

# High-pressure Phase Behavior of Ethylene Copolymer – Hydrocarbon Systems

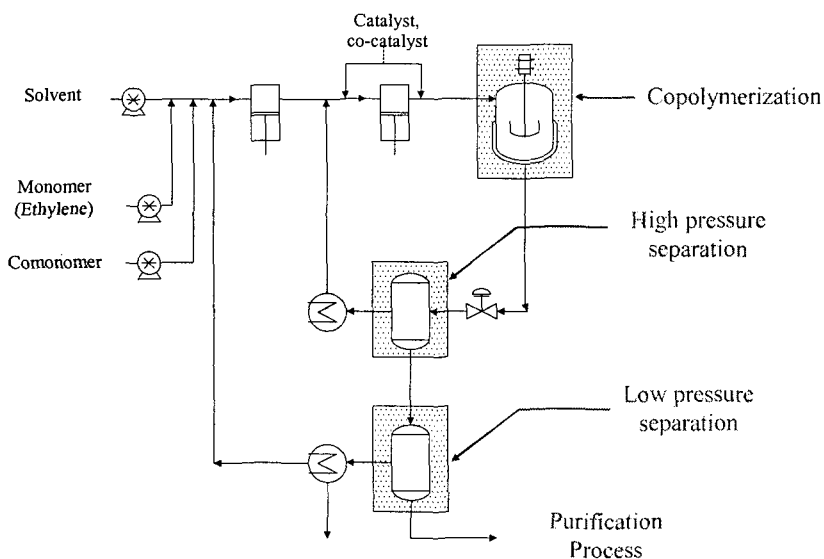
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## Where phase behavior information need?



### Which phase is preferred?

During Copolymerization: Homogeneous Phase

— Product Quality Control

{ Comonomer Composition and Molecular Weight Control }

After Copolymerization: Heterogeneous Phase

— Economical Separation Process

{ Separating copolymer, unreacted monomer, comonomer, solvent, and catalysts }

### Molecular Thermodynamics Polymer-Solvent mixtures

$$\Delta G_{\text{mixing}} = \Delta H_{\text{mixing}} - T\Delta S_{\text{mixing}}$$



$$\Delta H_{\text{mixing}} = \Delta U_{\text{mixing}} + \Delta(PV)_{\text{mixing}}$$

$$\Delta G_{\text{mixing}} \approx \Delta U_{\text{mixing}} - T\Delta S_{\text{mixing}}$$

### Enthalpy Contribution

Intermolecular Potential →  $\Delta U$

- Polarizability
- Dipole & Quadrupole Moments
- Polymer Structure, Steric Hindrance

Pressure increases the probability of interaction, it is used to “tune” the strength of interactions.



$$\Delta U/kT \approx A_0 + A_1 \rho(P,T) \int \Gamma(r) g(r) r^2 dr$$

↑  
For non-polar mixture, Dispersion forces is important.

### Intermolecular Forces That Govern Phase Behavior

$$\Gamma_{ij} = \Gamma_{ij\text{repulsive}} + \Gamma_{ij\text{attractive}} \quad (\Gamma_{ij} : \text{pair-potential energy})$$

Attraction (electrostatics)

$$\Gamma_{ij} \approx - C_1 \frac{\alpha_i \alpha_j}{r^6} - C_2 \frac{\mu_i^2 \mu_j^2}{r^6 kT} - C_3 \frac{Q_i^2 Q_j^2}{r^{10} kT} + A \cdots D$$

