

Phase Behavior of Binary and Ternary Mixtures of Poly(ethylene-co-octene)–Hydrocarbons

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ABSTRACT: Poly(ethylene-co-octene) (PEO) is a new thermoplastic elastomer that has the wide variation in mechanical, thermal, optical, and elastomeric properties. The variety of PEO properties results from incorporation octene comonomer in polyethylene backbone. Because of the wide difference in the copolymer properties, it is important to know the phase boundary to optimize the copolymerization and separation processes of PEO. The cloud-point and bubble-point curves for poly(ethylene-co-15.3 mol % octene) (PEO₁₅), which has 15.3 mol % octene repeat unit in the backbone structure, were determined in *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane. The miscibility of PEO₁₅ in normal alkane enlarges with the size of the normal alkane

because of the increasing dispersion interactions related to polarizability. The phase behavior for the ternary systems of PEO₁₅–ethylene–octene was also investigated, where ethylene and 1-octene are monomer and comonomer of PEO. As the concentration of ethylene in the ternary mixture increases, the miscibility of PEO₁₅ dramatically decreases. Adding 64 wt % ethylene into the ternary mixture increases the pressure, dissolving PEO₁₅ up to 1000 bar. In pure ethylene, PEO₁₅ was not dissolved up to 1900 bar, 160°C. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 161–165, 2005

Key words: phase behavior; miscibility; cloud-point; elastomer; high pressure

INTRODUCTION

Poly(ethylene-co-octene) (PEO) is a new polyolefin elastomer developed by using metallocene catalyst. Because PEO is an ethylene-based copolymer, its compatibility with thermoplastic olefins, such as polyethylene and polypropylene is excellent. The elastomeric characteristics of PEO is a consequence of incorporation of the long octene comonomer in the backbone of PEO, which pending the hexane group reduces the crystallinity and increases the flexibility of the copolymer. PEO can be used to improve impact property and resistance to low-temperature brittleness. The properties of PEO vary with the octene content in the backbone structure of the copolymer. Although 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. The phase behavior of copolymer solutions can be rather unpredictable because the properties of the copolymer vary greatly during copolymerization.

Therefore, the copolymerization may take place in heterogeneous phase. It is important to know the location of the phase boundaries for copolymer solutions to avoid potential fouling problems and the product quality problems, 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 copolymer from unreacted monomers and solvent recycled to the reactor.

The location of the cloud-point curve in pressure–temperature (P–T) space for the different polymer–solvent mixtures depends on the intermolecular forces in operation between solvent–solvent, solvent–polymer segment, and polymer segment–segment pairs in solution, and on the free-volume difference between the polymer and the solvent. Intermolecular potential energy of an *i*–*j* pair of segments or molecules, Γ_{ij} , depends on the physical properties of the polymer–solvent pair by using the following simplified expression provided by Prausnitz et al.¹

$$\Gamma_{ij} = -C_1 \frac{\alpha_i \alpha_j}{r^6} - C_2 \frac{\mu_i^2 \mu_j^2}{r^6 kT} - C_3 \frac{Q_i^2 Q_j^2}{r^{10} kT} + \text{Complex Formation} \quad (1)$$

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where the first term on the right-hand side, written in terms of the polarizabilities, α_i , represents dispersion interactions; the second term, written in terms of the

TABLE I
Properties of Poly(Ethylene-co-Octene) Used in this Study

Polymer	Octene content ³ (mol %)	Density (g/cm ³)	T_m (°C)	T_g (°C)	M_n	M_w	M_w/M_n
PEO ₁₅	15.3	0.86	50	-59	64,810	135,500	2.09

dipole moments, μ_i , represents dipolar interactions; the third term, written in terms of the quadrupole moments, Q_i , represents quadrupolar interactions; and the final term, written symbolically, represents hydrogen-bonding interactions. In this equation, r is the distance between the molecules, k is Boltzmann's constant, C_{1-3} are fixed constants, and T is the absolute temperature. Much smaller induced polar forces are neglected from consideration here. The key indicator of whether segment-solvent interactions are favorable is the interchange energy of mixing i - j pairs, ω , given by

$$\omega = z \left[\Gamma_{ij} - \frac{1}{2}(\Gamma_{ii} + \Gamma_{jj}) \right] \quad (2)$$

