

Solubility of Subcritical and Supercritical Propylene in Semicrystalline Polypropylene

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ABSTRACT: The solubility of propylene in semicrystalline isotactic polypropylene (iPP) was measured at temperatures from (348.15 to 383.15) K and pressures up to 8 MPa by a pressure-decay method. The results demonstrated that solubility of propylene in iPP is increased with elevated pressure and decreased with elevated temperature. The results could be correlated using the Sanchez–Lacombe equation of state (SL EOS) with temperature-dependent binary interaction parameters k_{ij} . It was shown that the SL EOS can well predict the solubility of propylene in polypropylene over a wide range even above the critical temperature and pressure. The deviations between experimental data and calculated results were within 5%. It is important to point out that the value of k_{ij} varied almost linearly with respect to temperature, and the solubility of propylene in semicrystalline polypropylene in other conditions can be estimated.

INTRODUCTION

With the rapid development of catalyst and process technology, polyolefins, including polyethylene, polypropylene, and ethylene-propylene copolymers, become more and more indispensable. Gas-phase polymerization, slurry polymerization, and supercritical polymerization are important methods to produce different types of polyolefins. In these polymerization processes, the catalytic activity is an important factor deciding the process design and economic efficiency. It is well-known that the olefin polymerization rate depends on the concentration of the monomer at catalyst active sites in the polymer phase.^{1–3} Because the active sites are surrounded by a layer of polyolefins, the concentration of monomer is limited by its solubility in polyolefins. Therefore, it is necessary to have the solubility data of the olefins in given polyolefins at different temperatures and pressures to calculate the reaction rate and design polymerization process. Furthermore, the freshly produced polyolefin has significant amounts of absorbed monomers, which must be removed to meet safety standards. The knowledge of the solubility in polyolefins is also desired to control the monomer removal process.^{4,5}

Solubilities of olefins in polyolefins have been investigated by several researchers. Yoon et al. published the solubility of 1-butene, 1-hexene, and 1-octene in LLDPE.⁶ Sliepcevich et al. reported the diffusivity and solubility of olefins in polypropylene using a gas chromatography technique.³ Moore et al. measured the solubility of ethylene, 1-butene, and 1-hexene in different kinds of polyethylenes with the gravimetric method.⁷ Sato et al. proposed a pressure-decay method to obtain the solubility of propylene in semicrystalline polypropylene and propylene copolymer.^{8,9} The solubility of olefins in propylene copolymers also have been measured by Bartke et al. and Yoon et al.^{10,11} However, there is still a lack of solubility data of olefins in

polyolefins under high-pressure or supercritical conditions. The present work is aimed to experimentally study the solubility of propylene in semicrystalline polypropylene at elevated pressure and temperature. A pressure-decay method was used to measure the solubility equilibrium of propylene in semicrystalline isotactic polypropylene (iPP), and the PVT behavior of the polypropylene was predicted by Sanchez–Lacombe equation of state (SL EOS). The results were also correlated with SL EOS.

EXPERIMENTAL SECTION

Materials. The propylene (mass purity > 0.995) was supplied by Foshan Kodi Gas Chemical Industry Co. (Guangzhou, China), and the argon (mass purity ≥ 0.99999) was purchased from Hangzhou Jingong Special Products Co. (Hangzhou, China). The iPP pellets (F401) were provided by Sinopec Yangzi Petrochemical Company Co. (Nanjing, China). The weight-average and number-average molecular weight of the iPP samples were determined by a gel permeation chromatography (PL-GPC220, Polymer Lab, U.S.A.) at 423.15 K with 1,2,4-trichlorobenzene as the solvent. Mass fraction crystallinities (X_c) and the melting temperature (T_m) of the samples were obtained by a differential scanning calorimeter (TA Q200) in nitrogen at ambient pressure. The crystallinity X_c of iPP was calculated in the following equation:

$$X_c = \frac{\Delta H}{\Delta H_m^0} \cdot 100\% \quad (1)$$

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Table 1. Characteristics of the Given Polypropylene

sample	M_n	M_w	T_m	X_c
iPP	46004	229162	167.0	50.2

where ΔH is the enthalpy of crystallization per gram of the sample and ΔH_m^0 is the enthalpy of crystallization per gram of the 100 % crystalline polyolefin, which is $209 \text{ J}\cdot\text{g}^{-1}$ for polypropylene.¹² The characteristics of polypropylene used in this work are listed in Table 1.

