

# The Miscibility and Phase Behavior of Polyethylene with Poly(dimethylsiloxane) in Near-Critical Pentane

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**Abstract**—Miscibility and phase behavior of solutions of polyethylene (PE) and poly(dimethylsiloxane) (PDMS) mixtures in near-critical n-pentane have been investigated in a special variable-volume view-cell equipped with a computerized data acquisition system. This is a study on dissolving mutually incompatible polymers in a common solvent at high pressures. The fluid-fluid and fluid-solid demixing pressures of the solutions were determined for different polymer concentrations (5% PE, 5% PE+1% PDMS, 5% PE+2% PDMS and 5% PE+5% PDMS). In the PE+n-pentane solutions, the system shows LCST (lower critical solution temperature) type behavior and the fluid-fluid demixing pressures increase with increasing temperature. The PE+PDMS+n-pentane systems, however, show UCST (upper critical solution temperature) type behavior and the fluid-fluid demixing pressures decrease with increasing temperature. Even with small addition of PDMS to PE, the demixing pressures show dramatic increases compared to the demixing pressures of PE alone. At high PDMS concentrations (5% PDMS), complete miscibility could not be achieved at pressures up to 70 MPa. The fluid-solid boundary that is associated with the melting or crystallization of PE was also studied as a function of cooling and heating rates. It is shown that these temperatures tend to approach the same value in the limit of very low heating and cooling rates.

Key words: Miscibility, Phase Behavior, Polyethylene, Poly(dimethylsiloxane), Pentane

## INTRODUCTION

The phase behavior of polymer solutions at high pressure is of great interest in polymer formation, modification and processing [Kiran, 1994, 2000; Kiran and Zhuang, 1997]. Pressure plays an important role in the transport, kinetics and thermodynamic properties of polymer solutions. A specific area of recent activity is the pressure (density) tuning of a supercritical fluid-based process to control the miscibility conditions to bring about selective extractions, fractionations or separation.

We have already conducted several systematic studies on the miscibility, phase separation and volumetric properties of polyethylene in n-alkanes (such as n-butane and n-pentane) and poly(dimethylsiloxane) in carbon dioxide and the phase behavior of polyethylene in binary fluid mixtures that contain carbon dioxide as a component [Kiran, 1994, 2000; Kiran and Zhuang, 1997; Kiran et al., 1993; Bayraktar and Kiran, 2000]. The ternary mixtures of the type “polymer+solvent+carbon dioxide” are of interest in processes that aim at reducing the use of the traditional solvents in the process, or using carbon dioxide as an anti-solvent to produce polymers of specific morphologies ranging from powders to fibers. In this article, we report on different ternary systems of the type “Polymer A+Polymer B+solvent.” The specific system is the polymer-polymer mixture of polyethylene with poly(dimethylsiloxane) and their miscibility in n-pentane. This polymer mixture is interesting in that PE and PDMS are mutually incompatible [Bayraktar and Kiran, 2001; Chalykh and Avdeyev, 1985; Huglin and Idris, 1985].

Polyethylene is soluble in n-pentane at high pressures. PDMS is a liquid at room temperature and is highly soluble in pentane at ambient pressures. Their blends are not compatible and the miscibility of such incompatible systems in a common solvent would offer opportunities in solution blending [Kiran et al., 2000; Kiran, 2001]. The phase behavior of PE+PDMS in pentane has not been previously reported in the literature. In the present study, we have investigated the miscibility conditions and the fluid-fluid and fluid-solid demixing pressures of solutions of PE + PDMS in near-critical n-pentane for different PE and PDMS concentrations in a pressure range from 10-50 MPa. A new computerized data acquisition system was used to record transmitted light as a function of temperature, pressure or time, from which demixing pressures, or temperatures can then be determined.

