Phase Behavior Study of Poly(ethylene-*co*-octene) in normal-Hydrocarbons

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ABSTRACT : Cloud-point and bubble-point data to 170 °C and 50 bar are presented for four different solvents, normal pentane, n-hexane, n-heptane, and n-octane with poly(ethylene-*co*-42 wt% octene) (PEO_{42}) copolymer. The pressure-concentration isotherms measured for PEO_{42} - normal pentane have maximums at around 5 wt% of the copolymer concentrations in the solution. PEO_{42} - normal pentane system exhibits LCST-type phase behavior at temperatures greater than 130 °C. Below 120 °C, bubble-point type transitions are observed. However, the binary mixtures for PEO_{42} in n-hexane, n-heptane, and n-octane have only bubble-point type transitions at the pressure-temperature region investigated in this study. The single-phase region of PEO - alkane mixtures increases with the molecular size of alkane solvent due to the increasing dispersion interactions between PEO and the alkane.

Keywords : Poly(ethylene-co-octene), phase behavior, cloud-point, bubble-point

Ⅰ. Introduction

Ethylene-based copolymers have properties sufficiently different relative to the homopolymer low density polyethylene (LDPE) and high density polyethylene. For instance, poly(ethylene-*co*-acrylate) has superior thermal stability, stress crack resistance, and adhesive strength relative to LDPE.[1-2] Poly(ethylene-*co*-acrylic) and poly(ethylene-*co*-methacrylic acid) also have excellent strength, toughness, adhesive strength, and chemical resistance than PE does.[3-4] Poly(ethylene-*co*-vinyl acetate), another important ethylene-based copolymer, is recognized its clarity, low-temperature flexibility, stress-crack resistance, and impact strength.[5] All these excellent properties relative to PE increase with vinyl acetate content of the copolymer. Recently, poly(ethylene-*co*-octene) (PEO) is synthesized using metallocene catalyst. The long pending

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octene comonomer in PEO gives elastomeric characteristics to the copolymer. PEO can be used to improve impact property and resistance to low temperature brittleness. Since PEO is ethylene-based copolymer, its compatibility with thermoplastic olefins, such as PE and PP, is expected excellent.

The superior properties of the ethylene-based copolymers are consequence of the incorporation of a comonomer into PE. The extents of the different properties of the copolymers vary with the comonomer content in the backbone structure of the copolymers. While copolymerization occurs in a reactor, small change of comonomer concentration in the feed can cause a great change of comonomer composition in the copolymer. The physical and chemical properties of copolymer vary not only with molecular weight and degree of chain branching but also with composition of comonomer in the copolymer. Therefore the copolymerization may take place in heterogeneous phase. The phase behavior

of copolymer-solutions can be rather unpredictable since the properties of the copolymer greatly vary during copolymerization. It is important to know the location of the phase boundaries for copolymer solutions in order to avoid potential fouling problems or runaway reactions which may occur if a two-phase region is allowed to form inside the reactor. Also information on the phase behavior of copolymer solutions is required to efficiently separate product copolymers from unreacted monomers and solvent recycled to the reactor.

This paper presents experimental investigation about the phase behavior of four PEO - normal alkane systems. PEO has 42 wt% of octene repeat unit in the backbone structure, which the relatively long octene unit endows elastomeric characteristic to PEO. First we determined the effect of PEO

concentration on the cloud-point behavior in normal pentane. Then the phase behavior for PEO is investigated in n-hexane, n-heptane, and n-octane that the all are non-polar solvents and have simple molecular structures.

