Macromolecules **1997,** *30,* 4887−4890

Phase Equilibria of Polypropylene with Compressed Propane and Related Systems. 2. Fluid-Phase Equilibria of Polypropylene with Propane Containing Alcohols as Cosolvents and of Some Other Branched Polyolefins with Propane

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Received October 21, 1996; Revised Manuscript Received May 16, 1997[⊗]

ABSTRACT: The phase equilibrium measurements for the pseudobinary supercritical polypropylene−propane system reported in the previous paper are extended to include pseudoternary systems where a polar cosolvent, in this case a low molecular weight alcohol, has been added. The cloud-point isopleths near the critical composition show the range of behavior to be expected as the type V pseudobinary system, polypropylene−propane, described in the previous paper, is transformed into the type IV pseudobinary system polypropylene−alcohol. This type of system contains an additional critical locus with upper critical solution temperatures (UCSTs) emanating from an upper critical end point (UCEP). The pseudoternary systems polypropylene−propane−alcohol possess in most cases a merged critical locus which contains a set of UCSTs and lower critical solution temperatures (LCSTs) and which does not touch the vapor pressure curve of the solvent. The phase equilibrium measurements of the system polypropylene−propane were also extended to include some polymers and copolymers which vary in branch length and frequency. The cloud-point pressures of these systems correlate with the wt % carbon in the branches but not with the branch frequency.

Introduction

The phase equilibria of isotactic and atactic polypropylene (iPP and aPP) with propane were described in the preceding paper,[1] which should be referred to where necessary. This report deals with the phase equilibria of aPP with propane, in the presence of the cosolvents ethanol, 1-propanol, and 1-butanol. The alcohols were expected to act as antisolvents, as they have been shown to do for the mixture poly(ethylene-*co*-methyl acrylate)−propane.[2] This was expected to change the aPP−propane system, which is type V, into a type IV system or into one where the two critical lines of a type IV system merge, eliminating the miscibility window between the upper critical end point (UCEP) and the lower critical end point (LCEP) along the vapor pressure curve of the solvent. A preliminary report on the system aPP−propane−1-propanol is available.[3]

We also describe the effect of additional branching in the polymer backbone on the fluid-phase equilibria, by comparing the cloud-point curves of aPP−propane with those of propane with poly(1-butene), poly(4-methyl-1-pentene), and the copolymers poly(ethylene-*co*-propylene) and poly(ethylene-*co*-octene). This branching is expected to reduce the cloud-point pressure, as it does in polyethylene (PE).[4,5] Detailed studies on the effect of branching on the LCEP of branched olefin polymers and of ethylene−propylene copolymers in *n*-butane and in a series of higher alkanes were carried out by Charlet, Ducasse, and Delmas[6,7] and analyzed according to the Flory−Patterson theory.[8] More recently, the phase behavior of alternating copolymers of ethylene and propylene in olefinic solvents was determined by Chen, Radosz, and co-workers and analyzed in terms of statistical associating fluids theory (SAFT).[9−12]

Experimental Section

Materials. Molecular weight information and sources of the polymers are listed in Table 1. Information on the composition, density, and molecular weight of a set of poly(ethylene-*co*-octene) samples is given in Table 2. The reference unbranched sample is a fraction of a linear polyethylene, PE1484.[13]

Table 1. Weight Average Molecular Weight and Polydispersity Information for Polyolefins with Different Side-Chain Branching

sample designation	M_w	M_w/M_n
polyethylene PE1484[a]	119 600	1.19
poly(ethylene-*co*-propylene) (PEP)[b]	153 000	2.8
atactic polypropylene (aPP)[c]	400 000	2.0
poly(1-butene) (PB)[d]	570 000	n.a.[f]
poly(4-methyl-1-pentene) (PMP)[e]	n.a.[f]	n.a.[f]

[a] Data of Condo et al.[13]. [b] Obtained from Dr. S. J. Chen of Exxon Chemical, Annandale, NJ. [c] Obtained from Dr. Howard Turner of Exxon Chemical, Baytown, TX. [d] Obtained from Aldrich Chemical. [e] Obtained from Mitsui Plastics, White Plains, NY. [f] Not available.

