric materials. The separation of 42 styrene oligomers has been reported [1, 2]. The separation of every oligomer in a mixture is routinely possible, in contrast to size exclusion chromatography in which resolution is much lower. For example, Figure 7.1a shows the separation of a polydimethyilsiloxane mixture. Not only are the individual linear oligomers resolved, but also a series of small peaks is assigned to branched-chain oligomers. The analysis of numerous other polymers and surface-active agents by SFC had been reported, including methylphenylsiloxanes, styrene and other vinyl aromatic polymers, polyolefins and waxes, polyethers, polyglycols (underivatised, since analysis temperatures are well below the decomposition temperature), polyesters, and more polar polymers such as epoxies (Figure 7.1b) and isocyanates.

Such analyses generally involve density programming to bring out oligomers at fairly regular intervals. Simultaneous temperature programming also extends the range of compounds eluted and gives greater chromatographic efficiencies by increasing solute diffusion coefficients in the mobile phase.

For very high molecular weight polymers, hydrocarbon (e.g., pentane) mobile phases modified with polar additives such as alcohols and ethers are required. Many such separations have been reported by SFC using packed columns, often with gradient elution, but such an approach poses special problems in capillary SFC because of the low flow rates. Capillary SFC with solvent programming is a likely future growth area.

A number of advantages accrue from combining the separating power of capillary SFC with the explicit structural information of mass spectroscopy (MS). Most of the common ionisation modes have been shown to be compatible with SFC, including electron impact, chemical ionisation, and charge exchange [3]. The variety of structural data available from SFC with negative-ion chemical ionisation detection has been demonstrated: while methane reagent gas gave mainly the methane positively charged ion plus I ion (M + I), both methane with carbon dioxide and ammonia with carbon dioxide as reagent gases gave many more fragment ions.
Figure 7.1 (a) SFC chromatogram of polydimethylsiloxane. Conditions: column, 20 m x 50 µm id SB-methyl; mobile phase: CO\textsubscript{2} at 120 °C with asymptotic density programming, detector: flame ionisation detection (FID); and (b) SFC chromatogram of epoxy acrylate oligomers. Conditions: column: 20 m x 50 µm id, SB-biphenyl-100; mobile phase: CO\textsubscript{2} at 70 °C with linear density programming, detector: FID. Source: Author’s own files
By changing the density of the supercritical fluid, different fractions may be selectively extracted from the complex mixture or simple matrix. On decompression, the extracted solutes are precipitated and may be collected from injection into a gas chromatography or SFC for analysis. Figure 7.2 shows a simple apparatus for on-line supercritical fluid extraction (SFE)/SFC: solutes extracted from the sample matrix are deposited from the end of a restrictor into the internal loop of the microinjection valve of the capillary SFC. The valve loop contents are subsequently switched into the SFC column by means of liquid or supercritical carbon dioxide.

**Figure 7.2** Apparatus for coupled supercritical fluid extraction.
Source: Author’s own files

SFC has been used to determine oligomers in polyethylene glycol [4] and low molecular weight, high-density polyethylene wax [5]. Carbon dioxide, propane and propane-modified carbon dioxide have been studied as eluents.

SFC coupled to time-of-flight – secondary ion mass spectroscopy has been applied to the fractionation of polydimethylsiloxane oligomers in the molecular weight range of 1,000–10,000 [6].

Nerin and co-workers [7] used supercritical fluid extraction coupled to MS to determine potential migrants from paper and board intended for food packaging.
One attractive approach in this context is the use of SFE with carbon dioxide as the supercritical fluid, which can provide a fast and efficient extraction of a wide range of compounds. SFE has been shown as an excellent extraction system of different matrixes [8-19].

References


Chromatography Mass Spectroscopy in Polymer Analysis