Phase Behavior of Polycaprolactone in Dimethyl Ether, Dimethyl Ether + carbondioxide, HCFC-22, HCFC-22 + Carbondioxide

Tae-Hyoung Kim, Ji-Young Park, Jong-Sung Lim and Ki-Pung Yoo*

Hoseo University, Asan City, Korea

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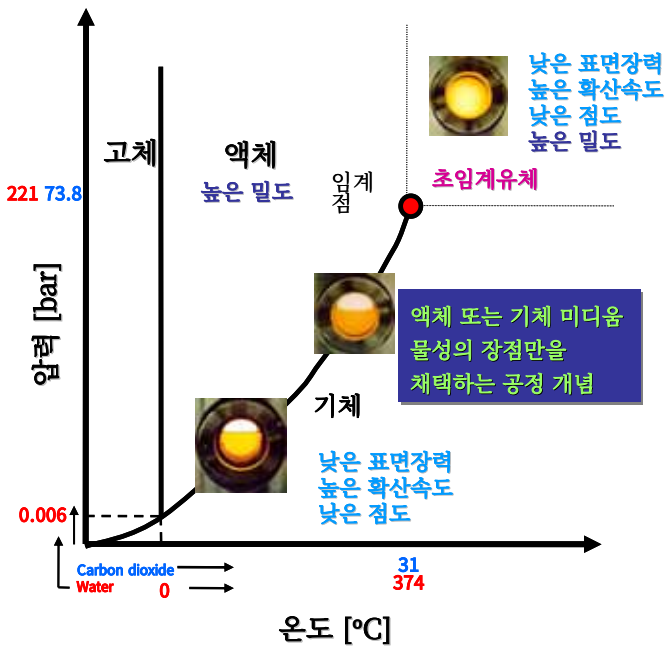
Dept .of Chemical Engineering, Sogang University

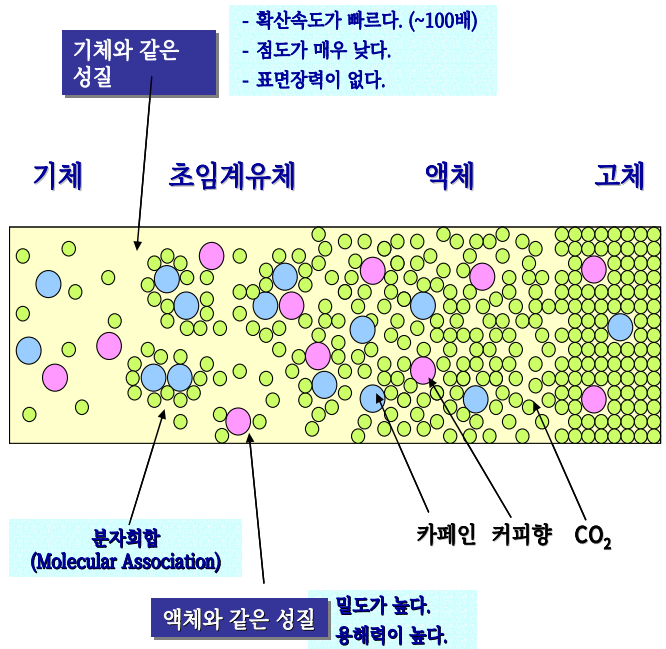
*KIST**

Objectives

- **The phase behavior of PCL in DME, DME+CO_2, HCFC-22, HCFC-22+CO_2**
- **CO_2 could be used as an anti-solvent, and the cloud point of PS and PCL could be controlled by changing the concentration of CO_2**

Introduction – what is the supercritical fluid?