## EXPERIMENTAL

### 1. Materials

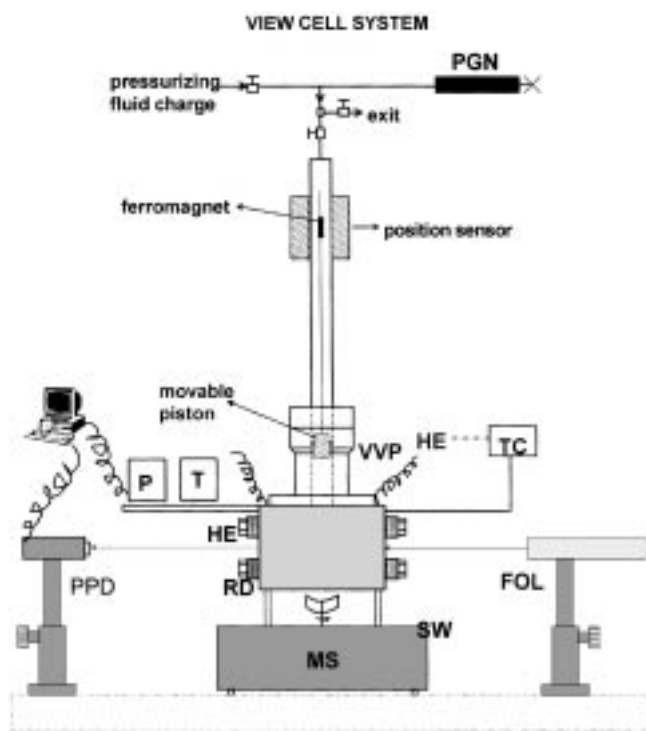
The poly(dimethylsiloxane) had a weight-average molecular weight of  $M_w=38,900$  with a polydispersity index of  $M_w/M_n=2.84$ . The polyethylene sample had a molecular weight of  $M_w=121,000$  with a polydispersity index of  $M_w/M_n=4.3$ . The solvent n-pentane (Purity>99.9%) was obtained from Aldrich and used as received.

### 2. Determination of Demixing Pressures or Temperatures

Fig. 1 is a schematic diagram of the experimental system. It consists of a variable-volume view-cell, a fiber-optic light source and related optical components to monitor the transmitted light intensity, and a dedicated computer system for real-time data acquisition. The details of the view-cell and the loading procedure have been reported in our earlier publications [Bayraktar and Kiran, 2001].

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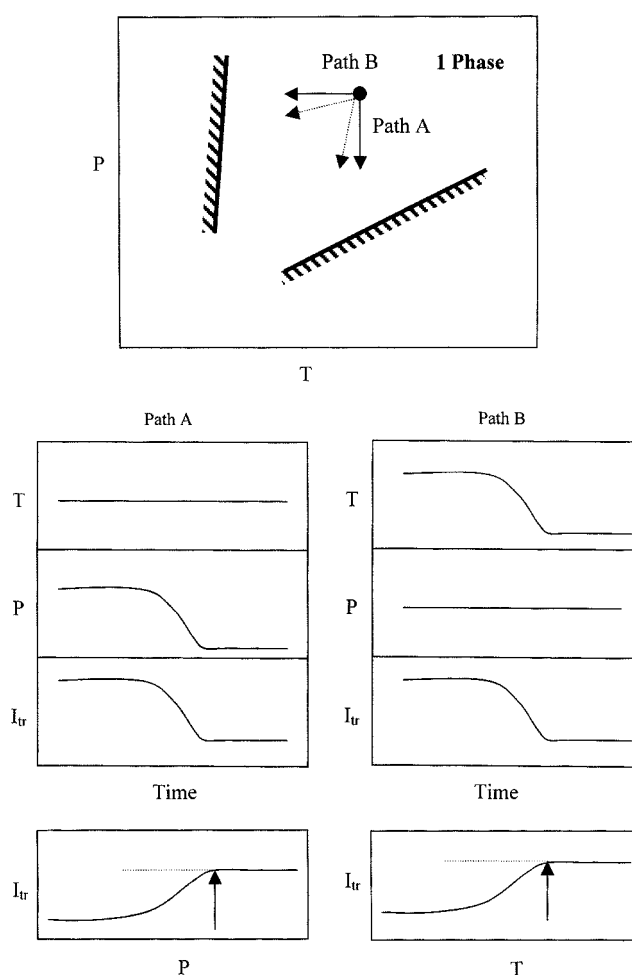


**Fig. 1. Schematic diagram of the view-cell and data acquisition system.**

PGN: Pressure Generator  
TC: Temperature controller  
HE: Cartridge heating elements  
VVP: Variable volume-part housing the movable piston  
RD: Rupture disc  
MS: Magnetic stirrer  
PPD: PIN photodiode  
FOL: Fiber optic illuminator

