

Strategies for Supercritical CO₂ Fractionation of Polydimethylsiloxane

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SYNOPSIS

The fractionation of polydimethylsiloxane (PDMS) using supercritical CO₂ was studied to determine the parameters of pressure and temperature required to separate specific molecular weights. On a laboratory scale, we show that this fractionation method can quickly provide gram quantities of the polymer with a polydispersity of around 1.2 for molecular weights in excess of 200 kg/mol. This technique has obvious applications in the preparation of PDMS for surface-related uses. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polydimethylsiloxane (PDMS), shown in Figure 1, is an important member of the family of silicones that have a diverse range of applications in adhesives,¹ antifoaming agents,^{1,2} insulator coatings,¹ and other surface-related uses.¹ The desirable properties of PDMS that account for its usefulness are attributed to its low surface tension ($\gamma_{T=20^\circ\text{C}} = 20.9$ mN/m),^{3,4} high flexibility ($T_g \sim -123^\circ\text{C}$),⁵ and high affinity for a variety of solid substrates. In fundamental studies of polymer adsorption^{6,7} and wetting,^{8,9} PDMS is often used as a model system for the same reasons that it is effective in applications.

Commercial PDMS, however, has a polydispersity (M_w/M_n) on the order of 2 or greater and, in addition, the commercial samples commonly contain a significant fraction of low molecular weight cyclic oligomers.^{9,10} These lighter components are not even included in the calculation of the polydispersity.

The low molecular weight fractions can have an adverse effect on the application properties of the material. For example, the increased mobility of the lighter fractions may lead to those components dominating the wetting behavior on a surface in contact with the PDMS. Indications of this effect may be seen in the wetting of colloid spheres by PDMS elastomers.¹¹ In another example, the anti-foaming properties of PDMS depend on its insol-

bility in the bulk liquid.² If the lower molecular weight components are soluble, foaming would be enhanced, rather than suppressed. On a more fundamental level, the interpretation of the experimental results of PDMS adsorption requires the use of a well-defined and narrow polymer molecular weight distribution.

The ability for supercritical fluids to efficiently fractionate polymers by molecular weight has been known for some time^{4,12-19} and the fractionation of PDMS by supercritical CO₂ extraction was first reported by Krukoni nearly a decade ago.¹²⁻¹⁵ He pointed out that narrow fractions with molecular weights over 100 kg/mol could be isolated from a parent fraction with a broad distribution.¹²⁻¹⁵ In addition, end-functionalized PDMS, used for the fabrication of silicone elastomers and fundamental studies of end effects in polymer adsorption, has also been fractionated with CO₂.⁴

Here, we extend the existing reports of PDMS fractionation¹²⁻¹⁵ with a detailed extraction procedure for PDMS that is intended to guide others interested in using the CO₂ fractionation method. Our own motivation for this study was the recovery of gram quantities of the fractionated material with molecular weights higher than 50 kg/mol to be used for polymer adsorption studies.

EXPERIMENTAL

For amorphous polymers, supercritical fluid fractionation can be carried out by holding the pressure

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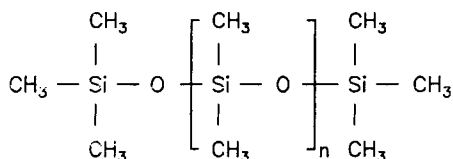


Figure 1 Chemical structure of PDMS. We used samples with trimethylsiloxy terminations.

constant and collecting fractions as the temperature of the extraction vessel is increased or decreased (depending on whether or not the liquid/liquid phase separation is of the lower or upper critical solution temperature type [LCST and UCST]). Alternatively, for systems that demonstrate LCST behavior, one can hold the temperature constant and collect fractions of increasing molecular weight as the pressure is increased in a stepwise fashion; this is the procedure that we have adopted.

