

# S - L TRANSITION OF PEG 35000 UNDER PRESSURE OF NITROGEN AND CARBON DIOXIDE

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**Abstract:** The aim of the present work was to investigate thermal behavior such as melting temperature ( $T_{\text{onset}}$  and  $T_{\text{endset}}$ ) of PEG in presence of compressed  $\text{CO}_2$  and  $\text{N}_2$  and to compare new measured data with the results obtained previously by capillary method. Completely new data on heat of fusion under pressure of gas and degree of crystallinity for PEG ( $M_w$  35000) under pressure of nitrogen and carbon dioxide in the pressure range up to 100 bar have been determined. Measurements were performed on HP DSC1 STAREe, METTLER TOLEDO. Samples of PEG were heated from 293K to 373 K with the heating rate of 5 K/min. The results showed that  $\text{CO}_2$  under pressure significantly affect thermal behavior of PEG.  $T_{\text{onset}}$  and  $T_{\text{endset}}$  of PEG under pressure of  $\text{CO}_2$  were lowered for approximately 5-10 °C depending on pressure compared to melting point at atmospheric conditions while in presence of  $\text{N}_2$  decrease in melting is negligible. Comparison of both HP methods (DSC and capillary) shows very small deviation of measured data. Crystallinity degree (CD) of PEG after exposure to the  $\text{CO}_2$  at elevated pressure, calculated on the basis of enthalpies of fusion, markedly decreased (up to 40% more amorphous phase was present), while after exposure to the  $\text{N}_2$ , CD was more or less constant.

## INTRODUCTION

Poly(ethylene glycol) (PEG) is a condensation polymer of ethylene oxide, having the general formula  $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ , where  $n$  is the average number of repeating oxyethylene units ( $n = 4$  to 180). The low relative molecular mass compounds ( $MW < 700$ ) are colorless, odorless, viscous liquids, while compounds with relative molecular mass higher than 1000 are waxlike or solids.

PEGs are water-soluble polymers and are widely used in the pharmaceutical and cosmetic industries because of their physiological acceptance [1]. Their hydrophilicity, antithrombogenicity, and good biocompatibility recommend PEGs for biomedical applications, such as drug delivery devices [2,3,4] and tissue engineering scaffolds. The traditional methods for polymer processing involve either high temperatures, necessary for melting or viscosity reduction, or hazardous volatile organic solvents (VOCs) and chlorofluorocarbons (CFCs).

Due to the undesirable environmental impact of these solvents, extensive research is focused on seeking new and cleaner methods for the processing of polymers. One such method is the use of supercritical fluids as processing solvents or plasticizers. The special combination of gaslike viscosity and diffusivity and liquid-like density and solvating properties of a supercritical fluid makes it an excellent solvent for various applications [5].  $\text{scCO}_2$  can be used as solvent or antisolvent for obtaining PEG microparticles used as drug carriers [6,7].

The technique offers two important advantages. The first advantage refers to a better control of particle size, particle size distribution, and morphology, which can be achieved by tuning process parameters such as the amount of dissolved CO<sub>2</sub>, temperature, pressure, nozzle diameter, and depressurization rate. The second advantage refers to the lack of organic solvent or, when necessary, the efficient removal and recovery of the solvent. This allows sensitive bioactive molecules, such as proteins and drugs, to be introduced during polymer processing stages [8].

## MATERIALS

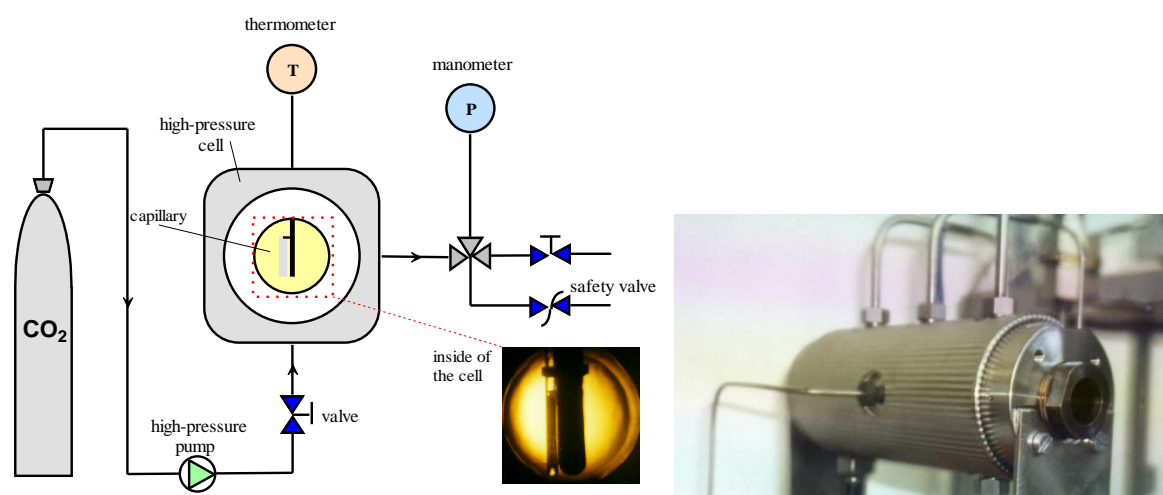
Poly(ethylene glycol) (PEG) with molecular weight 35 000 was obtained from Merck, Germany, and was used without further purification.

