

Supercritical Fluid Processing of Polymers

In Situ Spectroscopy Of CO₂-Induced Plasticization Of Glassy Polymers

We have applied *in situ* FTIR, ATR-IR and photoacoustic spectroscopy to identify for the first time specific molecular interactions between CO₂ and polymers that may be responsible for the plasticization of glassy polymers. The changes in IR spectra of CO₂ incorporated into various polymers indicate a specific interaction between CO₂ and polymer functional groups. Increased polymer segmental mobility has also been observed, indicative of the plasticization phenomenon.

Supercritical fluids, mainly supercritical CO₂, have been widely applied in the chemistry and processing of polymers. Elevated pressure CO₂ is known to swell and plasticize glassy polymers. The increase in the polymer interchain distance upon plasticization by CO₂ is accompanied by the enhanced mobility of polymer segments, similar to the plasticizing effect by ordinary solvents. One of the differences between common liquid plasticizers and CO₂ is that CO₂ is easily removable from the processed polymers, and thus may be used for “solvent-free” incorporation of additives. It is possible to change the degree of plasticization and swelling of such a polymer, and consequently its free-volume, merely by changing the density of the CO₂.

A polymer film is placed into a high-pressure optical cell for *in situ* spectroscopic measurements. Then the cell is pressurized with high-pressure or supercritical CO₂, and the spectrum through the polymer and surrounding high-pressure gas is measured. The amount of carbon dioxide absorbed into the polymers may be quite large, thus making the studies of relatively thick (0.1 mm–1 mm) polymer films difficult due to the high optical absorbance of sorbed CO₂. Also, the presence of CO₂ surrounding the film strongly interferes. There are ways to avoid or overcome these difficulties. First, the spectrum of the polymer films can be measured after processing with CO₂, thus yielding the information on the state of trapped CO₂ molecules or any changes in the spectrum of the polymer itself.

An alternate approach is to use a [dual-windowed high-pressure cell](#) that allows one to measure the spectrum of the surrounding gas at the same conditions. The spectra of the gas or fluid phase can be subtracted from the spectra measured through both the polymer and the gas/fluid phases under identical high pressure conditions to yield the information on the absorbed gas within the polymer. Spectra are measured through each path separately simply by moving the cell within the spectrometer compartment.

In situ ATR (attenuated total reflectance)-IR spectroscopy has been applied for the first time to measure the spectrum of a polymer film subjected to high-pressure gas or

supercritical fluid (11). The results demonstrate a great potential of this spectroscopic technique in the studies of polymers subjected to high-pressure gases.

Some of our spectral results are:

- The bending mode of CO₂ incorporated into glassy polymers has been studied. A splitting of the band corresponding to this mode was observed, indicative of a specific interaction between CO₂ and basic functional groups in glassy polymers, such as carbonyl groups. This interaction appears to be a Lewis acid-base type, where the carbon atom of CO₂ acts as an electron acceptor, although the contribution of electrostatic forces cannot be excluded. This assignment is consistent with *ab initio* calculations and liquid solution studies.
- Our observation of increased segmental mobility in PMMA subjected to CO₂ also provides molecular-level evidence for suggestions by Sanders et al., and by Handa et al. on the mechanism of CO₂-induced plasticization of PMMA.
- A small splitting of the bending mode of CO₂ was observed for fluorine-containing polymers, providing evidence for the weak CO₂-fluorine interactions proposed by Shah et al. Such splitting was not observed for polymers without basic functional groups, such as poly(ethylene).
- Spectral changes in polymers (such as PMMA) subjected to high-pressure CO₂ indicated an increased segmental mobility of the ester groups in PMMA, because the changes were observed on the bands associated with the coupled vibration of the ester group. These spectral changes mimic the changes in PMMA induced by heating close to the glass transition temperature of the polymer.
- An *in situ* spectroscopic approach can be used to study supercritical fluid impregnation, diffusion, drying, dyeing and extraction of polymeric materials (see below).

Partitioning of Solutes And Cosolvents Between Supercritical Fluids And Polymer Matrices

Many polymeric matrices can uptake significant amounts of supercritical solvents, which can lead to beneficial changes in the polymer. For example, glassy polymers can be plasticized at relatively low temperatures, and free volume in rubbery polymers increases considerably. Both thermodynamic properties and mass transport processes can be “tuned” for selectivity by changing the processing pressure or temperature. We present partitioning and diffusion results for PMMA and crosslinked PDMS taken by a novel *in situ* spectroscopic method. The applications of this research range from low temperature dyeing of glassy polymers to tuning of chromatographic stationary phases with cosolvents for specific separations.

Supercritical fluids (SCFs) have been widely used in the synthesis and processing of polymers. Supercritical CO₂ is known to reduce the T_g for many glassy polymers. Furthermore, it is possible to change the degree of swelling simply by changing the

system pressure, and the polymer free volume can easily be “tuned”. Thus it is feasible that CO₂ dissolved in a glassy polymer could significantly influence mass transfer properties of solutes in the polymer matrix. Indeed, researchers have exploited this increase in solute mass transfer rate in polymeric matrices for supercritical fluid extraction and to a lesser extent supercritical fluid impregnation processes.

Supercritical dyeing of polymeric matrices is a particular case of impregnation with several potentially encouraging applications. The replacement of aqueous dyeing solvents with a benign supercritical fluid solvent can reduce waste streams in the textile industries significantly. Further, after the supercritical fluid dyeing process is complete, there is virtually no residual CO₂ in the polymer. Volatile components, such as residual monomer or organic solvents used in the polymer production process, are effectively removed with supercritical CO₂. Thus after the process the polymeric matrix is very clean. There has been significant effort to commercialize SCF PET dyeing in other countries due to these environmental advantages. While there has been interest in exploiting supercritical fluids as a dyeing solvent, most researchers have concentrated on the solubility of the dyes in the fluid phase. Very little research has concentrated on partitioning of dyes between the polymeric phase and the fluid phase.

