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ScienceDirect
Polymer 48 (2007) 805−812
polymer
www.elsevier.com/locate/polymer

# Phase behavior of the poly(neopentyl methacrylate) + supercritical fluid solvents + neopentyl methacrylate system and $CO_2$ + neopentyl methacrylate mixtures at high pressure

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Received 15 July 2006; received in revised form 1 December 2006; accepted 6 December 2006
Available online 9 January 2007

**Abstract**

High-pressure phase behaviors are measured for the $CO_2$ + neopentyl methacrylate (NPMA) system at 40, 60, 80, 100, and 120 °C and pressure up to 160 bar. This system exhibits type-I phase behavior with a continuous mixture-critical curve. The experimental results for the $CO_2$ + NPMA system are modeled using the Peng−Robinson equation of state. Experimental cloud-point data up to the temperature of 180 °C and the pressure of 2000 bar are presented for ternary mixtures of poly(neopentyl methacrylate) [poly(NPMA)] + supercritical solvents + NPMA systems. Cloud-point pressures of poly(NPMA) + $CO_2$ + NPMA system are measured in the temperature range of 60−180 °C and to pressures as high as 2000 bar with NPMA concentration of 0.0, 5.2, 19.0, 28.1 and 40.2 wt%. It appears that adding 51.2 wt% NPMA to the poly(NPMA) + $CO_2$ mixture does significantly change the phase behavior. Cloud-point curves are obtained for the binary mixtures of poly(NPMA) in supercritical propane, propylene, butane, 1-butene, and dimethyl ether (DME). The impact of dimethyl ether concentration on the phase behavior of the poly(NPMA) + $CO_2$ + $x$ wt% DME system is also measured at temperature of 180 °C and pressure range of 36−2000 bar. This system changes the pressure−temperature ($P-T$) slope of the phase behavior curves from upper critical solution temperature (UCST) region to lower critical solution temperature (LCST) region as the NPMA concentration increases.

*Keywords:* Supercritical fluid solvents; Phase behavior; Poly(neopentyl methacrylate)

## 1. Introduction

There has been a great interest in supercritical fluid (SCF) in the past three decades. SCF solvents have been widely applied to several industrial processes including in the processing of pharmaceuticals, environments, foods, polymers and monomers. In more recent years, SCF solvents have been used in a much more diverse array of processes as environmentally preferable solvents for liquefaction and mixing of crystalline materials, powder formation, particle and surface impregnation, and antisolvent precipitation [1,2].

The fundamental knowledge of the driving force about SCF solubility are needed for experimental data for polymers + SCF solvents mixture and SCF solvents + monomers system. Specially, the binary monomers + supercritical fluids' mixture is of importance for a number of applications related with polymerization condition, separation processes and fine chemical industry. The methacrylates are also one of the important classes widely used in the manufacture of plastic products, reaction media and color resists [3].

Until recently, we have demonstrated that it is possible to dissolve the polymers in SCF solvents over a large temperature

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doi:10.1016/j.polymer.2006.12.006

range at modest pressure if a cosolvent is used [4−7]. For many free radical polymerization reactions, the time needed to form polymer is on the order of seconds, while the residence time in the reactor is typically on the order of minutes. The cosolvents can greatly enhance polymer solubility in a given SCF solvents for several reasons. If the solvent is highly expanded, the addition of a dense, liquid cosolvent reduces the free-volume difference between the polymer and the supercritical solvent [7,8]. If the cosolvent provides favorable physicochemical interactions, such as polar interactions, the region of miscibility should be increased [9]. Interpreting the effect of a cosolvent added to a supercritical solvent is slightly complicated since increasing the pressure of the system reduces the free-volume difference between the polymer and the solvent, and it increases the probability of interaction between polymer, solvent, and cosolvent in mixture [10]. The polymer + supercritical solvent + cosolvent studies at high pressure reported in the literature show that cloud points monotonically decrease pressure and temperature with the addition of a cosolvent as long as the cosolvent does not form a complex with the polar repeat units in the polymer [9,11]. In these cases, cosolvent effect is directly related to the polar forces of attraction contributed by the cosolvent and to the increase in solvent density resulting from the addition of a liquid cosolvent to a supercritical fluid solvent.

The phase behavior of straight chain alkyl tail ($-CH_3$) and branch isoalkyl tail (di-$CH_3$) polymers in SCF solvents has been reported by several researchers. Lora and McHugh [12] reported the phase behavior data for poly(methyl methacrylate) + $CO_2$ + methyl methacrylate mixture. Byun and McHugh [13] also studied the phase behavior of poly(ethyl methacrylate) and poly(butyl methacrylate) in supercritical $CO_2$ + monomer mixture at temperature up to 250 °C and pressure up to 2500 bar. Recently, Byun and McHugh [14] reported cloud-point experimental data for poly(isopropyl methacrylate) + $CO_2$ + isopropyl methacrylate system at temperature from 50 to 170 °C and pressure up to 2500 bar using static phase equilibria apparatus. However, the experimental data in this work present the phase behavior of branch neopentyl tail (tri-$CH_3$) polymer in SCF solvents. No experimental data on the solubility of $CO_2$ + NPMA and poly(NPMA) + SCF solvents + NPMA mixtures have been reported in the literature.

