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Phase Behavior of Poly(ethylene-*co*-norbornene) - Hydrocarbon Binary Systems at High Pressures

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Introduction

Poly(ethylene-*co*-norbornene) (PEN) is one of the major cyclo olefin copolymers that have potential applications for optical storage devices, such as high density compact disk and digital video disk. PEN also has the potential to be used in optical fiber, protecting sheets for displays, pick-up lenses for CD and DVD, and lenses for cameras and projection displays.[1-3] Because of the wide variation in the copolymer properties, phase behavior information is essential to ensure that copolymerization takes place under homogeneous phase conditions to obtain a high yield of copolymers. The information is also needed to efficiently separate product copolymers from unreacted monomers and solvent recycled to the reactor. In this study, we present the cloud-point behavior for binary mixtures of poly(ethylene-*co*-53 mol% norbornene) (PEN_{53}) and hydrocarbon solvents to 170 °C and 1,400 bar. PEN_{53} contains 53 mol% of norbornene repeat unit in the backbone structure. The hydrocarbon solvents used in this study were four normal alkanes (n-pentane, n-hexane, n-heptane, n-octane) and three cyclo-alkanes (c-pentane, c-hexane, c-heptane).

Experimental

Figure 1 and Table 1 show the molecular structure and properties of PEN_{53}, respectively. Normal-pentane, n-hexane, n-heptane, and n-octane were obtained from Aldrich Chemical Company. Cyclo-pentane, cyclo-hexane, and cyclo-heptane, which have cyclic molecular structure, were also obtained from Aldrich Chemical Company. All hydrocarbon solvents have a minimum purity of 99.5 % and were used as received. Table II lists properties of hydrocarbon solvents used in this study.[4-6]

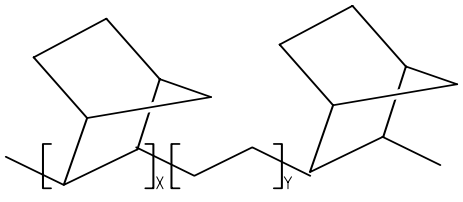

Fig. 1. Molecular structure of poly(ethylene-*co*-norbornene). X and Y represent the number of repeat unit in the backbone structure.

Cloud points measured at a fixed copolymer concentration of 5~10 wt%, which is the expected maximum in the pressure-composition curve,[7,8] are obtained using a high-pressure, variable-volume view cell described in detail elsewhere.[7,9]

Table I. Properties of Poly(ethylene-*co*-53 mol% norbornene) Used in This Study

T_g (°C)	M_n	M_w	Polydispersity (M_n / M_w)	Norbornene Content (mol%)
156.3	45,800	111,300	2.4	53

Table II. Properties of Hydrocarbon Solvents Used in This Study [4-6]

Property	n-pentane	n-hexane	n-heptane	n-octane	c-pentane	c-hexane	c-heptane
T_c (°C)	196.9	234.9	266.9	295.8	238.6	280.9	331.1
P_c (bar)	33.7	30.4	27.4	24.9	45.1	40.7	38.2
ρ_c(g/cm^3)	0.232	0.234	0.234	0.232	0.270	0.272	0.278

Results and Discussion

Figure 2 shows the pressure-temperature (P-x) isotherms of PEN_{53} in n-hexane at 60, 90 and 120 °C. The P-x isotherms have a maximum at the concentrations around 5 wt% PEN_{53}, suggesting that at these polymer concentrations, the cloud-point pressures are reasonably close to the true mixture-critical point. At 90 and 120 °C, the P-x isotherms for the mixture of PEN_{53} and n-hexane are relatively flat between copolymer concentrations of 5 to 12 wt%. Therefore, cloud-point pressures are measured at fixed PEN_{53} concentrations 5 ~ 12 wt% in this study.