Another application is related to supercritical fluid chromatography (SFC). Distribution or partitioning of a solute between scCO₂ and a polymer as a stationary phase occurs in supercritical fluid chromatography (SFC). The addition of small quantities of cosolvent to the scCO₂ mobile phase in SCF usually improves the applicability of SFC for more polar analytes. However, absorption of cosolvent in the polymeric stationary phase will significantly influence the retention of a solute and thus will affect thermodynamic properties measured by SFC.

In situ spectroscopy under supercritical conditions allows one not only to measure the partitioning of a solute or cosolvent between the supercritical fluid phase and the polymer phase, but also can also reveal specific intermolecular interactions. The objective of this work was to identify and quantify the interactions between solutes and cosolvents dissolved in scCO₂ and a polymer phase using *in situ* FT-IR and UV/vis spectroscopy.

Partitioning of azo-dyes between scCO₂ and PMMA.

The use of CO₂ to incorporate dyes into polymers has potential not only in the textile industry but also in the production of advanced polymeric materials for nonlinear optical (NLO) applications. Fortunately some azo-dyes, such as 4-(diethylamino)-4'-nitroazobenzene (DENAB) or Disperse Red 1 (DR1) are applicable to both: color for dyeing processes as well as an NLO effect when the molecules oriented within the polymer matrix via poling.

Unfortunately, such polar dyes have rather low solubilities in scCO₂(the solubility of DR1 is 10⁻⁶ M at 400°C and 90 bar). However, a [PMMA film placed into a vessel containing scCO₂ and Disperse Red 1 for a period of one day changes color to a dark](#)

[red](#). This observation shows that in spite of low solubility, scCO_2 can well be used as a transport medium, because the partition coefficient of DR1 between the CO_2 -swollen PMMA phase and scCO_2 is high.

In situ spectroscopy was applied to measure the spectra of both phases, and the partition coefficient of Disperse Red 1 between PMMA and scCO_2 approaches 10^4 under the conditions specified above. This large partition coefficient allows impregnation of about 0.5 weight% of dye into PMMA. We compared the partition coefficient for DR1 with that of another azo-dye, DENAB, which differs from DR1 only by having a hydrogen atom instead of a hydroxyl group. Although this dye has a somewhat higher solubility in scCO_2 (10^{-5} M), its concentration in an impregnated PMMA film was approximately the same as that of DR1 at the same conditions. Specific interactions such as H-bonding between DR1 and PMMA may play less of a role in the partitioning of this dye. These results show that supercritical fluid dyeing can be effective due to the high partition coefficients even if the solubility of a dye in the fluid is quite low. Other investigators have focused on studying the solubility of dyes in supercritical fluids; we show that a high affinity of the dye for the polymer environment relative to the fluid may be a key to supercritical fluid dyeing of glassy polymers.

Partitioning of cosolvents and solutes between PDMS film and scCO_2 .

The use of a cosolvent in SFC is a common technique in studying polar solutes because the solvent power of scCO_2 alone is often not sufficient. However, the use of a cosolvent may affect the stationary phase. These effects are:

- (i) the adsorption (or partitioning) of cosolvents into a stationary phase may alter the chemical nature of the stationary phase thus affecting the retention of a solute under such conditions;
- (ii) the presence of cosolvents may change swelling of the stationary phase as compared to pure scCO_2 .

We have combined our spectroscopic approach of measuring concentrations in PDMS films and cosolvent modified scCO_2 phases with measurement of swelling of PDMS films subjected to modified scCO_2 . We measured the partitioning of deuterated methanol, isopropanol and acetone between PDMS and scCO_2 . The partition coefficient for isopropanol between polymer and fluid phases decreased by over an order of magnitude as the pressure increases from 50 to 175 bar. This trend is similar to the behavior of toluene partitioning between scCO_2 and PDMS measured by inverse supercritical fluid chromatography. We have also applied *in situ* spectroscopy to measure the partitioning of solutes (acridine and 2-naphthol) between cosolvent modified scCO_2 and a PDMS phase.

Modeling the Effects of Supercritical Fluids on Polymers with a Lattice Fluid Equation of State

The Sanchez-Lacombe lattice fluid equation of state, modified to account for a crosslinked polymer, has been used to model both phases for a polymer-supercritical fluid-cosolvent system. This method represents well over a wide pressure range both volumetric and phase equilibrium properties for a crosslinked poly(dimethyl siloxane) phase in contact with CO₂ modified by a number of cosolvents. A single adjustable binary interaction parameter, obtained from swelling data of the polymer, is used to correlate both polymer dilation and solvent sorption.

The goal of this work is to model volumetric properties and the composition of the stationary phase in supercritical fluid chromatography, both to understand better how the stationary phase affects chromatographic separation, and also to determine thermophysical properties more accurately. In particular, the cosolvent effects of acetone and methanol on a non-functionalized crosslinked PDMS phase over a large pressure range have been studied.

This treatment could easily be extended to calculate partition coefficients of solid solutes between a swollen polymer phase and cosolvent modified supercritical fluid phase, but no experimental data are currently available. Condo *et al.* used this equation of state to calculate partition coefficients of several solutes between a polymer phase and a pure fluid phase. Since the partition coefficient is directly related to chromatographic retention and this partition coefficient is a function of pressure, the model could be a valuable tool to develop specific methods for chromatographic separations.

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