Briefly, a pressure generator and a movable piston are used to bring about volume (thus pressure) changes in the view-cell after the cell is loaded. The position of the piston is monitored with an LVDT (Linear Variable Differential Transformer). The LVDT detects the position of a ferromagnet attached to the extension stem connected to the movable piston. Knowing the internal volume of the cell at a given temperature and pressure permits calculation of the density of the mixture from the cell loading. The optical components and the real-time data acquisition system are designed to monitor the temperature, pressure and the intensity of the transmitted light through the view-cell as conditions in the cell are changed. An optical fiber illuminator is used as the light source and the transmitted light intensity is monitored with a fast-response PIN photodiode detector.

Fig. 2 describes the methodology in determining the demixing (commonly known as the cloud point) conditions. The figure illustrates the case where from a fully homogenized one-phase solution, phase boundaries are approached by lowering the pressure at a fixed temperature (Path A), or by lowering the temperature at a given pressure (Path B). The dotted paths A and B are included to emphasize the fact that if the pressure is changed rapidly, there will be a cooling associated with it, and the actual path will not be a constant-temperature path. Likewise if the temperature is lowered, the pressure in the system will decrease unless corrective action is taken to maintain the pressure at its initial value. The figure demonstrates the changes in temperature (T), pressure (P) and the transmitted light



**Fig. 2. Schematic representation of data collected during pressure reduction or temperature reduction in determining the demixing pressures (at a given temperature) or demixing temperature (at a given pressure) from changes in the transmitted light intensity.**

intensity ( $I_{tr}$ ) with time for paths A and B. From these data, plots of the variation of the transmitted light intensity with pressure (at a given temperature) or temperature (at a given pressure) are generated. The pressure or temperature corresponding to the departure from the base value of the transmitted light intensity (corresponding to the one-phase, fully homogeneous conditions) is identified as the demixing pressure or the demixing temperature. These are illustrated with the arrows in the lower portion of Fig. 2.

In the present study we have conducted experiments along Path A to assess the demixing pressures (fluid-fluid phase boundary) at different temperatures in the range from 375 to 440 K. We have also determined the demixing temperatures at different pressures in the range from 35 to 55 MPa to assess the solid-fluid boundary that is associated with the crystallization of polyethylene. The solid-fluid boundary was approached by cooling (to induce crystallization of PE) from one-phase homogeneous conditions at high temperatures, or by heating (to induce melting of PE) from low temperatures starting from phase-separated conditions. The influence of the heating or cooling rates on the observed value of the melting and crystallization temperatures was also investigated. In these ex-

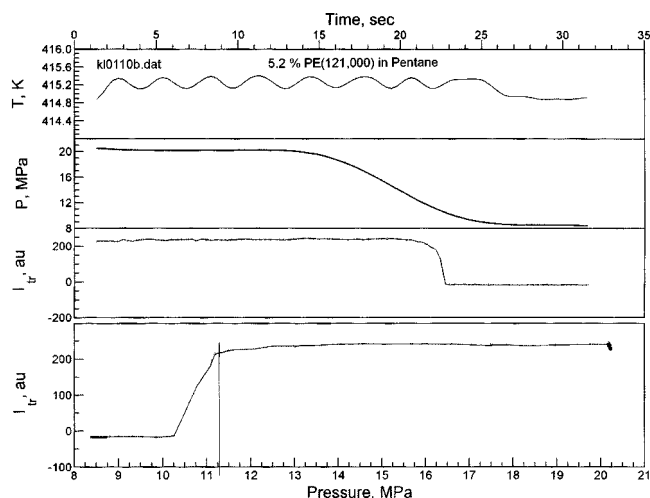


Fig. 3. Variation of temperature  $T$ , pressure  $P$ , and transmitted light intensity  $I_{tr}$  with time and  $I_{tr}$  with pressure during a pressure reduction in 5.2% PE solution in n-pentane. Transmitted light intensity is in arbitrary unit (au).

periments the rate of heating or cooling of the cell was altered either by simply putting extra insulation or by introducing airflow (with a fan) around the view-cell. The system pressure was maintained constant through the cooling or heating process by manually adjusting the pressure with the pressure generator.