Phase Diagram of Polymer-Solvent

1) The large molecular size differences between a polymer and an organic solvent induce the complicated phase behaviors

2) In the vicinity of the solvent critical temperature(Tc), a homogeneous polymer solution can spilt into polymer-rich phase and solvent-rich phase. (LCST behavior)

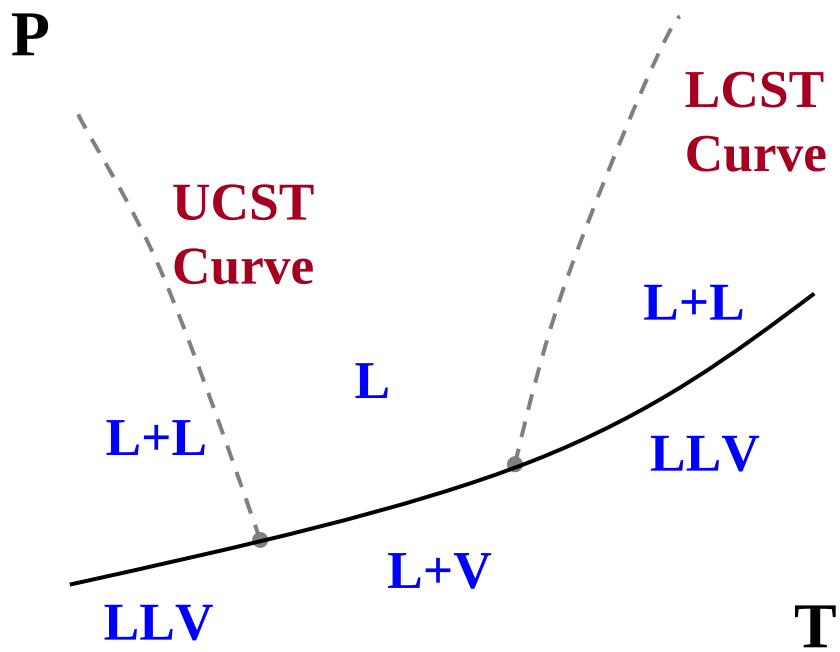
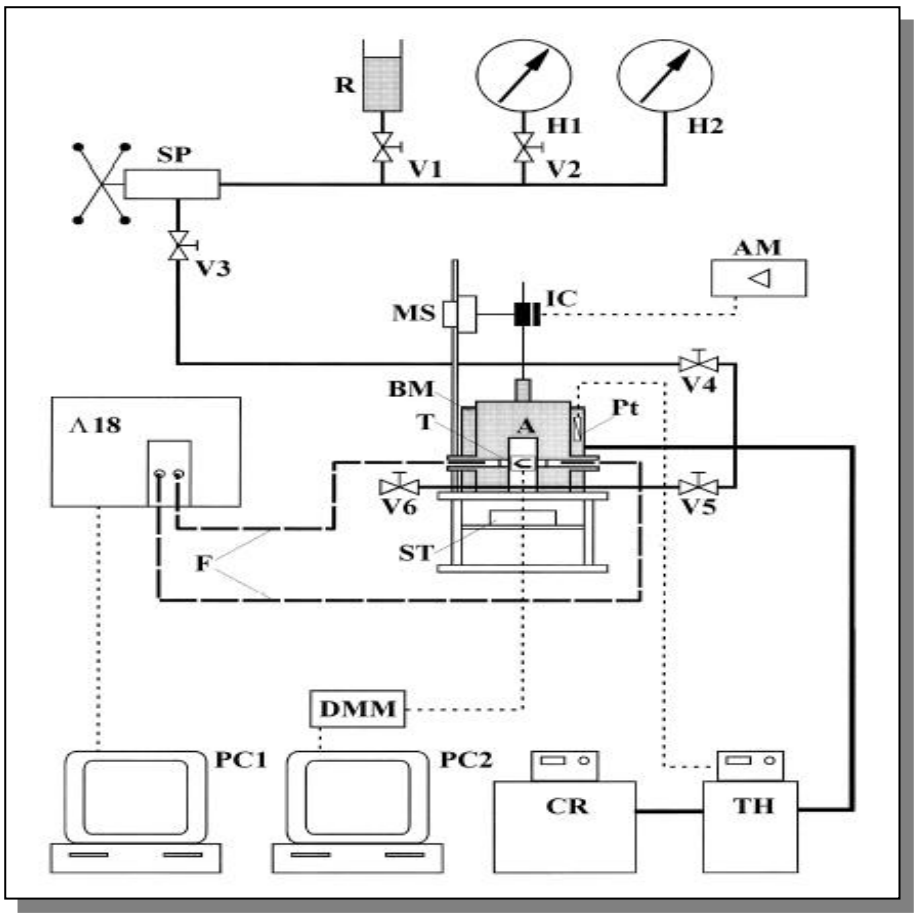


