

Research Article

Phase Behaviour of the System Propene/Polypropene at High Pressure

Oliver Ruhl,¹ Gerhard Luft,² Patrick Brant,³ and John Richard Shutt⁴

¹Lummas Novolen Technology GmbH, Gottlieb-Daimler-Strasse 8, 68165 Mannheim, Germany

²Institute of Chemical Engineering and Macromolecular Science, Darmstadt University of Technology, Petersenstrasse 20, 64287 Darmstadt, Germany

³ExxonMobil Chemical, 5200 Bayway Drive, Baytown, TX 77520-2101, USA

⁴ExxonMobil Chemical Europe Inc., Hermeslaan 2, 1831 Machelen, Belgium

Correspondence should be addressed to Gerhard Luft, luft@chemie.tu-darmstadt.de

Received 15 April 2011; Accepted 1 June 2011

Academic Editor: Tiziana Fornari

Copyright © 2011 Oliver Ruhl et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The phase behaviour of mixtures of supercritical propene and a number of polypropenes, which have a similar density but significantly different molecular weights and tacticities, was investigated in a broad range of polymer weight fractions and temperatures at high pressures. The cloud-point pressures were measured optically, using a view cell which was equipped with two windows made of synthetic sapphire and a metal bellows to accurately adjust the pressure. The cloud-point pressures were found in the range from 29 to 37 MPa decreasing with increasing polymer weight fraction and increasing with increasing temperature and polymer molecular weight. The critical weight fraction was found below 2 to 6 wt.-%. Whereas the cloud-point pressures of atactic and syndiotactic samples were high and very similar, the isotactic species exhibit distinctly lower values. The results, extrapolated to lower temperatures, show good agreement with the literature data.

1. Introduction

The phase behaviour of mixtures of monomers and polymers exerts a major influence on the performance of polymerisation reactions and the properties of the resulting products. The formation of microcellular materials in the polymerisation under supercritical conditions is of growing interest. Whereas the phase behaviour of ethylene and low density polyethylene systems has been investigated in detail [1–5], little data of the high-pressure phase equilibrium of polypropene solutions are presented in the open literature [6, 7], and then only at lower temperatures and lower polymer concentrations. For this reason in this work, the phase behaviour of mixtures of some polypropene grades in supercritical propene were evaluated over a broad range of temperature, pressure, and composition.

2. Experimental Section

2.1. Materials. The data of the polymers are listed in Table 1. The density of all samples is in the range of 0.9 g/mL, but they differ in molecular weight, polydispersity, and structure.

Polymer PP4062 is a commercial grade of high molecular weight and moderate polydispersity. The molecular weight of PP 45379 is much lower. Both polymers are produced with Ziegler-Natta catalysts and exhibit isotactic structures. Achieve 1635, produced with a metallocene catalyst, is also isotactic and has medium molecular weight but a low polydispersity which is typical for metallocene-based polymers. The sample PP W01 has a low molecular weight and isotactic structure. It was prepared in a semicontinuously operated laboratory unit by means of a metallocene catalyst in solution under a medium pressure of 7 MPa. The remaining polymers were also produced by metallocene catalysts and exhibit low polydispersities. Gemini aPP has a high molecular weight and an atactic structure, whereas Fina 9306 is a syndiotactic polypropene with medium molecular weight.

Propene was supplied by Linde AG, Wiesbaden, Germany in cylinders of 36 kg. Its data are listed in Table 2. It was used without further purification.

2.2. Apparatus and Procedure. The cloud-point pressures were measured using a view cell developed in Darmstadt

TABLE 1: Data of the polymer grades. MFR: Melt flow rate, and M_N : Number-average molecular weight, M_W : Weight-average molecular weight.