## RESULTS AND DISCUSSION

Fig. 3 shows the actual change in temperature, pressure, and transmitted light intensity with time during a pressure reduction experiment in a 5.2% PE solution in n-pentane at 415 K. The data shows that temperature remains fairly stable as the pressure is reduced from 20 to 8 MPa over a 10 s time interval. The demixing pressure is determined to be 11.25 MPa. Fig. 4 shows the corresponding data for the solution that contains 1.1% PDMS+5.2% PE in n-pentane

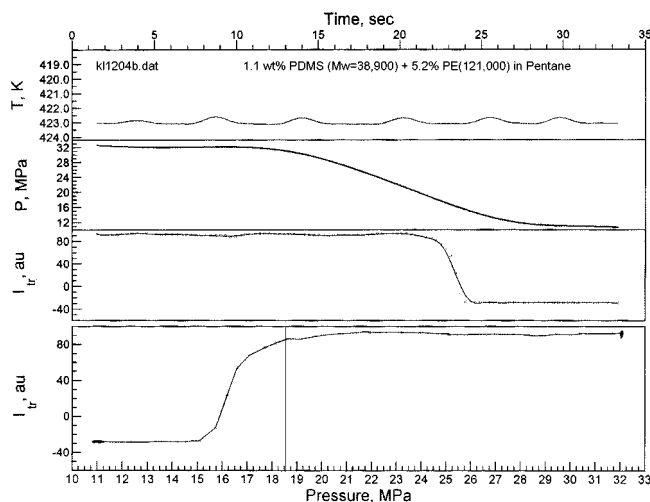


Fig. 4. Variation of temperature  $T$ , pressure  $P$ , transmitted light intensity  $I_{tr}$  with time and  $I_{tr}$  with pressure during a pressure reduction in 1.1% PDMS+5.2% PE solution in n-pentane.

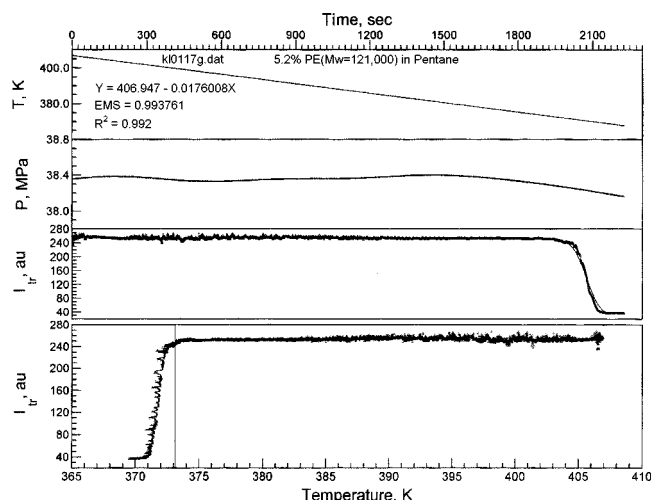


Fig. 5. Variation of temperature  $T$ , pressure  $P$ , transmitted light intensity  $I_{tr}$  with time and  $I_{tr}$  with temperature during a temperature reduction in 5.2% PE solution in n-pentane with a cooling rate of 0.0176 K/second. The pressure was maintained constant at 38.4 MPa.

at 423 K. The fluid fluid demixing pressure at this temperature for this ternary system is determined to be 18.5 MPa.

Fig. 5 shows the data for 5.2% PE in n-pentane for the case where temperature is reduced from 423 K to 370 K over a 2,200 s time interval. Pressure is sustained (by manual adjustments with the aid of the pressure generator) fairly constant at 38.4 MPa. The demixing temperature is determined to be 373 K. During this experiment, the cooling rate was highly linear at 0.0176 K/s. Fig. 6 is a similar set of plots showing the change in temperature, pressure, and transmitted light intensity during cooling at a rate of 0.0185 K/s in the ternary system 1.1% PDMS+5.2% PE in n-pentane. For this system the demixing temperature at 42 MPa is found to be 375 K.