Table 2. Weight Average Molecular Weight, Density, and Octene Content of Poly(ethylene-*co*-octene) Samples

sample designation	M_w	density (g/cc)	mol % octene
PE1484[a]	119 600	n.a.[b]	n.a.[b]
P(E-*co*-O)-1	99 300	0.9350	0.38
P(E-*co*-O)-2	94 600	0.9100	2.10
P(E-*co*-O)-3	143 600	0.9020	3.30
P(E-*co*-O)-4	151 800	0.8850	5.30
P(E-*co*-O)-5	111 300	0.8750	6/60
P(E-*co*-O)-6	159 700	0.8700	7.40
P(E-*co*-O)-7	203 400	0.8630	8.40

[a] Data of Condo et al.[13]

Methods and Apparatus. The methods and apparatus were those of the previous study, except for the use of the antioxidant Irganox 1010 (Ciba-Geigy) at 0.5 wt % in the aPP−1-propanol and aPP−1-butanol systems to avoid polymer degradation during the prolonged exposure to high temperatures.

Results

Polypropylene with Propane Containing Alcohols as Cosolvents. The 2 wt % isopleths, which provide a good approximation of the critical lines, were

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

S0024-9297(96)01546-X CCC: $14.00

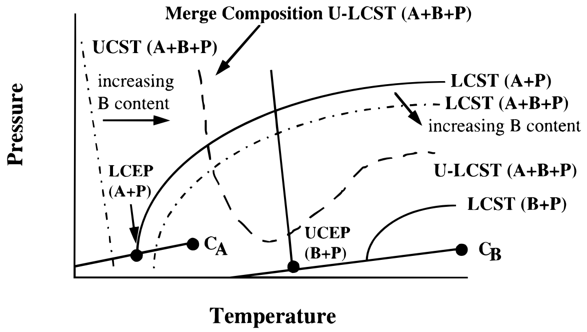

Figure 1. Ternary phase behavior diagram: change in critical lines upon changing polarity of solvent (A = alkane, B = alcohol, and P = polymer). C_A and C_B represent the critical points of A and B, and the associated solid lines, their vapor pressures.

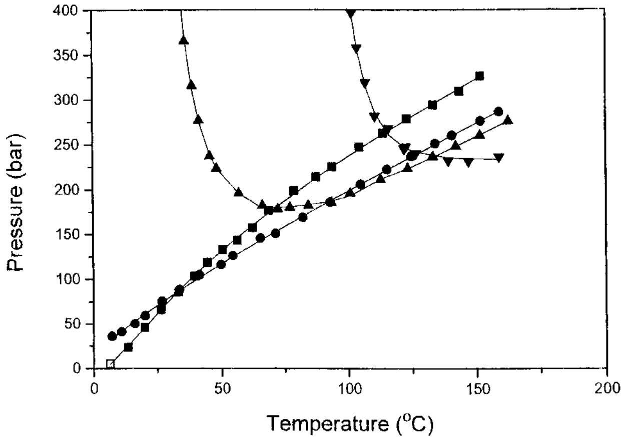

Figure 2. Cloud-point isopleths for the ternary system atactic polypropylene—propane—ethanol (2 wt % polymer solutions). The solvent compositions in wt % ethanol are as follows: (■) 0%; (●) 16.8%; (▲) 31%; (▼) 47.3%. (□) LCEP for 0% system.

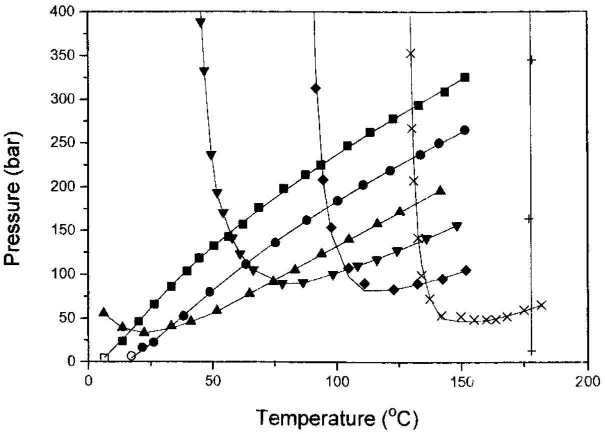

Figure 3. Cloud-point isopleths for the ternary system atactic polypropylene—propane—1-propanol (2 wt % polymer solutions). The solvent compositions in wt % 1-propanol are as follows: (■) 0%; (●) 16.8%; (▲) 31%; (▼) 47%; (◆) 65.4%; (×) 82%, (+) 100%. The lowest pressure on the 100 wt % isopleth represents an UCEP; the open symbols on other isopleths represent an LCEP.