$\uparrow$   
**Dispersion**

$\uparrow$   
 Dipole

$\uparrow$   
 Quadrupole

$\uparrow$   
 Complex  
Formation

Repulsion

$$\Gamma_{ij} \approx \frac{\text{Collision diameter}}{r^{12}}$$

### Interchange Energy

$$Z \left[ \Gamma_{ij} - \frac{1}{2} \cdot (\Gamma_{ij} + \Gamma_{ij}) \right]$$

$\uparrow$   
 Polymer-Solvent

$\uparrow$   
 Solvent-Solvent

$\uparrow$   
 Polymer-Polymer

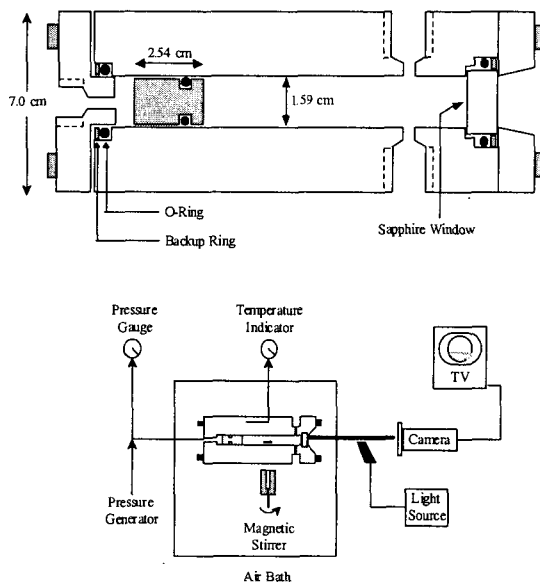
### Entropy Contribution

$\Delta S \Rightarrow$  Configurational Properties

- Polarizability
- Dipole & Quadrupole Moments
- Polymer Structure, Steric Hindrance

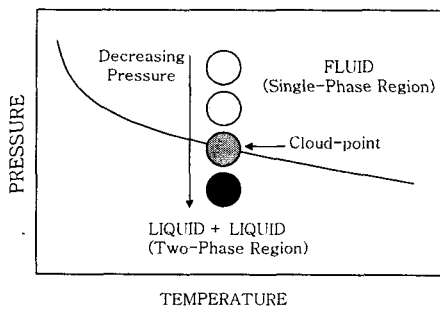
*! Decoupling  $\Delta U$  &  $\Delta S$  is not exact !*

## Apparatus for Measuring Polymer-Solvent Phase Behavior

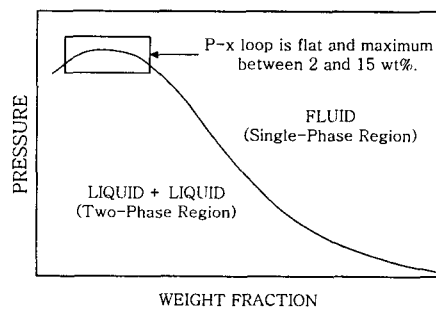


## Polymer-Solvent Cloud-points

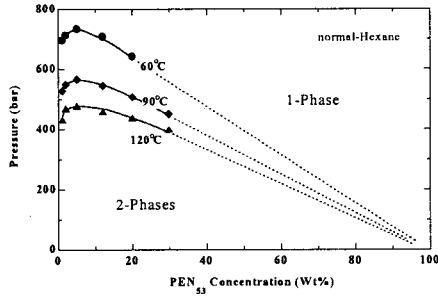
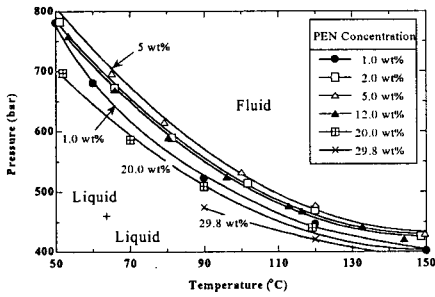
**Pressure-Temperature diagram**  
(polymer concentration constant)



**Pressure-Concentration diagram**  
(temperature constant)



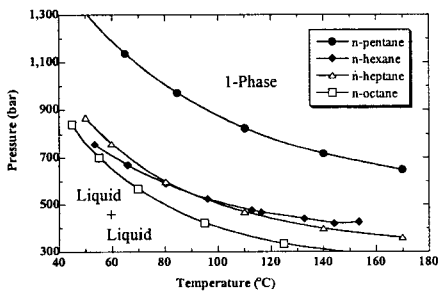
### Effect of Polymer Concentration PEN<sub>53</sub> - Hexane System



✓ In Pressure-Temperature (P-T) space, single-phase region increases with temperatures

✓ The Pressure-concentration (P-x) loops have flat maximums between 2 ~ 15 wt% PEN<sub>53</sub>

### PEN<sub>53</sub> - n-Alkane System



$T > T_g$  (156 °C)

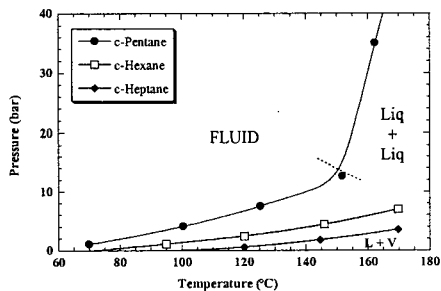
✓ Single-phase region increases with the size of solvent

✓ As the molecular size of the alkane increases, the impact of the size decreases

$T < T_g$  (156 °C)

✓ UCST-type phase behavior (Configurational properties?)

