Phase behavior and modeling of CO_2 + 2,2,2-trifluoroethyl methacrylate and CO_2 + poly (2,2,2-trifluoroethyl methacrylate) systems

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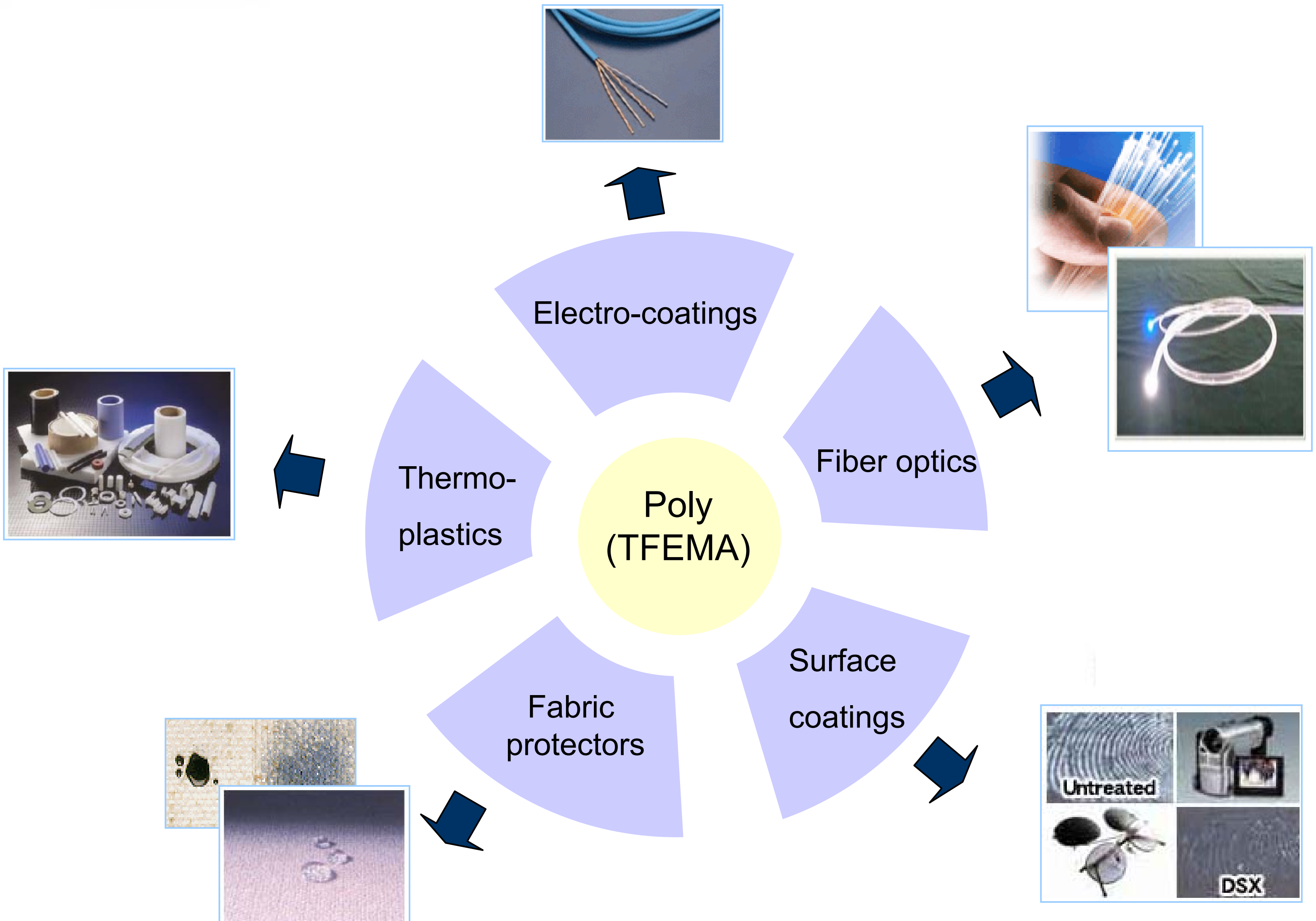
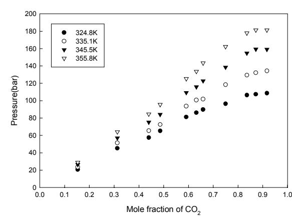
Objectives – Applications of poly (TFEMA)