II. Experimental

Figure 1 shows the schematic diagram of the experimental apparatus used in this study. Cloud-point curves are obtained using a high-pressure, variable-volume cell, which has a 1.59 cm I.D., an O.D. of 7.0 cm, and a working volume of ~28 cm^3. A 1.9 cm thick sapphire window is fitted in the front part of the cell to allow visual observation of the phases. Typically 350 $\pm$ 2 milligrams of polymer are loaded into the cell that is then purged at room
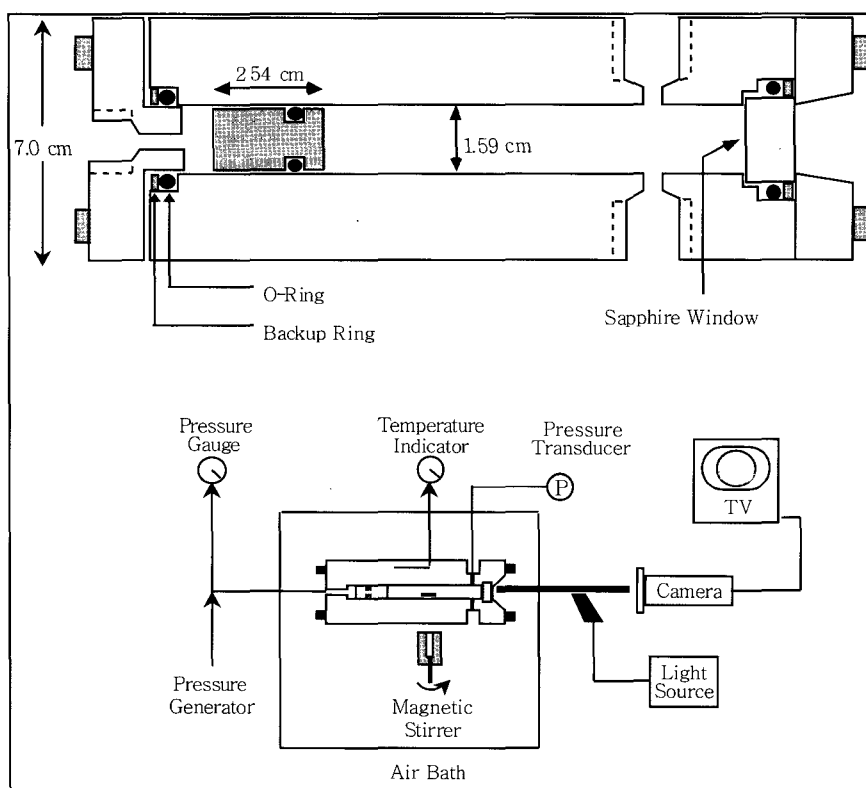

Figure 1. Schematic diagram of the experimental apparatus used to measure cloud-point and bubble-point in this study.

temperature with nitrogen at 3 to 6 bar to remove any entrapped air. Generally 6 to 7 $\pm$ 0.020 grams of solvent are transferred into the cell using a syringe. The mixture is compressed to the desired pressure with an internal piston that is moved using water displaced by a high-pressure generator. Before compressing the mixture, nitrogen is removed through the top port of the cell by moving the piston to window direction. The pressure of the mixture is measured with a Konics pressure transducer (model PT-3300, 0 to 49 bar, accuracy $\pm$ 0.3%) directly connected to the cell. The temperature of the cell is measured using a platinum-resistance thermometer (Thermometrics Corp., Class A) and a digital multimeter (Keithley Instruments, Inc., Model 195T, accuracy $\pm$ 0.03%). The system temperature is typically maintained to within $\pm$ 0.2 ℃. The mixture in the cell can be viewed on a video monitor using a camera coupled to a borescope (Olympus Corp., model R080-024-000-50) placed against the outside of the sapphire window. A fiber pipe connected to a high-density illuminator (Dolan-Jenner Industries, Inc., model 180) and to the borescope is used to transmit light into the cell. The solution in the cell is well mixed using a magnetic stir bar activated by an external magnet beneath the cell.

The cloud-point pressure is defined as the point at which the mixture becomes so opaque that it is no longer possible to see the stir bar in the solution. The cloud points are measured at least twice at each temperature, and are typically reproducible to within $\pm$ 0.01 bar. Cloud-point pressures of polymer solutions have maxima between 2 and 11 wt% polymer. Therefore, in this study cloud-point pressures are measured at fixed copolymer concentration around 5 wt% except obtaining pressure-concentration (P-x) diagram for PEO - normal pentane system.