The extraction setup is shown in Figure 2. Filtered, bone-dry CO_2 was introduced into a two-stage compressor (Fluitron, Ivyland, PA) that elevated the CO_2 pressure to the desired value. The pressure was coarsely set by adjusting the inlet pressure of an air compressor used to drive the two-stage pump and finely adjusted with a 10,000 psi (694 bar) back-

pressure regulator (Tescom, Elk River, MN). With the back-pressure regulator, the set pressure remained stable for several hours to within 3.5 bar. Without the back-pressure regulator, the pressure had to be monitored constantly; we could keep the set pressure within ± 13 bar. A 0.1 L surge tank (Fluitron) was used to reduce the pressure fluctuations that arose due to the pump. Next, the tubing leading from the surge tank to the extraction column was wrapped with heating tape to preheat the CO_2 to the extraction temperature. The extraction vessel was a 0.250 M long, 0.032 L, 316 stainless-steel reactor (High Pressure Equipment, Erie, PA) that was heated with silicone heating tape wrapped around the outside and temperature controlled by PID feedback from a thermocouple (Omega Engineering, Stamford, CT) centered inside the column, close to the middle of the column length. The temperature of the extraction vessel and preheating line was kept within 2°C of the set value. To support the sample, a 316 s.s. gauze was inserted in the column and the PDMS, which was a viscous liquid, was poured or spread across the gauze to ensure a large surface area of the sample for the extraction. From the extraction vessel, the fluid flowed through a heated precision valve (High Pressure Equipment) and

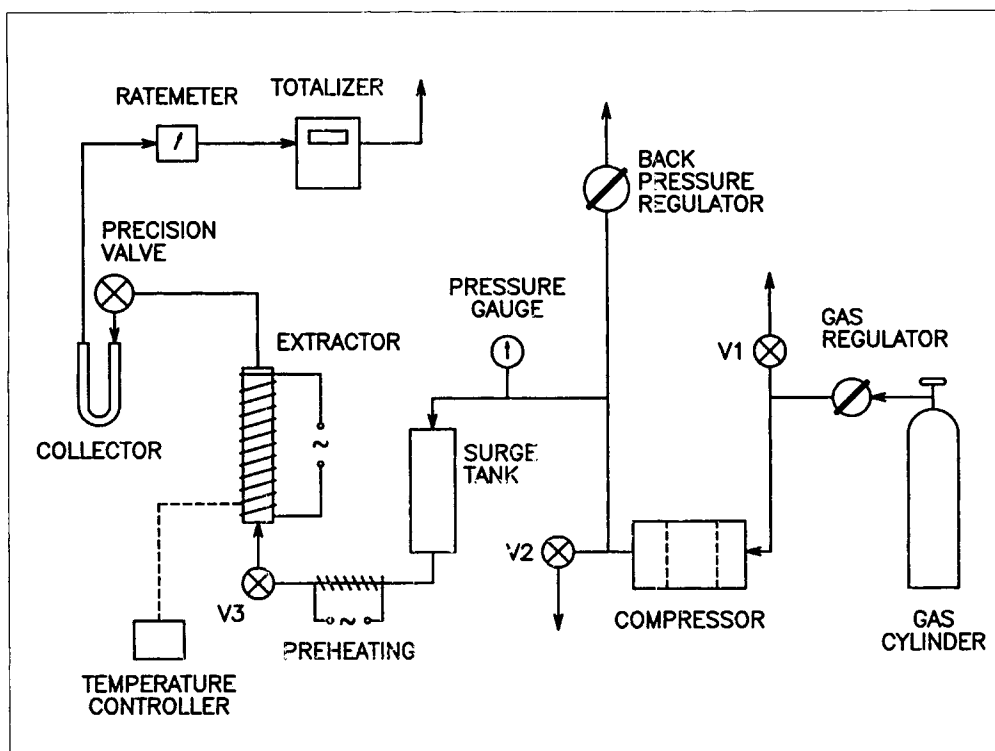


Figure 2 Schematic of supercritical fluid extraction apparatus.

Table I Extraction Data for Higher Molecular Weight Fractions of PDMS at 70°C; The GPC Data Are Shown in Figure 3

Fraction	Yield (g)	% Yield	M_w (kg/mol)	M_w/M_n	P (bar)	V_{CO_2} (Std. L)
Parent	5.2	100	122.50	2.00		
2	1.53	29.4	83.56	1.18	360	1716
3	1.30	25.0	140.61	1.13	380	2640
4	0.80	15.4	237.50	1.20	415	924

sprayed into a Pyrex u-tube. The rate and volume of CO₂ used was measured by a flowmeter and an integrating totalizer, respectively (Brooks Instruments, Hatfield, PA). Typical flow rates were 2 standard L of CO₂ per min.

