Solubility of polyethylene in n-pentane at high pressures

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The high pressure solubility of polyethylene standards ($M_w = 2100$, 16400, 108000 and 420000 and $M_w/M_n = 1.14$, 1.16, 1.32 and 2.66, respectively) in n-pentane has been studied. Concentrations of up to 15 wt% polymer have been investigated. For each polymer sample and concentration, pressures that are required to achieve single-phase solutions have been determined over a range of temperatures. The solutions are found to all show lower critical solution temperatures. Demixing pressures are observed to depend strongly on the molecular weight of the polymer.

(Keywords: polyethylene; high pressure; solubility; *LCST*; n-pentane; supercritical)

INTRODUCTION

There is a growing interest in the experimental determination and theoretical prediction of the solubility of polymers in high pressure fluids, especially at near and supercritical conditions. In our previous studies, the solubility of monodisperse polystyrene standards ($M_w = 4000$ and 9000) was studied in near and supercritical n-butane, n-pentane and their binary mixtures[1-4]. More recently we have reported on the solubility of polyethylene (PE, $M_w = 121\,000$; $M_w/M_n = 4.3$) in binary mixtures of carbon dioxide with cyclohexane, toluene and n-pentane[5].

The present study is focused on the solubility of PE samples with known molecular weights and narrow molecular weight distributions (*MWD*s) in n-pentane.

Even though the solubility of PE has been extensively studied in ethylene[6-21], reports on its solubility in n-pentane are very limited[22-26]. One of the earliest observations of the solubility of PE in n-pentane was reported by Freeman and Rowlinson[22] in their now classic paper on the lower critical solution temperature (*LCST*) in polymer solutions. A sample of $M_w = \sim 10^6$ was found to swell but not dissolve in experiments that were carried out in sealed glass tubes. Pressures were not reported.

In a later study[23], the solubility of PE was investigated in a series of alkanes including n-pentane, n-hexane, n-heptane and n-octane as a function of the molecular weight of the sample. Dissolutions were achieved and the phase separation temperatures were determined at polymer volume fractions up to 0.1 for samples with $M_w = 4900$, 12500, 14300 and 22760. All the solutions were shown to display *LCST*s. The *LCST* was found to decrease with increasing molecular weight of the polymer sample. However, these experiments were also conducted in sealed glass tubes and pressures were not measured. Furthermore, the glass tubes were sealed in a nitrogen atmosphere, and thus the actual values of the *LCST*s reported do not strictly correspond to the pure n-pentane case. The values are most likely lower than those corresponding to solutions in pure n-pentane since the presence of nitrogen would have an effect similar to an increase in molecular weight. Two further studies on the solubility of PEs in alkanes have been reported using sealed glass tubes[24,25].

The only study in which some data on both the demixing pressures and temperatures are given is that by Ehrlich and Kurpen[26]. These authors used an optical high pressure cell to determine the solubility of PE in a series of alkanes including n-pentane. However, the data in n-pentane are reported only for a sample with $M_w = 246\,000$ at 5 wt% polymer concentration.

The present study has been conducted to expand the limited data base on the solubility of PE in n-pentane by covering a wide range of molecular weights (from 2100 to 420000) and polymer concentrations (up to 15 wt%). Data on well characterized model polymer–solvent systems are needed for improving our understanding of the factors that influence solubility in high pressure fluids.

EXPERIMENTAL

Materials

The PE molecular weight standards with narrow *MWD*s were obtained from Scientific Polymer Products (Ontario, New York, USA). They are linear PEs produced by the hydrogenation of polybutadienes. The molecular weights and polydispersities are given in *Table 1*. For each sample a crystalline melting temperature of

Table 1 Polyethylene molecular weight standards (hydrogenated polybutadienes)

Molecular weight (M_w)	Polydispersity (M_w/M_n)
2100	1.14
16400	1.16
108000	1.32
420000	2.66