Fig. 1. Phase behavior of polymer-solvent

Static method



Advantage
- easy to make equilibrium state
- no clogging
- a small leakage available

Disadvantage
- fixed path length
  - cannot measure the high solubility of solution
- high cost

Fig. 2. Schematic diagram of static method reactor

Experimental Materials - Polycarprolacton

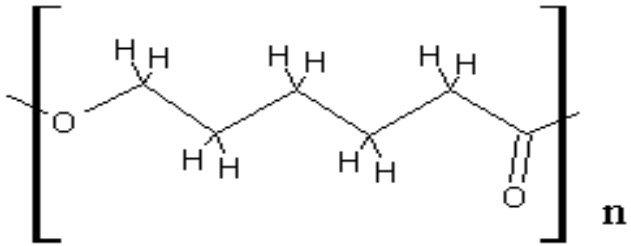
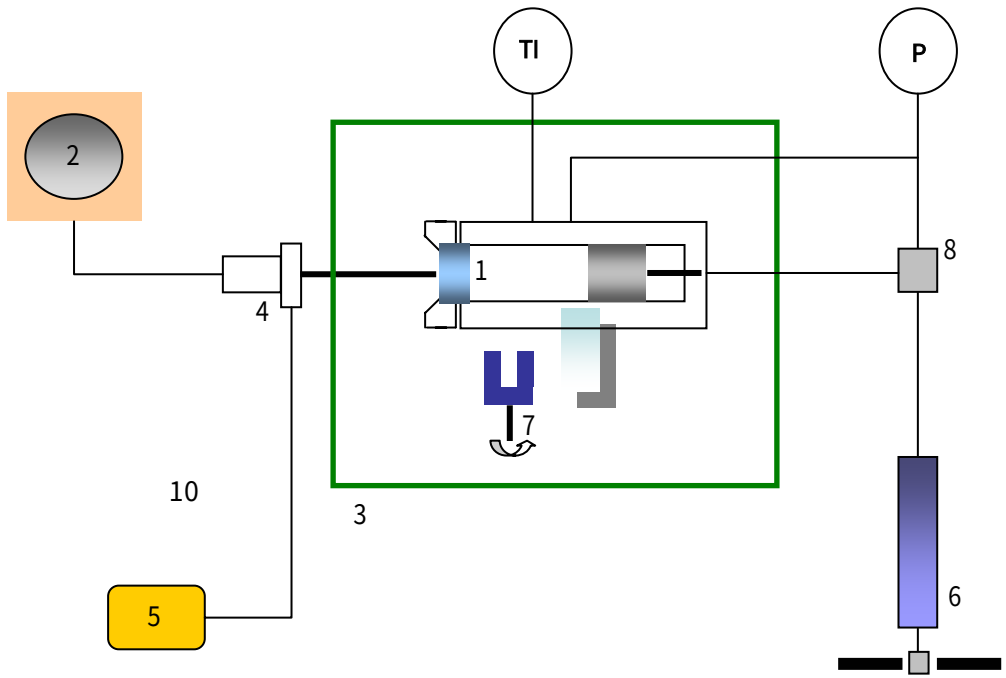


Table. Physical properties of solvents and polymers

Solvent	M.wt	Tc(K)	Pc(MPa)	Company
Dimethylether	46.06	400.00	5.24	Aldrich Co.
Chlorodifluoromethane	84.46	369.30	4.97	Aldrich Co.

Polymer	M.wt	Tm(K)	Company
Polycarprolacton	14,000	331.15 – 333.15	Aldrich Co.