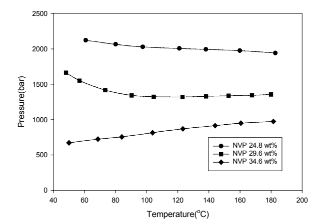


Objectives – 초임계 상거동 자료의 용도 예

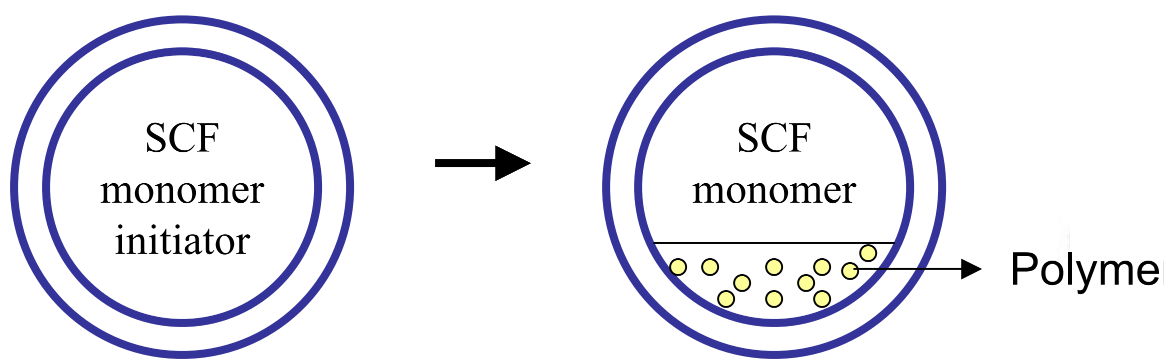
초임계 유체를 이용한
고분자 합성

Binary mixture of
CO_2+monomer or polymer





Ternary mixture of Polymer
+ monomer + CO_2

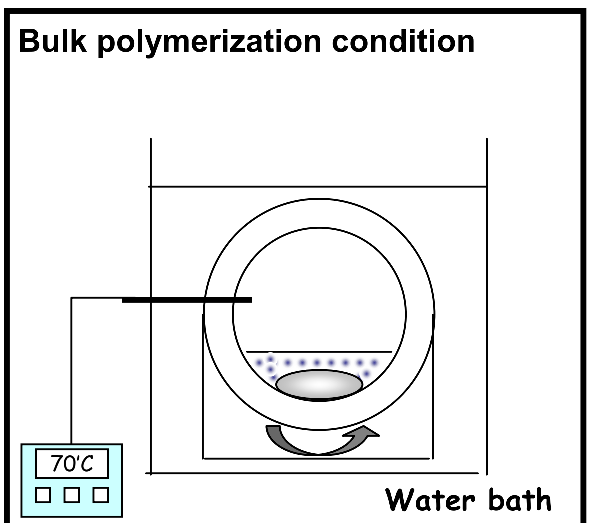


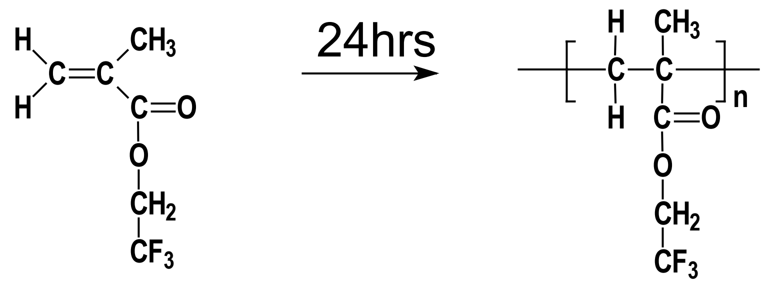
Initial State **Final State**

- 최적 중합조건 결정
- 중합 후 잔류 단량체 제거

Materials

- Carbon dioxide (min. 99.99% purity) - Korea industrial Gases
- 2,2,2-trifluoroethyl methacrylate: (TFEMA: min. 99% purity) - Aldrich
- poly (2,2,2-trifluoroethyl methacrylate): bulk polymerization