where z is the number of dissimilar solvent-segment pairs. The choice of a suitable solvent for a polymer depends on the physical properties of the solvent that will intimately affect the interchange energy. It is important to be aware of how the quality of the solvent depends on its density. Lee² shows that the internal energy of a mixture, u_{total} , depends on the density of the solvent for a homogeneous-isotropic solution

$$\frac{u_{\text{total}}}{kT} \approx A_0 + A_1 \rho(T, P) \int \Gamma(r) g(r) r^2 dr \quad (3)$$

where $\Gamma(r)$ is the pair potential energy of ii , jj , and ij interactions, $g(r)$ is the radial distribution function, A_0 and A_1 are constants that depend on the properties of the components in solution, and ρ is the solvent density if the solution is moderately dilute in solute. This simplified formula provides an explanation that, to a first approximation, the solubility of a solute in a solvent is proportional to density. Equations (1), (2), and (3) provide some insight when choosing an appropriate solvent for a polymer. It is important to match the physical properties of the solvent with those of the solute so that the interchange energy is of sufficient strength to insure finite polymer solubilities. Also, eq. (1) shows that if polymer and solvent are nonpolar, the interchange energy can be adjusted only by polarizability through the Γ_{ii} and Γ_{jj} values to allow for increased solubility of the polymer.

In this article, the effect of PEO concentrations on the cloud-point behavior is first determined with n -pentane in P-T space. The effect of solvent quality on

the phase behavior of binary PEO-hydrocarbon systems is demonstrated by switching solvent from n -butane to n -octane. Because normal alkanes and PEO are nonpolar, the phase behavior of the binary mixtures is governed by the polarizability and density of solvents. Incorporation of octene into polyethylene changes the polymer architecture from highly structured polyethylene to highly branched copolymer with octene comonomer. The highly branched structure reduces the free volume of the polymer and increases the miscibility of PEO in a solvent. When nonpolar ethylene repeat units with a polarizability of $42.5 \times 10^{-25} \text{ cm}^3$ are replaced by octene repeat units, the crystallinity of the polymer is reduced, so the contribution of dispersion forces to polymer-polymer interactions. In addition, octene with a polarizability of $153.3 \times 10^{-25} \text{ cm}^3$ endows increasing dispersion interaction with a solvent, which is favorable to dissolve the polymer. The phase behaviors of PEO are also investigated in the mixture of ethylene and 1-octene that are the monomer and the comonomer of PEO.

EXPERIMENTAL

The PEO₁₅ were obtained from DuPont Dow Elastomers Corp. Table I shows the properties of PEO₁₅ used in this study. n -Butane, n -pentane, n -hexane, n -heptane, n -octane, and n -octene (all CP grade, 99.0% minimum purity) were obtained from Sigma-Aldrich Co. Ethylene with 99.9% purity was obtained from Korea Standard Gas. Table II shows the properties of the solvents.

TABLE II
Physical Properties of Hydrocarbon Solvent Used in This Study^{4,5}

Substance	$\alpha \times 10^{25} \text{ (cm}^3\text{)}$	$T_c \text{ (}^\circ\text{C)}$	$P_c \text{ (bar)}$	$\rho_c \text{ (g/cm}^3\text{)}$
n -Butane	82.0	151.9	38.0	0.228
n -Pentane	99.9	196.6	33.7	0.232
n -Hexane	119.0	234.5	30.3	0.228
n -Heptane	137.0	267.1	27.4	0.234
n -Octane	159.0	295.8	24.9	0.232
c -Pentane	91.5	238.6	45.1	0.270
c -Hexane	100.9	280.9	40.7	0.273
Ethylene	42.5	9.4	50.6	0.214
1-Octene	153.3	293.5	26.8	0.236