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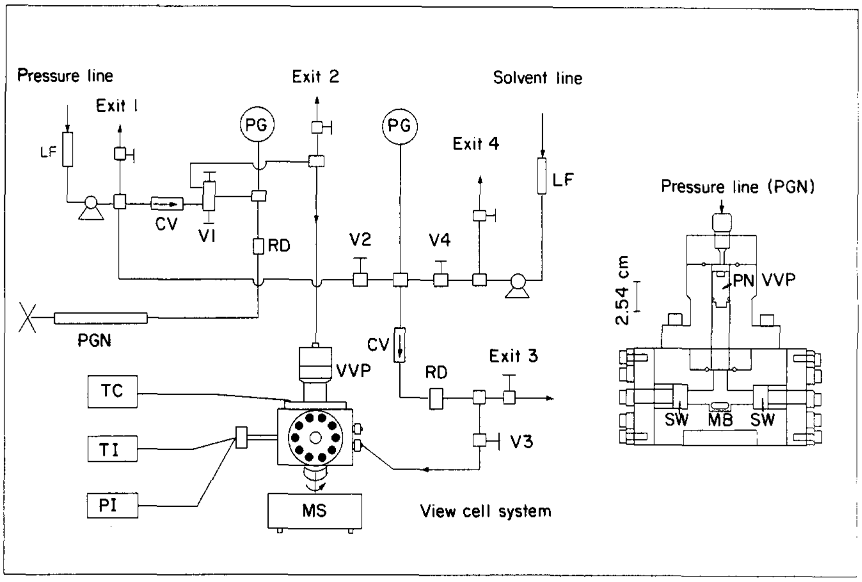

Figure 1 Experimental system: LF, line filter; CV, check valve; PG, pressure gauge; PGN, pressure generator; TC, temperature controller; TI, temperature indicator; PI, pressure indicator; VVP, variable volume part of the view cell; MS, magnetic stirrer; RD, rupture disc; PN, movable piston; SW, sapphire window; MB, magnetic stirrer bar

~380 K was determined by d.s.c. runs conducted at a heating rate of 5 K min^{-1}.

Pentane (>99% purity) was obtained from Aldrich (Milwaukee, WI, USA) and used without further purification.

Apparatus and operational procedure

A schematic diagram of the experimental system is shown in *Figure 1*. Details have been described in our previous publications[2,5]. Briefly, the system consists of a variable volume view cell which has two sapphire windows (for visual or optical observations of the cell content), a solvent delivery manifold and a pressure generation line. Pressure is measured to an accuracy of ±0.06 MPa using a Dynisco flush mount type transducer (model TPT 432A-20M) and read with a resolution of 0.007 MPa. The pressure readings are frequently checked against a calibrated Heise gauge (model CC-90037). Temperature is measured to an accuracy of ±1.5 K using a J-type thermocouple mounted to the Dynisco pressure transducer and read with a resolution of 0.1 K.

In a typical experiment, the cell is loaded with polymer and solvent (corresponding to a given concentration), and the temperature and pressure are adjusted to achieve homogeneous solutions. Pressures up to 70 MPa and temperatures up to 200°C are scanned. Once the cell is loaded, the pressure manipulations at a given temperature are accomplished through movement of the piston inside the variable volume attachment of the cell which is connected to the pressure generation line. After thermal equilibration, demixing pressures are determined by repeated cycling through the phase separation and dissolution point at each temperature.

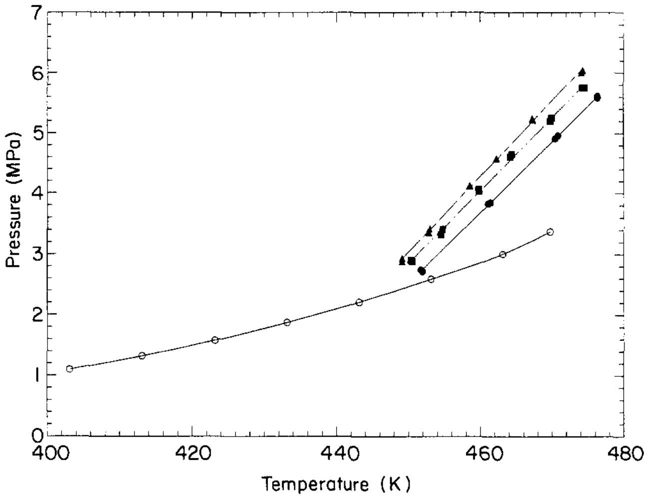

Figure 2 Demixing pressures for PE ($M_w = 2100$; $M_w/M_n = 1.14$) in n-pentane: (●) 3.0 wt% PE; (■) 5.0 wt% PE; (▲) 10.0% PE; (○) 100% pure n-pentane. The 100% pure n-pentane curve is the vapour pressure curve for n-pentane