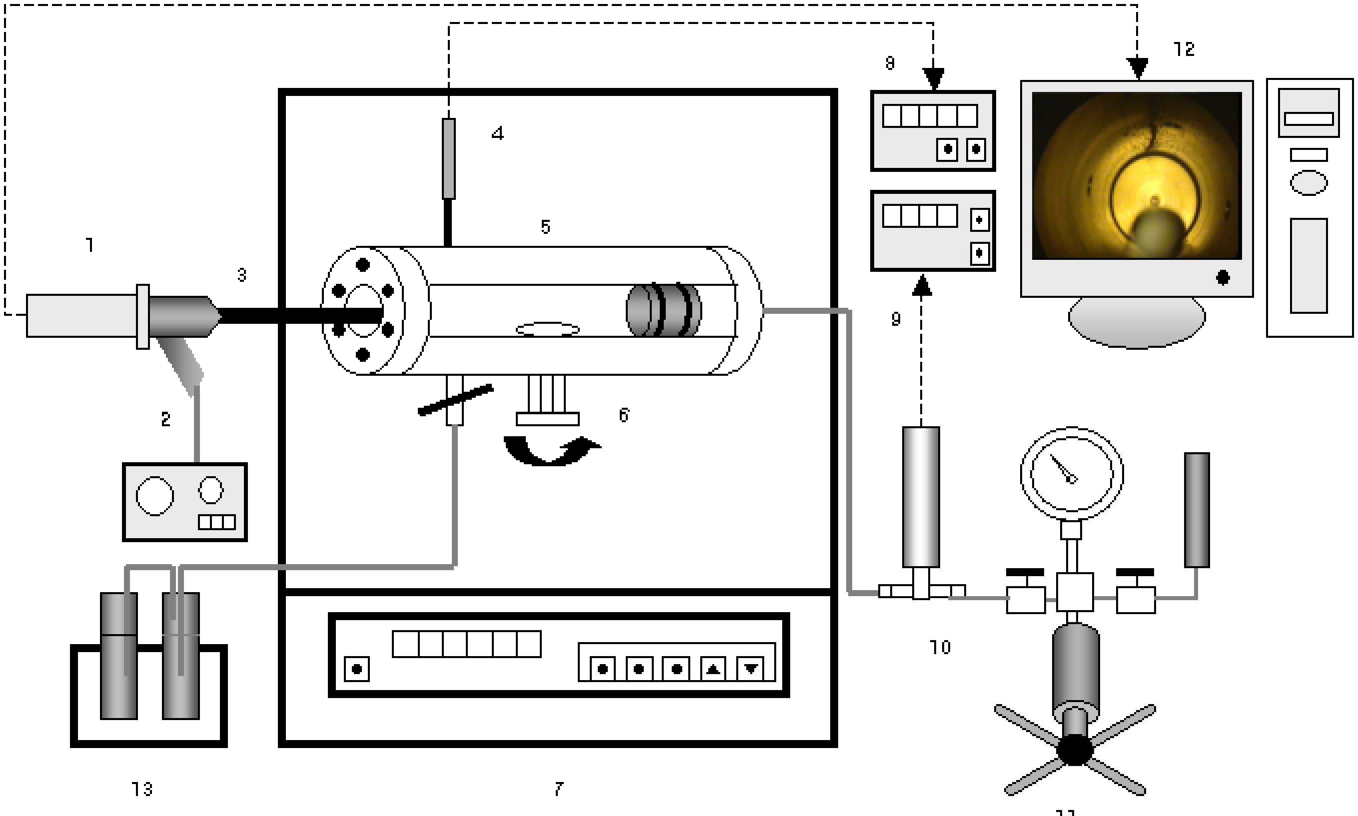




- Initiator ; AIBN [1.0 wt% of monomer]
- Temperature ; 70$\pm 0.5^{\circ}$C
- $\overline{M}_w$; 268,000 PDI ; 1.6

→ characterization by GPC

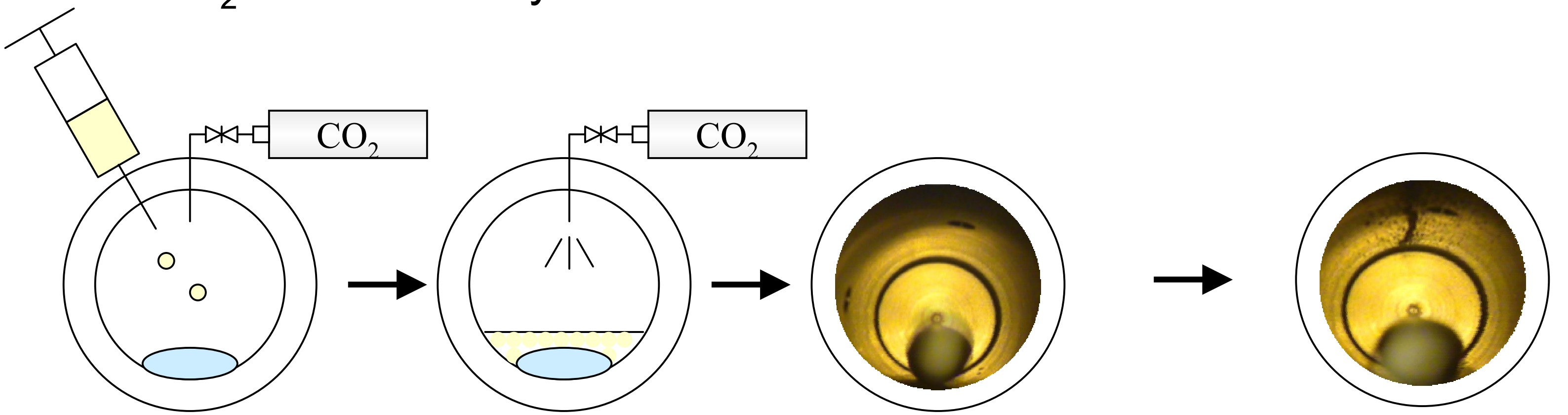
Experimental apparatus – variable volume cell



1. Camera
2. Light source
3. Borescope
4. Thermocouple
5. View cell
6. Magnetic stirrer
7. Air bath
8. Digital thermometer
9. Digital pressure transducer
10. Pressure gauge
11. Hand pump
12. Computer monitor
13. Trap

Experimental procedure

- CO_2 + monomer system



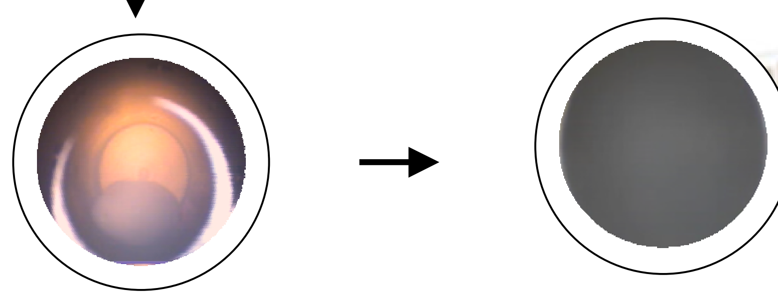
단량체 혹은 고분자 주입 후 CO_2, N_2로 purge

CO_2 주입 (실린더 혹은 실린지 펌프이용)

