

# Production of narrow fractions of polymers using supercritical fluids with a density program

A.A. Clifford\*, K.D. Bartle, I. Gélébart and S. Zhu  
*School of Chemistry, University of Leeds, Leeds LS2 9JT, UK*  
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The supercritical fluid extraction of a low polymer using supercritical fluids with a linear density program is modelled. It shows that this density program gives an approximately constant polydispersity in the polymer being extracted at a particular time. Experiments are carried out on the supercritical extraction of polyisobutene and polydimethylsiloxane which show qualitative agreement with the predictions, both with respect to the shapes of the curves and also the effect of density ramp speed. © 1998 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

Narrow fractions of polymers are used as analytical standards for calibration in size-exclusion or gel permeation chromatography (g.p.c.). A wide range of polymer samples are available, typically with polydispersities of 1.05, for this purpose. The standard methods of fractionating polymers have been comprehensively reviewed in one of the Springer Lab. Manual series<sup>1</sup>. For example, polymers can be fractionated by extracting them with a liquid using a solvent gradient: initial extraction being a 'poor' solvent, which extracts the lowest molar masses, to which a 'better' solvent is added in higher and higher proportions to extract fractions of progressively higher molar mass. For some polymers of lower molar mass, this and other methods are not successful because of their high solubility and the polymer fractions are made by preparing directly polymers of low polydispersity. However, the fractions made in this way have higher polydispersity than is desirable and at the same time these samples are more expensive.

A possible solution is to extend the solubility range downwards by using supercritical fluid extraction (SFE). The use of SFE for polymer fractionation is now well known, and a comprehensive review of methods of general and large scale fractionation has been made<sup>2</sup>. Fractionation in supercritical fluids has been a feature of polymer production from the 1940s, and subsequent fractionation using a compressed gas was patented at that time<sup>3</sup>. Narrow fractions of polymers have also been made on a laboratory scale using conventional supercritical extraction equipment, for example fractions of polyethylene with polydispersities of 1.07–1.09 were made using CO<sub>2</sub> by a procedure of extraction in a series of increasing pressure steps<sup>4</sup>. The aim of the present study is to use density programming in SFE as an analogue of solvent programming in the present method described above. Density programming is a well-established technique in SFC<sup>5</sup>. These authors used a method for describing the behaviour of the solubility of oligomers, which is adopted here and is first used to model the SFE of

low polymers (typically liquids) using a linear density program.

## MODELLING OF POLYMER FRACTIONATION USING A SUPERCRITICAL FLUID

A number of assumptions were made to simplify the model used, as described below. These assumptions are not unrealistic, as is argued and do not affect the qualitative behaviour predicted. Firstly, the characteristic time for (a) diffusion out of the polymer films and (b) the residence time of the fluid in the extraction cell is assumed to be small enough that it has little effect on the polydispersity of the polymer being extracted at any time. This assumption can be made realistic in practice by choice of experimental conditions and, for example, supporting the polymer on sand so that the liquid film is thin. Secondly, the fluid substance does not dissolve in the polymer film and the concentrations of oligomers in the fluid are negligible. These second assumptions will be approximately true at lower pressures, but may have to be rethought at higher pressures. Thirdly, it is assumed that the polymer behaves as an ideal mixture of oligomers and that there is a relationship  $y_i/x_i = S_i$  between the mole fraction of the  $i$ th oligomer in the polymer,  $x_i$ , and that in the fluid,  $y_i$ , with  $S_i$  being a solubility, which is constant at constant pressure and temperature.

The polymer is considered to contain  $n_i$  mol of the  $i$ th oligomer with  $n$  mol in total with initial values of  $n_i^0$  and  $n^0$ ;  $r$  is defined as the ratio of moles of the supercritical fluid substance that has passed through the cell at a particular time,  $t$ , to the initial amount of polymer,  $n^0$ . The rate of removal of each oligomer will be equal to the flow rate times the mole fraction of the oligomer in the fluid, therefore

$$\frac{dn_i}{dt} = -n^0 \frac{dr}{dt} y_i = -n^0 \frac{dr}{dt} S_i x_i = -n^0 \frac{dr}{dt} S_i \frac{n_i}{n}, \quad (1)$$

