

HIGH PRESSURE POLYMER CRYSTALLIZATION IN SUPERCRITICAL OR DENSE FLUIDS

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Crystallization of polymers in dense fluids offers new pathways for polymer separation and purification, polymer modification, or formation of microstructures with unique morphologies. The rate of approach to solid-fluid boundary, degree of undercooling that is imposed, the pressure and the fluid media from which crystallization is carried out influence the outcome and can be used as tuning parameters. Crystallization from fluid mixtures, especially those mixtures containing carbon dioxide as a component offers additional flexibilities in terms of the fluid composition which influences the solvent quality and the location of the phase boundaries.

In this presentation, we describe recent results on the crystallization of polyethylene in n-pentane and n-pentane + carbon dioxide fluid mixtures over a temperature range from 370 to 390 K at pressures from about 20 to 60 MPa. The crystals were formed at selected temperatures below the fluid-solid phase boundary by reducing the temperature while holding the pressure constant along selected constant pressure paths in a variable volume cell. Differential scanning calorimetry results show that the polyethylene crystals formed from these high pressure solutions display multiple (three) melting transitions observed at around 395, 399 and 403 K. Degree of crystallinity was observed to be higher by about 7 to 11 % compared to the original polyethylene samples.

INTRODUCTION

Several studies have already been reported on the phase behavior of polyethylene and other polyolefins in n-alkanes and n-alkane + carbon dioxide fluid mixtures [1-2]. Majority of these studies have been on the liquid-liquid (L-L) phase transition. The L-L phase transition of polyolefins in these fluids displays lower critical solution (LCST)-type behavior. In the presence of carbon dioxide the phase boundary shifts to higher pressures and the character of system gradually transforms to an upper critical solution (UCST) - type behavior. Even though limited in scope, several studies have also been carried out on the fluid-solid (F-S) phase transition in polymer solutions in pressurized or supercritical fluids [2,3,4]. These studies show that the fluid-solid phase boundary is usually confined to a narrow temperature range.

The influence of pressure on the morphology of polyethylene crystals has been of special interest. Studies have been reported at pressures up to about 800 MPa. [5-7]. These studies show that the polyethylene crystals that are formed under pressure, either from melt or from common organic solvents, may display different morphologies and / or display multiple melting transitions. These have been attributed to either the

rearrangement of metastable crystal structures or to the recrystallization of the folded chain crystals during the DSC heating scan.

In this paper, we present the results of crystallization of polyethylene from both n-pentane and from the fluid mixture of CO₂ + n-pentane along constant pressure paths in the range from 22 to 52 MPa by lowering the temperature to conditions below the fluid-solid phase boundary while adjusting the pressure during the process.

MATERIALS AND METHODS

The measurements were performed using previously characterized polyethylene samples with $M_w = 121,000$, $PDI = 4.3$. A variable-volume view cell equipped with optical sensors was used for determining (a) the miscibility and phase separation conditions (from changes in the transmitted light intensity), and (b) the mixture densities (from knowing the initial mass loading and the actual cell volume determined at a given temperature and pressure with the aid of an LVDT sensor that monitors the position of a movable piston inside the cell). The view cell was also used to carry out the crystallization of the polymer from its solutions at high pressures. The details of the systems and operational procedures have been previously published [1,2]. A computerized data acquisition system was used to record the temperature, pressure and transmitted light intensity (I_{tr}) during a given experiment as a function of time.

In crystallization experiments, the temperature was lowered at a rate of 0.02 K/min at constant pressure to a target crystallization temperature T_c (typically 363K) below the solid-fluid phase boundary. While the temperature decreased the pressure in the view cell was continuously adjusted (by moving a movable piston inside the cell) to compensate for volume changes that take place during cooling. The system was then maintained at the crystallization temperature T_c for a certain duration (typically 60 min) for crystallization to further proceed. Then the view cell was depressurized and cooled down to ambient temperature, and the polymer crystals were collected for further characterization by DSC and electron microscopy.

The polyethylene crystals were characterized with a DSC (Perkin Elmer DSC 7) at ambient pressures under a nitrogen atmosphere with a scanning rate of 10K/ min both for heating and cooling. For each sample three consecutive scans were carried out. The first scan included heating to a temperature higher than the melting transitions and then cooling to room temperature, which was then followed by a second scan with identical heating and cooling rates to the same temperatures. This was followed by a third heating scan. There was no holding time after each heating or cooling scan.