일정 온도에서 1-phase 되도록 가압 후 안정화

2-phase 될 때까지 천천히 감압 (bubble, dew, mixture critical point)

- CO_2 + polymer system



천천히 감압하면 임계 현상보임

압력을 더 내리면 Cloud point (운점) 관측 가능

Calculation: Peng-Robinson equation of state

- **_Peng-Robinson EOS_**

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V^2 + 2bV - b^2}$$

$$a = 0.45724\, R^2 T_c^2 / P_c$$

$$b = 0.07780\, R\, T_c / P_c$$

$$\alpha = [1 + (0.37464 + 1.54226\,\omega - 0.26992\,\omega^2)(1 - T_r^{0.5})]^2$$

pure parameters

→ T_c, P_c, ω

- **_van der Waals 1-fluid mixing rule_**

$$a_{mix} = \sum_i \sum_j x_i x_j a_{ij} \qquad a_{ij} = \sqrt{(a_{ii} a_{jj})}(1 - k_{ij})$$

$$b_{mix} = \sum_i \sum_j x_i x_j b_{ij} \qquad b_{ij} = \frac{(b_{ii} + b_{jj})}{2}$$

binary parameter

→ k_{ij}

$$OBF = \sum_i^N \left(\frac{P_{exp} - P_{cal}}{P_{exp}} \right)^2$$

Calculation: Sanchez-Lacombe lattice-fluid equation of state

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1-\tilde{\rho}) + (1-\frac{1}{r})\tilde{\rho}] = 0$$

or $$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{1}{r} - \left[1 + \tilde{v}\ln\left(1-\frac{1}{\tilde{v}}\right)\right] - \frac{1}{\tilde{v}\tilde{T}}$$

$$\tilde{T} \equiv \frac{T}{T^*} \qquad T^* = \frac{\varepsilon^*}{k}$$

$$\tilde{P} \equiv \frac{P}{P^*} \qquad P^* = \frac{\varepsilon^*}{v^*}$$

$$\tilde{v} \equiv \frac{1}{\tilde{\rho}} \equiv \frac{V}{V^*} \equiv \frac{\rho^*}{\rho} \qquad V^* = N(rv^*)$$

pure parameters

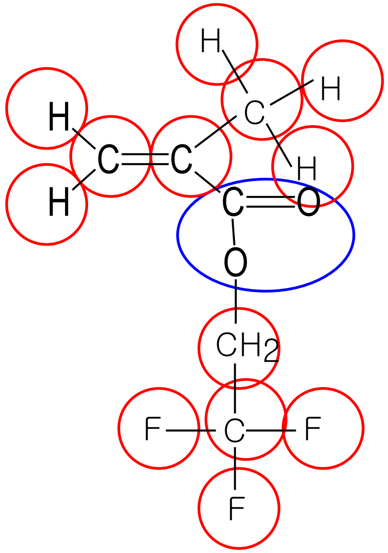
$\longrightarrow$ T^*, P^*, ρ^* or ε^*, v^*, r

Estimation method of pure parameters : TFEMA

- ***Group Contribution method***

: Method of Wilson and Japerson

Critical constants T_c, P_c, Estimation based Zero, first and second order methods (1996)



$$T_b = 380.15K$$ **F-Tech Inc. data**

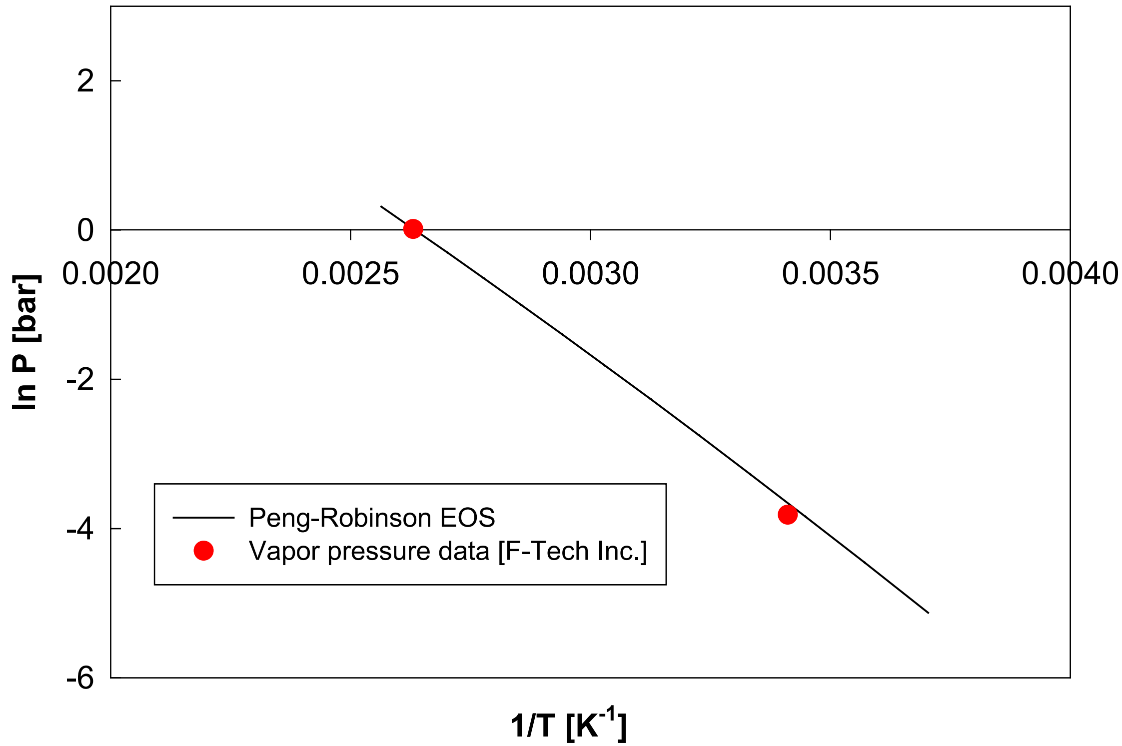
$$T_c = T_b /[(0.048271 - 0.019846 N_r + \sum_k N_k (\Delta tck) + \sum_j M_j (\Delta tcj) +]^{0.2}$$