and thus

$$d \ln n_i = \frac{n^0}{n} S_i dr. \quad (2)$$

\* To whom correspondence should be addressed

To introduce a density program,  $S_i$  is made a function of  $r$ . More typically in experimental work, a density program is described as a function of  $t$ , but the former method is chosen because it makes scaling-up more straightforward and because of the difficulty in controlling the flow rate in a process, whereas the amount of fluid that has passed through the system by a particular time is easily measured. The density programs used in supercritical fluid chromatography were designed to have the oligomer peaks equally spaced with respect to time, and for this an asymptotic density programme was developed<sup>5</sup>. In the case of polymer fractionation by SFE, the requirements may be different and a likely situation is that constant polydispersity is required. At constant polydispersity, a greater range of oligomers are present at higher average molar masses. Thus for constant polydispersity, successive peaks needs to emerge more rapidly as the process continues. This effect occurs in SFC with a linear density gradient and so a linear density program is used here.

The solubility behaviour used by Fjeldsted *et al.*<sup>5</sup>, which was successful for developing density programming for SFC, is an assumption that the solubility of oligomers is given by

$$S_i = b_1 \exp[-(b_2 - b_3\rho)i] \quad (3)$$

where  $b_i$  are constants for a particular polymer and fluid. If a linear density program of  $\rho = b_4 + b_5r$  is applied, where  $b_4$  and  $b_5$  are similar constants,  $S_i$  is given by

$$S_i = b_1 \exp[-(b_2 - b_3b_4 - b_3b_5r)i] = c_1 \exp[-c_2(1 - c_3r)i], \quad (4)$$

where the  $c_i$  are constants for a particular polymer, fluid and density programme. For the model used here, values of  $c_1 = 2$  and  $c_2 = 0.693$  are chosen and three different values of  $c_3$  are used, as described below. Thus at the beginning of the extraction, when  $r = 0$ ,  $S_i = 1/2^{i-1}$ , which assumes each oligomer has half the solubility of the previous oligomer. As the extraction proceeds and  $r$  increases, the ratio between the solubility of oligomers decreases until, when  $r = (1/c_3)$ , the solubility of all oligomers is the same.

Calculations are carried out numerically, using equation (2) and equation (4). Boundary conditions are required, i.e. values of  $n_i^0$  must be set in advance and this amounts to designing an artificial model low polymer. A fairly realistic model of a low polymer is used in which there are 100 oligomers with amounts according to a Gaussian distribution of  $n_i^0 = \exp[-(i - 50)^2/1250]$ , which gives a value for  $n^0$  of 60. For the initial calculation, a value for  $c_3 = 6 \times 10^{-4}$  used. The calculations are presented in Figure 1a in the form of plots of the mole fraction of oligomer  $i$  in the polymer being extracted (not including the fluid),  $z_i$ , as a function of  $r$ . Oligomers 10–15 are shown and then every 10th oligomer. As can be seen, the oligomers emerge successively and more and more rapidly, as occurs with a linear density program in SFC<sup>5</sup>.

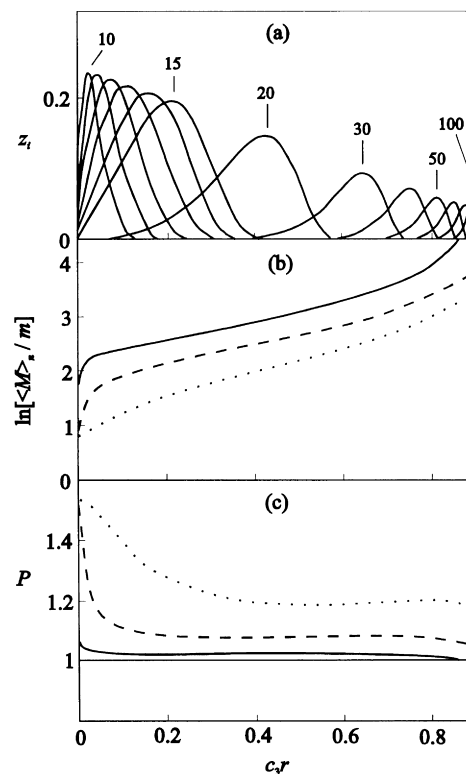
The number-averaged molar mass can be written, in terms of the present notation, as

$$\langle M \rangle_n = (1/n) \sum_i n_i i m, \quad (5)$$

where  $m$  is the mass of the monomer unit and the polydispersity as

$$P = n \sum_i n_i i^2 / (\sum_i n_i i)^2. \quad (6)$$

These parameters can therefore also be calculated as a function of  $r$  from the earlier results, and are shown as the