RESULTS AND DISCUSSION

Phase Boundaries. Figure 1 shows the phase boundaries for the 5 wt % PE solutions in n-pentane and in 85 % n-pentane + 15 % carbon dioxide mixture. The fluid-solid boundary (F-S) was determined by lowering the temperature starting from 52.1, 44.5, 40.8, 38.5, 37, 33.3, 29.5 and 22MPa in the one-phase homogeneous conditions. Each data point at a given pressure corresponds to a new loading of the cell with 5 wt % polyethylene in n-pentane. The liquid-liquid phase boundary (L-L), which is determined by lowering the pressure at selected temperatures from homogenous conditions shows a positive slope (typical of LCST behavior), with increasing demixing pressures from about 6 to 15 MPa

over the experimental temperature range. The fluid-solid boundaries in solutions of polyethylene in carbon dioxide + n-pentane mixture were determined in a similar way by lowering the temperature from homogeneous conditions at 52.1, 44.5, 40.8, 38.5, 37.0 and 33.3 MPa. In this system of polyethylene + carbon dioxide + pentane, the liquid-liquid phase boundary was observed to be shifted by more than 17 MPa to higher demixing pressures compared with the liquid-liquid phase boundary of the polyethylene -pentane system. Whereas the fluid-solid phase boundary showed only a very small shift to higher demixing temperatures compared to the boundary in n-pentane.

Density. The density data were generated along the constant pressure paths from the one-phase to the two-phase region during all fluid-solid phase boundary determination experiments. Densities were in the range about 0.56 to 0.64 g/cm³ for these solutions. No major changes in the density were noted while crossing the phase boundaries.

DSC Transitions. Figure 2 shows the DSC scan for polyethylene, crystallized from a n-pentane solution at 38.5 MPa and 363 K for 60 min. The first scan shows the behavior of the polyethylene crystals as collected from the view cell, which displays multiple melting transitions. At 394.8 K we can see a small shoulder followed by two additional endothermic peaks at 399.0 and 401.8 K. The sample was immediately cooled back when temperature reached 410 K at the end of the first scan. During cooling, a single exothermic crystallization peak is observed at 387.0 K. In the second heating scan which is carried out immediately after cooling to 303 K, the DSC result shows only one broad melting peak at around 403.5 K. The sample was cooled and heated again. The DSC output during the second cooling and third heating scans were identical to the first cooling and second heating scans. DSC scans were conducted for all samples in a similar way.

Figure 3 compares the first heating scans of crystals formed at 363 K over 60 min at the pressures indicated. The scan for the initial polyethylene sample is also included for comparison. These polyethylene crystals formed in n-pentane all show a shoulder peak plus two additional better resolved melting peaks. The first DSC heating scans of polyethylene samples crystallized from a 15 wt % CO₂ + 85 wt % n-pentane solution at 363 K for 60 min display similar general features.

As indicated earlier, previous studies in polyethylene crystallization under pressure from melt have also been reported to show multiple melting transitions [5-7]. In those studies, these melting peaks were attributed to the presence of folded chain (FCC) and extended chain (ECC) crystals, the extended chain crystals being promoted at high pressures. The multiplicity of melting peaks that are observed in the present study may stem from the existence of either (a) crystals with distinct size range, (b) crystals with different crystalline morphology as in FCC vs. ECC, or may be due to the presence of a mixture with non-equilibrium transient structures that undergo rearrangements during heating in the DSC. In the present study, the formation of different size crystals is a distinct possibility. At a given undercooling level during crystallization from these solutions it is possible that a fraction, i.e., the lower molecular weight fractions of the polymer, remain in the dissolved state while the higher molecular weight chains undergo the fluid-solid transition and thus crystallization. The chains that remain in the solution are then forced to phase separate and rapidly crystallize in the second stage during depressurization of the cell. This could lead to formation of small crystals with lower

melting temperatures. Additional studies that we conducted on the effect of undercooling suggest that the appearances of distinct melting peaks are promoted for a ΔT range of about 12 – 13 K. For deeper quenches of 15 – 16 K or shallow quenches of 8 K or smaller, the melting transition appears broad. These observations support the notion of the system's ability to produce crystals from higher and lower molecular weight fraction in a distinct way. The broadening of the DSC peak for crystals formed very close to the demixing temperature may be interpreted as implying that in this case, the majority of the polymer actually undergoes the crystallization process in the depressurization stage. It should be noted that as demonstrated in Figure 2 the melting temperature observed in the second DSC scan is higher than the melting temperatures observed in the first scan. With increasing undercooling or decreasing crystallization temperature the difference in the DSC melting transition between the first scan (intermediate peak value) and second scan were observed to increase from about 1.8 K at 377.6 K which is very close to the incipient demixing temperature (solid-fluid phase boundary in the solution) to 4.5 K at a crystallization temperature of 363 K. The crystallization carried out with higher degree of undercooling results in polyethylene crystals that have lower melting temperatures, suggesting smaller crystals.