In this work, the experimental data on high-pressure phase behavior of $CO_2$ + NPMA system are obtained at temperature of 40−120 °C and pressure in the range of 40−160 bar. The experimental data on $CO_2$ + NPMA system are fitted to the Peng−Robinson equation of state [15], and the phase behavior of this binary monomer + SCF solvent mixture is calculated at elevated operating temperatures and pressures. The focus of this work is to determine the impact of NPMA cosolvent on the phase behavior of the poly(NPMA) + $CO_2$ system. Given that $CO_2$ has been considered a desirable reaction medium for free radical polymerizations [16], the phase behavior of these ternary poly(NPMA) + supercritical $CO_2$ + NPMA mixtures provides the information needed for the regions where homogeneous polymerization can occur in the presence of excess monomer.

## 2. Experimental section

### 2.1. Apparatus and procedure

Fig. 1 shows the experimental apparatus used for obtaining cloud-point curves for poly(NPMA) + SCF solvents + NPMA ternary mixtures [13] and vapor−liquid equilibrium data on pressure−composition ($P$−$x$) isotherms for the $CO_2$ + NPMA mixtures [17]. The vapor−liquid equilibrium data and cloud-point curves at high pressure are obtained through variable-volume cell described in detail elsewhere [13,17]. The experimental procedure for ternary systems is briefly described here. Cloud points are measured for the polymer solutions at a fixed poly(NPMA) concentration of about 5.0 wt%, which is typical of the concentrations used for polymer + SCF solvent studies. Polymer is loaded into the cell accurate to within ±0.002 g and then the cell is purged with nitrogen followed by $CO_2$ to ensure that all of the air and organic matter are removed. The NPMA is injected into the cell accurate to within ±0.002 g using a syringe and $CO_2$ is transferred into the cell gravimetrically accurate to within ±0.004 g using a high-pressure bomb. The ternary mixture is compressed to the desired pressure with an internal piston displaced by water in a high-pressure generator (HIP Inc., model 37-5.75-60). A Heise gauge is used to measure the pressure of the poly(NPMA) + supercritical solvents + NPMA (Dresser Ind., model CM-108952, 0−3450 bar, accurate to within ±3.5 bar) and $CO_2$ + NPMA mixture (Dresser Ind., model CM-53920, 0−340 bar, accurate to within ±0.3 bar). The temperature in the cell is measured using a platinum-resistance thermometer (Thermometrics Corp., Class A) connected to a digital multimeter (Yokogawa, model 7563, accurate to within ±0.005%). The system temperature is typically maintained to within ±0.2 °C below 200 °C. The mixture inside the cell is viewed on a video monitor using a camera coupled to a borescope (Olympus Corp., model F100-038-000-50) placed against the outside of the sapphire window. Light is transmitted into the cell with a fiber optic cable connected at one end to a high-density illuminator

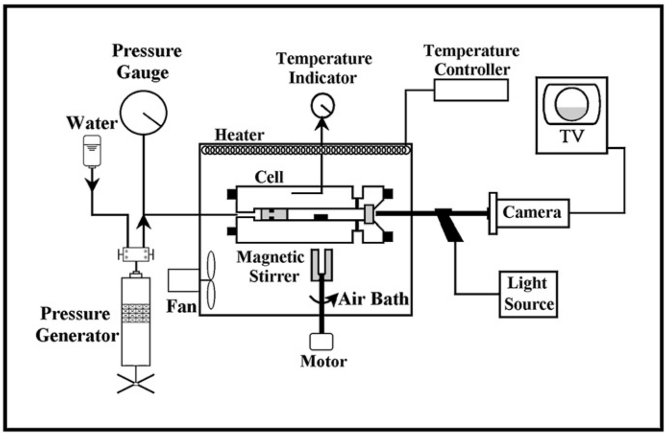

Fig. 1. Schematic diagram of the experimental apparatus used for the poly(neopentyl methacrylate) + SCF solvents + neopentyl methacrylate and $CO_2$ + neopentyl methacrylate system.

(Olympus Optical Co., model ILK-5) and at the other end to a borescope.

### 2.2. Materials

Poly(neopentyl methacrylate) ($M_w = 480{,}000$; model dynamic light scattering-7000DH, Otsuka Co., Japan) was obtained from Scientific Polymer Product, Inc. and used as received. The neopentyl methacrylate (NPMA) (>98% purity) was obtained from Scientific Polymer Product, Inc. and used as received. $CO_2$ (99.8% purity) was obtained from Daesung Industrial Co., propane (98% purity) from LG Gas (E1), and propylene (99.6% purity), butane (97.0% purity), 1-butene (99.5% purity) and dimethyl ether (DME) (99.5% purity) were obtained from Yeochun NCC Co., and all of them were used as received. To prevent NPMA polymerization, 2,6-di-*tert*-butyl-4-methyl phenol (Aldrich, 99% purity) was used as an inhibitor at a concentration of 0.005 times the amount of NPMA.

## 3. Results and discussion

### 3.1. Phase behavior of $CO_2 + NPMA$ mixture

The phase behavior experimental data for the $CO_2$ + NPMA systems are measured and reproduced at least twice to within ±0.3 bar and ±0.2 °C for a given loading of the cell. The mole fractions of experimental data are accurate to within ±0.002. The solubility for $CO_2$ + NPMA mixtures at temperature range of 40–120 °C are arranged according to the value at least two independent data points that have an estimated accumulated error of less than ±1.0%.

