Polymer Bulletin 12, 491–497 (1984)

Polymer Bulletin

Supercritical Fluids

Novel Supercritical Fluid Techniques for Polymer Fractionation and Purification.

1. Background

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Summary

Supercritical fluids which combine the properties of both gases and liquids also show very unusual pressure dependent dissolving power. When such fluids are used as solvents in various separation processes, it is possible to achieve effective fractionation or purification in a number of different systems which are difficult to obtain by conventional techniques. In this communication a brief summary of the basic aspects of supercritical fluids will be given. The application of this novel technique for the fractionation and purification of polymeric and oligomeric organofunctional siloxanes will be illustrated.

Introduction

When a liquid is heated in a closed container its vapor pressure increases and it eventually reaches its boiling point. However, since it is in a closed system, as it is heated the pressure also rises. Therefore there is always a liquid-vapor equilibrium in the system. If the heating is continued further, a point is finally reached (a constant temperature and pressure depending on the liquid) at which all the liquid vaporizes and the system is transformed into a single phase. This is called the critical point and beyond this point a fluid is in the supercritical state and cannot be reliquified by increasing the pressure. A simple picture of this behavior is given in Figure 1, which shows the phase diagram of carbon dioxide including the critical point and the supercritical region.

Supercritical fluids combine the properties of both liquids and gases. However, perhaps the most interesting behavior of these systems (especially for our purposes) is their unusual, pressure-dependent dissolving power. The ability of supercritical fluid solvents to dissolve materials of low volatility was first reported over a century ago (1), however only recently it has begun to receive appropriate attention due to the technique's unique feature in the design and operation of entirely new separation processes (2-4). By proper choice of the solvent fluid, temperature and pressure, it may be possible to perform separations that are otherwise extremely difficult or impossible to achieve by conventional

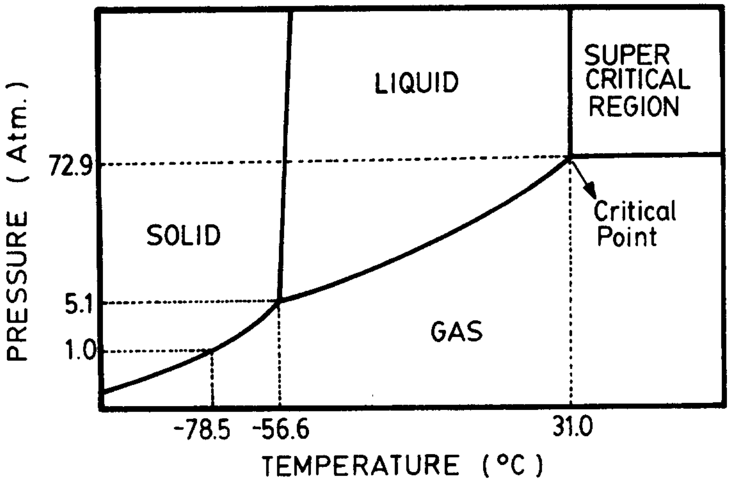

Figure 1. Phase Diagram of Carbon Dioxide (scales are not linear)

unit operations such as distillation, extraction, fractional precipitation, etc.

Table I provides a list of critical Temperatures (Tc) and Pressures (Pc) for various compounds (5). It is clear that except for water, the supercritical state for carbon dioxide, chloroform, methanol and for most of the hydrocarbons can be attained at fairly low pressures and low to moderate temperatures.

TABLE I

Critical Temperatures (Tc) and Pressures (Pc) for Various Compounds

Compound	Tc, (°C)	Pc, (Atm)
Methane	-82.1	45.8
Ethane	32.2	48.2
Butane	152	37.5
Hexane	234.2	29.9
Cyclohexane	280.4	40
Ethylene	9.9	50.5
Toluene	320.8	41.6
Chloroform	143.4	65.9
Methanol	240	78.5
Carbon dioxide	31.0	72.9
Water	374.1	218.3

In the literature most of the work on supercritical fluid fractionations (or separations) has been done by using carbon dioxide, water or ethylene. In some cases hexane, toluene and higher parafins have also been employed as the fluid solvents. The principal applications of this technique have been in areas such as food processing (6), coal and oil technology (7), separation of organic chemicals and waste treatment. Very recently there have also been some studies on the fractionation of various polymers (2) and oligomers which we will discuss in detail in the next paper of this issue.