Polymer	Density [g/mL]	MFR [g/10 min]	M_N [g/mol]	M_W [g/mol]	Polydispersity [—]	Tacticity [—]
PP 4062	0.90	3.7	168 400	527 900	3.13	Isotactic
Achieve 1635	0.90	32	147 100	254 100	1.73	Isotactic
PP 45379	0.90	300	43 000	147 700	3.43	Isotactic
PP W01	0.90	80	20 900	76 360	3.64	Isotactic
Gemini aPP	0.85	4	225 800	456 600	2.02	Atactic
Fina 9306	0.88	7	123 670	217 910	1.76	Syndiotactic

TABLE 2: Data of propene.

Propene	C_3H_6
Molecular weight	42.08 g/mol
Density (0°C, 1013 mbar)	1.91 kg/m ³
Melting temperature	-185.25°C
Melting enthalpy	69.9 kJ/kg
Boiling point (1013 mbar)	-47.75°C
Enthalpy of vaporization (1013 mbar)	438 kJ/kg
Critical temperature	91.85°C
Critical pressure	4.62 MPa
Purity	>99.8%
Other C_nH_m	<1000 ppm

[8]. The cell had a volume of 20 mL and was designed for a maximum pressure of 250 MPa and a temperature of 513 K. For optical observation, two windows made of synthetic sapphire are arranged one opposite the other. One is used to illuminate the interior of the autoclave, through the other, the phase behaviour can be observed. The pressure was generated by a membrane compressor and could be adjusted by a metal bellows inside the cell. For this purpose, the bellows is connected to a pump operated by a pressure controller.

First, the polymer is placed in the cell. As next, the cell is evacuated and finally propene is fed. While heating to the preset temperature, the apparatus is shaken to mix the components. Three plates are arranged around the bellows to support the mixing.

After homogenization, the pressure is reduced stepwise by means of the bellows, while the phase state is observed visually. The phase separation is indicated by cloudiness. The procedure was repeated at different temperatures to measure the cloud-point curve. The reproducibility of the measurements was better than 3%.

3. Results

3.1. Influence of the Polymer Concentration. The cloud-point pressures of mixtures of propene with the different polymers are presented in Figure 1 for temperatures of 140, 160, 180, and 200°C. They are in the range from 28 to nearly 40 MPa. With increasing concentration of polymer in the mixture, the cloud-point pressure generally decreases. Only