Degree of Crystallinity. The degree of crystallinity was calculated by comparing the area A which represents the heat of fusion $\Delta h(T)$ under the melting peak to a reference value of the heat of fusion $\Delta h^*(T)$ corresponding to a completely crystalline sample [8]. The results show that the average degree of crystallinity for all samples determined from the second DSC scan is about 65.1. The degree of crystallinity of the original polyethylene was about 64.3 %. This leads to the assumption that the thermal history of the samples is completely erased after the first heating scans. Figure 4a shows the result of analysis of the DSC data. The samples crystallized from n-pentane display about 9 percentage units higher crystallinity irrespective of the crystallization pressure. For polyethylene crystallized from a 15 wt % CO_2 + 85 wt % n-pentane solution, the increase in the degree of crystallinity was found to be in the range from 7 to 11 percentage units. Additional evaluations were carried out on the effect of undercooling. It was observed that polyethylene crystals formed at 377 K in pentane show nearly 15 percentage units greater crystallinity compared to the original polyethylene, whereas the samples crystallized at 363 K show a 9 percentage units increase. The degree of crystallinity for samples crystallized from n-pentane at 38.5 MPa for different crystallization time show that the crystallinity increase is about 8 units for 30 min, and about 10 units at 120 min crystallization time. The morphological features of these crystals are being further investigated. Figure 4b is a representative micrograph of crystals formed at 38.4 MPa.

CONCLUSIONS

Polyethylene samples crystallized from pentane or pentane + carbon dioxide fluid mixtures at high pressures show multiple melting peaks in the DSC scans, with degree of crystallinities that are observed to be higher by about 7 to 11 percentage units compared to the original polyethylene sample. The degree of crystallinity is affected most by the degree of undercooling during crystallization.

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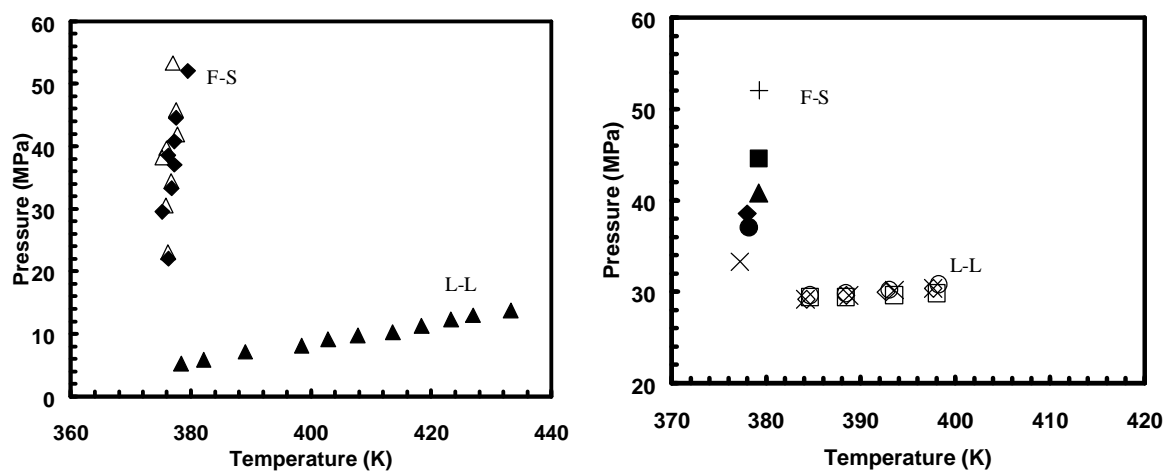


Figure 1. Fluid-solid (F-S) and liquid-liquid (L-L) phase boundaries in solutions of 5 wt % polyethylene in n-pentane (left), and in 85 % n-pentane + 15 % carbon dioxide (right)