Table 1 and Fig. 2 show the experimental pressure–composition ($P$–$x$) isotherms at 40, 60, 80, 100 and 120 °C and at the range of pressures of 42–160 bar for the $CO_2$ + NPMA system. As shown in Fig. 2, three phases were not observed at any of the five temperatures studied. The phase behavior experimental results obtained in this work are modeled using the Peng–Robinson equation of state [15]. These two binary interaction parameters were determined by regression experimental data with Peng–Robinson equation of state. Objection function (OBF) [18] and root mean squared relative deviation (RMSD) percent of this calculation were defined as follows:

$$\mathrm{OBF} = \sum_{i}^{N} \left( \frac{P_{\mathrm{exp}} - P_{\mathrm{cal}}}{P_{\mathrm{exp}}} \right)^2 \qquad (1)$$

$$\mathrm{RMSD}(\%) = \sqrt{\frac{\mathrm{OBF}}{\mathrm{ND}}} \times 100 \qquad (2)$$

ND in Eq. (2) means the number of bubble point among experimental data. Table 2 lists pure component critical temperatures, critical pressures, and acentric factors for $CO_2$ [19], NPMA that are used with the Peng–Robinson equation of state [15]. The boiling point of NPMA was obtained by Scientific Polymer Product, Inc. The properties of NPMA were calculated by group-contribution method [19], but the vapor pressures were calculated by Lee–Kesler method [19].

Table 1
Experimental data for the $CO_2$ + neopentyl methacrylate (NPMA) system measured in this study

| Mole fraction of the NPMA | $P$ (bar) | Transition |
|---|---|---|
| $T = 40$ °C | | |
| 0.025 | 84.5 | B.P |
| 0.052 | 81.9 | B.P |
| 0.104 | 77.7 | B.P |
| 0.163 | 71.7 | B.P |
| 0.195 | 70.3 | B.P |
| 0.252 | 64.8 | B.P |
| 0.319 | 60.3 | B.P |
| 0.382 | 55.5 | B.P |
| 0.525 | 42.4 | B.P |
| $T = 60$ °C | | |
| 0.025 | 106.6 | C.P |
| 0.052 | 106.2 | B.P |
| 0.104 | 103.0 | B.P |
| 0.163 | 98.4 | B.P |
| 0.195 | 92.1 | B.P |
| 0.252 | 84.5 | B.P |
| 0.319 | 76.2 | B.P |
| 0.382 | 69.7 | B.P |
| 0.525 | 53.4 | B.P |
| $T = 80$ °C | | |
| 0.025 | 123.3 | D.P |
| 0.052 | 128.1 | C.P |
| 0.104 | 126.7 | B.P |
| 0.163 | 122.8 | B.P |
| 0.195 | 115.9 | B.P |
| 0.252 | 103.8 | B.P |
| 0.319 | 93.1 | B.P |
| 0.382 | 83.6 | B.P |
| 0.525 | 63.1 | B.P |
| $T = 100$ °C | | |
| 0.025 | 129.3 | D.P |
| 0.052 | 144.8 | D.P |
| 0.104 | 147.1 | C.P |
| 0.163 | 143.3 | B.P |
| 0.195 | 137.6 | B.P |
| 0.252 | 123.3 | B.P |
| 0.319 | 110.5 | B.P |
| 0.382 | 97.2 | B.P |
| 0.525 | 71.9 | B.P |
| $T = 120$ °C | | |
| 0.025 | 119.8 | D.P |
| 0.052 | 152.1 | D.P |
| 0.104 | 160.7 | C.P |
| 0.163 | 160.0 | B.P |
| 0.195 | 154.5 | B.P |
| 0.252 | 140.4 | B.P |
| 0.319 | 125.9 | B.P |
| 0.382 | 108.8 | B.P |
| 0.525 | 81.0 | B.P |

Fig. 3 shows the comparison of experimental results of $CO_2$ + NPMA and calculated values obtained using Peng–Robinson equation at a temperature of 80 °C. The binary interaction parameters of Peng–Robinson equation of state fit well with the experimental data at 80 °C. The values of the optimized parameters (bubble-point data = 7, RMSD = 1.12%)

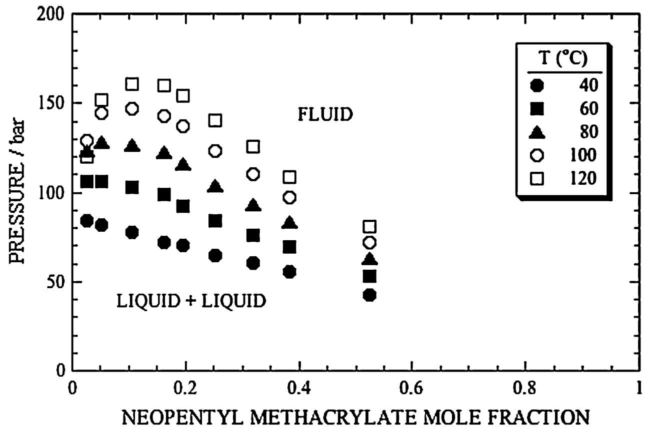

Fig. 2. Experimental isotherms for the $CO_2$ + neopentyl methacrylate system obtained in this work at 40, 60, 80, 100, and 120 °C.