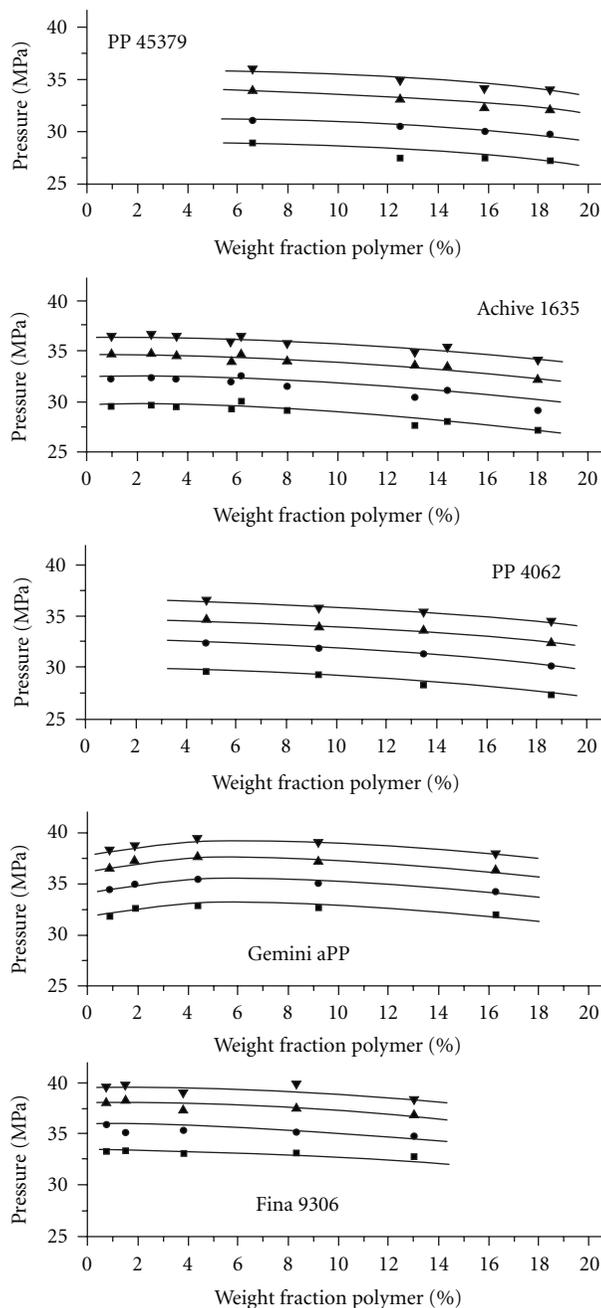


FIGURE 1: Influence of polymer weight fraction on cloud-point pressure at 200 (down triangle), 180 (up triangle), 160 (circle), and 140°C (square).

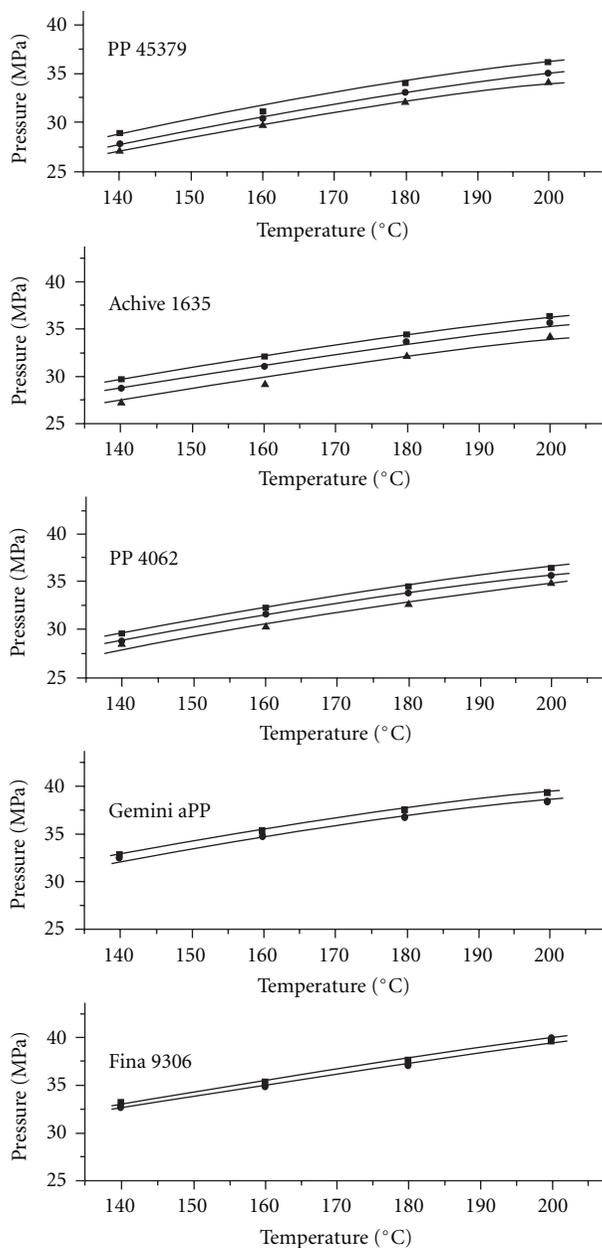


FIGURE 2: Influence of temperature on cloud-point pressure at a polymer content of 6 (square), 12 (circle), and 18 wt.-% (triangle).

the isotherms of the atactic polypropene show a maximum at polymer concentrations of 1 to 6 wt.-% and then decrease with increasing polymer weight fraction.

3.2. Influence of the Temperature. In Figure 2 the isopleths are presented for polymer concentrations of 6, 12, and 18 wt.-%. They increase nearly linearly with increasing temperature. At 140°C, the cloud-point pressures are in the range of 26 to 29 MPa and at the highest temperature of 200°C values of 34 to 36.5 MPa were obtained.