By carrying out similar experiments at different temperatures and

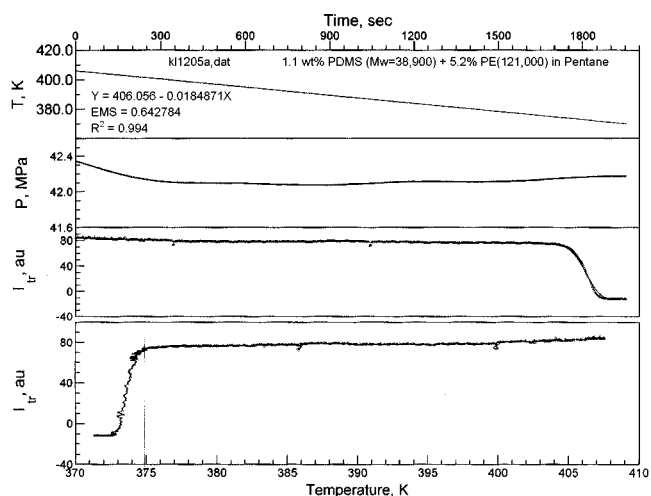


Fig. 6. Variation of temperature  $T$ , pressure  $P$ , transmitted light intensity  $I_{tr}$  with time and  $I_{tr}$  with temperature during a temperature reduction in the solution of 1.1% PDMS+5.2% PE in pentane. The cooling rate is 0.0184 K/second. The pressure was kept constant at 42.1 MPa.

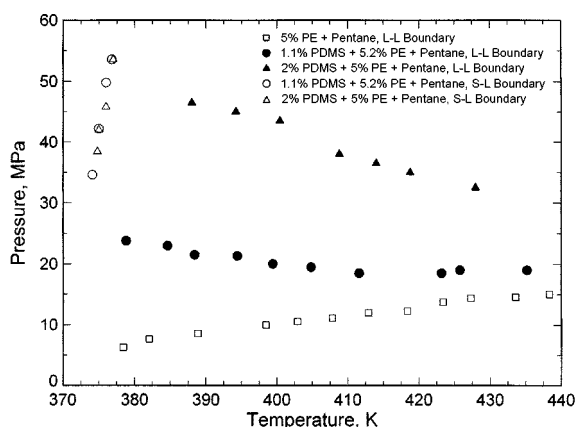


Fig. 7. Demixing pressures and temperatures in solutions of PE+PDMS mixtures in n-pentane. L-L and S-L refer to the liquid-liquid and solid-liquid boundaries.

pressures detailed phase boundary information for these solutions was generated. Fig. 7 is a comparative plot for solutions of PE and PE+PDMS polymer blends in n-pentane. The figure shows that compared to PE, the fluid-fluid phase boundary shifts to significantly higher pressures in the presence of PDMS. This is especially magnified at lower temperatures. For example at 390 K, the demixing pressures increase from about 10 to 20 MPa for the 1% PDMS and to 50 MPa for 2% PDMS case. A 5% PDMS+5% PE mixture could not be dissolved at pressures up to 70 MPa. Another characteristic feature displayed in Fig. 7 is that the slope of the demixing curve changes in going from PE to PE+PDMS system. In PE+n-pentane system, the two-phase region is entered upon an increase in temperature at a given pressure at temperatures above the crystalline melting temperature of polyethylene. This is typical of systems showing lower critical solution temperature, or the LCST-type behavior. In PE+PDMS+n-pentane systems, the one-phase region is entered upon an increase in temperature, provided again the temperature is above the melting temperature of polyethylene. This is typical of systems showing upper critical solution temperature, or the UCST-type behavior. This type of crossover from LCST to UCST type behavior has been observed in systems such as PE+pentane+carbon dioxide [Kiran, 1994, 2000; Kiran and Zhuang, 1997]. PDMS is not compatible with PE, and its effect is similar to that of carbon dioxide which is not a solvent for polyethylene.

Fig. 7 shows that the solid-fluid boundary in these systems observed in the temperature range below 375 K does not appear to be influenced much with the presence of PDMS in the solution.