Table 2
Pure component parameters for the Peng–Robinson equation of state [19]

| Compound | $M_w$ | $T_c$ (°C) | $P_c$ (bar) | $\omega$ |
|---|---|---|---|---|
| $CO_2$ | 44.01 | 31.1 | 73.8 | 0.225 |
| Neopentyl methacrylate | 156.23 | 371.9 | 24.7 | 0.4732 |

of the Peng–Robinson equation of state for the $CO_2$ + NPMA system are $k_{ij} = 0.0066$ and $\eta_{ij} = -0.0477$. A reasonable fit of the data is obtained over most of the composition range even if no mixture parameters are used. But if two mixture parameter, $k_{ij} = 0.0066$ and $\eta_{ij} = -0.0477$, are used the fit of the experimental results is significantly better. The RMSD at five temperatures for $CO_2$ + NPMA system was 5.88% of the bubble-point number 36. We compared the experimental results with the calculated $P$–$x$ isotherms at temperatures of 40, 60, 100, and 120 °C for the $CO_2$ + NPMA system using the optimized values of $k_{ij}$ and $\eta_{ij}$ determined at 80 °C. As shown in Fig. 4, a good fit of the data is obtained with Peng–Robinson equation using an adjustable mixture parameter for the $CO_2$ + NPMA system.

Fig. 4 shows the comparison of experimental data and the mixture-critical curve for the $CO_2$ + NPMA system calculated by the Peng–Robinson equation of state. The experimental data and calculated mixture-critical curve are type-I, in agreement with experimental observations. The traits of type-I phase behavior are that only a single liquid phase exists throughout the phase diagram and that the mixture-critical curve runs continuously from the critical point of more volatile component to that of less volatile component [1]. As shown in Fig. 5, the solid lines represent the vapor pressure for pure $CO_2$ [19] and NPMA [19]. The solid circles represent the critical point for pure $CO_2$ and NPMA. The upper part of the dashed line is fluid state, while the lower part of it is vapor–liquid state (two-phases).

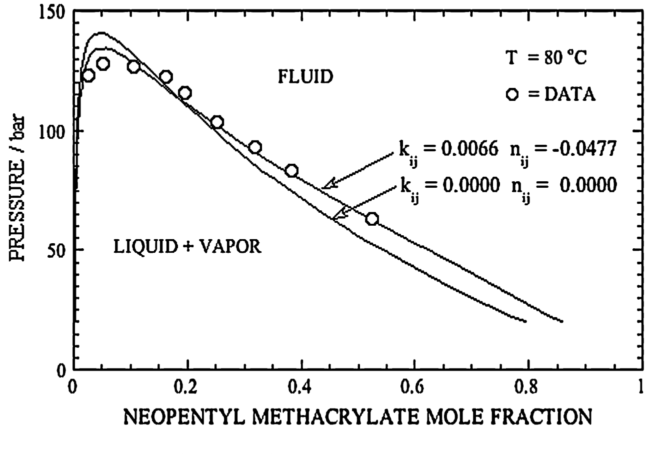

Fig. 3. Comparison of the best fit of Peng–Robinson equation of state to the $CO_2$ + neopentyl methacrylate system at 80 °C.

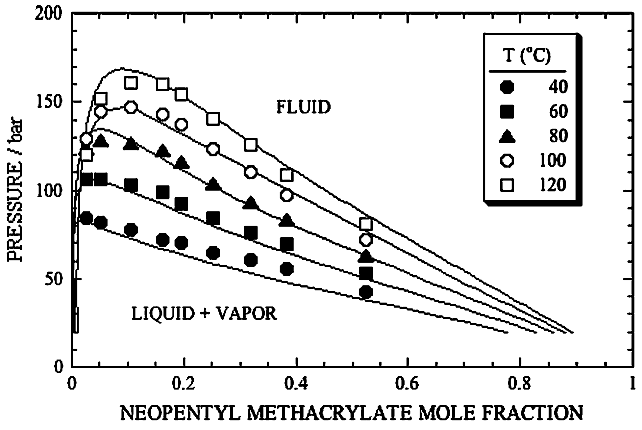

Fig. 4. Comparison of the experimental data (symbols) for the $CO_2$ + neopentyl methacrylate system with calculations (solid lines) obtained with the Peng–Robinson equation of state $k_{ij}$ equal to 0.0066 and $\eta_{ij}$ equal to −0.0477.

### 3.2. Phase behavior of poly(NPMA) + $CO_2$ + NPMA system

The cloud points for poly(NPMA) + supercritical solvents + NPMA mixture are measured and reproduced at least twice to within ±2.8 bar and ±0.3 °C. Table 3 and Fig. 6 show

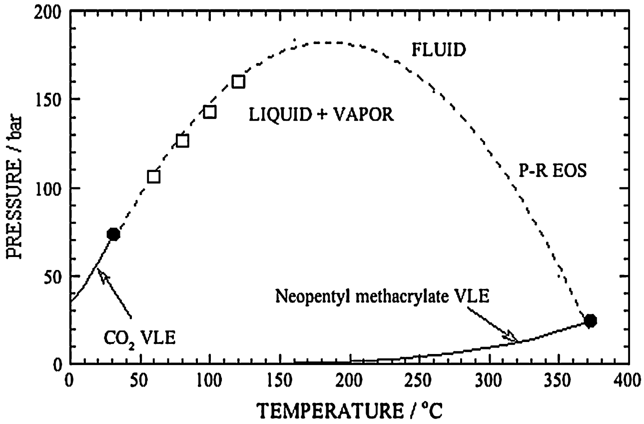

Fig. 5. Pressure–temperature diagram for the $CO_2$ + neopentyl methacrylate system. The solid lines and the solid circles represent the vapor–liquid lines and the critical points for pure $CO_2$ and neopentyl methacrylate. The open squares are critical points determined from isotherms measured in this work. The dashed lines represent calculations obtained using Peng–Robinson equation of state with $k_{ij}$ equal to 0.0066 and $\eta_{ij}$ equal to −0.0477.