**Figure 1** Calculations of the SFE of a model low polymer containing 100 oligomers with the number of moles of the  $i$ th oligomer,  $n_i^0 = \exp[-(i - 50)^2/1250]$ , and with a density programme linear with  $r$ , the ratio of the amount of fluid passed to the initial amount of polymer. The results are plotted versus  $c_3 r$ , where  $c_3$  is proportional to the rate of density increase with  $r$ . (a)  $z_i$ , the mole fraction of the  $i$ th oligomer being extracted, for  $c_3 = 6 \times 10^{-4}$ ; (b) the number-averaged molar mass,  $\langle M \rangle_n$  divided by that of the monomer unit,  $m$ ; and (c) the polydispersity,  $P$ . In (b) and (c):  $c_3 = 6 \times 10^{-4}$  (solid lines);  $c_3 = 6 \times 10^{-3}$  (dashed lines); and  $c_3 = 6 \times 10^{-2}$  (dotted lines)

solid lines in Figure 1b,c. The solid line in Figure 1b shows the natural logarithm of the average molar mass, which can be seen to be roughly linear, with a slight 'S' shape visible at the ends, where little material is being extracted. The solid line in Figure 1c shows the polydispersity, which is approximately constant over most of the range, although it peaks slightly in the middle and falls at both ends. Calculations are also carried out for the same model polymer, but with more rapid density programmes in which  $c_1$  and  $c_2$  have the same values as before, but in which  $c_3 = 6 \times 10^{-3}$  and  $c_3 = 6 \times 10^{-2}$ . More rapid density programmes are seen to give similar shaped curves, but with a lower molar mass curve and a higher polydispersity.

#### COLLECTION OVER AN EXTENDED PERIOD

Previously, only the results of instantaneous collection have been discussed, but to recover polymer in a process it must be collected over a finite period, corresponding to a finite increase,  $\Delta r$ , in the parameter  $r$ . This will increase the polydispersity of the polymer obtained. An approximate calculation of this effect can be made in each case by assuming that during the collection period the average quantity  $\langle M \rangle_n / m$  is varying linearly with  $r$  and also that the values of  $n_i^0$  are approximately equal for all the oligomers being appreciably extracted in this period.

Suppose the polymer is collected from  $r - 1/2\Delta r$  to  $r + 1/2\Delta r$ , and that mean values of quantities collected over the period are represented by  $\langle \dots \rangle_{\Delta r}$ . Because of the

assumptions, the mean number average molar mass  $\langle\langle M \rangle_n\rangle_{\Delta r}$  is equal to the value of  $\langle M \rangle_n$  at  $r$ . The mean square of number average molar mass  $\langle\langle M \rangle_n^2\rangle_{\Delta r}$  can be calculated by integration to be related to previously known quantities by

$$\langle\langle M \rangle_n^2\rangle_{\Delta r} - (\langle\langle M \rangle_n\rangle_{\Delta r})^2 = (1/12)(d\langle M \rangle_n/dr)^2(\Delta r)^2. \quad (7)$$

Both sides of equation (7) are equal to an additional variance in the mean squared molar mass that has been introduced as a result of collection over a time period. As a result an additional term must be added to the polydispersity, i.e.

$$\langle P \rangle_{\Delta r} = P + (1/12)[(d\langle M \rangle_n/dr)(\Delta r)/\langle M \rangle_n]^2. \quad (8)$$

The quantity in the square brackets in equation (8) is the fractional increase in the average molar mass during the collection period. Thus the additional polydispersity due to the finite collection period can be easily calculated. For example, if  $\langle M \rangle_n$  increases by 25% over the collection period, the polydispersity of the material collected in this period will be increased by 0.005 over the polydispersity of the instantaneously collected material. The design of the process or experiment can therefore ensure that the effect on the polydispersity is acceptable in different cases. In the experiments described below, the effect of the finite collection periods is less than the experimental uncertainty in the measured polydispersity.