3.3. Influence of the Average Molecular Weight. The influence of the average molecular weight was investigated with the

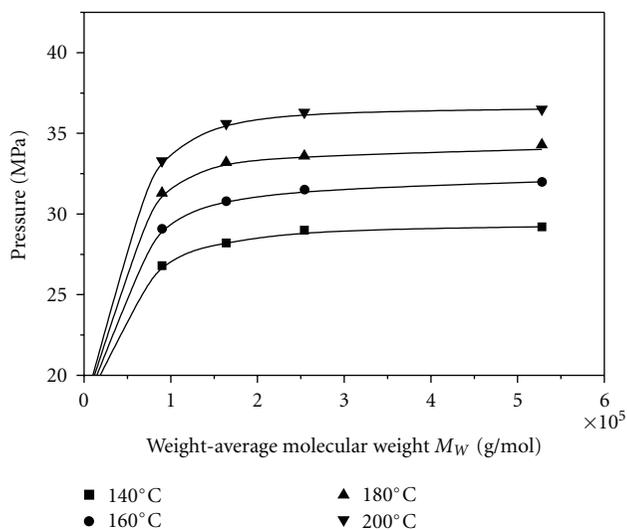


FIGURE 3: Influence of average molecular weight M_W at 10 wt.-% polymer in propene. M_W in g/mol polystyrene units.

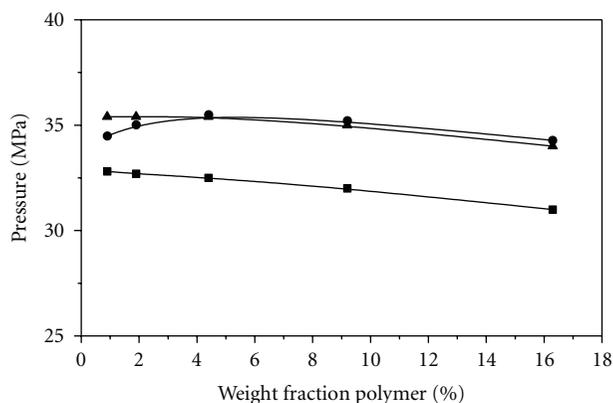


FIGURE 4: Influence of tacticity at 160°C. Polymers are isotactic PP4062 (square), atactic Gemini aPP (circle), and syndiotactic Fina 9306 (triangle).

isotactic samples. In Figure 3, the cloud-point pressures measured at temperatures of 140, 160, 180, and 200°C are plotted versus M_W for 10 wt.-% polymer in propene. The curves start at the zero point. With increasing molecular weight, the cloud-point pressure increases first steeply and then converges to an upper limit at a molecular weight of 500,000 to 600,000 g/mol.

3.4. Influence of the Tacticity. In order to show the influence of the tacticity, in Figure 4, the cloud-point pressures of an atactic (Gemini aPP), an isotactic (PP 4062), and a syndiotactic (Fina 9306) polypropene are plotted versus the weight fraction of the polymer in the mixture with propene. The temperature is 160°C. Whereas the cloud-point pressures of the atactic (curve marked by circles) and the syndiotactic (triangles) species are very similar, the isotactic polypropene exhibits distinctly lower cloud-point pressures (squares).

