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Solubility of modified poly(propylene oxide) and silicones in supercritical carbon dioxide

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Abstract

In this paper, the solubility of several modified poly(propylene oxide) (PPO) derivatives and silicones has been investigated by measuring cloud point pressure (CPP) values in supercritical carbon dioxide (Sc CO_2) at a temperature range of 308–328 K and in the pressure range of 7.40–23.00 MPa. The end group and molecular weight strongly affect the solubility of the PPO derivatives. The solubility of modified silicones in Sc CO_2 is generally larger than that of polyethers of the same chain length. In addition, the solubility of some silicones with pendant phosphine groups in Sc CO_2 was also determined. The CPP values of the phosphine-modified silicone oils increases with the number of phosphine side chains along the silicone backbone. The relationship between the solubility and structure of the PPOs and silicones is discussed.

Keywords: Supercritical carbon dioxide; Solubility; Poly(propylene oxide); Silicone; Phosphine

1. Introduction

The utilization of Sc CO_2 has attracted significant attention [1–3], owing to its low toxicity, non-flammability, low cost, and abundance. Furthermore, Sc CO_2 is considered an environmentally benign alternative for conventional organic solvents because the CO_2 properties of density, dielectric constant, diffusion coefficient, and the solubility parameter can be continuously tuned by simply changing the pressure and/or temperature at the Sc condition, especially in the near-critical region. CO_2 has already been used in the processes of extraction, cleaning systems, micro-electronics development, and polymer production [4]. CO_2-based solvents offer new opportunities in chemical manufacturing, such as for heterogeneous reactions, protein chemistry, and separation processes [5]. However, the solubility of high molecular weight polymers or hydrophilic molecules, such as proteins, high polar organic compounds, and metal ions in CO_2 is very low due to its non-polarity. This limitation of lower solubility restricts the application of Sc CO_2 [6,7]. To overcome this drawback, surfactants and/or cosolvents have been employed. In the presence of a surfactant, some polymerizations and transition metal catalyzed reactions have been carried out in Sc CO_2 [8–14]. To be effective the surfactant should have properties that promote solubility in Sc CO_2. At this time, some fluoropolymers, silicone polymers, and poly(ether-carbonate) copolymers are reported to be soluble in CO_2 [15], while some fluorinated, siliconated, and polyether-modified materials have been used as surfactants [9,12,14]. So far, the most efficient surfactants used in Sc CO_2 are fluorinated surfactants, but they are very expensive and difficult to synthesize. Therefore, the design and development of alternative surfactants with higher efficiency would greatly benefit the potential applications of CO_2 as a solvent and/or reagent. Although several kinds of oligomers and polymers have been used as model materials to determine phase behavior with Sc CO_2 [1–3,5,16–18], further studies on the relationship between solubility and structure will be valuable for accumulating more information for designing novel surfactants. Herein, we determine the solubility of several modified PPO and siliconated materials by measuring their CPP values in Sc CO_2 and discuss the relationship between the solute structure and its solubility.

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2. Experimental

2.1. Materials

CO_2 was obtained from Tianjin BOC gas industry. The hydroxyl silicone oil and hydrogen-containing silicone oil were purchased from Jilin Huafeng chemical factory and used as received. All modified PPOs and silicones were synthesized according to our previously described procedures[1]. The structures and corresponding abbreviations are listed in Chart 1.

2.2. Apparatus

A high-pressure stainless steel view cell of 50 mL capacity was used to measure the CPP values. The temperature was controlled by a SXHW model controller with an accuracy of better than ±0.05 K. The pressure gauge was composed of a SCYB3111 model pressure transducer and an indicator, which was accurate to ±0.01 MPa in the pressure range of 0–25 MPa. The sample in the cell was stirred by a magnetic stirrer.