Gel permeation chromatography (GPC) was used to determine the molecular weight distributions of the parent and fractionated samples. Toluene was used as the solvent and the molecular weights were calibrated using polystyrene standards. The PDMS samples were purchased from Scientific Polymer Products (Ontario, NY) and were listed as secondary standards.

Below, we present data for fractionations starting with material in which the weight-average molecular weight of the parent was 122 kg/mol. The reported M_w/M_n value for the parent sample was 2.00.[†] At 70°C, a detailed fractionation was performed, where we kept track of the volume of CO₂ used to extract each fraction. In extraction procedures at other temperatures, from 60 to 90°C, the polymer was extracted at a given pressure until the elution rate of the polymer coming from the column was noticeably reduced. The selection of the temperature range was

[†] Only the main peak at high molecular weight (shorter retention times) was used in calculating the reported polydispersity.

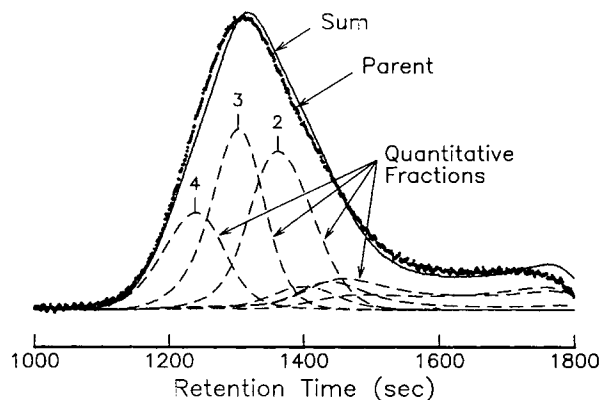
Table II Selected Extraction Data for PDMS Fractionations at Temperatures from 60 to 90°C; Values in Parentheses Are the Polydispersities, and These Data Are Plotted in Figure 4

T (°C)	$M_n(M_w/M_n)$ (kg/mol)			
	P (bar)			
	417	438	458	479
60	90.5 (1.33)	144.4 (1.24)	181.0 (1.22)	226.6 (1.26)
70	62.2 (1.65)	104.4 (1.34)	174.2 (1.26)	236.3 (1.25)
80	62.4 (1.61)	87.8 (1.39)	136.5 (1.35)	175.8 (1.25)
90	39.1 (1.6)	76.1 (1.52)	101.1 (1.53)	151.9 (1.39)

chosen so that we were neither too close to the liquid/vapor critical temperature for the CO₂ (31°C) nor so high that the higher molecular weights would be insoluble (LCST behavior). (Temperatures close to the liquid-vapor critical point were not desirable because the density of the CO₂ increases rapidly with pressure in the vicinity of T_{crit} . Since the solubility is determined by the solvent density, it was difficult to control an extraction procedure where the density was sensitive to small changes in pressure.)

RESULTS AND DISCUSSION

Tables I and II summarize the results from typical fractionations. One can see that gram quantities of material can be extracted from the parent fraction. The nominal dispersity is around 1.2 for the more narrow fractions. For our adsorption studies, this M_w/M_n value is entirely acceptable and represents a colossal improvement over the original parent material. The GPC traces for the fractions described in Table I are shown in Figure 3. The fractions were redissolved in the same amount of toluene and diluted identically for GPC analysis. One can see that the sum of the peaks is close to the parent trace,


Figure 3 Gel permeation chromatograms of the parent and fractionated PDMS samples removed at 70°C.

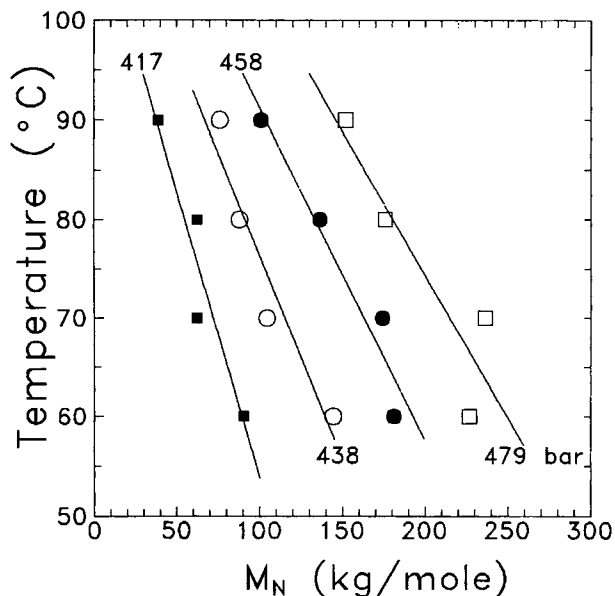


Figure 4 Extraction isobars: weight-average molecular weight of PDMS extracted at different temperatures and pressures. The nos. labeling each curve refer to the pressure (in bars) for the extraction.