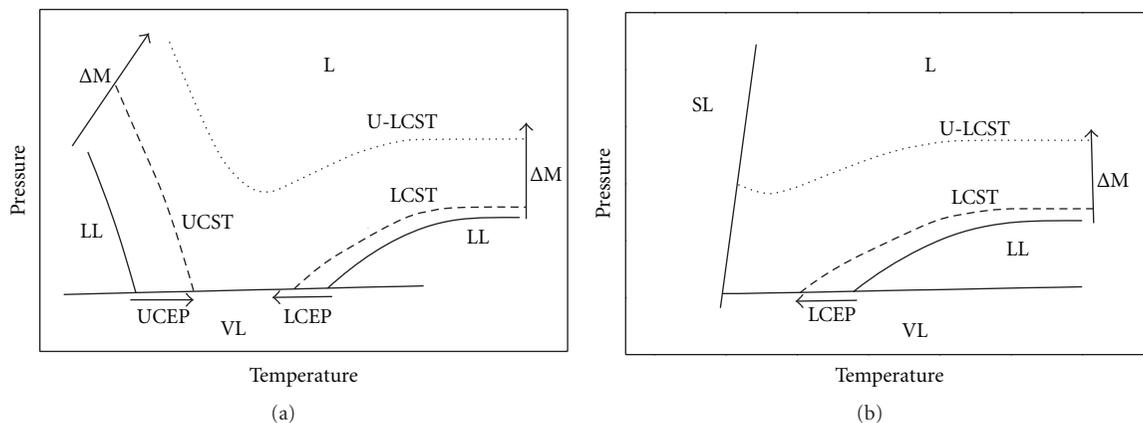


FIGURE 5: Generic phase diagrams of polymer/monomer mixtures (cutaway from TYP IV phase behaviour diagram). (a) low melting polymer; (b) high melting polymer. L: homogeneous fluid phase; LL: two fluid phases; VL: vapor and fluid phase; SL: solid and fluid phase; ΔM : difference in molecular weight.

4. Discussion

In order to discuss the observed phase behaviour of propene/polypropene mixtures the classification of phase equilibria proposed by Van Konynenburg and Scott is considered [9]. An excellent understanding of phase diagrams is given by Kikic and De Loos [10]. Schematic phase diagrams are shown in Figures 5(a) and 5(b). Figure 5(a) shows schematically the pressure versus temperature phase diagram of a polymer with low melting point, such as the atactic polypropene, and a low molecular weight solvent. Similarly, Figure 5(b) shows the pressure versus temperature phase diagram of a polymer with higher melting point, such as the isotactic polypropene, and a low molecular weight solvent. The curves are critical curves and describe the temperature and pressure conditions at which two heterogeneous phases merge into one homogeneous phase.

The following areas can be distinguished in Figure 5(a): The solid line at the bottom represents the vapour pressure curve of the solvent when the mixture contains polymer. At pressures below this line, two phases (VL) exist with a liquid and a vapour. The areas on the extreme left and right (LL) represent regions where two fluid phases are present. Above the VL-L and LL-L curves a homogeneous liquid phase (L) exists. The dashed line at the left between LL and L is the upper critical solution temperature (UCST). The corresponding curve on the right is called lower critical solution temperature curve (LCST). The intersection of the UCST-curve and the vapor-pressure curve is the so-called upper critical end point (UCEP). Similarly, the intersection of the LCST-curve with the vapor-pressure curve is the lower critical end point (LCEP).

The separation of polypropene and propene can be explained by the Gibbs free energy of mixing

$$\Delta G_m = \Delta H_m - T \cdot \Delta S_m. \quad (1)$$

UCST and LCST behaviours have slightly different explanations. The separation at UCST curve occurs when the temperature drops while the separation at the LCST curve appears with a temperature increase.

ΔG_m is the difference of the free energy between the mixture and the two pure components. ΔH_m and ΔS_m represent the according enthalpy and entropy. A mixture is homogeneous when the difference of the free energy is negative whereas it separates into two phases when $\Delta G_m < 0$. For the investigated system, the mixing enthalpy can be considered as positive because the interactions within the pure components are larger than those between the polymer and the propene. Consequently, the second term of the above equation is the determinant term for the separation.

The behaviour at the UCST curve can be explained by the positive mixing entropy. A mixture of two components is more disordered than a pure component. Therefore, the mixing entropy shall be larger than zero and higher temperatures make the second term more dominating.