2.3. Typical procedure for determining the CPP values

In a typical experiment, 0.5000 g of the sample was charged into a high-pressure view cell which was flushed with CO_2, and the cell was immersed in a constant temperature water bath for 1 h to obtain thermal equilibrium. Then CO_2 was slowly compressed into the cell by a syringe pump, and the sample was stirred while the pressure in the cell rose. When the sample in the cell became homogeneous, the stirrer was stopped for observation. The pressure was released slightly until the system became cloudy again. At this point, the pressure was recorded as the CPP value. Then the pressure was increased gradually until the cloudy mixture became transparent again. This procedure was repeated three times at each condition and the uncertainty for the respective pressure was ±0.05 MPa [2].

Safety note: The experiments described in this paper involve the use of high pressure and require equipment with an appropriate pressure rating.

3. Results and discussion

3.1. Solubility of modified PPO derivatives

The PPO molecule is reported to be soluble in CO_2, but the solubility depends on the end groups and the molecular weight [5]. The end group can reduce the intermolecular attraction of PPO by eliminating hydrogen bonding. In order to obtain more information about the end-group effect on the solubility of PPO in CO_2, modified PPOs were prepared by the reaction of trimethylsilyl (TMS) and acetyl chlorides with the hydroxyl groups of the PPO molecule. The CPP values of modified PPO derivatives were measured and the plot of CPP values versus temperature is shown in Fig. 1.

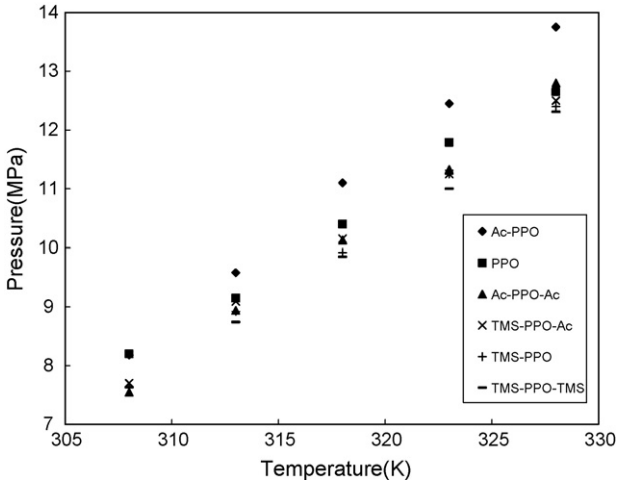

Fig. 1. CPP values vs. temperature for modified PPO derivatives.

Generally, the CPP value of a modified PPO increases with temperature (shown in Fig. 1). Nonetheless, the temperature dependence of each PPO is different. At low temperature, the CPP values of Ac-PPO and PPO are higher than those of the other four substances, owing to stronger self-association through hydrogen bonding. In order to clearly show the solubility difference of the modified PPOs in Sc CO_2, the density of the Sc CO_2 solution containing PPO has been calculated by the Sanchez-Lacombe model [16]. The basic equation is given as follows:

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

where ρ^*, P^*, and T^* are the characteristic parameters; ρ, P, and T are the density, pressure, and temperature of the system; and r represents the number of lattice sites occupied by a molecule. The characteristic parameters used in this calculation are listed in Table 1 [16]. The value of $r = 7.2814$ is obtained from reference data [2] as listed in Table 2. In order to evaluate the accuracy of this method, both calculated and measured density data are listed in Table 3. The percentage error between the calculated and measured density is in the range of −0.16 to 4.14%. We consider the average error of 1.32% to be acceptable. The density and solubility data of the modified PPOs are listed in Table 4.

As a whole, the solubility of the modified PPOs increases with temperature (as shown in Figs. 1. and 2), and the end-group effect shown in Fig. 2 becomes much clearer than in Fig. 1. A PPO molecule with different end groups has an unusual assembly. Mono end-capped and unsubstituted PPO molecules can associate together by hydrogen bonding. Two end-capped

Table 1
Characteristic parameters for the calculation process

	P^* (MPa)	T^* (K)	ρ^* (g/cm^3)
CO_2	574.5	305.0	1.510

[1] The synthesis of these compounds will be published in another paper, which is in preparation.