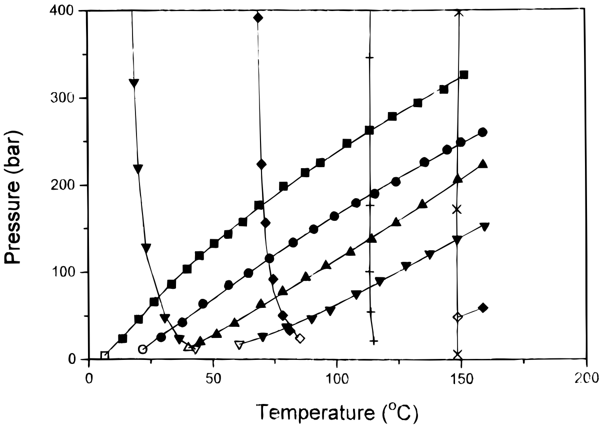

Figure 4. Cloud-point isopleths for the ternary system atactic polypropylene—propane—1-butanol (2 wt % polymer solutions). The solvent compositions in wt % 1-butanol are as follows: (■) 0%; (●) 16.8%; (▲) 31%; (▼) 47%; (◆) 65.4%; (×) 82%; (+) 100%. The lowest pressure on the 82 and 100 wt % isopleths represents an UCEP; the open symbols on other isopleths represent an UCEP or an LCEP.

determined for the quasi-ternary mixtures containing the cosolvents ethanol, 1-propanol, and 1-butanol. All data can be represented by the schematic shown in Figure 1. The replacement of the alkane solvent (A) with an alcohol (B) in the binary mixture with polymer (P) turns the type V system into a type IV one, such that the upper critical solution temperature (UCST) of B + P lies at higher temperatures than the lower critical solution tempeature (LCST) of A + P, while the LCST branch moves up in temperature. As A is added to B + P, generating the ternary system A + B + P, both branches move down in temperature. As the ternary mixture is made richer in B, both branches will first move up in temperature, and then there will come a point at which the LCEP and the UCEP will become identical, eliminating the miscibility window along the vapor pressure curve (not shown in Figure 1). The two branches will finally merge into a continuous curve with a pressure minimum that does not touch the vapor pressure curve. Such a curve, first described by Zeman and Patterson,[14] was termed a U-LCST curve by Chen and Radosz.[15] The same type of change in character of the critical locus, as the solvent becomes poorer, can also be seen when the molecular weight of the polymer is increased at constant solvent quality.[10,14]

Figure 2 shows the 2 wt % isopleths for the ternary systems containing ethanol. These isopleths are assumed to represent critical lines. The two richest compositions in ethanol, containing 47.3 and 31.0 wt % ethanol, respectively, show an U-LCST locus. No LCEP is visible in the operable temperature range for the mixture with the lowest alcohol content, so that an U-LCST locus might exist rather than a separate UCST branch. The 1-propanol cosolvent system shows an LCEP and, presumably, a separate UCST branch outside the acessible temperature window for the lowest propanol content of 16.8 wt % and merged U-LCSTs for the other three mixed solvent systems (Figure 3). The UCST branch for the pure *n*-propanol solvent is now visible within the temperature window, with an UCEP at 178 °C. For the butanol system, critical lines move up in temperature as the system becomes richer in butanol, but no merging into an U-LCST locus occurs at any composition. The UCEPs for the 82 and 100 wt % butanol systems now occur within the operating range (Figure 4). A summary of the character of the critical lines and the location of critical end points, if accessible, is shown for all of the systems in Table 3.

Some Other Branched Polyolefins with Propane. Figure 5 shows cloud-point isopleths for PE, aPP, poly(ethylene-*co*-propylene) (PEP), poly(1-butene) (PB), and poly(4-methyl-1-pentene) (PMP). The low polymer concentrations chosen should not be too different from those corresponding to the maxima in the rather flat

Table 3. UCEP and LCEP Temperatures for Atactic Polypropylene–Propane–Alcohol Systems

	ethanol		1-propanol		1-butanol	
wt % alcohol	UCEP (°C)	LCEP (°C)	UCEP (°C)	LCEP (°C)	UCEP (°C)	LCEP (°C)
0.0	none	6	none	6	none	6
16.8	U-LCST	U-LCST	OTW[b]	17	OTW	22
31.0	U-LCST	U-LCST	U-LCST	U-LCST	OTW	40
47.3	U-LCST	U-LCST	U-LCST	U-LCST	43	61
65.4	NM[a]	NM	U-LCST	U-LCST	85	149
82.0	NM	NM	U-LCST	U-LCST	115	OTW
100.0	NM	NM	178	OTW	149	OTW

[a] NM = not measured. [b] OTW = outside experimental temperature window.