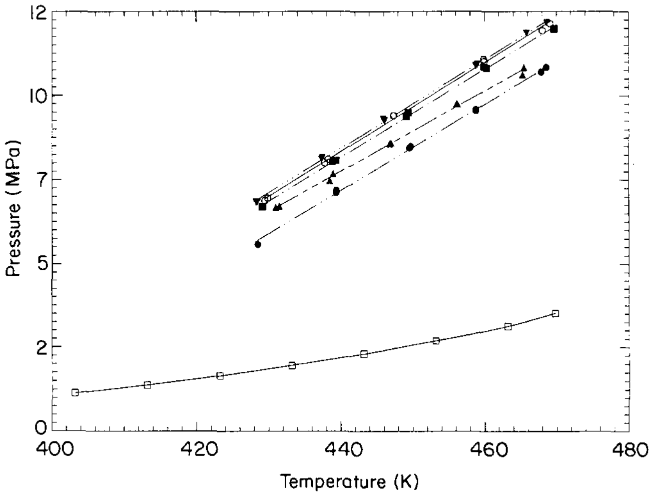

Figure 3 Demixing pressures for PE ($M_w = 16400$; $M_w/M_n = 1.16$) in n-pentane: (●) 1.0 wt% PE; (■) 3.0 wt% PE; (○) 5.0 wt% PE; (▼) 10.0 wt% PE; (▲) 15.0 wt% PE; (□) 100% pure n-pentane

RESULTS AND DISCUSSION

Demixing pressures are shown for each polymer sample in *Figures 2–5*. Polymer concentrations cover a range of 1–15 wt%. The pure n-pentane curve corresponds to a portion of the vapour pressure curve of n-pentane and

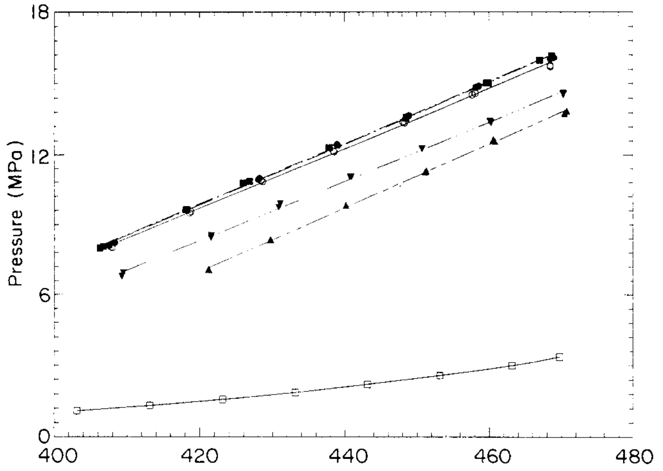

Figure 4 Demixing pressures for PE ($M_w = 108000$; $M_w/M_n = 1.32$) in n-pentane. Symbols as in *Figure 3*