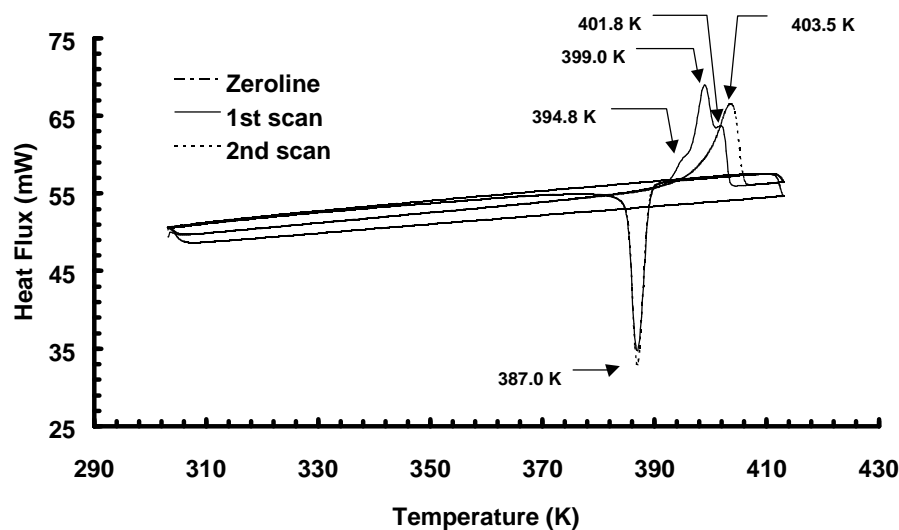


Figure 2. DSC scans of polyethylene crystals formed at 363 K and 38.5 MPa

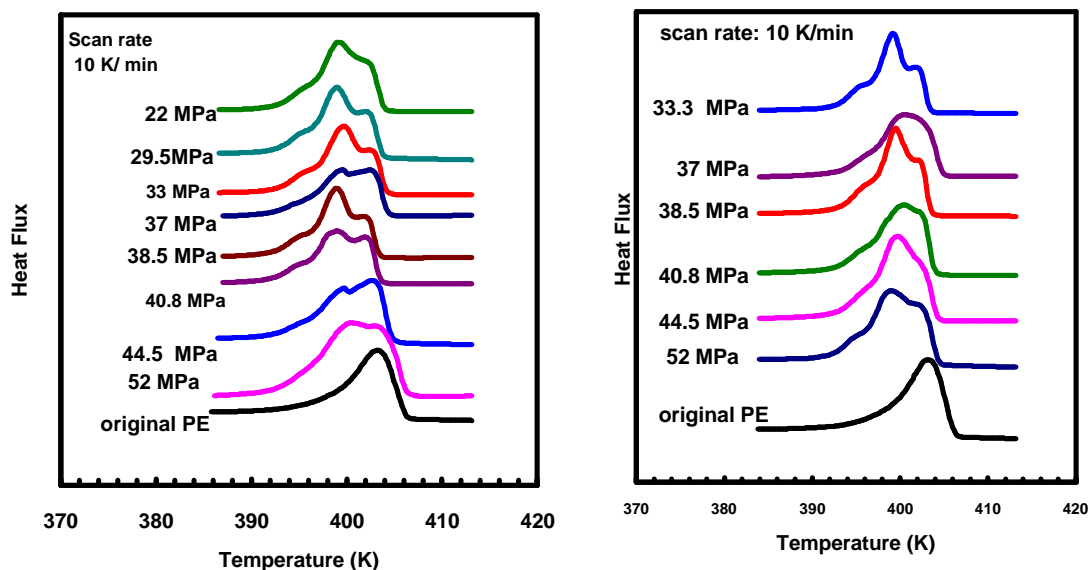


Figure 3. First DSC scans of polyethylene crystals formed at 363 K at the indicated pressures in n-pentane (Left) and in 85 % pentane + 15 % carbon dioxide solutions (Right).

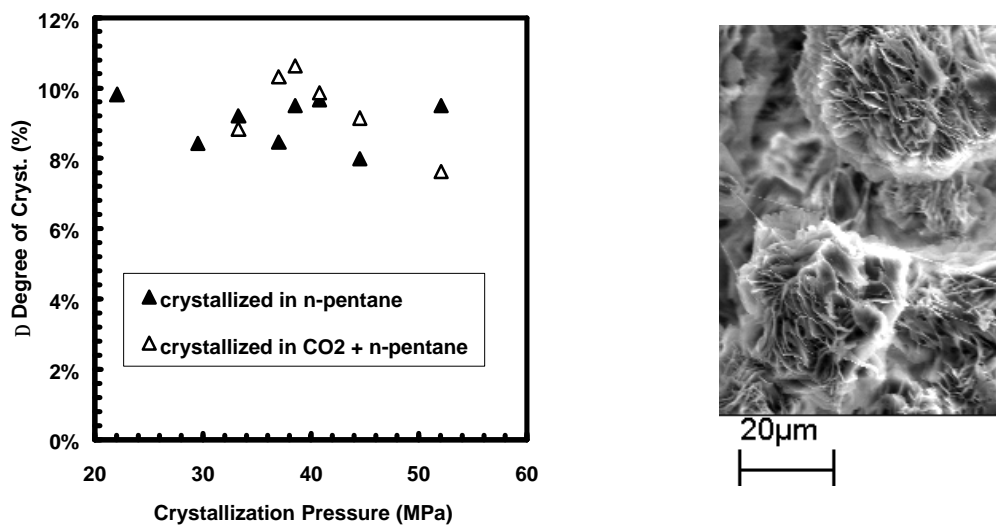


Figure 4a (Left). The change in the degree of crystallinity of polyethylene crystals formed in n-pentane or in 85 % n-pentane + 15% carbon dioxide mixtures compared to the crystallinity of the initial polyethylene.

Figure 4b (Right). Micrograph of polyethylene crystals formed from 5 % solution in n-pentane at 38.5 MPa at 12.4 K below the solid-fluid phase separation temperature. Scale bar is 20 microns.