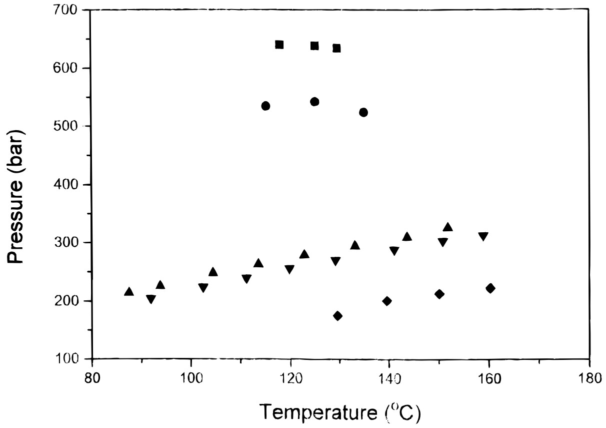

Figure 5. Cloud-point isopleths for various polyolefins with different branching in propane: (●) a poly(ethylene-*co*-polypropylene) with 70 wt % propylene content at 5 wt % polymer; (▲) aPP at 2 wt %; (▼) poly(1-butene) at 5 wt %; (◆) poly(4-methyl-1-pentene) at 5 wt %; (■) PE1484 (see Table 1).

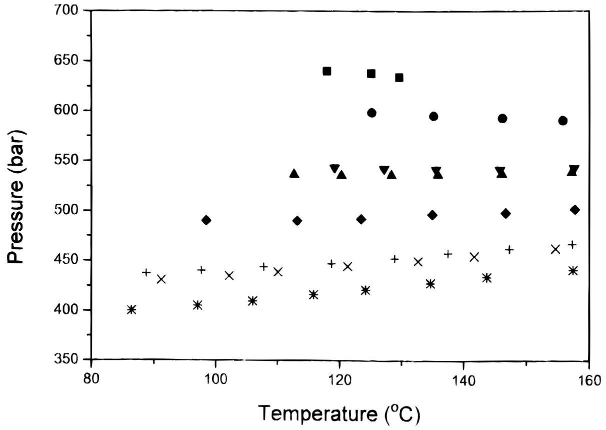

Figure 6. Cloud-point isopleths for poly(ethylene-*co*-octene) copolymers with different octene contents in propane. For characterization of copolymers, see Table 2. (●) P(E-*co*-O)-1; (▲) P(E-*co*-O)-2; (▼) P(E-*co*-O)-3; (◆) P(E-*co*-O)-4; (+) P(E-*co*-O)-5; (×) P(E-*co*-O)-6; (*) P(E-*co*-O)-7, (■) represents PE1484 (see Table 1).

cloud-point isotherms.[1] The cloud-point pressures evidently decrease with increasing branch length. Figure 6 shows that cloud-point pressures also decrease with increasing octene content, and hence with increasing branch frequency, for a series of poly(ethylene-*co*-octene) polymers (Table 2). This effect was also described by Hasch et al.[5] and by Chen et al.[11,15] The effects of branch length and branch frequency on the cloud-point pressures must therefore both be taken into consideration. Whereas a single plot based on branch frequency alone cannot correlate the cloud-point pressures of polymers with different branch lengths (Figure 7), such a plot can be made if it is based on branch density combined with branch length and expressed as wt % carbon in the branches (Figure 8).

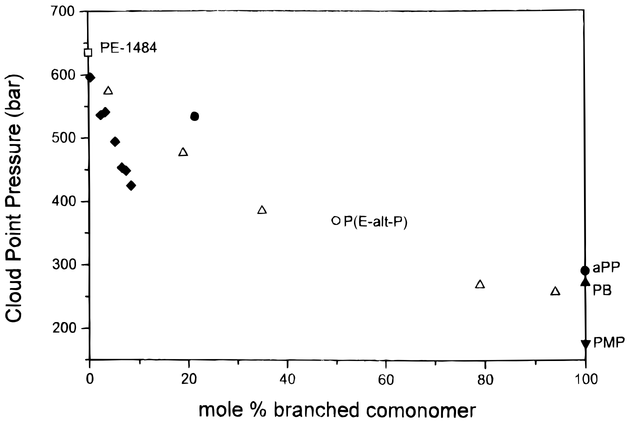

Figure 7. Plotted cloud-point pressures of polyolefins in propane as a function of branch frequency. Symbols for branch length are as follows: (□) unbranched; (●, ○) methyl; (▲, △) ethyl; (▼) butyl; (◆) hexyl. PE1484 is a high-density polyethylene; P(E-*alt*-P) is poly(ethylene-*alt*-propylene); aPP is atactic polypropylene; PB is poly(1-butene); PMP is poly(4-methyl-1-pentene); □ are the data of Condo et al.;[13] and ○, △ are the data of Chen et al.[15,16] (See Table 1).