In general the unique features of supercritical fluids that favor their use in various applications may be summarized as follows:

> Sensitivity to Both Temperature and Pressure: Small changes of temperature and/or pressure, especially in the region near the critical point of the solvent can affect the solubility by two or three orders of magnitude.
>
> High Mass-Transfer Rates Between Phases: A supercritical fluid phase has a low viscosity similar to that of gases but it also has a high liquid like diffusivity which consequently provides higher mass transfer rates than those observed in liquid extractions.
>
> Ease of Solvent Removal and Regeneration: After the extraction, when the pressure of the system is reduced the solute precipitates and supercritical fluid can then be easily removed or recycled.
>
> Environmental Considerations: Carbon dioxide and water, the most widely used fluid solvents are non-toxic, non-flammable and non-polluting. Moreover, supercritical fluid extractions are reported to be less expensive than other conventional methods, due to the savings in energy needed for operations.

Operation of a Supercritical Extraction Process

As it was stated before, the dissolving power of a supercritical fluid is strongly pressure dependent. Therefore, in principle, it is possible to design processes to extract, fractionate or purify materials based on changes in pressure at various points during the process. The material which is extracted at high pressures can be precipitated out simply by reducing the pressure and the solvent (fluid) can then be recompressed and recycled to the extractor. Figure 2 gives a simplified flow diagram of such a process. A detailed explanation of the naphthalene-carbon dioxide supercritical fluid extraction process is given in Reference (2) for a better understanding of the basic principles and operation of such systems.

Application of Supercritical Fluids to the Fractionation of Oligomers and Polymers

Synthetic polymers are well-known to usually show a broad molecular weight distribution. In addition, the presence of unreacted monomers and/or low molecular weight oligomers influence the overall physical and perhaps toxicological behavior of these materials very dramatically. In many cases effective removal of these species from the system is fairly difficult. Another important problem in polymer chemistry and engineering is the fractionation of a specific polymer into its corresponding low molecular weight components. Since vapor pressures of these species are too low for effective distillation, the techniques used in polymer purification and fractionation are generally based on solution (solvent/ nonsolvent) behavior of the respective components (8,9). However, most of these processes are extremely time consuming and also difficult. Pressure dependent dissolving power properties of supercritical fluids may provide the capability to effectively remove the low molecular weight species from these systems and/or achieve narrow cuts that cannot be matched by other fractionation or synthetic techniques (10). Preliminary studies on various simple or functionally terminated silicones, halocarbon oils, perfluoropolyethers, polycarbosilanes, etc. (2) have shown the effectiveness of the

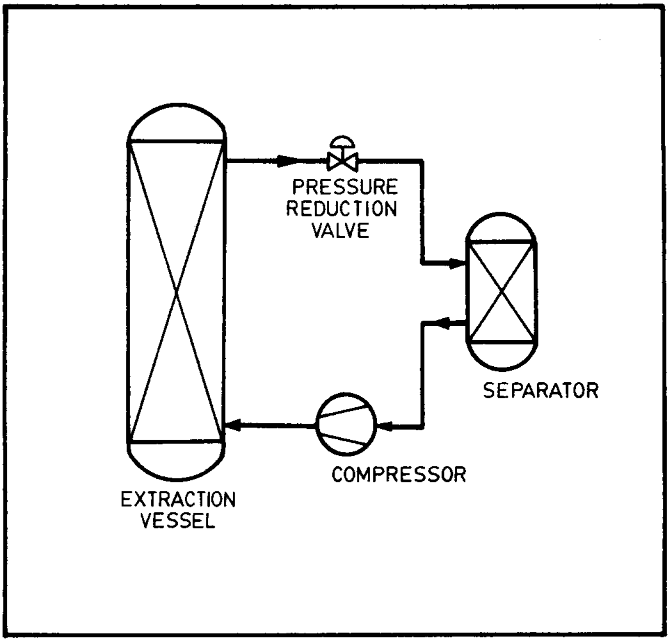

Figure 2. Supercritical Fluid Extraction Process

supercritical fluids on the fractionation or purification of these polymeric materials.

Fractionation of polymers is carried out by the subject technique in a multiple pressure reduction system which is an extension of the operation described in Figure 2. A schematic diagram of a continuous system employed in the fractionation of a polymer is shown in Figure 3. The number of vessels can be varied depending on the system and the number of fractions desired. In practice, first the polymer and then the supercritical fluid are pumped into the contactor. The density of the extractant is usually lower than that of the polymer. After complete solution of polymer in the fluid is obtained, the pressure is reduced. This causes the highest molecular weight fraction to precipitate. Then the stream leaves the primary contactor and is subjected to another