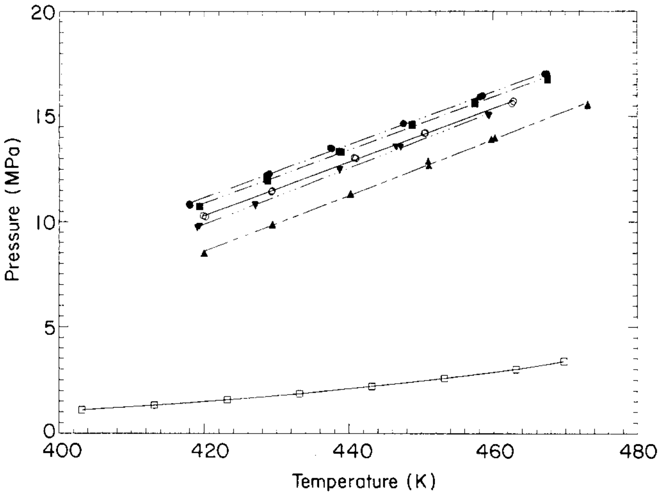

Figure 5 Demixing pressures for PE ($M_w = 420000$; $M_w/M_n = 2.66$) in n-pentane. Symbols as in *Figure 3*

terminates at the critical point (critical temperature, $T_c = 469.56$ K; critical pressure, $P_c = 3.36$ MPa) of n-pentane. The regions above each demixing curve are the single-phase regions for these polymer solutions. All the solutions show *LCST* behaviour. For all molecular weights and concentrations, $(\mathrm{d}P/\mathrm{d}T)_c$ is positive, and the two-phase regions are entered either by an increase in temperature at constant pressure or by a decrease in pressure at constant temperature.

The intersection of the demixing curves with the vapour pressure curve of n-pentane would represent the lower critical end points (*LCEPs*) which are easily visualized for the low molecular weight sample ($M_w = 2100$) shown in *Figure 2*.

As can be seen from *Figures 2–5*, in the concentration range of 1–15 wt%, demixing pressures for these solutions are not very sensitive to polymer concentrations, and vary by only ~2 MPa. They are, however, strongly influenced by temperature and molecular weight.

Figure 6 is a comparison of the demixing pressures for different molecular weight samples at 10 wt% polymer concentration. It is shown that at a given temperature higher pressures are required to dissolve the higher molecular weight samples. *Figure 6* also illustrates that at a given pressure, two-phase regions are entered at lower temperatures with increasing molecular weight of the sample. That the *LCST* moves to lower temperatures with increasing molecular weight of the polymer sample has also been noted in an earlier study[23].

The vapour pressure curve for n-pentane has also been included in *Figure 6*. It is noted that the intersections of the demixing curves with the vapour pressure curve of n-pentane are shifted to progressively lower temperatures with increasing molecular weight of the polymer. Such a shift is also observed when the solvent T_c is lowered by adding a second component with a lower T_c, such as carbon dioxide, to pentane[5,27]. The influence of molecular weight and composition of solvent on the *LCEP* has been described for other polymer–solvent systems in the literature[28,29].

Figures 7–10 show pressure–composition (*P–X*) and temperature–composition (*T–X*) diagrams which have been generated by taking constant temperature and constant pressure cuts from *Figures 2–5*.

The *P–X* diagram shown in *Figure 7* corresponds to a temperature of 460 K. In this figure, even though not presented in *Figures 2–5*, data obtained at concentrations

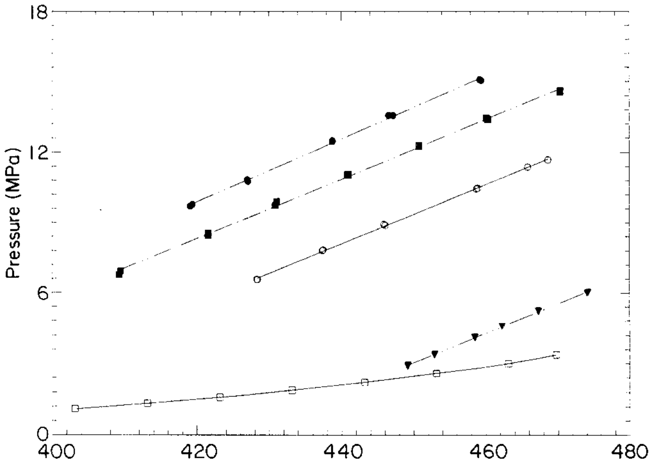

Figure 6 Effect of molecular weight on the demixing pressures for 10 wt% PE solutions in n-pentane: (●) $M_w = 420000$; (■) $M_w = 108000$; (○) $M_w = 16400$; (▼) $M_w = 2100$; (□) 100% pure n-pentane