indicating that extraction was quantitative. Note the significant amount of low molecular weight material (higher retention time) in the parent and its absence in the high molecular weight fractions.

In Figure 4, we plotted the fractionation data from Table II as the temperature vs. the M_n of PDMS extracted at different pressures. These extractions were made as before, with the temperature held constant and the fractions removed with increasing pressure. The plot represents an *ersatz* phase diagram; it is clear from the negative slope of the temperature vs. the extracted molecular weight that we have an LCST system in which the Flory χ parameter is determined mainly by the free-volume dissimilarity between the polymer and the solvent.²⁰ Thus, at constant pressure, as the temperature is increased and the solvent density decreases, the higher molecular weight polymer components will become insoluble. Roughly speaking, at a given pressure and temperature, a particular molecular weight of PDMS is soluble if it lies to the left of the isobaric extraction curves drawn in Figure 4.

In Figure 5, we followed the mass yield of PDMS

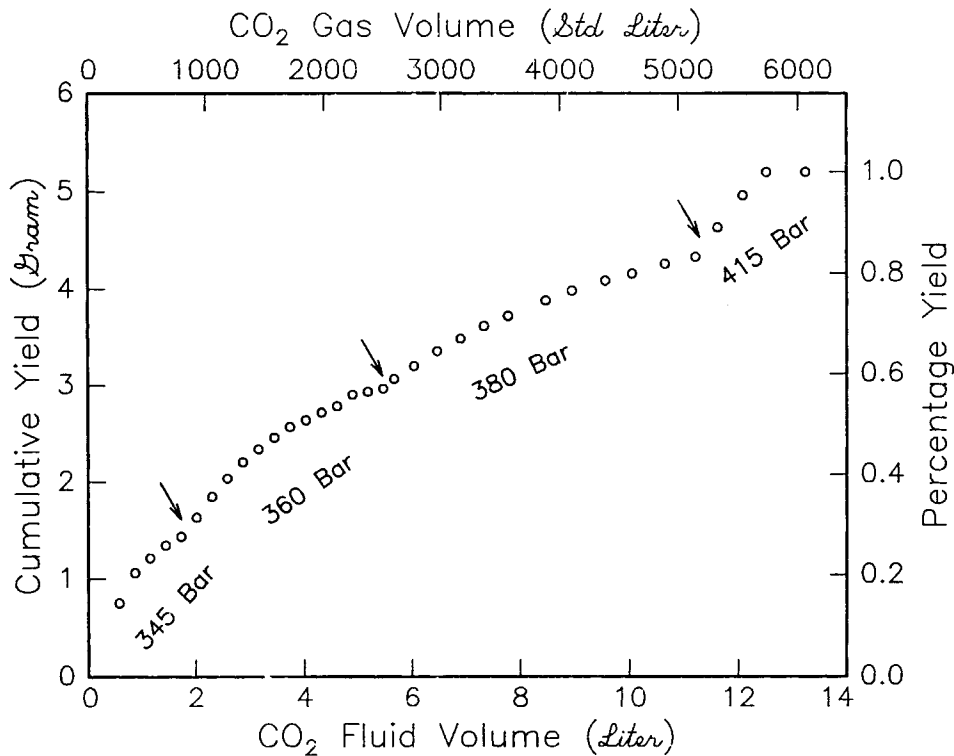


Figure 5 Percentage yield vs. volume CO_2 . The lower abscissa is the volume in standard liters and the upper abscissa is the volume of CO_2 calculated from the average density at 381 bar and 70°C .

as a function of the CO₂ extraction volume for a series of pressures. The arrows in the plot indicate the point at which the pressure was increased to the next value. We saw the tendency toward saturation as a greater volume of CO₂ was used to extract the polymer at each pressure. (One never sees a true saturation due to the limited, but finite, solubility of the higher molecular weights.) The volume of CO₂