Carbon dioxide (CO<sub>2</sub>) and nitrogen (N<sub>2</sub>) were obtained from Messer, Slovenia, and were used without further purification.

## METHODS

### *Determination of melting point under pressure*

Two methods were used for the determination of melting points of PEG under pressure of gas. *Capillary method.* A basic scheme of the capillary method used for the determination of the influence of pressure on the melting point of the substance in the presence of a gas is presented in Fig. 1. The optical cell has been designed for a pressure of 500 bar and temperature of 250 °C. The volume of the cell is 14 ml. The observation windows are made of sapphire and are fixed to the cell with screws. The cell is equipped with three additional openings for introducing and emptying the gas and to introduce a thermocouple. Pressurized gas was introduced via a high-pressure pump. The pressure was measured (accuracy within  $\pm 0.1$  %) by an electronic pressure gauge (Digibar PE 500, Hottinger-Baldwin), and the cell was electrically thermostated by a heating jacket (accuracy within  $\pm 0.5$  °C).



**Figure 1:** Capillary method for measuring melting points – basic scheme of the experimental apparatus.

DSC. Measurements were performed on HP DSC1 STAREe, METTLER TOLEDO (Fig. 2). Samples of PEG were heated from 293K to 373 K with the heating rate of 5 K/min. Melting temperature ( $T_{\text{onset}}$  and  $T_{\text{endset}}$ ), heat of fusion and degree of crystallinity of PEG ( $M_w$  35000) under pressure of  $N_2$  and  $CO_2$  were investigated in the pressure range up to 10 MPa.



**Figure 2:** HP DSC1 STAREe, METTLER TOLEDO apparatus.

## RESULTS

Comparison of both methods for determining the melting point of PEG 35 000 under pressure of  $CO_2$  is shown in Table 1.

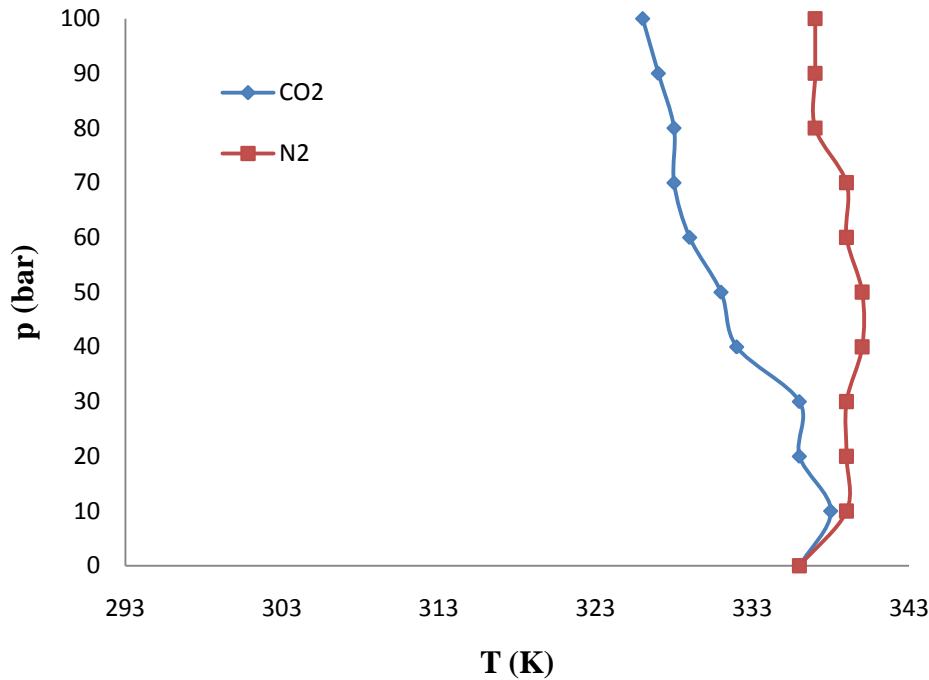
Table 1: Melting point of PEG 35 000 under pressure of  $CO_2$  and  $N_2$ .