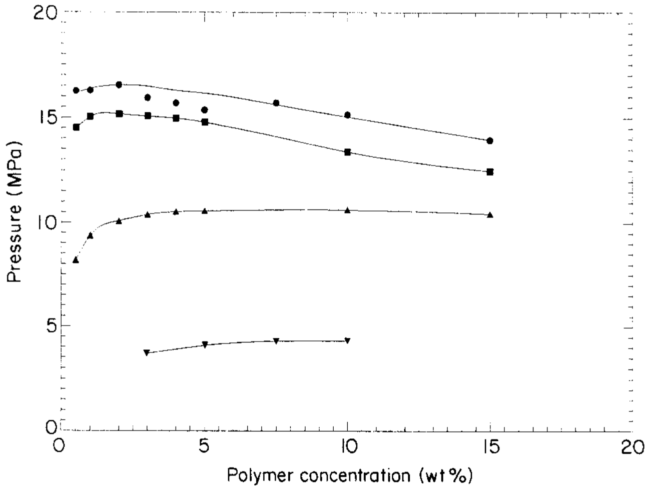

Figure 7 Variation of demixing pressures of PE solutions with polymer concentration and molecular weight at 460 K in n-pentane: (▼) $M_w = 2100$; (▲) $M_w = 16400$; (■) $M_w = 108000$; (●) $M_w = 420000$

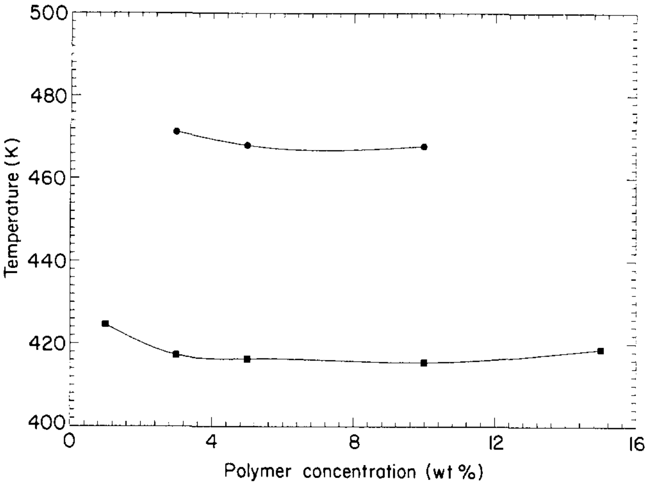

Figure 8 Variation of demixing temperatures of PE solutions with polymer concentration and molecular weight at 5 MPa in n-pentane: (●) $M_w = 2100$; (■) $M_w = 16400$

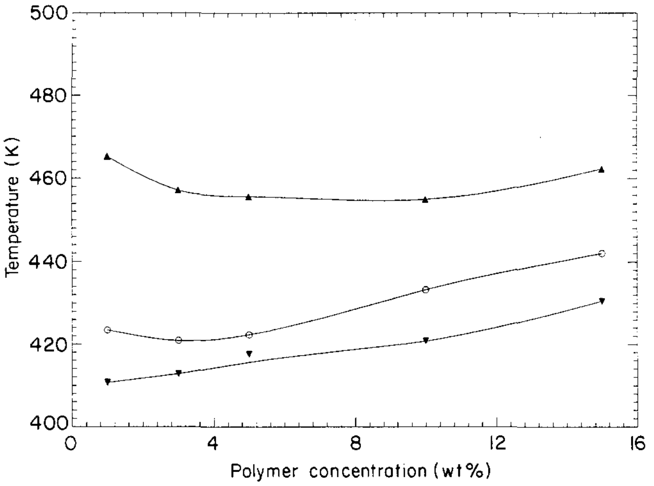

Figure 9 Variation of demixing temperatures of PE solutions with polymer concentration and molecular weight at 10 MPa in n-pentane: (▲) $M_w = 16400$; (○) $M_w = 108000$; (▼) $M_w = 420000$