## EXPERIMENTAL

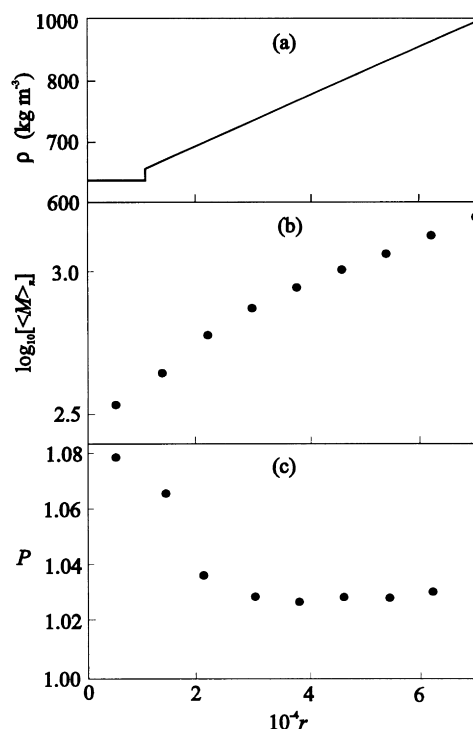
The SFE experiments were carried out using a 'Spe-ed' SFE (Applied Separations, Allentown, PA, USA). This apparatus satisfied the requirements of the study, which were manual and separate control of pressure and flow rate and a pressure rating up to 680 bar. A weighed amount of the polymer was thoroughly mixed with fine sand with a loading of 2.5% (w/w). The polymers used were polyisobutene, supplied as 'Hyvis 10' (BP, Grangemouth, UK), and polydimethylsiloxane supplied as silicone oil (Hopkins and Williams, Chadwell Heath, UK). A 3.5 ml extraction cell was used. All experiments were conducted with carbon dioxide as the fluid, which was SFC/SFE grade with helium overpressure (Air Products, Crewe, UK). As a result, extraction could not be carried out below 130 bar. The extracts were collected in high-purity reagent-grade tetrahydrofuran (THF) (Fisher Scientific, Loughborough, UK) and the collection vial was exchanged after a predetermined time interval, thus producing a series of fractions. For each density programme, a table was prepared of pressure *versus* time at 1 min intervals using a recently published equation of state for carbon dioxide<sup>6</sup>.

The weight-averaged molar mass and polydispersity of the fractions were determined by gel permeation chromatography (g.p.c.). The analytical system consisted of a Model 422 liquid pump (Kontron, Watford, UK), a 'Rheodyne' injection valve (Jones Chromatography, Hengoed, UK), a guard column and a 60 cm, 100 Å, 10 µm 'PLGEL' column (Polymer Labs, Shropshire, UK) and a mass detector (Varex, MD, USA). The solvent used was THF, supplied as above and the flow rate was 1 ml min<sup>-1</sup>. The method was calibrated using polystyrene standards (Polymer Labs, Shropshire, UK). Calibration with polystyrene is known to give errors when used to analyse other polymers. For example, number-averaged molar masses of polyisobutene, obtained using polystyrene can be 10% below their true value. However, this procedure is adequate for the present study, where comparisons between the fractions and also

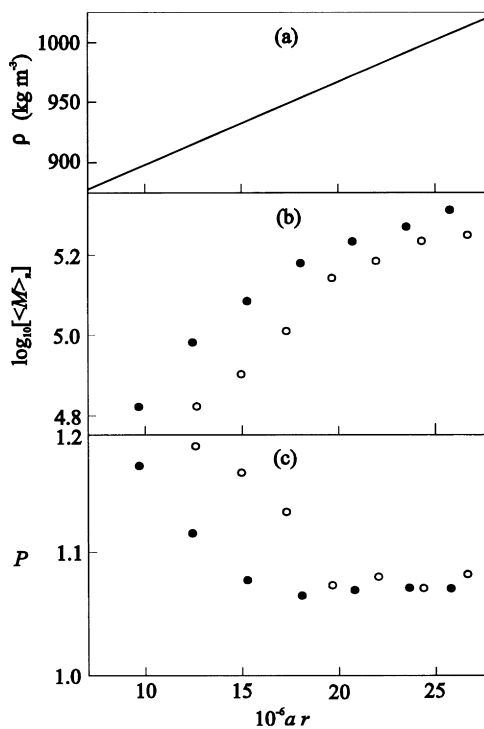
with the starting material are what is required and qualitative behaviour was being investigated.