### 3. Further Discussion on the Solid-Fluid Boundary

The solid-fluid boundary in these systems is associated with the crystallization or melting of polyethylene. Crystallization is induced when cooling from high temperatures. Melting occurs when the system is heated from low temperatures. Fig. 8 shows the system response during such a heating experiment in 5.2% PE in n-pentane. After the solution was cooled to temperatures below 363 K, it was heated back to enter the one-phase region at 38.4 MPa. The heating rate was 0.0111 K/s. As shown in the figure, during this heating mode, the transmitted light intensity shows a marked increase upon entering the one-phase region. From variation of the transmitted light intensity with temperature, a melting temperature of

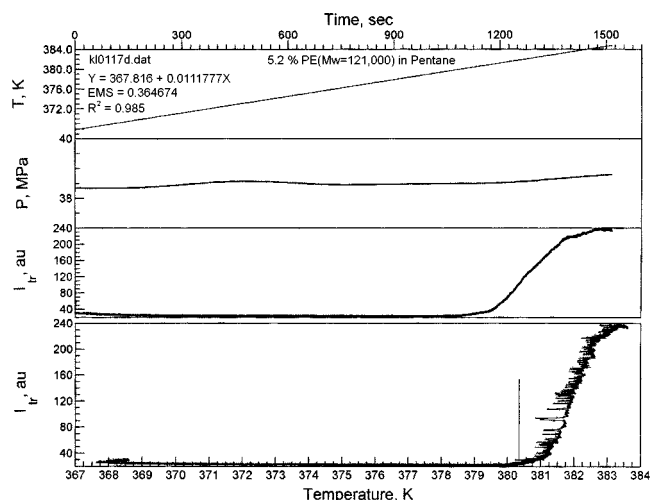


Fig. 8. Variation of temperature  $T$ , pressure  $P$ , transmitted light intensity  $I_t$  with time and  $I_t$  with temperature during a temperature increase in 5.2% PE in pentane with a heating rate of 0.0111 K/second. The pressure was maintained at 38.4 MPa.

Table 1. The observed melting temperature of PE in pentane at different heating rates

Heating range (K)	Pressure (MPa)	Heating rate (K/s)	Melting temperature (K)
360-400	34.48	0.0434	389
360-400	34.48	0.0313	384
360-400	34.48	0.0111	380.3

Table 2. The observed crystallization temperature of PE in pentane at different cooling rates

Cooling range (K)	Pressure (MPa)	Cooling rate (K/s)	Crystallization temperature (K)
400-300	34.48	0.0176	374
400-300	34.48	0.0421	373.2
400-300	34.48	0.0547	372.8

380.3 K is observed for this heating rate. A number of additional experiments were conducted to document the influence of the heating and cooling rates on the observed melting and crystallization temperatures. These are shown in Tables 1 and 2.

As shown in Table 1, the observed melting temperature increases when the heating rate increased. Table 2 shows that the observed crystallization temperature decreases when the cooling rate is increased. At these heating and cooling rates that were employed, the melting and crystallization temperatures differ by about 10-15 K. Fig. 9 shows the variation of melting and crystallization temperatures with the rate of heating and cooling, and shows their extrapolations to extremely slow rates, which ideally should merge. The figure suggests an equilibrium crystalline melting temperature of about 376 K for polyethylene in n-pentane at 38.4 MPa. The heating and cooling rate dependence of crystallization or melting in polymers is well known, and the present observations demonstrate these phenomena at high pressures in the presence of a solvent. It is interesting to

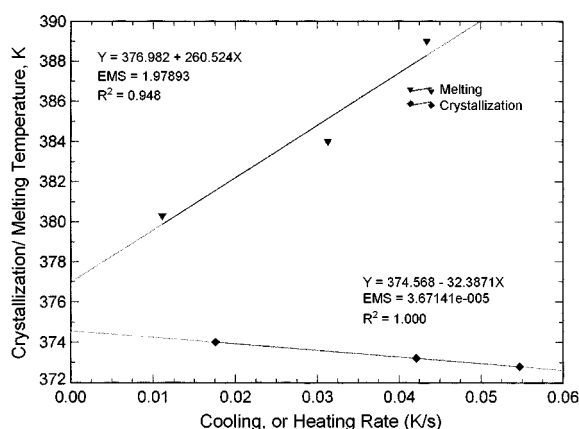


Fig. 9. The dependence of the observed melting and crystallization temperature on the heating and cooling rates.