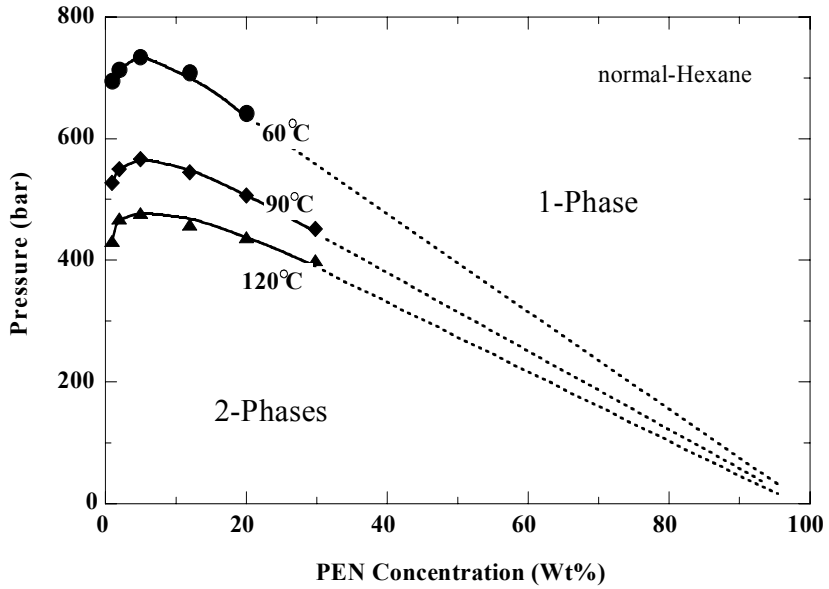

Fig. 2. Pressure-composition diagram for the PEN_{53} (53 mol% norbornene) n-hexane systems at 60, 90, and 120 °C.

Figure 3 shows the cloud-point curves for PEN_{53} in n-pentane, n-hexane, n-heptane, and n-octane. In pressure-temperature space, the cloud-point curves all have negative slopes that decrease in pressure with increasing temperatures. In pressure-temperature (P-T) space, a

single-phase region of PEN_{53} enlarges as the molecular size of n-alkane increases. However, the effect of molecular size of n-alkane gradually diminished. For example, the cloud-point pressure for PEN_{53} - n-hexane mixture is lower than the pressure for PEN_{53} - n-pentane mixture upto 500 bar. With changing solvent from n-heptane to n-octane, the decrease in the cloud-point pressure was reduced to ~ 100 bar. The cloud-point curve for PEN_{53} in n-heptane locates a little lower than the curve in n-hexane at temperatures higher than 80 ℃. The location of the two curves switched at 80 ℃ in P-T space. It was not try to identify what causes the two cloud-point curves switch at 80 ℃.

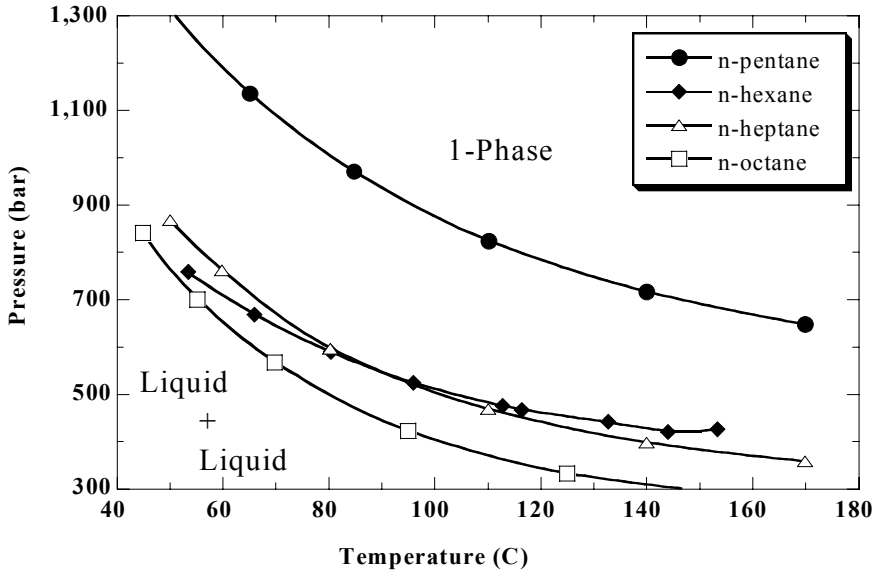

Fig. 3 Cloud-point curve for PEN_{53} in n-pentane, n-hexane, n-heptane, and n-octane.