$$P_c = 0.0186233 T_c /[-0.96601 + \exp(Y)]$$

$$Y = -0.00922295 - 0.0290403 N_r + 0.041 \left(\sum_k N_k (\Delta pck) + \sum_j M_j (\Delta pcj) \right)$$

Estimation method of pure parameters : TFEMA

	Unit	TFEMA
T_b	K	380.15
T_c	K	541.12
P_c	bar	29.13
ω	-	0.4773



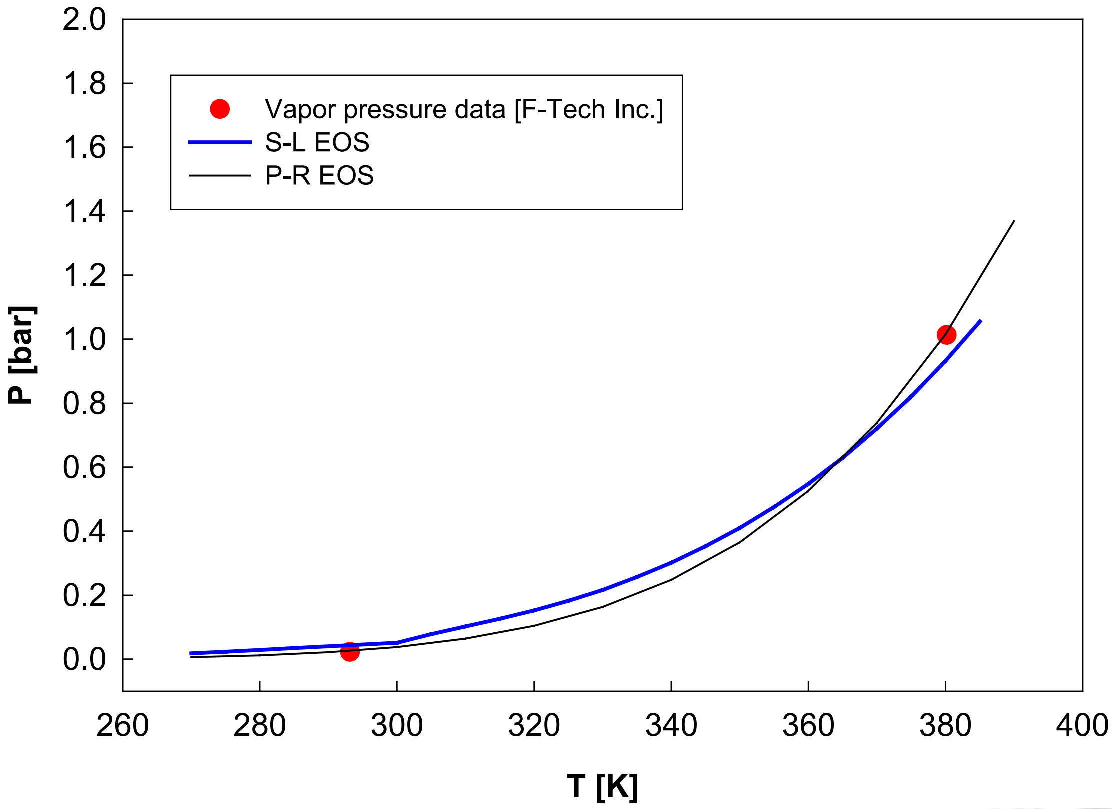
ω : Lee-Kesler method

→ Vapor pressure data 이용하여 S-L parameters구함

Estimation method of pure parameters : TFEMA

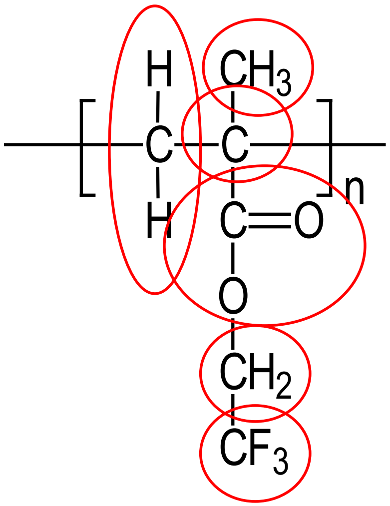
	Unit	TFEMA	CO_2
T*	K	711.40	305.00
P*	MPa	294.79	574.50
ρ*	kg/m³	1167.20	1510.00

