

# Supporting Information for “Effect of Temperature and Pressure on Surface Tension of Polystyrene in Supercritical Carbon Dioxide”: Density determination and Surface Tension comparison

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## 1. Density determination

The densities of polystyrene saturated with carbon dioxide and carbon dioxide were determined by the Sanchez and Lacombe (S-L) equation of state (EOS) [26], as expressed below:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] = 0 \quad (\text{S1})$$

where  $\tilde{\rho}$  is the reduced density,  $\tilde{P}$  is the reduced pressure,  $\tilde{T}$  is the reduced temperature and  $r$  is the number of sites occupied by a molecule; they are defined as

$$\tilde{P} = \frac{P}{P^*}, \tilde{\rho} = \frac{\rho}{\rho^*}, \tilde{T} = \frac{T}{T^*}, r = \frac{MP^*}{RT^* \rho^*} \quad (\text{S2})$$

where  $\rho$  is the density,  $P$  is the pressure,  $T$  is the temperature,  $M$  is the molecular weight and  $R$  is the gas constant. In the equation, the characteristic parameters,  $P^*$ ,  $\rho^*$ , and  $T^*$ , of the S-L EOS for the mixture were evaluated using the following mixing rules:

$$P^* = \sum_i \sum_j \phi_i \phi_j P_{ij}^*, P_{ij}^* = (1 - k_{ij})(P_i^* P_j^*)^{0.5}, T^* = P^* \sum_i \frac{\phi_i^0 T_i^*}{P_i^*},$$

$$\frac{1}{r} = \sum_i \frac{\phi_i^0}{r_i^0}, \phi_i^o = \frac{(\phi_i P_i^* / T_i^*)}{\sum_j (\phi_j P_j^* / T_j^*)}, \phi_i = \frac{(w_i / \rho_i^*)}{\sum_j (w_j / \rho_j^*)} \quad (\text{S3})$$

where  $T_i^*$ ,  $P_i^*$ ,  $\rho_i^*$ , and  $r_i^0$  represent the characteristic parameters of the component  $i$  in its pure state, and in particular, two of the characteristic parameters are defined as

$$T_i^* = \frac{\varepsilon_i^*}{k_B}, P_i^* = \frac{\varepsilon_i^*}{v_i^*}$$

where  $\varepsilon_i^*$  is the interaction per mer, and  $v_i^*$  is the close-packed mer volume [1].

The characteristic parameters for calculating the density using the S-L EOS are given in Table S1[2]. The binary interaction parameter,  $k_{12}$ , was determined in order to minimize the relative experimental deviation at each given temperature, and the determined binary interaction parameters at different temperatures are included in Table S2 [3].

## 2. Surface Tension comparison

Figure 1 shows the comparison of the surface tension results between this work and the literature at 200 °C [4]. The figure shows a similar trend of lower surface tension values at higher pressures. Although it shows deviations at a given pressure, considering the experimental difficulties to attain equilibrium pendant drops of the high viscosity polymer, such deviations can be acceptable. More importantly the focus of the current study is to explain the surface tension trends based on both modeling and experiment.

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3. Li, G.; Wang, J., Park, C. B.; Moulinie, P.; Shimha, R., Annu. Tech. Conf.-Soc. Plast. Eng., **2004**, Paper No.421.
4. Li, H.; Lee, L. J.; Tomasko, D. L. Ind. Eng. Chem. Res. **2004**, 43, 509-514.

TableS1. Characteristic parameters for the Sanchez-Lacombe equation of state [28]

Substance	$P^*$ [MPa]	$\rho^*$ [kg/m <sup>3</sup> ]	$T^*$ [K]
PS	387.0	1108	739.9
Carbon dioxide	720.3	1580	$2089+0.459T-7.56 \times 10^{-4}T^2$

TableS2. Binary interaction parameters ( $k_{12}$ ) of polystyrene and carbon dioxide for different temperatures

Temperature(°C)	Interaction parameter(-)
170	-0.1572
180	-0.1712
190	-0.1851
200	-0.1990
210	-0.2129

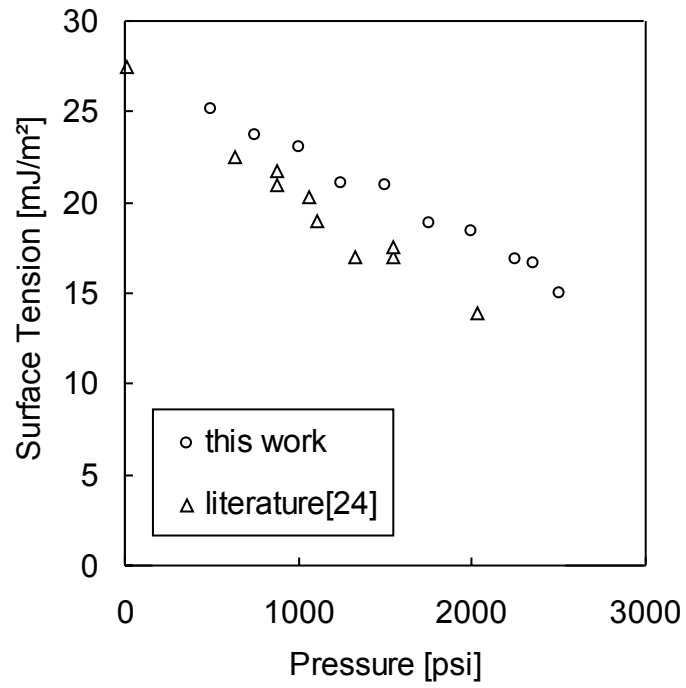


Figure 1. Comparison of the surface tension values between this work and the literature of polystyrene in supercritical carbon dioxide under various pressures at 200 °C, where the polystyrene used was of the same type and from the same supplier.