Table 3
Experimental cloud-point data for the poly(neopentyl methacrylate) [poly(NPMA)] + $CO_2$ + neopentyl methacrylate [NPMA] system measured in this study

| $T$ (°C) | $P$ (bar) |
|---|---|
| 4.1 wt% Poly(NPMA) + 0.0 wt% NPMA | |
| 76.6 | 2001.7 |
| 90.9 | 1244.5 |
| 104.6 | 1124.1 |
| 121.6 | 1063.8 |
| 135.9 | 1043.1 |
| 150.7 | 1034.5 |
| 166.0 | 1035.5 |
| 181.3 | 1046.6 |
| 5.5 wt% Poly(NPMA) + 5.2 wt% NPMA | |
| 58.7 | 856.9 |
| 80.3 | 808.6 |
| 100.7 | 815.5 |
| 120.2 | 836.2 |
| 142.2 | 863.8 |
| 161.5 | 884.5 |
| 181.6 | 929.3 |
| 5.6 wt% Poly(NPMA) + 11.1 wt% NPMA | |
| 59.2 | 563.8 |
| 80.5 | 605.2 |
| 100.0 | 648.3 |
| 120.5 | 684.5 |
| 142.4 | 722.4 |
| 162.2 | 753.5 |
| 180.4 | 770.7 |
| 4.7 wt% Poly(NPMA) + 19.0 wt% NPMA | |
| 58.2 | 346.6 |
| 79.1 | 412.1 |
| 102.6 | 484.5 |
| 122.2 | 529.3 |
| 142.0 | 574.1 |
| 161.3 | 603.5 |
| 181.7 | 636.2 |
| 4.7 wt% Poly(NPMA) + 28.1 wt% NPMA | |
| 59.5 | 298.3 |
| 79.8 | 363.8 |
| 101.5 | 422.4 |
| 121.2 | 467.2 |
| 142.0 | 506.9 |
| 161.5 | 537.9 |
| 180.8 | 546.6 |
| 4.6 wt% Poly(NPMA) + 40.2 wt% NPMA | |
| 59.2 | 222.4 |
| 80.2 | 291.4 |
| 101.9 | 353.5 |
| 121.7 | 394.8 |
| 139.4 | 431.0 |
| 162.6 | 474.1 |
| 181.0 | 498.3 |

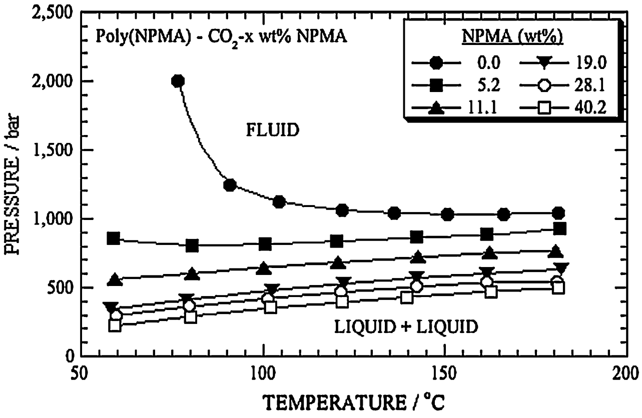

Fig. 6. Experimental cloud-point curves for the poly(neopentyl methacrylate) [poly(NPMA)] + $CO_2$ + neopentyl methacrylate (NPMA) system with different NPMA concentration. The concentration of polymer is about 5.0 wt% for each solution.

the cloud-point behavior of the poly(NPMA) + $CO_2$ + $x$ wt% NPMA mixture. The poly(NPMA) does dissolve in pure $CO_2$ at the temperature below 181 °C and the pressure of 2000 bar. At temperatures greater than 100 °C, the cloud-point curve is shifted to moderately lower pressures due to the decrease in the free-volume difference between polymer and mixed solvent. With 5.2 wt% NPMA added to the solution, the cloud-point curve exhibits upper–lower critical solution temperature (U–LCST) type phase behavior from positive slope to slightly negative slope. As shown in Fig. 6, for the curve with 5.2 wt% NPMA, it shows negative slope at low temperature and the slope changes to a positive slope as the temperature increases and virtually, the cloud-point pressure increases slightly over a temperature range from 58 to 180 °C. The U–LCST curve in the cloud-point pressure with decreasing temperature is attributed to the increase of polymer + solvent (or + cosolvent) interactions over solvent + solvent, cosolvent + cosolvent and polymer + polymer interactions. With 11.1 wt% NPMA in solution, the cloud-point pressure curve shows the LCST behavior of positive slope at pressures from 564 bar to 770 bar and a temperature range of 60–180 °C. If 19.0, 28.1 and 40.2 wt% NPMA are added to the solution, the cloud-point curve exhibits lower critical solution temperature (LCST) type phase behavior of the positive slope at lower pressures from 298 bar to 636 bar and a temperature range of 58–181 °C. The location of the LCST type is mainly controlled by entropic interactions, which are more sensitive to the changes in pressure. This type is due to the decrease in free-volume difference between the poly(NPMA), $CO_2$, and NPMA. The phase behavior of poly(NPMA) + $CO_2$ + 19.0, 28.1 and 40.2 wt% NPMA systems shows a positive slope in 2.34 bar/°C (19.0 wt%), 2.08 bar/°C (28.1 wt%) and 2.24 bar/°C (40.2 wt%), respectively. The effect of NPMA cosolvent on the phase behavior is similar to that observed for the poly(ethyl methacrylate) + $CO_2$ + 38.2 wt% ethyl methacrylate systems [13]. These slopes are about 40% greater than those observed for binary poly(isobutylene) + alkane mixtures reported by Zeman and Patterson [20], which are due to the enhanced influence of hydrostatic pressure on the free-volume difference between poly(NPMA) and the $CO_2$ + NPMA mixture.