Ⅲ. Materials

The PEO$_{42}$ were obtained from DuPont Dow Elastomers Corporation. Table 1 shows the pro-

Table 1. Physical Properties of Poly(ethylene-*co*-42 wt% octene) Used in This Study.[6]

| Material	Octene Content (wt%)	Density (g/cm^3)	Melt Index 190℃, 2.16kg (dg/min)	T$_m$ (℃)	T$_g$ (℃)
PEO$_{42}$	42	0.864	13	50	-59

Table 2. Physical Properties of normal Pentane, n-Hexane, n-Heptane, and n-Octane Solvents Used in This Study.[7-8]

| Properties	n-pentane	n-hexane	n-heptane	n-octane
T$_c$ (K)	470.0	508.0	540.0	569.0
P$_c$ (bar)	33.7	30.3	27.4	24.6
ρ_c (g/cm^3)	0.232	0.234	0.234	0.233
$\alpha \times 10^{25}$ (cm^3)	100	118	136	142

perties of PEO$_{42}$ used in this study.[6] Normal pentane, n-hexane, n-heptane and n-octene (all CP grade, 99.0% minimum purity) were obtained from Sigma-Aldrich Company. All of the solvents were used as received. Table 2 lists physical properties of solvents used in this study.[7-8]

Ⅳ. Results and Discussion

The effect of PEO$_{42}$ concentration on the location of the cloud-point curve was determined for normal pentane. Figure 2 shows the effect of PEO$_{42}$ concentration on the phase behavior of PEO$_{42}$ - normal pentane system in pressure-temperature space. At temperatures below 120 ℃, PEO$_{42}$ - normal pentane system has bubble-point type transitions. In the pressure-temperature space above each curve, PEO$_{42}$ is homogenously dissolved in n-pentane. As pressures decrease below 10 bar, the single phase separates to two phases, vapor phase containing almost no PEO$_{42}$ and liquid phase. The liquid phase is supposed to have almost identical amount of PEO$_{42}$ to the total PEO$_{42}$ in the homogeneous PEO$_{42}$ - normal pentane mixture since PEO$_{42}$ is not expected dissolved in the less dense normal pentane vapor at these low pressures. The pressures that
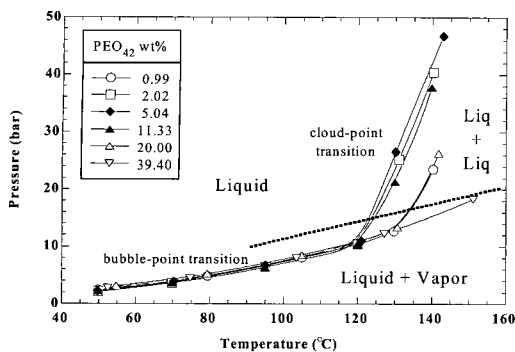
Figure 2. The effect of PEO$_{42}$ concentrations on the phase behavior of PEO$_{42}$ - normal pentane mixture. In lower region than dashed line, one liquid phase separates liquid and vapor phases below the each curve (bubble-point type transition), whereas in the upper region one liquid phase separates two liquid phases below the each curve (cloud-point type transition).
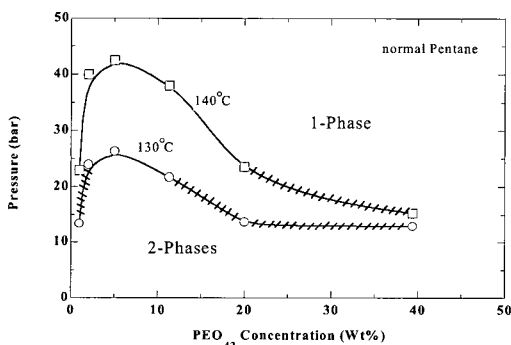
Figure 3. Pressure-concentration diagram for the PEO$_{42}$ - normal pentane mixture at 130 and 140 ℃. The x-shaped lines represent bubble-point type transition curves. Below x-shaped line, the PEO$_{42}$ - normal pentane mixture separates to liquid and vapor phases. Below solid line, the mixture separates to two liquid phases.

bubble-point transitions occur are not distinguishable between the curves at different PEO$_{42}$ concentrations, since differences in the transition pressures are in the error range of the measuring device used in this study. As temperatures increase above 120 ℃, transition type changes to cloud-point type transition. PEO$_{42}$ fells out of the homogeneous solution and the copolymer rich liquid phase separates from normal pentane rich liquid phase. Notice that cloud-point transitions take place at

higher temperatures and pressures if PEO$_{42}$ concentration is less than 2 wt% and greater than 11 wt%.