## FRACTIONATION OF POLYISOBUTENE

Polyisobutene is not very soluble in carbon dioxide and only low oligomers can be extracted. However, this also means that high polydispersities can be obtained. The starting material was, in fact, a polymer of a mixture of butenes, predominantly isobutene. It had a number-averaged molar mass, measured by the procedures described above, of 1274 and a polydispersity of 1.54. A preliminary extraction was carried out at 50°C and 636 kg m<sup>-3</sup> (the minimum 130 bar) for 10 min to remove the tail at low molar masses and to produce the first fraction. Extraction was then carried out at 50°C with a linear density programme rising from 656 to 1011 kg m<sup>-3</sup> at a rate of 6.32 kg m<sup>-3</sup> min<sup>-1</sup>. The flow rate of carbon dioxide, calculated as liquid carbon dioxide at the pump, was 10 ml min<sup>-1</sup>. The density programme, as a function of  $r$ , is illustrated in *Figure 1a*. Eight further fractions were collected at equal density intervals of 45 kg m<sup>-3</sup>. Fifty-two percent by weight of the polymer was extracted. The number-averaged molar masses of the fractions were between 342 and 1528 and are plotted as logarithms in *Figure 2b* against  $r$ . The shape of the curve is similar to the first part of the curves in *Figure 1b*, bearing in mind that only half of the polymer was extracted. The polydispersity, shown in *Figure 2c*, falls and then rises slightly, as in the first part of the theoretical curves of *Figure 1c*. These results show agreement between experiment and prediction and also that, with the right density programme, low and approximately constant polydispersities can be obtained, except at the beginning.



**Figure 2** SFE of polyisobutene of number-averaged molar mass 1274 with carbon dioxide at 50°C. The results are plotted *versus*  $r$ , the ratio of the amount of fluid passed to the initial amount of polymer. (a) The density programme used, with  $\rho$  the density; (b) the number-averaged molar mass,  $\langle M \rangle_n$ ; and (c) the polydispersity,  $P$



**Figure 3** SFE of polydimethylsiloxane of number-averaged molar mass 127 682 with carbon dioxide at 40°C, using two density programmes; one twice as fast with respect to  $r$  as the other. The results are plotted versus  $ar$ , where  $r$  is the ratio of the amount of fluid passed to the initial amount of polymer and  $a = 1$  for the slower programme and  $a = 2$  for the faster programme. (a) The density programme used, with  $\rho$  the density; (b) the number-averaged molar mass,  $\langle M_n \rangle$ ; and (c) the polydispersity,  $P$ , with filled circles for the slower programme and open circles for the faster programme

#### FRACTIONATION OF POLYDIMETHYLSILOXANE

The purpose of these experiments was to demonstrate that the effect of density ramp speed on the molar mass and polydispersity agrees with the theoretical predictions of *Figure 1*. The large changes in the rate of rise of density, possible in calculations, are impracticable and a ratio of 2 was used. For this reason conditions were chosen so that the effect of ramp speed would be observable, which means that low polydispersities were not obtained in this experiment.

The starting material had a number-averaged molar mass, measured by the procedures described above of 127 682 and a polydispersity of 1.32. Both extractions described were carried out at 40°C and with a flow rate of carbon dioxide, calculated as liquid carbon dioxide at the pump, of 6.5 ml min<sup>-1</sup>. In each case a preliminary extraction was carried out at low densities to remove the tail at low molar masses, and were discarded. Two linear density programmes are reported, different in the rate of rise of density by a factor of 2, and are shown in *Figure 1a* plotted against  $ar$ , where  $a = 1$  for the slower program and  $a = 2$  for the faster program. For the lower speed ramp, shown in the filled circles in *Figure 3b,c*, seven fractions were collected at equal density intervals of 18 kg m<sup>-3</sup>. For the higher speed ramp, shown in the open circles in *Figure 3b,c*, seven fractions were collected at equal density intervals of 16 kg m<sup>-3</sup>. Eighty-six and 84% by weight of the polymer was extracted in the two experiments, respectively. The number-averaged molar masses of the fractions for both runs are plotted as logarithms in *Figure 3b* against  $r$ , and it can be seen that the filled circles for the lower speed ramp lie above those for the higher speed ramp, as predicted in *Figure 1b*. The polydispersities, shown in *Figure 3c*, have the filled circles for the lower speed ramp below those of the higher speed ramp, as predicted by *Figure 1c*. Thus the effect of ramp speed has the same qualitative effect on the experimental results as it does on the theoretical predictions.

#### ACKNOWLEDGEMENTS

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