When 51.2 wt% NPMA is added to the poly(NPMA) + $CO_2$ solution, as shown in Fig. 7 and Table 4, the cloud-point curve takes the typical appearance of a LCST boundary. At 140 °C the phase boundary has shifted from 431 bar to 328 bar as the concentration of NPMA increases from 40.2 to 51.2 wt%. The poly(NPMA) + $CO_2$ + 51.2 wt% NPMA phase behavior

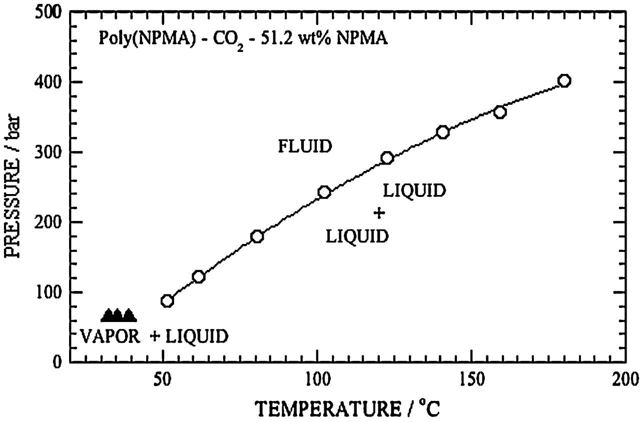

Fig. 7. Impact of 51.2 wt% neopentyl methacrylate (NPMA) monomer (on a polymer-free basis) on the phase behavior of the poly(neopentyl methacrylate) [poly(NPMA)] + $CO_2$ system. ○, fluid → liquid + liquid transition; ▲, fluid → liquid + vapor transition. The concentration of polymer is about 5 wt% for each solution.

curve intersects a fluid → liquid + vapor (LV) curve at about 40 °C and about 67 bar. A liquid and vapor phase coexists at pressures below this curve. The initial slope of the poly(NPMA) + $CO_2$ + NPMA LCST curve at the lowest pressures is about 3.1 bar/°C. The results obtained in this study demonstrate clearly that it is possible to obtain a single phase that extends over a large temperature range at modest pressures if sufficient amounts of free methacrylate monomer are added to the solution.

### *3.3. Phase behavior of poly(NPMA) + $CO_2$ + DME and poly(NPMA) + SCF solvents system*

Table 5 lists the properties of the solvents used in this study [19,21–24]. For the poly(NPMA) + solvent systems, $CO_2$, propylene, propane, butane, 1-butene and dimethyl ether (DME) were used as solvents. Propane and propylene have similarity in critical properties and polarizabilities, though propylene possesses both dipole and quadrupole moments. In propane and propylene, the effect of solvent polarity can be studied independently about polarizability. On the other hand, the comparison of propane and butane, or propylene and 1-butene yields information about the effect of solvent size and polarizability on the phase behavior independent of polarity effects.

Table 6 and Fig. 8 show the phase behavior of the poly(NPMA) + $CO_2$ + DME mixture. The poly(NPMA) + $CO_2$

Table 4
Experimental cloud-point and bubble-point data for the poly(neopentyl methacrylate) [poly(NPMA)] + $CO_2$ + neopentyl methacrylate (NPMA) system measured in this study

| $T$ (°C) | $P$ (bar) | Transition |
|---|---|---|
| 4.6 wt% Poly(NPMA) + 51.2 wt% NPMA | | |
| 51.5 | 87.9 | C.P |
| 61.5 | 122.4 | C.P |
| 80.7 | 179.3 | C.P |
| 102.6 | 242.8 | C.P |
| 122.7 | 291.4 | C.P |
| 140.7 | 328.3 | C.P |
| 159.2 | 356.9 | C.P |
| 180.1 | 403.1 | C.P |
| 32.4 | 66.7 | B.P |
| 35.5 | 67.0 | B.P |
| 39.1 | 67.2 | B.P |