Using the data in Figure 2, P-x diagram of PEO$_{42}$ in normal pentane is plotted at various temperatures. Figure 3 shows P-x isotherms for the PEO$_{42}$ - normal pentane at 130 and 140 ℃. "X"-shaped lines in the diagram are not cloud-point curves. The x-shaped lines indicate that bubble-point type transitions occur along the curves, which the cloud-point is expected to locate at a little higher pressures than the bubble-point locates The P-x curves of the PEO$_{42}$ - normal pentane system have plateau between the copolymer concentrations of 2 to 11 wt% and have the maximums near 5 wt% polymer in the solution, suggesting that at near 5 wt% of the copolymer the cloud-point pressures are reasonably close to the true mixture-critical point.[9-12] The same characteristic P-x shapes are observed in many homopolymer and copolymer systems.[10-14]

Figure 3 also shows that the single-phase region deceases with increasing temperatures. (LCST-type phase behavior) However, the copolymer concentrations having cloud-point transition broaden to 1 ~ 20 wt% at 140 ℃ as compared to the concentrations at 130 ℃, 2 ~ 11 wt%. Therefore it is expected that at high temperatures the complete P-x loops can be obtained for PEO$_{42}$ - normal pentane mixture.

Figure 4 shows the pressure-temperature diagram for PEO$_{42}$ in n-pentane, n-hexane, n-heptane, and n-octane. Except the curve for PEO$_{42}$ - normal pentane mixture, all curves in n-hexane, n-heptane, and n-octane have bubble-point type transitions at temperatures less than 170 ℃. PEO$_{42}$ - normal pentane system exhibits liquid to liquid-liquid transition at temperatures greater than 120 ℃, which means the single-phase region is abruptly shrunk as compared to the single-phase region for PEO$_{42}$ in the higher normal alkanes. Figure 4 also shows that the single-phase region for PEO$_{42}$ - normal alkane system enlarges with the molecular size of the normal alkane. Since PEO and n-alkanes are all
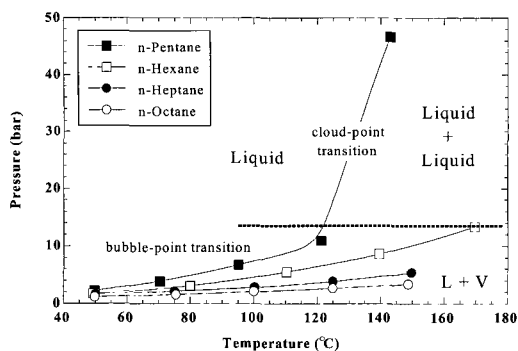
Figure 4. Pressure-temperature diagram for the PEO_{42} in normal pentane, n-hexane, n-heptane, and n-octane. Below dashed line, the PEO_{42} - normal alkane mixtures have bubble-point type transitions. Above dashed line, the mixture has cloud-point type transitions.

non-polar, the intermolecular potential between the copolymer and alkane is fundamentally derived from dispersion forces. Therefore, the phase behavior for the PEO - alkane system is greatly influenced by the dispersion forces that increase with polarizability. As shown in table 2, polarizability of alkane increases with the molecular size of the alkane. The increase of PEO solubility in the higher alkanes is the consequence of the increasing polarizability.

V. Conclusions

In the pressure-temperature space, PEO_{42} - normal pentane system has the maximum around 5 wt% copolymer in solution, suggesting that at 5 wt% of the copolymer the cloud-point pressures for PEO_{42} - normal alkane systems are reasonably close to the true mixture-critical point. As the molecular size of alkane solvent increases, the single-phase region of PEO - alkane mixtures increases. Since PEO and n-alkane are all non-polar, the increase in the solubility of PEO in higher normal alkanes results from the dispersion forces increasing with the molecular size of the alkane.

Acknowledgments

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