Experimental Apparatus



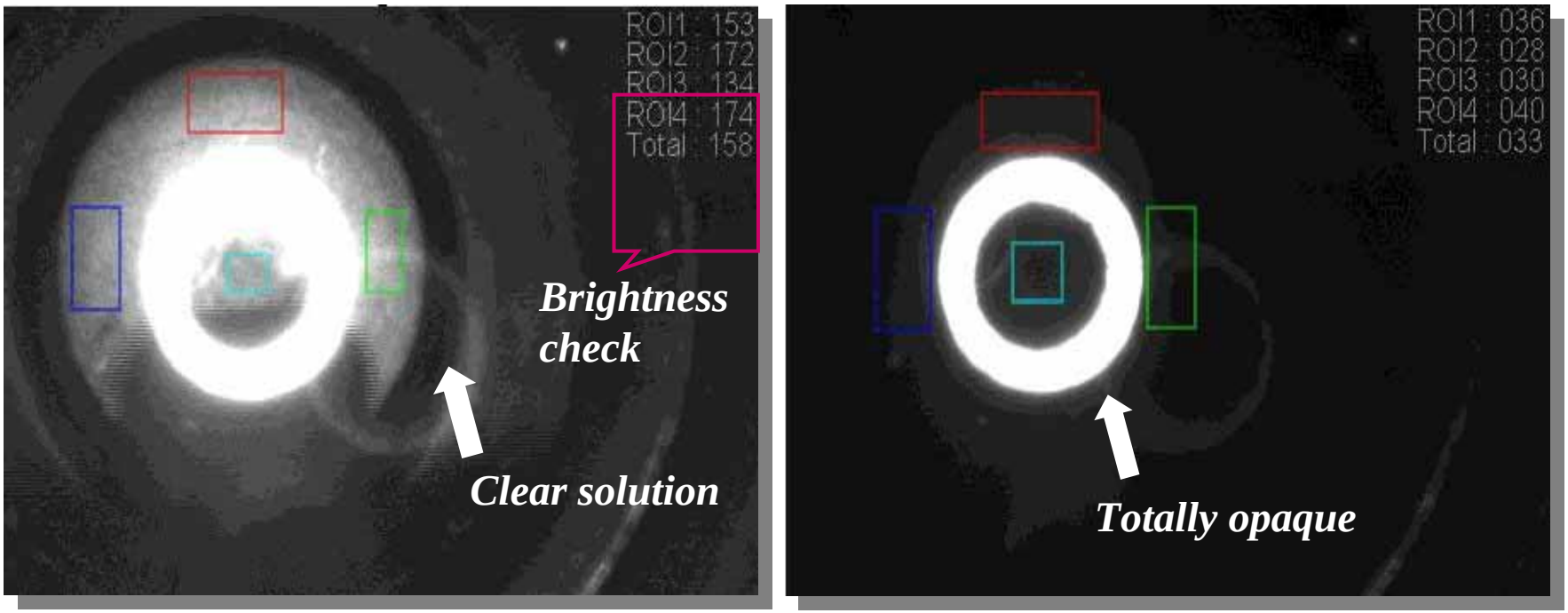
(1) variable-volume view cell; (2) monitor; (3) air oven; (4) CCD camera;
(5) halogen light source; (6) pressure generator; (7) magnetic stirrer;
(8) fluid transport line

Fig. 3. Schematic diagram of high-pressure variable-volume view cell

Experimental Apparatus

Fig. 4. View of experimental variable volume view cell

Investigation of LCST Curve



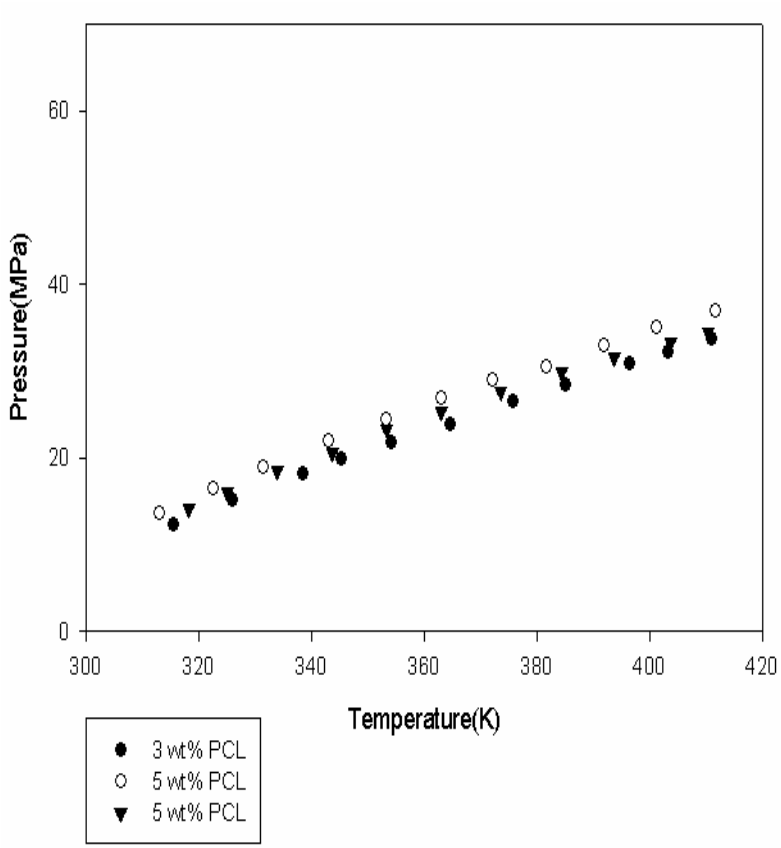
(a) Homogeneous Polymer Solution *(b) Cloud Point*