In order to explain the phase separation at the LCST curve, one should consider the densities of the pure components. At or above the critical point, the density is significantly decreasing with increasing temperature, while the influence of the temperature on the polymer density is minor. If the difference of the densities of the solvent and the polymer becomes larger, the mixing entropy turns negative and the influence of the temperature turns into the opposite.

The cloud-point curves in our polypropene/propene system can be assigned to this LCST behaviour. Also, the lower demixing pressure of the isotactic PP arises from this effect. As Antoniadis et al. [11] claimed for polypropene melts, the isotactic PP occurs in coils of higher density than the syndio- or atactic PP. As a result, a higher free volume can be assumed for the isotactic PP, which leads to the better solubility in propene.

The UCST- and LCST-curves are typical for less asymmetric mixtures with small difference in molecular weight of the components. Mixtures become more asymmetric as the molecular weight of the polymer increases. In this case, the UCST- and LCST-curves come closer and eventually merge into a single curve, the so called U-LCST-curve (dotted line). Such phase behaviour, which was found by Chen and Radosz [12] for mixtures of organic solvent and poly(ethene-propene) of different molecular weights ($M_N = 790$ to

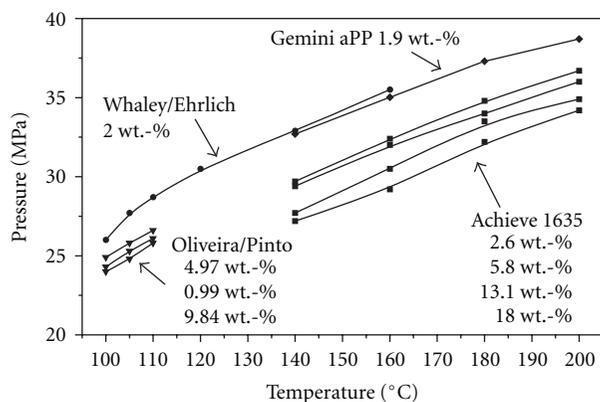


FIGURE 6: Comparison with data from literature: Cloud-point isopleths for selected polymer/propene mixtures. (weight fraction is given for polymer in propene).

59,000 g/mol), corresponds to basic type IV. Mixtures with other polymers having low melting points, such as low density polyethylene (LDPE) or ethylene-vinylacetate copolymers in mixtures with their monomers, show the same behaviour with UCST- or U-LCST-curves [13].

A different phase diagram is observed when higher melting point polymers such as isotactic PP are used. As shown in Figure 5(b), at higher temperatures (above the polymer melting point) the picture is similar. The same phase areas (L, LL, and VL) as with mixtures of polymers having a lower melting point exist together with the LCST-curve. Differences can be seen at low temperatures. With increasing melting temperature of the polymer, a solid-liquid two phase area (SL) can be observed. With increasing melting temperature of the polymer, this area overlaps the UCST-curve. If an UCST-curve can be observed it is intersected by the borderline of the SL-area. Cloud-point pressures can be measured only at temperatures above this limit.

Finally, the results should be compared with data of Oliveira et al. [7] and those of Whaley et al. [6]. For this purpose, isopleths are presented in Figure 6. Oliveira et al. used a commercial PP grade from Polibrasil Resinas S.A. which was produced with a supported Ziegler-Natta catalyst. The isotactic polymer had a molecular weight of $M_W = 245,000$ g/mol, a polydispersity of $M_W/M_N = 5.0$, and a melting point of 159.3°C . The isopleths which were measured with polymer weight fractions of 5 to 10 wt.-% at temperatures of 100 to 110°C are marked by triangles. Whaley et al. used a sample of atactic PP having a molecular weight of $M_W = 400,000$ g/mol and $M_W/M_N = 2.0$. The data which were obtained with 2% polymer and temperatures of 10 to 150°C are marked by circles.