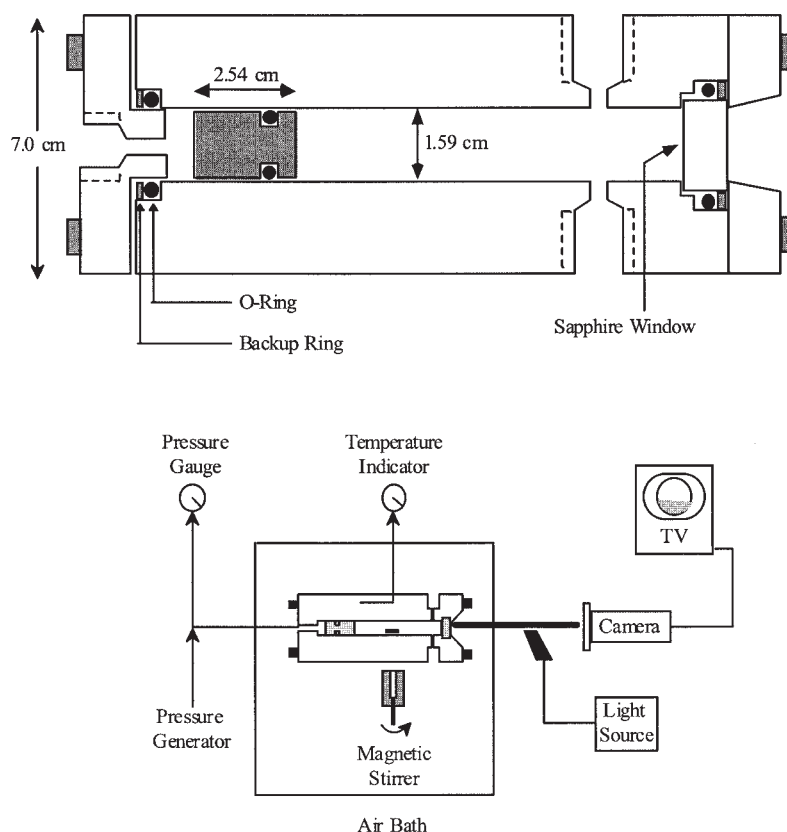


Figure 1 Schematic diagram of the experimental apparatus used to measure cloud-point and bubble-point in this study.

Cloud points are obtained by using a high-pressure, variable-volume view cell shown in Figure 1. The view cell, which is constructed of high nickel content stainless steel, has an ID of 1.59 cm, an OD of 7.0 cm, and a working volume of $\sim 22 \text{ cm}^3$ and is fitted with a 1.9-cm-thick sapphire window. Experimental procedures are described in detail elsewhere.⁶⁻⁸

RESULTS

Figure 2 shows the effect of PEO₁₅ concentration on the phase behavior of PEO₁₅-normal pentane mixture. In the region below the dashed line of Figure 2, PEO₁₅-normal pentane system has bubble-point-type transitions. As pressures decrease < 10 bar, the homogeneous mixture of PEO₁₅-normal pentane separates to two phases: liquid phase and vapor phase containing almost no PEO₁₅. The liquid phase is supposed to have almost an identical amount of PEO₁₅ to the total PEO₁₅ in the homogeneous PEO₁₅-normal pentane mixture because PEO₁₅ is not expected to dissolve in normal pentane vapor at these low pressures. In the region above the dashed line, PEO₁₅-normal pentane mixture has cloud-point type transition. PEO₁₅ dropped out of the homogeneous solution and the single liquid phase separates into two liquid phases, copolymer-rich liquid phase and normal pentane-rich

liquid phase. It should be noted that cloud-point transitions take place at higher temperatures and pressures if PEO₁₅ concentration is < 2 wt % and > 11 wt %.

Figure 2 also shows that the P-x curves of the PEO₁₅-normal pentane system have a plateau be-

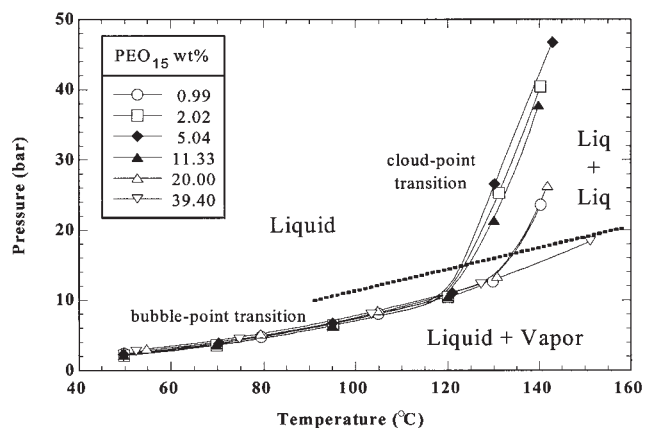


Figure 2 The effect of PEO₁₅ concentrations on the phase behavior of PEO₁₅-normal pentane mixture.⁶ In the region below the dashed line, homogeneous phase separates one liquid phase and one vapor phase (bubble-point type transition), whereas in the upper region, single liquid phase separates two liquid phases below the each curve (cloud-point-type transition).