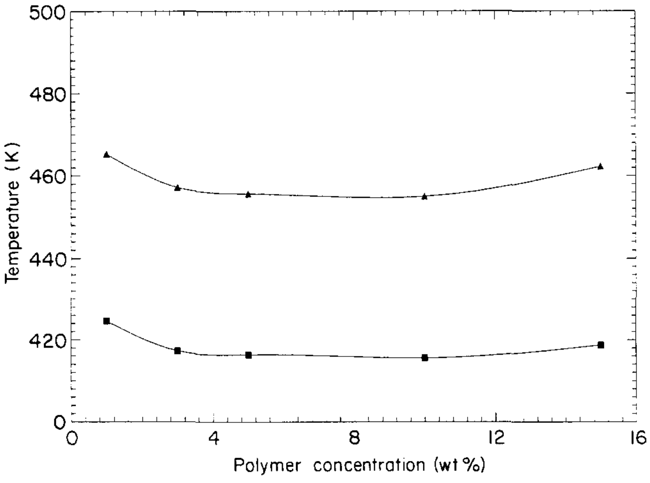

Figure 10 Dependence of demixing temperatures of PE ($M_w = 16400$; $M_w/M_n = 1.16$) solutions on polymer concentration and pressure in n-pentane: (■) 5 MPa; (▲) 10 MPa

<1 wt% have also been included. The figure shows the relatively flat nature of the demixing pressures, and also indicates that the critical polymer concentrations may be ~1 wt%. The molecular weight dependence of dissolution or demixing pressures is clearly illustrated for all concentrations studied. The regions above each curve correspond to the single-phase regions. The curves represent the upper critical solution pressures.

The *T–X* diagram shown in *Figure 8* corresponds to a pressure of 5 MPa for polymer samples with $M_w = 2100$ and 16400. *Figure 9* corresponds to a pressure of 10 MPa for samples with $M_w = 16400$, 108000 and 420000. In contrast to the *P–X* diagrams, in these figures, the regions below each curve are the single-phase regions. Comparisons of samples with $M_w = 2100$ and 16400 at 5 MPa and $M_w = 16400$, 108000 and 420000 at 10 MPa illustrate well the shift in *LCST*s to lower temperature with increasing molecular weight at a given pressure. *Figure 10* is a comparison of the *LCST* curves for the sample with $M_w = 16400$ at 5 and 10 MPa, and shows the shift in *LCST*s to higher temperatures with increasing pressure.

LCST is often explained in terms of an unfavourable entropy effect which in non-polar polymer–solvent systems arises from the difference in free volume of the solvent and the free volume of the polymer. At a given pressure, when the temperature is increased, the solvent molecules undergo an expansion towards a larger free volume state, but find themselves confined within the more rigid polymer matrix. As the T_c is approached, the difference between the free volume of the polymer and the solvent that would otherwise be achievable becomes sufficiently large, leading to a decreased entropy of mixing and consequently phase separation. The difference in free volume is expected to become larger when the molecular weight becomes higher, thus causing the phase separation to take place at even lower temperatures. When pressure is increased, the free volume of the solvent decreases much faster than that of the polymer, thus the difference in the free volume of the polymer and the solvent decreases and phase separation does not occur until high enough temperatures (much closer to the T_c of the solvent) to cause sufficient difference in free volume are approached. *Figures 8–10* illustrate these points extremely well. At 10 MPa, increasing the molecular weight from 16400 to 420000 causes the *LCST* to decrease from ~460 to 415 K. For the sample with $M_w = 16400$, increasing the pressure from 5 to 10 MPa shifts the *LCST* from ~420 to 460 K.

CONCLUSIONS

Solutions of PE standards of molecular weights in the range 2100–420000 in n-pentane are shown to display *LCST* behaviour. In the concentration range from 1 to 15 wt% polymer, the demixing pressures do not show high sensitivity to polymer concentration. The demixing pressures increase with polymer molecular weight. At a given molecular weight, the *LCST*s shift to higher temperatures with increasing pressure. At a given pressure, the *LCST*s shift to lower temperatures with increasing molecular weight.

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