The data from the literature are compared with own results gained with different weight fractions of the isotactic polymer Achieve 1635 ($M_W = 254,100$ g/mol) and the atactic polymer Gemini aPP ($M_W = 456,600$ g/mol) in a range of 140 to 200°C . Our data for mixtures with the isotactic polymer Achieve 1635 agree well with the data of Oliveira et al. measured also on an isotactic grade. The agreement of the results gained with the atactic PP Gemini

and the data published by Whaley et al. for mixtures with an atactic resin of similar molecular weight is excellent.

References

- [1] A. Lindner and G. Luft, "Zum Einfluss des Polymermolekulargewichts auf das Phasenverhalten von Gas-Polymer-Systemen unter Hochdruck," *Die Angewandte Makromolekulare Chemie*, vol. 56, pp. 99–114, 1976.
- [2] R. Spahl and G. Luft, "Entmischungsverhalten von Ethylen und niedermolekularem Polyethylen," *Berichte der Bunsengesellschaft für Physikalische Chemie*, vol. 85, pp. 379–384, 1981.
- [3] T. W. De Loos, W. Poot, and G. A. M. Diepen, "Fluid phase equilibria in the system polyethylene + ethylene. 1. Systems of linear polyethylene + ethylene at high pressure," *Macromolecules*, vol. 16, no. 1, pp. 111–117, 1983.
- [4] B. Folie, C. Gregg, G. Luft, and M. Radosz, "Phase equilibria of poly(ethylene-co-vinyl acetate) copolymers in subcritical and supercritical ethylene and ethylene-vinyl acetate mixtures," *Fluid Phase Equilibria*, vol. 120, no. 1-2, pp. 11–37, 1996.
- [5] H. Dörr, M. Kinzl, and G. Luft, "The influence of inert gases on the high-pressure phase equilibria of EH-copolymer/1-hexene/ethylene-mixtures," *Fluid Phase Equilibria*, vol. 178, no. 1-2, pp. 191–201, 2001.
- [6] P. D. Whaley, H. H. Winter, and P. Ehrlich, "Phase equilibria of polypropylene with compressed propane and related systems. 1. Isotactic and atactic polypropylene with propane and propylene," *Macromolecules*, vol. 30, no. 17, pp. 4882–4886, 1997.
- [7] J. V. Oliveira, C. Dariva, and J. C. Pinto, "High-pressure phase equilibria for polypropylene-hydrocarbon systems," *Industrial and Engineering Chemistry Research*, vol. 39, no. 12, pp. 4627–4633, 2000.
- [8] H. Dörr, M. Kinzl, G. Luft, and O. Ruhl, "Influence of additional components on the solvent power of supercritical ethylene," in *Supercritical Fluids as Solvents and Reaction Media*, G. Brunner, Ed., pp. 39–60, Elsevier, New York, NY, USA, 2004.
- [9] P. H. van Konynenburg and R. L. Scott, "Critical lines and phase equilibria in binary van der Waals mixtures," *Philosophical Transactions of The Royal Society A*, vol. 298, no. 1442, pp. 495–540, 1980.
- [10] I. Kikic and T. W. De Loos, "Thermodynamic properties at high pressure," in *High Pressure Process Technology*, A. Bertucco and G. Vetter, Eds., pp. 17–63, Elsevier, Amsterdam, The Netherlands, 2001.
- [11] S. J. Antoniadis, C. T. Samara, and D. N. Theodorou, "Effect of tacticity on the molecular dynamics of polypropylene melts," *Macromolecules*, vol. 32, no. 25, pp. 8635–8644, 1999.
- [12] S. J. Chen and M. Radosz, "Density-tuned polyolefin phase equilibria. 1. Binary solutions of alternating poly(ethylene-propylene) in subcritical and supercritical propylene, 1-butene, and 1-hexene. Experiment and Flory-Patterson model," *Macromolecules*, vol. 25, no. 12, pp. 3089–3096, 1992.
- [13] B. Folie and M. Radosz, "Phase equilibria in high-pressure polyethylene technology," *Industrial and Engineering Chemistry Research*, vol. 34, no. 5, pp. 1501–1516, 1995.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