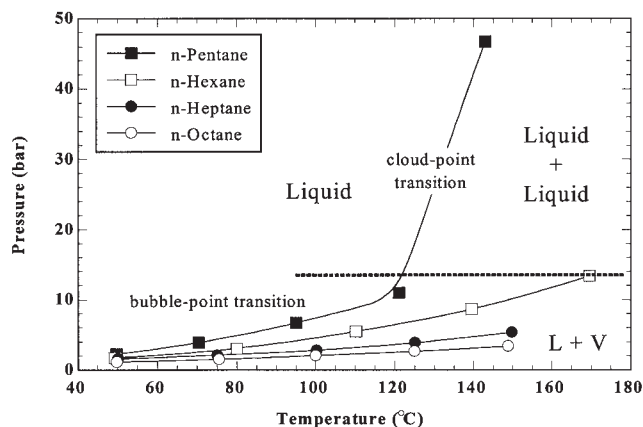


Figure 3 Pressure–temperature diagram for the PEO₁₅ in normal pentane, *n*-hexane, *n*-heptane, and *n*-octane. Below the dashed line, the PEO₁₅–normal alkane mixtures have bubble-point type transitions. Above the dashed line, the mixture has cloud-point-type transitions. The concentrations of PEO₁₅ in the mixtures are ~5 wt %.

tween the copolymer concentrations of 2 to 11 wt %. The P-x curve has the maximum near 5 wt % polymer in solution, suggesting that at a near 5 wt % of the copolymer the cloud-point pressures are reasonably close to the true mixture-critical point.^{7,9–11} The same characteristic P-x shapes are observed in many homopolymer and copolymer systems.^{9–13} Therefore, polymer concentrations are typically maintained around 5 wt % in this study.

Figure 3 shows the effect of solvent quality on the phase behavior of PEO₁₅ in normal alkanes. At temperatures < 170°C, binary mixtures of PEO₁₅ in *n*-hexane, *n*-heptane, and *n*-octane have bubble-point-type transitions. However, the PEO₁₅–normal pentane mixture exhibits liquid (L) to liquid–liquid (L-L) transition at temperatures > 120°C. The single-phase region abruptly decreases with increasing temperatures. Figure 3 also shows that the single-phase region for PEO₁₅–normal alkane system enlarges with the molecular size of the normal alkane. PEO and *n*-alkane are all nonpolar. Therefore, the phase behavior for the PEO–alkane system is fundamentally influenced by the dispersion interaction that is directly related to polarizability, as shown in eq. (1) and Table II.

Figure 4 exhibits the P-T diagram of PEO₁₅ in cyclopentane and cyclohexane. All transitions are bubble-point-type. As temperature increases, the homogeneous binary mixtures of PEO₁₅ and the cycloalkanes separate one PEO₁₅-rich liquid phase and one solvent-rich vapor phase. The phase behavior is similar to the phase behavior in normal alkane solvents. However, the single-phase regions are greater than the regions in the homologous normal alkanes. L to L-L transition does not occur even at 150°C. Because polarizability of cycloalkane is less than the homologous normal alkane, the enhanced miscibility of PEO₁₅ in cycloalkane

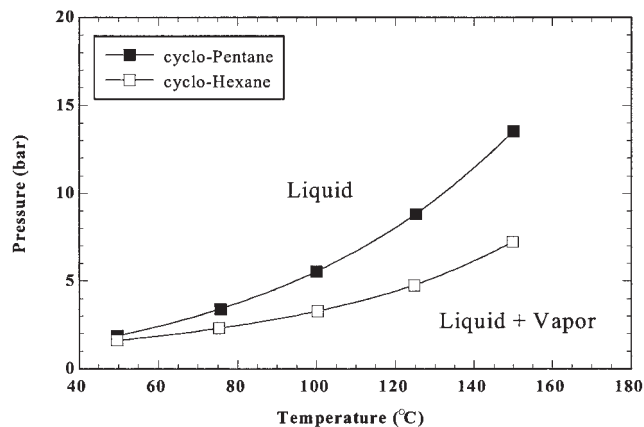


Figure 4 Pressure–temperature diagram for the PEO₁₅ in cyclopentane and cyclohexane. Homogeneous liquid phase separated to one liquid and one vapor phase along the curve. The concentrations of PEO₁₅ in the mixtures are around 5 wt %.

is supposed to be the consequence of higher density of cycloalkane compared to normal alkane.