Fig. 5. Visual Determination of L-LL Phase Transition

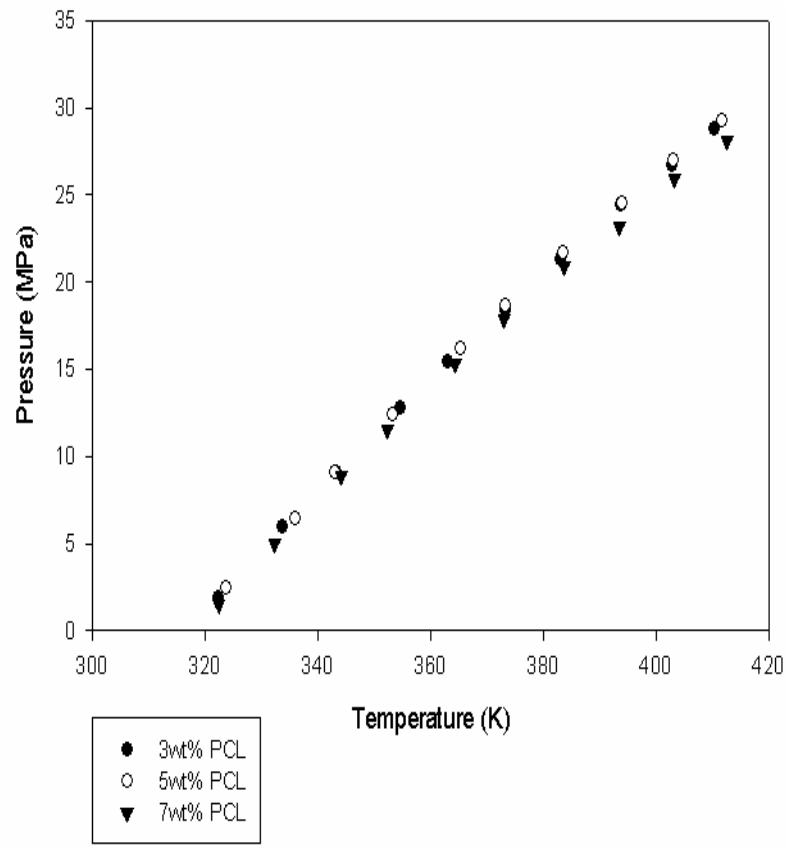
Results

● Polycaprolactone + Dimethyl Ether, Polycaprolactone + HCFC-22

PCL(Mw=100,000) + DME



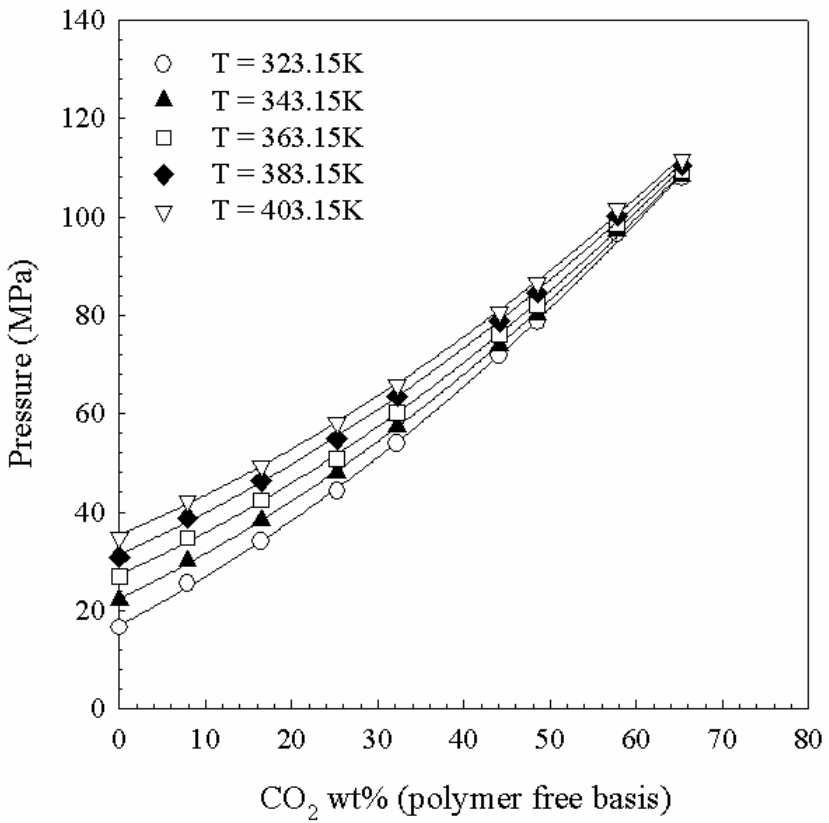
PCL(Mw =100,000) + HCFC-22



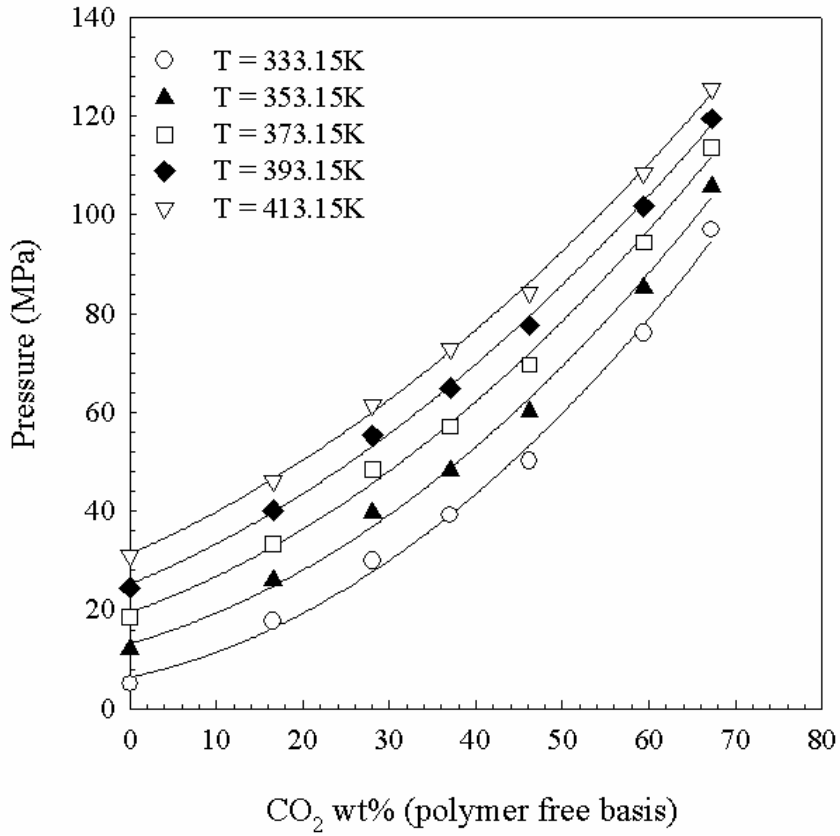
Results

● PCL + DME + CO_2, PCL + HCFC-22 + CO_2

PCL(Mw=100,000) + DME + CO_2



PCL(Mw=100,000) + HCFC-22 + CO_2



Concluding Remarks

- **Using variable volume view cell, visual investigation of L-LL coexistence curve was performed for polymer-solvent system.**
- **The correlated results are in good agreements with the experimental data.**
- **The molecular weight of the solvent was increased, the LCST phase behavior was observed**
- **CO_2 could be used as an anti-solvent, and the cloud point of PCL could be controlled by changing the concentration of CO_2**