Figure 4 shows the phase behavior for PEN_{53} in c-pentane, c-hexane, and c-heptane. Bubble-point type transition was observed for all PEN_{53} - c-alkane mixtures. Again, the effect of the molecular size on the solubility of PEN_{53} was observed in c-alkanes. In all the c-alkane solvents, PEN_{53} was dissolved below 10 bar whereas the copolymer was dissolved at pressures greater than at least 300 bar in n-alkanes. The enhanced solubility of PEN_{53} in c-alkanes is likely consequence of a relatively high density of c-alkane. Moreover, as shown in figure 1, PEN_{53} has cyclic-shape repeat unit (norbornene unit) in the backbone structure. The similarity of molecular structure between cyclo-alkane and norbornene repeat unit is favorable to dissolve the copolymer.

Notice that PEN_{53} - c-pentane system has bubble-point transition at temperatures lower than 150 ℃. However, at temperatures over 150 ℃ the pressures dissolving PEN_{53} abruptly increase and phase transition changed to cloud-point transition type. LCST-type phase behavior was observed for PEN_{53} - c-pentane system. It is expected that Liquid-Liquid-Vapor (L-L-V) coexistence line locates around 150 ℃. No attempt accomplished to determine L-L-V coexistence line.

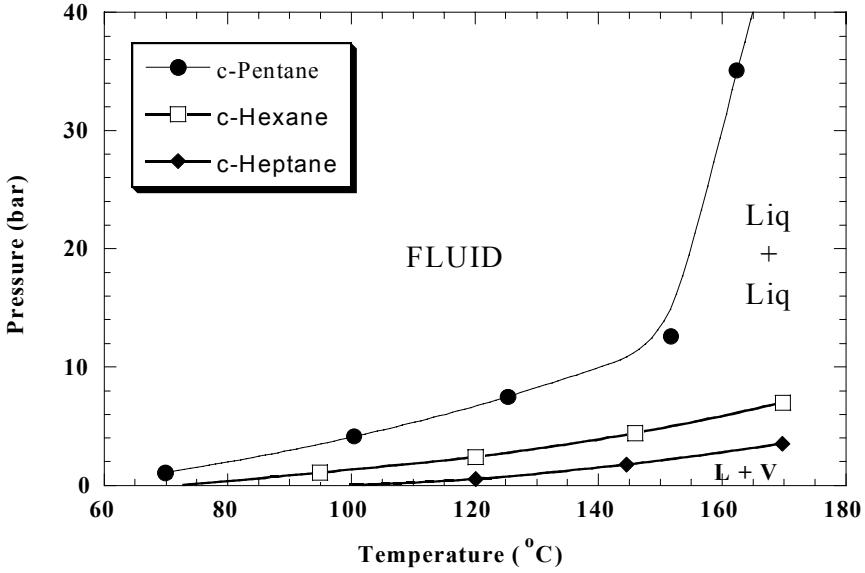

Fig. 4 Cloud-point curve for PEN_{53} in c-pentane, c-hexane, and n-heptane.

Conclusions

The solubility of PEN_{53} increases with the molecular size of hydrocarbon solvent. However, the effect of alkane size on the solubility diminished as the molecular size of hydrocarbon increases. A single-phase region of PEN_{53} in c-alkane is much larger than the region in n-alkane due to relatively high density of c-alkane and the similarity of molecular structure between PEN_{53} and c-alkane.

References

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