Figure 5 shows the phase behavior of ternary PEO₁₅–ethylene–1-octene mixtures. The cloud-point curves for the ternary mixtures were measured at PEO₁₅ concentrations of 5.0 ± 0.3 wt %. Ethylene and 1-octene are monomer and comonomer of PEO. PEO₁₅ was dissolved in 1-octene < 5 bar. The enhanced miscibility of PEO₁₅ in 1-octene, which is similar to the miscibility in *n*-octane, is the consequence of the large polarizability of 1-octene. However, the miscibility of PEO₁₅ decreases with increasing ethylene concentrations in the ternary mixture. Adding 25 wt % ethylene into the PEO₁₅–1-octene mixtures dramatically reduces the miscibility of PEO₁₅ in the mixtures. The cloud-point pressures increase up to 50–200 bar higher than the pressure dissolving PEO₁₅ in pure 1-octene. Adding 64 wt % ethylene shifts the cloud-

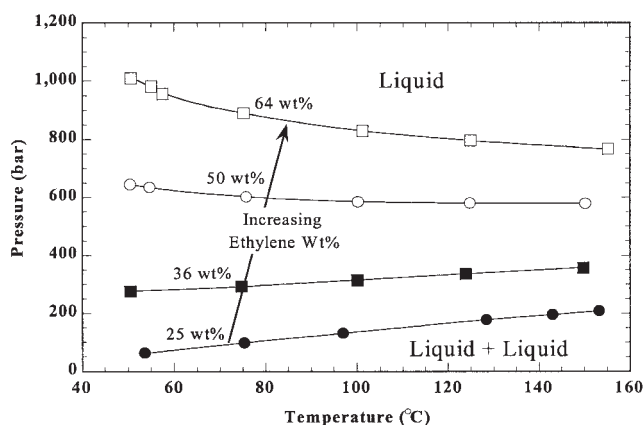


Figure 5 Cloud-point curves for PEO₁₅–ethylene–1-octene ternary mixtures. The concentrations of PEO₁₅ in the ternary mixtures are 5.0 ± 0.3 wt %.

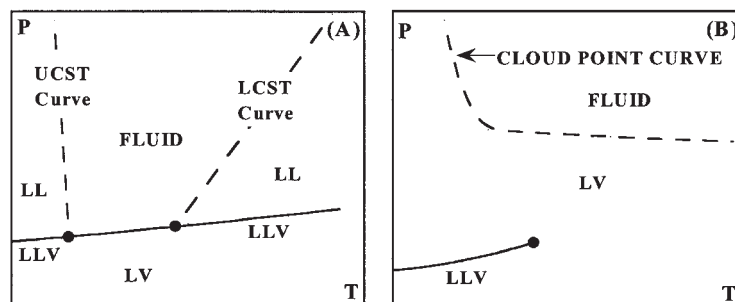


Figure 6 The typical P-T diagrams for polymer-solvent systems: (A) polymer-solvent type-III system; (B) polymer-solvent type-IV system.¹⁴

point pressures from 4 to 1000 bar. The reduced solubility of PEO₁₅ by ethylene results from the low polarizability of ethylene. PEO₁₅ was not dissolved in pure ethylene even at 160°C and 1900 bar. Figure 5 also shows that PEO₁₅-ethylene-1-octene mixtures have LCST-type phase behavior at ethylene concentration < 36 wt %, whereas the ternary mixture has UCST-type phase behavior at the ethylene concentration > 50 wt %. The phase behavior changed from Type III to Type IV as ethylene concentrations increase, of which the typical phase diagrams are shown in Figure 6.

CONCLUSION

In the P-x diagram, PEO₁₅-normal pentane system has a plateau between the copolymer concentrations of 2-11 wt %, suggesting that near 5 wt % of the copolymer the cloud-point pressures are reasonably close to the true mixture-critical point. The miscibility of PEO₁₅ in normal alkane enlarges with the molecular size of the normal alkane. Because PEO and *n*-alkane are all nonpolar, the raised miscibility of PEO is the consequence of the enhanced dispersion interactions directly related with polarizability. In cycloalkane solvents, the single-phase regions are greater than the regions in the homologous normal alkanes. Because polarizability of cycloalkane is less than the homologous normal alkane, the enhanced miscibility of PEO₁₅ results from the high density of cycloalkane compared to normal alkane.

The single phase for PEO₁₅-ethylene-1-octene ternary mixture decreases with increasing ethylene con-

centrations due to the low polarizability of ethylene. The phase behavior of the ternary mixture changed from LCST-type (Type III) to UCST-type (Type IV) as ethylene concentrations increase.

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