Table 5
The properties of critical temperatures, critical pressures, critical densities, polarizabilities, dipole moments, and quadrupole moments of the solvents

| Solvents | $T_c$ (°C) | $P_c$ (bar) | $\rho_c$ (g/cm$^3$) | $\alpha \times 10^{25}$ (cm$^3$) | $\mu$ (D) | $Q$ (esu cm$^2$) |
|---|---|---|---|---|---|---|
| $CO_2$ | 31.0 | 73.8 | 0.469 | 26.5 | 0.0 | −4.3 |
| Propane | 96.7 | 42.5 | 0.217 | 62.9 | 0.1 | 1.2 |
| Propylene | 91.9 | 46.2 | 0.236 | 62.6 | 0.4 | 2.5 |
| Butane | 152.1 | 38.0 | 0.228 | 81.4 | 0.0 | |
| 1-Butene | 146.4 | 39.7 | 0.234 | 82.4 | 0.3 | 2.5 |
| Dimethyl ether | 126.8 | 53.0 | 0.258 | 52.2 | 1.3 | |

Table 6
Experimental cloud-point data for the poly(neopentyl methacrylate) [poly(NPMA)] + $CO_2$ + dimethyl ether (DME) system measured in this study

| $T$ (°C) | $P$ (bar) |
|---|---|
| 4.1 wt% Poly(NPMA) + 0.0 wt% DME | |
| 76.6 | 2001.7 |
| 90.9 | 1244.5 |
| 104.6 | 1124.1 |
| 121.6 | 1063.8 |
| 135.9 | 1043.1 |
| 150.7 | 1034.5 |
| 166.0 | 1035.5 |
| 181.3 | 1046.6 |
| 5.2 wt% Poly(NPMA) + 5.2 wt% DME | |
| 60.4 | 906.9 |
| 81.0 | 863.8 |
| 101.1 | 870.7 |
| 120.9 | 884.5 |
| 140.7 | 905.2 |
| 160.6 | 922.4 |
| 179.5 | 943.1 |
| 4.8 wt% Poly(NPMA) + 12.1 wt% DME | |
| 80.4 | 572.4 |
| 101.4 | 622.4 |
| 120.1 | 669.0 |
| 140.5 | 712.1 |
| 161.2 | 750.0 |
| 180.6 | 777.6 |
| 5.0 wt% Poly(NPMA) + 40.8 wt% DME | |
| 59.3 | 208.6 |
| 80.8 | 284.5 |
| 101.3 | 343.1 |
| 120.2 | 387.9 |
| 141.8 | 439.7 |
| 160.0 | 477.6 |
| 179.1 | 498.3 |
| 3.6 wt% Poly(NPMA) + 96.4 wt% DME | |
| 102.2 | 36.9 |
| 119.0 | 77.6 |
| 139.4 | 122.4 |
| 160.3 | 165.5 |
| 183.1 | 200.0 |

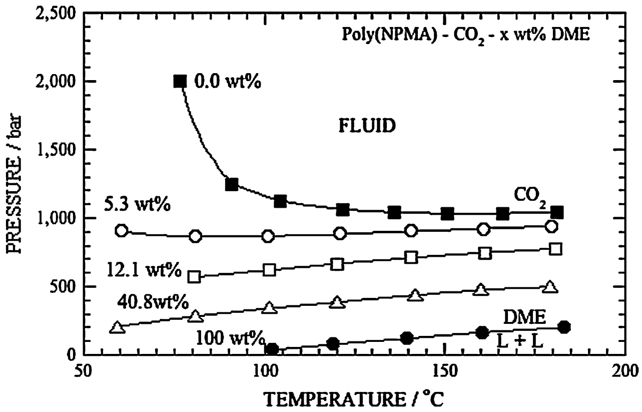

Fig. 8. Impact of dimethyl ether (DME) concentration on the phase behavior of the poly(neopentyl methacrylate) + $CO_2$ + $x$ wt% DME system. The concentration of polymer is about 5 wt% for each solution.

Table 7
Experimental cloud-point data for the poly(neopentyl methacrylate) [poly(NPMA)] + supercritical solvents system measured in this study

| $T$ (°C) | $P$ (bar) |
|---|---|
| 5.4 wt% Poly(NPMA) + 94.6 wt% propane | |
| 59.4 | 208.6 |
| 80.7 | 229.3 |
| 100.7 | 250.0 |
| 121.0 | 274.1 |
| 139.8 | 291.4 |
| 160.8 | 312.1 |
| 181.4 | 332.8 |
| 4.7 wt% Poly(NPMA) + 95.3 wt% propylene | |
| 60.3 | 115.5 |
| 82.5 | 169.0 |
| 101.1 | 208.6 |
| 121.9 | 244.8 |
| 142.4 | 274.1 |
| 161.6 | 298.3 |
| 180.8 | 322.4 |
| 4.6 wt% Poly(NPMA) + 95.4 wt% butane | |
| 101.1 | 60.3 |
| 118.4 | 91.4 |
| 139.3 | 122.4 |
| 159.8 | 153.5 |
| 181.7 | 170.7 |
| 4.4 wt% Poly(NPMA) + 95.6 wt% 1-butene | |
| 102.3 | 21.7 |
| 120.4 | 56.9 |
| 139.4 | 91.4 |
| 161.3 | 125.9 |
| 181.2 | 153.5 |