HP DSC/ $CO_2$		Optical cell/ $CO_2$		HP DSC/ $N_2$	
p (bar)	$T_{\text{ave}}$ (K)	p (bar)	$T_{\text{ave}}$ (K)	p (bar)	$T_{\text{ave}}$ (K)
1	336	1	336	1	334
10	338	10	338	10	336
20	336	20	336	20	334
30	336	30	336	30	332
40	332	40	332	40	330
50	331	50	331	50	328
60	329	60	329	60	327
70	328	70	328	70	326
80	328	80	328	80	325
90	327	90	327	90	322
100	326	100	326	100	321

Results obtained with both methods showed similar trend with very small deviation of measured data. Compared to the melting point at 1 bar, the liquefaction temperature increases with increasing the pressure- to about 10 bar. In this pressure range (1-10 bar) the solubility of  $CO_2$  in PEG is low, and therefore no decrease in the liquefaction temperature due to the solubilized

gas is observed. At pressures higher than 10 bar, the S-L transition temperature of the PEG decreases with increasing the pressure.

The melting course of PEG 35 000 under pressure of CO<sub>2</sub> and N<sub>2</sub> is presented in Fig. 3.



**Figure 3:** p – T diagram for PEG 35 000/CO<sub>2</sub> and PEG 35 000/N<sub>2</sub> systems.

The results showed that CO<sub>2</sub> under pressure significantly affect thermal behavior of PEG. T<sub>onset</sub> and T<sub>endset</sub> of PEG under pressure of CO<sub>2</sub> were lowered for approximately 5-10 °C depending on pressure compared to melting point at atmospheric conditions while in presence of N<sub>2</sub> decrease in melting is negligible.

Crystallinity degree was calculated on the basis of enthalpies of fusion by following equation:

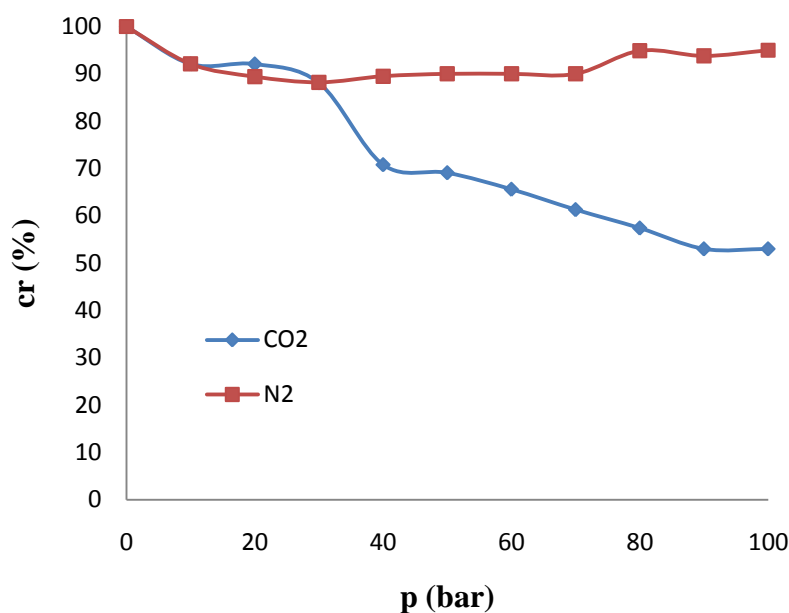
$$cr(\%) = \frac{\Delta H_{mx}}{\Delta H_{m0}} \times 100,$$

where:

$\Delta H_{mx}$  - enthalpy of fusion of PEG 35 000 after exposing under pressure of CO<sub>2</sub> and N<sub>2</sub>,

$\Delta H_{m0}$  - enthalpy of fusion of sample before exposing under pressure of CO<sub>2</sub> and N<sub>2</sub>.

The enthalpy of fusion of unprocessed PEG 35 000 was taken as 100 %. Fig. 4 presents comparison in crystallinity degree of PEG 35 000 at different pressures. Crystallinity degree (CD) of PEG 35 000 markedly decreased when sample was exposed to pressure of CO<sub>2</sub>. At 100 bar the content of amorphous phase was higher than 40 %. Degree of crystallinity after exposing to pressure of N<sub>2</sub> was almost equal to the degree before exposing.



**Figure 4:** Crystallinity degree of PEG 35 000 after exposing to pressure of CO<sub>2</sub> and N<sub>2</sub>.

## CONCLUSION

The knowledge of melting point variation in supercritical fluids is necessary for optimization of the high pressure spray processes. The melting points of polyethyleneglycol with molar mass of 35 000 under pressure of CO<sub>2</sub> and N<sub>2</sub> were measured with two methods; in optical cell and with high pressure DSC apparatus. It was found that the pressure and the gas influenced the S – L – V curve. The S – L – V curve for system PEG 35 000/CO<sub>2</sub> has a temperature maximum and temperature minimum which was not observed in system PEG 35000/N<sub>2</sub>. The course of the melting line for PEG/CO<sub>2</sub> is similar for both applied methods with small deviation of measured data. Melting point in presence of CO<sub>2</sub> was lowered for approximately 5-10 °C depending on pressure while under N<sub>2</sub> decrease in melting is negligible. Also sub- or supercritical state of CO<sub>2</sub> affected thermal behavior of PEG. Furthermore, with increasing the pressure of CO<sub>2</sub> the content of amorphous phase of PEG was significantly increased.

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