CO_2 parameter : Journal of Applied Polymer Science, Vol. 36, 583-597 (1988)



Estimation method of pure parameters : poly (TFEMA)

First order	n	T*	P*	ρ*
CH_3	1	-18.08	-105.41	-100.69
CH_2	2	-7.65	-29.67	-46.65
C	1	97.41	82.23	136.60
COO	1	-76.38	168.96	363.43
CF_3	1	-54.57	-134.86	67.12



$$f(X) = X - X_0 \quad (X = T^*, P^* \text{ or } \rho^*)$$

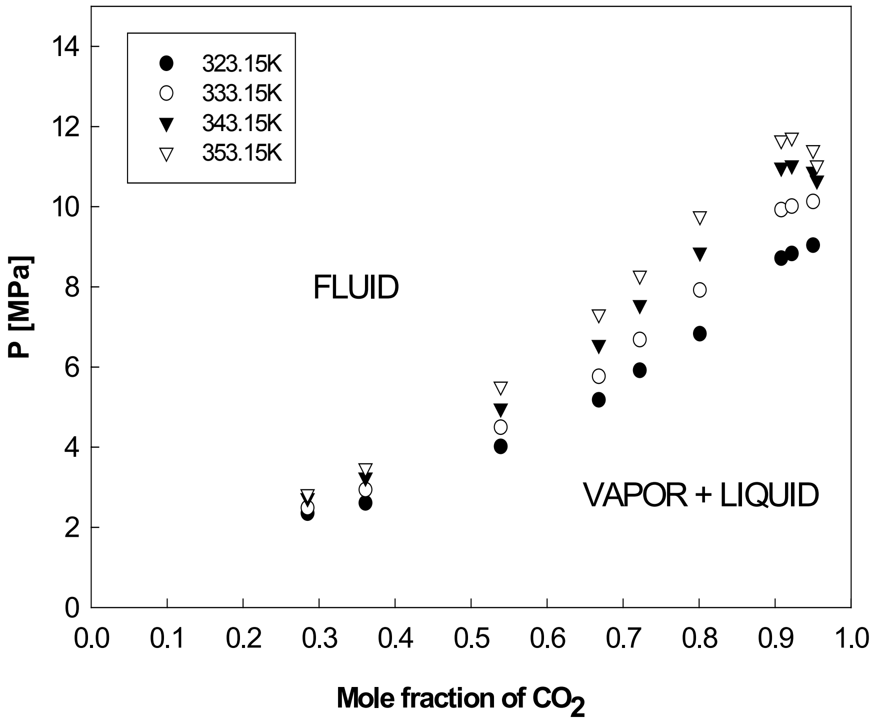
parameter	value
T^*_o	666.95 K
P^*_o	489.46 MPa
ρ^*_o	1019.47 kg/m³

	Unit	Poly(TFEMA)	CO_2
T*	**K**	**600.03**	**305.00**
P*	**MPa**	**441.04**	**574.50**
ρ*	**kg /m³**	**1392.63**	**1510.00**

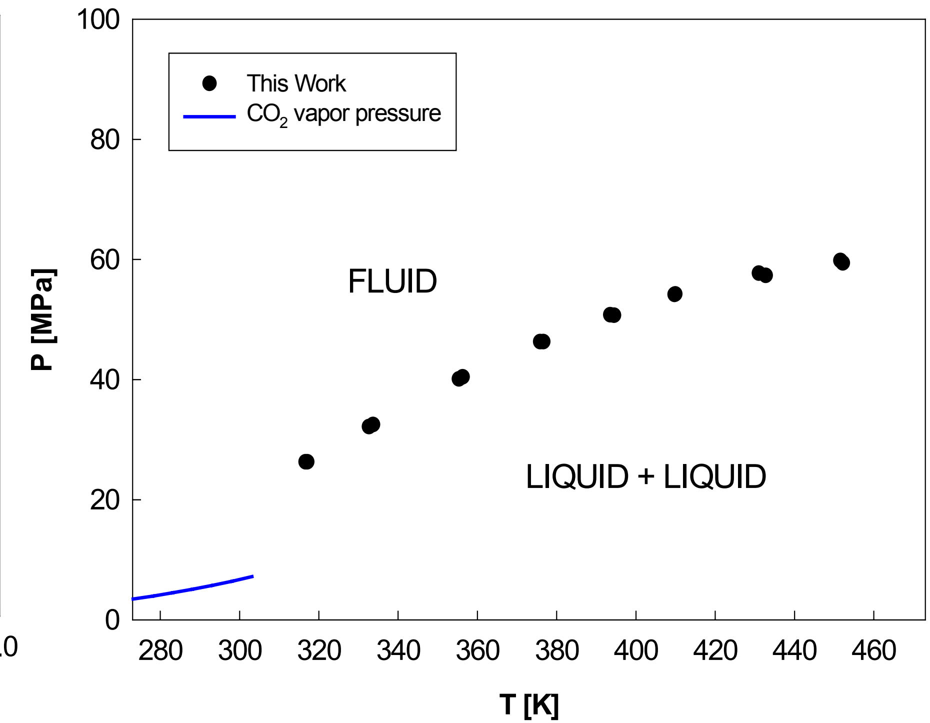
Ing. Eng. Chem. Res., Vol. 36, 3968-3973 (1997)