### PEN<sub>53</sub> - c-Alkane System



✓ cyclo-Alkane is much better solvent

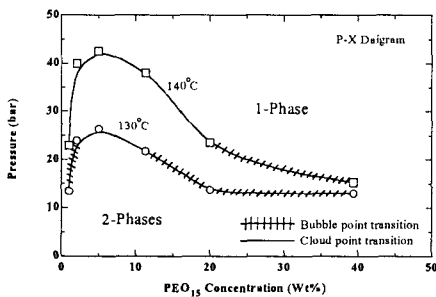
**Similar molecular structure to PEN  
Entropic Effect is important !!!**

✓ At high T, cloud-point type transition

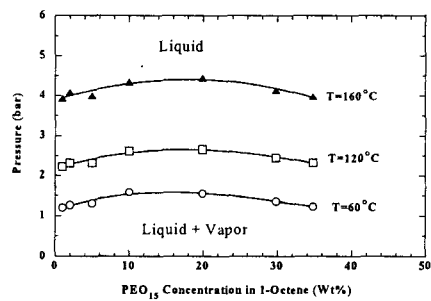
✓ Single-phase region increase with decreasing temperatures (LCST-type phase behavior)

## Effect of PEO<sub>15</sub> Concentration

### PEO<sub>15</sub> – n-Pentane System



### PEO<sub>15</sub> – 1-Octene System



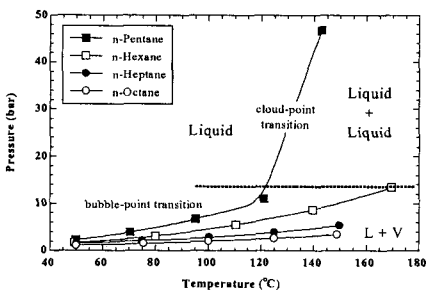
✓ The P-x loops have flat maximums between 2 – 12 wt%

✓ The P-x loops have flat maximums between 10 ~ 20 wt%

✓ PEO<sub>15</sub> solubility decreases with increasing temperatures

✓ Bubble point-type transitions occur at all concentrations

### PEO<sub>15</sub> – n-Alkane System

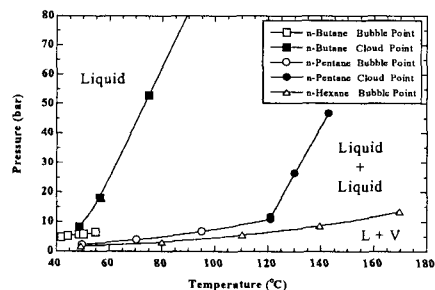


✓ P & T decrease with increasing solvent size due to the larger Polarizability

✓ In n-Pentane, cloud-point transition occurs at temperatures greater than 120 °C

✓ In n-Pentane, LCST-type Phase behavior

### PEO<sub>15</sub> – n-Alkane System



✓ In n-Butane, L → L-L → L-V transition

✓ As alkane molecular size increases, LCST-type transition occurs at higher T

n-Butane : 47 °C  
 n-Pentane : 121 °C  
 n-Hexane : ???

## Conclusions

### PEN<sub>33</sub> – Alkane System

- √ P-x loops have flat maximums between 2~15 wt% PEN<sub>33</sub>
- √ The solubility of PEN<sub>33</sub> increases with temperature
- √ As the molecular size of n-Alkanes increases the single-phase region of PEN<sub>33</sub> increases, but the effect of the size decreases
- √ The solubility of PEN<sub>33</sub> decreases with increasing temperatures in c-alkanes
- √ c-Hydrocarbons are better solvents than n-Alkanes
- √ Due to the molecular structure of PEN<sub>33</sub> backbone, configurational properties govern the phase behavior of PEN<sub>33</sub>- c-Alkane systems

### PEO<sub>15</sub> – Hydrocarbon System

- √ P-x loops have flat maximums at 2 ~ 12 wt% n-Butane
- √ P-x loops have flat maximums at 10 ~ 20 wt% 1-Octene
- √ Single phase increases with solvent size due to the larger Polarizability
- √ In n-Alkanes, PEO<sub>15</sub> shows LCST-type Phase behavior