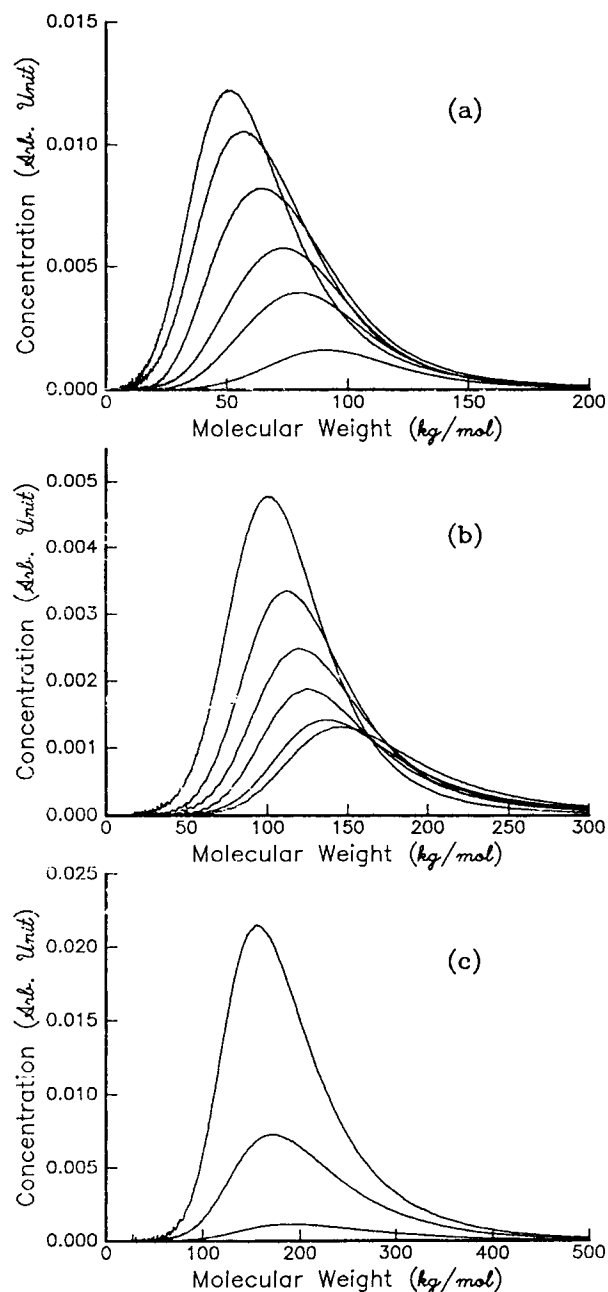


Figure 6 Gel permeation chromatograms for the PDMS fractions in Figure 5: (a) 360 bar; (b) 380 bar; (c) 415 bar. The peak heights are proportional to the yield.

is given in standard liters as well as the volume for CO₂ calculated at 70°C and a pressure of 381 bar,²¹ the pressure at the middle range of the extraction. The GPC traces for the data in Figure 5, scaled to the yield, are shown in Figure 6. As the extraction volume is increased, a steady increase in the molecular weight was observed, and during an extraction, one must of course sacrifice the narrowness of the distribution for yield.

We should comment on the solubility of PDMS in CO₂. The usual indicators for solubility suggest that PDMS should be insoluble in CO₂ at the temperatures and pressures that we used here. The index of refraction for PDMS is 1.43 (Ref. 22), and for CO₂ at the densities used for the extraction, the refractive index is around 1.25.[†] If *only* van der Waals forces existed between the PDMS segment and CO₂, then, based on the difference in refractive indices, one would predict that the two components would be immiscible.²⁴ Specific interactions must be present, and these are likely due to overlap between the oxygen lone-pair electrons on the CO₂ and the empty silicon *d*-orbitals in PDMS.¹⁰

SUMMARY

We have shown that the fractionation of PDMS by supercritical CO₂ is straightforward and relatively easy to implement. The fractions that we extracted are currently being used to study polymer adsorption from conventional solvents (toluene, 2-butanone). We are also in the process of measuring the cloud point curves for the fractions in supercritical CO₂ as a function of temperature and pressure and studying adsorption from supercritical CO₂. Our fractionation data give us an estimate of the range for the onset of liquid-liquid phase separation.

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