Experimental Results

Pressure-composition (P-x) isotherms

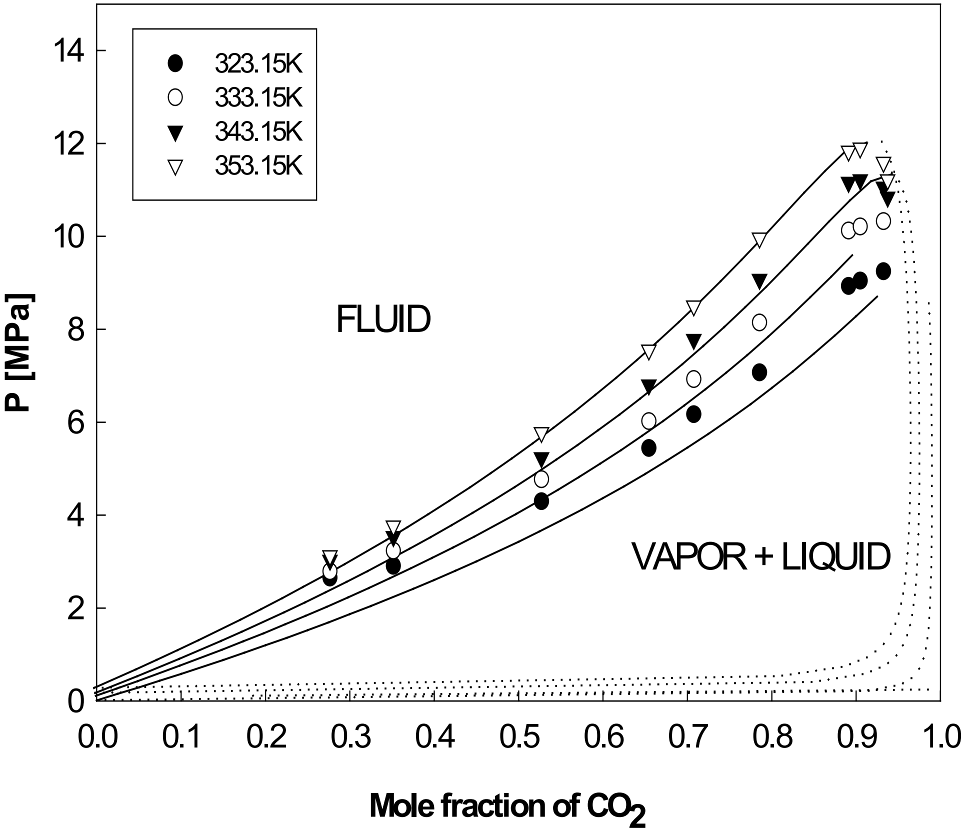


Temperature-Pressure (T-P) diagram of CO_2 + poly (TFEMA) system: LCST behavior



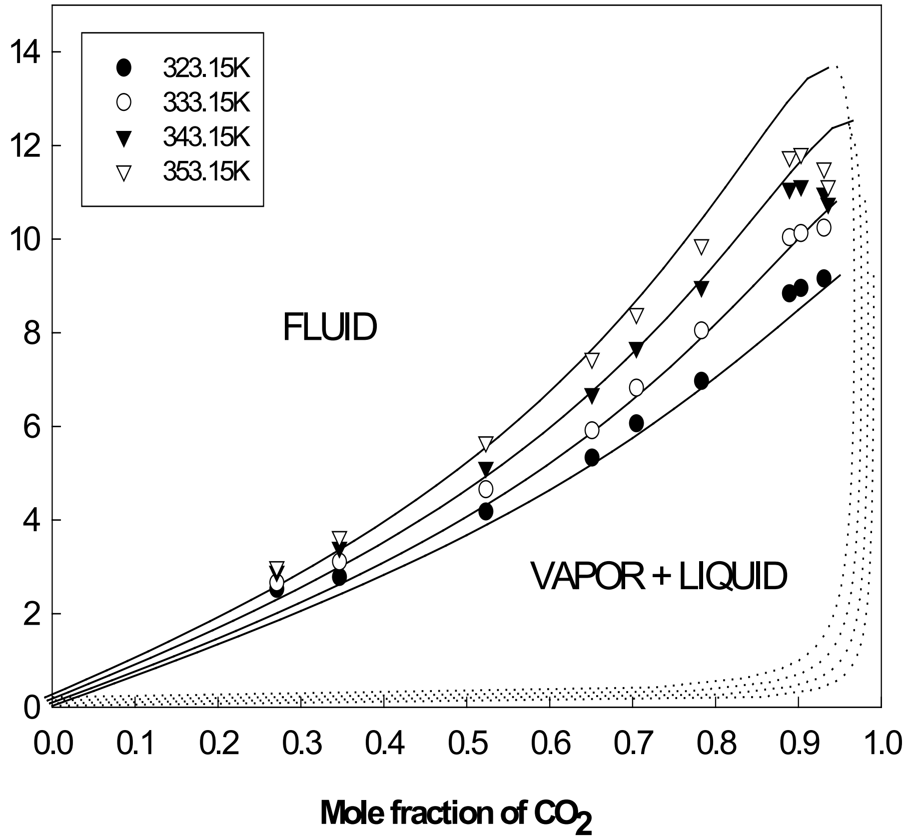
Modeling 1 – CO_2 + TFEMA system

Peng-Robinson EOS



k_{ij}	-0.0126

Sanchez-Lacombe lattice-fluid EOS

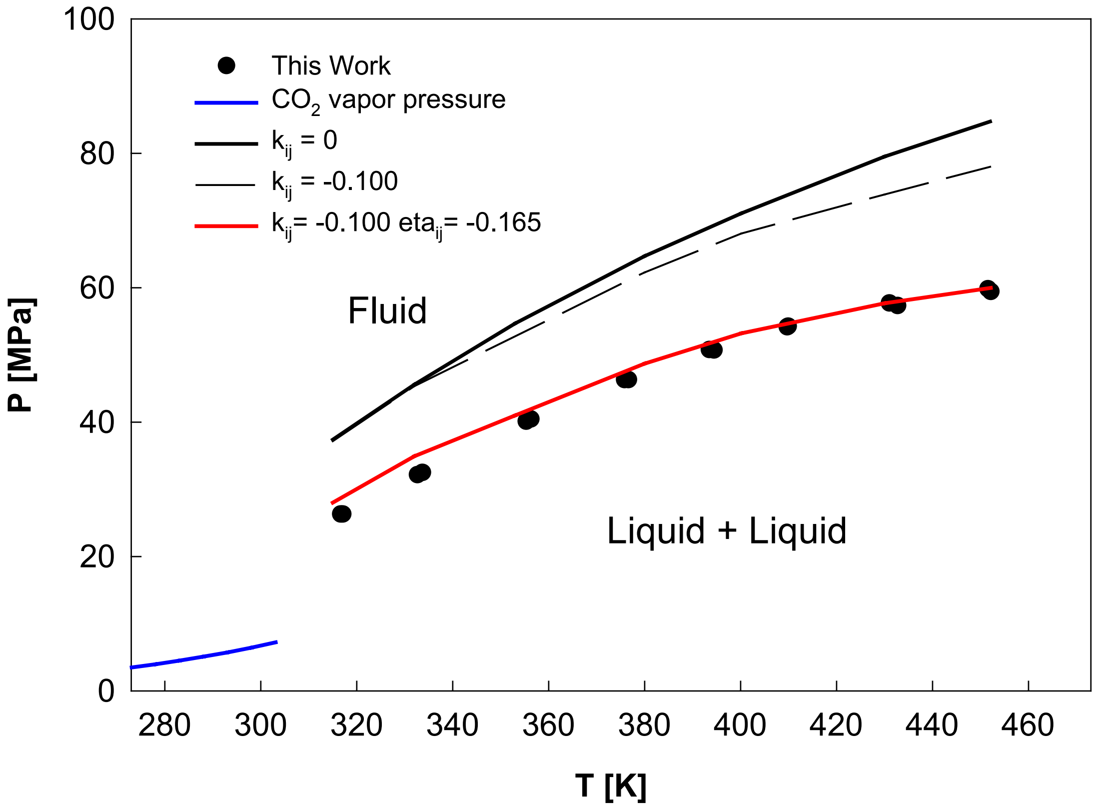


T [K]	323.15	333.15	343.15	353.15
k_{ij}	0.1159	0.1010	0.0933	0.0847

Modeling 3 – CO_2 + poly (TFEMA) system

P-T diagram : Sanchez-Lacombe lattice-fluid EOS

Lower Critical Solution Temperature



Poly (TFEMA) : 3.91wt%

Conclusions

- 온도 323.15 ~ 353.15K, 압력 20~120 bar 범위에서 CO_2 + trifluoroethyl methacrylate 계에 대한 고압 상평형 데이터(P-x diagram)를 variable volume view cell을 이용하여 얻었다.

- 온도 320 ~ 460 K, 압력 320~600 bar 범위에서 CO_2 + poly (trifluoroethyl methacrylate) 계에 관한 임계 거동(LCST critical locus)을 관측하였다.

- CO_2와 TFEMA, poly (TFEMA)의 상거동에 대하여 pure parameters를 그룹기여 방법을 이용하여 얻고 P-R EOS와 S-L EOS로 모델링 하였다.

  CO_2 + trifluoroethyl methacrylate 계의 경우 S-L EOS가 임계점을 높게 예측하는 것을 알 수 있었다. CO_2 + poly (trifluoroethyl methacrylate) 계는 두개의 binary parameters를 이용하여 모델링 하였다.

- 앞으로 CO_2 + poly (trifluoroethyl methacrylate) + trifluoroethyl methacrylate에 관한 ternary phase behavior에 관한 실험 및 모델링을 연구해보고자 한다.