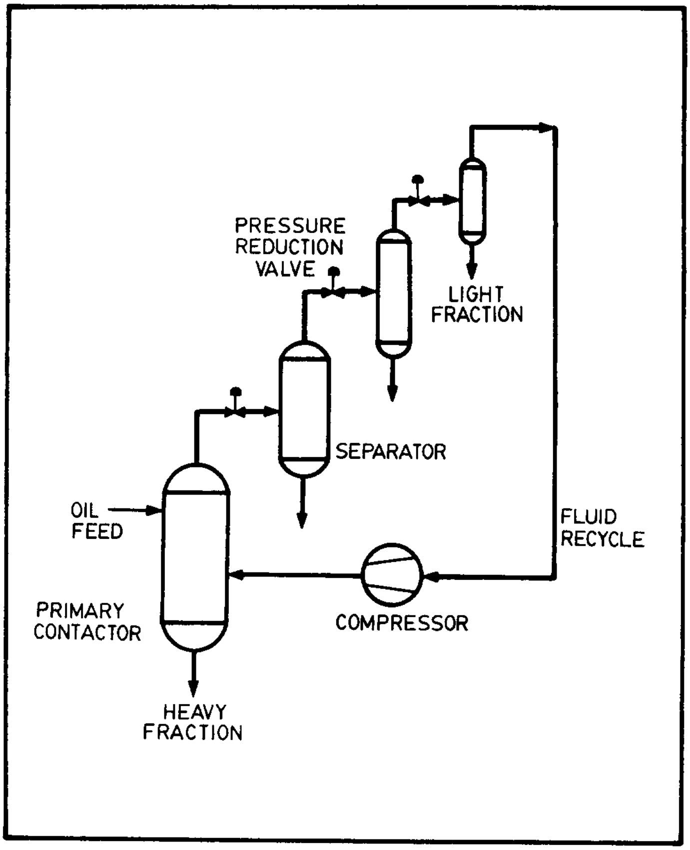

Figure 3. Flow Diagram of a Continuous Supercritical Fluid Fractionation Process.

pressure reduction (expansion) in the next vessel. The number of fractions obtained is consistent with the number of pressure reduction stages and the molecular weight distribution of each fraction is related to the pressure reduction per stage.

Figure 4 shows the GPC chromatograms of a polycarbosilane, fractionated by supercritical carbon dioxide. Efficiency of the method can easily be seen when we compare the GPC trace of the parent system with those of the fractions. Similar behaviors have also been observed in other systems (2). In the next paper of this issue we will discuss our results on the fractionation of reactive functionally terminated polydimethylsiloxane oligomers of molecular weights 2000-6000 using supercritical carbon dioxide.

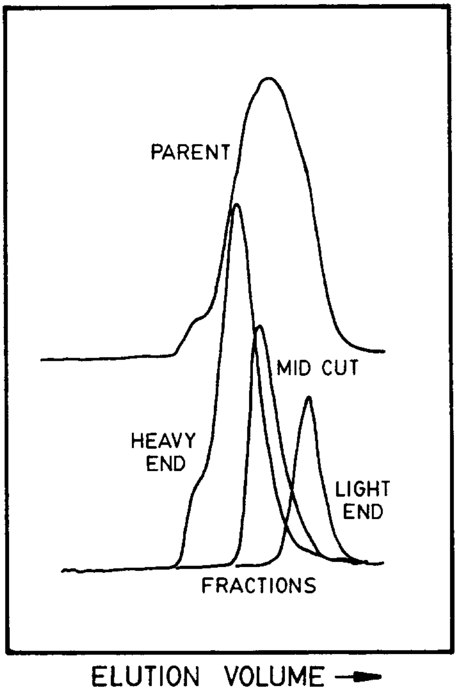

Figure 4. GPC Chromatograms of a Polycarbosilane Polymer and Its Fractions as Obtained by Supercritical Carbon Dioxide Fractionation.

Summary and Conclusions

Preliminary studies have indicated that polymers and oligomers can advantageously be fractionated with supercritical fluid solvents. This should be particularly useful for materials whose properties can be enhanced by fractionation, but which degrade when processed by high vacuum or molecular distillation. The process seems to be very effective for the fractionation of oligomers and for the removal of low molecular weight species from polymers. In addition to fractionation, another important application of supercritical fluid solvents may be their possible use as the reaction solvent in the polymerization reactions, especially when a thermodynamically good conventional solvent is not available for the polymers produced.

The importance of supercritical fluids on various aspects of polymer science will, of course, only be determined by future studies. Availability of various fluid solvents (Table I) and unique features of this novel process seem to be the most important factors on the possible future applications of this technique in the field of polymer chemistry and engineering.

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Accepted October 30, 1984