mixture was obtained at a range of temperature of 76–180 °C and at pressures of 1046–2000 bar, and for poly(NPMA) + DME mixture at the range of temperature of 102–183 °C and pressures of 37–200 bar. The pressure difference between two systems is due to whether or not dipole moment in DME (1.3 D) and $CO_2$ (0.0 D) as shown in Table 5. In case of the poly(NPMA) + $CO_2$ system, the rapid rise in the cloud-point pressure with decreasing temperature is attributed to the increase of solvent + solvent interactions over polymer + solvent interactions. The phase behavior of low pressure for poly(NPMA) + DME system is due to polar with a large dipole moment of DME. As shown in Fig. 8, the poly(NPMA) + $CO_2$ + 5.3 wt% DME mixture shows the U–LCST-type behavior from negative slope to positive slope, and then the pressure increases slightly at about 140 °C. With 12.1 wt% DME added to the solution, the cloud-point curve exhibits LCST region phase behavior of the positive slope in 2.07 bar/°C. The poly(NPMA) + $CO_2$ + 40.8 wt% DME system shows the LCST-type of the positive slope in 2.43 bar/°C. At 120 °C, the pressure difference of the poly(NPMA) + $CO_2$ + 12.1 from 40.8 wt% DME system shows about 280 bar, caused by the impact of free volume as DME concentration increases.

Table 7 and Fig. 9 show the cloud-point obtained in this work for poly(NPMA) dissolved in supercritical propane, propylene, butane and 1-butene. The phase behavior of poly(NPMA) + propane, +propylene, +butane and +1-butene system exhibits LCST curves of a positive slope in 1.02 bar/°C (propane), about 1.69 bar/°C (propylene), 1.39 bar/°C (butane) and 1.67 bar/°C (1-butene), respectively. The poly(NPMA) + propane and +propylene system is presented at the temperature range of 60–181 °C and pressure range of 115–333 bar. At 140 °C, the phase behavior boundary is the pressure of about 270 ± 10 bar, and it is due to the similarity in polarizability of propane ($62.9 \times 10^{-25}$ $cm^3$) and propylene ($62.6 \times 10^{-25}$ $cm^3$) as shown in Table 5. The poly(NPMA) + butane and +1-butene system is shown at temperature range of 100–180 °C and lower pressure of 21–170 bar. For the temperature of 140 °C, the cloud-point curve reduces from 122 bar (butane) to 91 bar (1-butene). As shown in Table 5, it seems to be due to a little of polarizability in butane ($81.4 \times 10^{-25}$ $cm^3$) and 1-butene ($82.4 \times 10^{-25}$ $cm^3$). The pressure difference between poly(NPMA) + propane and poly(NPMA) + butane system is considered to be due to polarity factor reducing pressures from 291 bar to 122 bar at temperature of 140 °C.

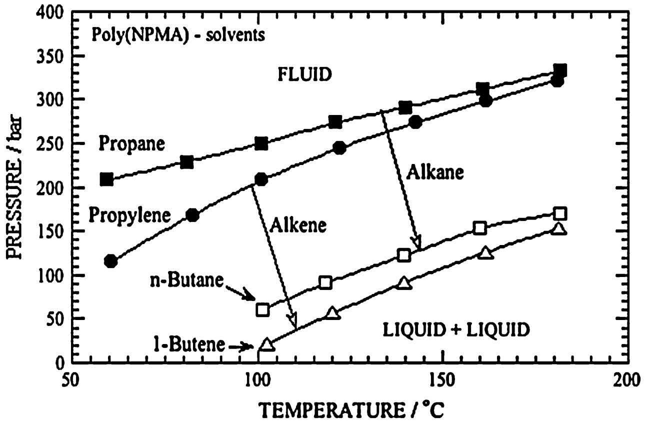

Fig. 9. Effect of the phase behavior of poly(neopentyl methacrylate) [poly(NPMA)] dissolved in supercritical propane, propylene, butane, and 1-butene. The concentration of polymer is about 5 wt% for each solution.

## 4. Conclusions

The $CO_2$ + NPMA system exhibits type-I phase behavior. The $P-x$ bubble-point curves are convex which indicates that $CO_2$ exhibits a high solubility in NPMA, probably due to the formation of a weak complex between the carboxylic oxygen in NPMA and the carbon in $CO_2$. The Peng–Robinson equation of state can be used with two adjustable parameters to calculate a reasonable representation of the phase behavior of the NPMA system. Cloud-point data are presented for binary and ternary mixtures of poly(NPMA) + $CO_2$ + $x$ wt% NPMA system. With 51.2 wt% NPMA added to the poly(NPMA) + $CO_2$ mixture, the cloud-point curve shows the typical appearance of a LCST boundary. Cloud-point behavior is presented for poly(NPMA) + $CO_2$ + NPMA mixtures with NPMA concentration of 0.0–40.2 wt%. The NPMA monomers provide favorable intermolecular interactions between the polymer segments and the solvent molecules, which help dissolution of the polymer. The cloud-point curves are shown for the binary mixtures for poly(NPMA) in supercritical propane, propylene, butane, 1-butene, and dimethyl ether at temperature up to 180 °C and pressure range of 21–332 bar. Also, the impact of DME concentration for the poly(NPMA) + $CO_2$ + 5.3, 12.1, 40.8 wt% DME system is measured at temperature up to 180 °C and pressure range of 36–943 bar.

## Acknowledgements

The author gratefully acknowledges the financial support from the Korea Ministry of Commerce, Industry & Energy and the Korea Energy Management Corporation.

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