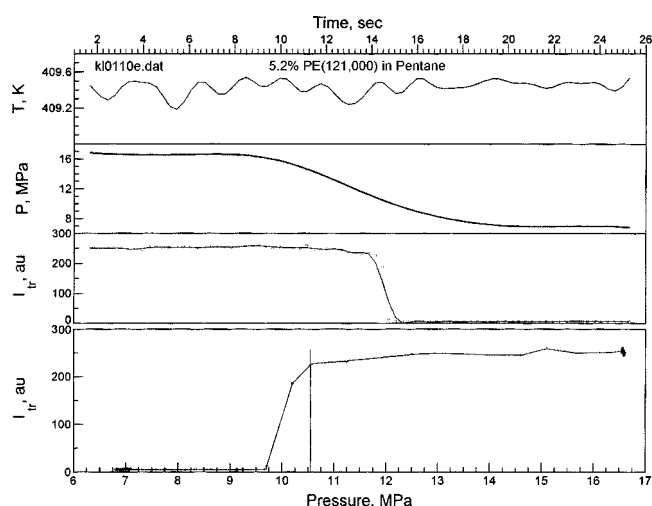


Fig. 10. Variation of temperature  $T$ , pressure  $P$ , and transmitted light intensity  $I_{tr}$  with time, and  $I_{tr}$  with pressure during a pressure reduction experiment in 5.2% PE solution in *n*-pentane at 409.4 K.

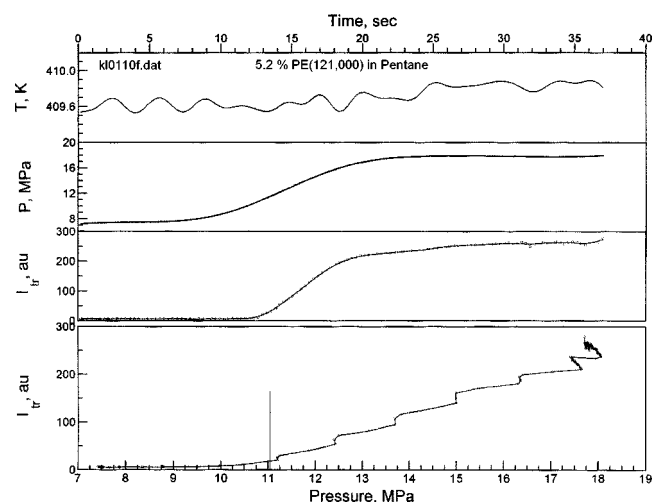


Fig. 11. Variation of temperature  $T$ , pressure  $P$ , and transmitted light intensity  $I_{tr}$  with time, and  $I_{tr}$  with pressure during a pressure increase experiment in 5.2% PE solution in *n*-pentane at 409.6 K.

note that Fig. 7 shows that the incipient crystallization temperature of PE is not influenced by the presence of PDMS at these levels of PDMS additions.

Unlike the difference in the observed temperature of phase change for the solid-fluid boundary, the fluid-fluid boundary at higher temperatures does not show any measurable difference whether the boundary is approached by decreasing the pressure, or by increasing the pressure, unless extremely fast rates are imposed. This is demonstrated in Figs. 10 and 11 for 5.2% solution of PE in *n*-pentane at 409.4 K. In this pressure decrease mode, the demixing pressure is identified as 11.5 MPa (Fig. 10), while in the pressure increase mode the dissolution pressure is identified as 11.25 MPa (Fig. 11). The pressure reduction and increase rates were about 0.4 MPa/s. The kinetic factors do not come into play for the liquid-liquid phase separation as in the case of crystallization.

## CONCLUSIONS

The present results show that with addition of even small amounts of PDMS to the PE+pentane solution, the liquid-liquid phase boundary is shifted to higher pressures and the character of the phase behavior of the system shifts from a system showing LCST to a system showing UCST. When the concentration of PDMS increases, the demixing pressures of the system increase accordingly. At PDMS levels greater than 5%, complete miscibility becomes unattainable at pressures up to 70 MPa. The solid-fluid boundary associated with the crystallization of PE does not show any measurable changes in the presence of PDMS. The observed crystallization and melting temperatures depend on the cooling and heating rates employed, and approach each other in the limit of extremely low rates.

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