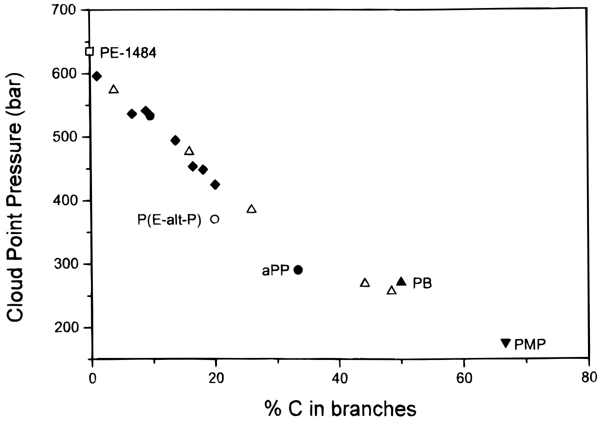

Figure 8. Correlation of cloud-point pressures of polyolefins in propane with wt % carbon in branches. Symbols for branch length are as follows: (□) unbranched; (●, ○) methyl, (▲, △) ethyl; (▼) butyl; (◆) hexyl. PE1484 is a high-density polyethylene; P(E-*alt*-P) is poly(ethylene-*alt*-propylene), aPP is atactic polypropylene; PB is poly(1-butene); PMP is poly(4-methyl-1-pentene); □ are the data of Condo et al.;[13] and ○, △ are the data of Chen et al.[15,16] (See Table 1).

Discussion

The modeling of ternary systems by the Sanchez–Lacombe equation, using a pseudobinary treatment for the solvent mixture, was attempted for the 1-propanol cosolvent systems. Simple temperature-dependencies for the ζ and δ parameters, as for the binary system,[1] could not be obtained, particularly, at the higher cosolvent concentrations. The success of Figure 8 in correlating the cloud-point pressures of branched polymers in propane solution is gratifying but probably has its limits in accuracy and scope. Although the trend observed of the lowering of the cloud-point pressure with increasing branching in the polymer is predicted by the Flory–Patterson theory, SAFT, and the solubility parameter theory, modeling even of a single characteristic point, like the LCEP, requires nearly always empirical adjustment parameters,[7,10,11] and special effects not taken into consideration by theory, such as randomness of branch distribution and correlations of molecular order,[7] appear to play a role. We therefore do not attempt to analyze the data obtained for the branched systems beyond the correlation of Figure 7.

Conclusions

The disappearance of the miscibility window between the UCEP and the LCEP, leading to the formation of an U-LCST locus containing a pressure minimum, which had been shown to occur upon increasing the molecular weight of the polymer,[10,14] can also be made to occur upon changing the quality of the solvent. In this particular case, it was accomplished by use of a binary solvent mixture in which the UCEP temperature of one component (the alcohol) was higher than the LCEP temperature of the other (propane), and by making the solvent richer in alcohol. Ternary systems containing the lower alcohol, ethanol, show the merging of the UCST and LCSTS loci, while the system containing the highest alcohol, 1-butanol, does not show a merging at any composition. In this latter case, the shift to higher temperatures of the UCST locus with an increase in the alcohol content is not sufficient to catch up with that of the LCST locus. In general, then, the alcohol acts as antisolvent, but it should be noted that, at high temperatures, alcohol enrichment can lead to a lowering of the cloud-point pressure. In this sense, alcohol becomes a promoter of polymer solubility at high temperature.

Cloud-point pressures for a variety of branched polyolefins and ethylene copolymers in supercritical propane correlate, to a first approximation, with the wt % carbon in the branches, which is a measure not only of branch frequency but also of branch length. Improved correlations may require that branch frequency and branch length be introduced as independent variables.

Acknowledgment. The financial support of the NSF through Grant 9202541 is gratefully acknowledged. We also appreciate the gift of polymer samples by Dr. S. J. Chen of Exxon Chemical, Annandale, NJ, by Dr. Howard Turner, Exxon Chemical, Baytown, TX, and by Mitsui Plastics.

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MA9615462