Apparatus for Solubility Measurements. The polymer samples were dried in a vacuum oven for 24 h before being used. Solubility measurements were performed using a pressure-decay method. The main feature of the experimental apparatus was shown in Figure 1.

The high-pressure containers A and B were made of stainless steel, which were placed in a temperature-controlled air bath. The temperature of the air bath was controlled with an accuracy of $\pm 0.1 \text{ K}$. A pressure sensor (Rosemount 3051S) with the accuracy of 10 kPa was located between the high pressure pin valve 6 and 7 (V-6 and V-7), which could cause $\pm 4 \%$ relative deviation on average. After putting a certain amount of polymer sample in the container B, the apparatus were evacuated by a vacuum pump. V-7 was closed before propylene was introduced into the container A. With the reading of the pressure sensor, the Benedict–Webb–Rubin (BWR) equation of state was used to calculate the density of the propylene (ρ_1).¹³ The mass of propylene introduced into the apparatus (m_t) was,

$$m_t = V_1 \cdot \rho_1 \quad (2)$$

where V_1 was the volume between V-5 and V-7.

After knowing the amount of propylene, V-7 was opened, allowing the propylene to enter container B. As the propylene was absorbed into the iPP sample, the pressure in the system was decreased until the equilibrium was reached. The mass of the residual propylene (m_r) was calculated as:

$$m_r = (V_1 + V_2 - V_p) \cdot \rho_2 \quad (3)$$

where V_2 was the volume behind V-7. V_1 and V_2 were measured by a pressure-decay approach, which the volume-known container with an accurate variable given, volume, was directly connected with valve V-3 substituted for the high-pressure supply pump in Figure 1. The accuracy of this method is 99.9 %. V_p was the volume of polymer sample, and ρ_2 was the density of propylene after solubility equilibrium, which was still calculated by the BWR equation of state as before.

Then the solubility of propylene (S) in the polymer sample could be obtained:

$$S = \frac{V_1 \cdot \rho_1 - (V_1 + V_2 - V_p) \cdot \rho_2}{m_p (1 - X_c)} \quad (4)$$

The value of m_p was the mass of polymer sample, and the amount of V_p in eq 4 under various temperature and pressure values without considering the correlation of solubility can be calculated by the SL EOS, which is described below.⁹

RESULTS AND DISCUSSION

Thermodynamic Model for Solubility. There are several predictive models which can calculate the equilibrium solubilities of absorbed species in polymers. The PC-SAFT EOS (statistical

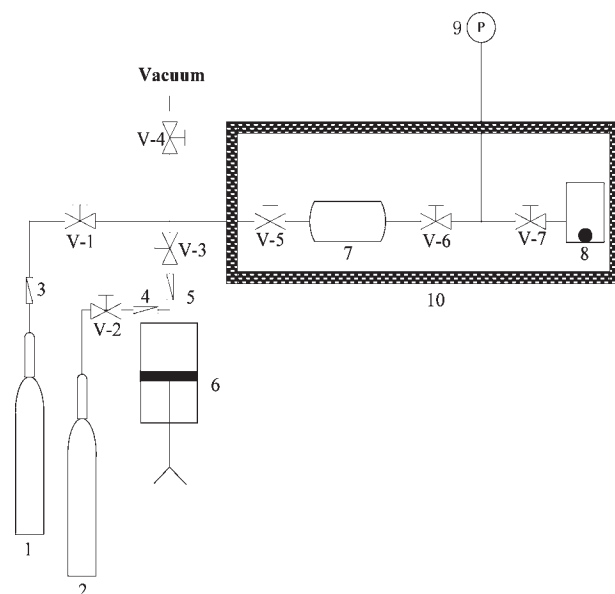


Figure 1. Schematic diagram of the pressure-decay experimental setup. 1, argon capsule; 2, propylene capsule; 3, 4, 5, filter; 6, high pressure supply pump; 7, high pressure container A; 8, high pressure container B; 9, pressure sensor; 10, constant temperature drying oven; V-1, V-2, V-3, V-4, V-5, V-6, V-7, high-pressure pin valve.

Table 2. Characteristic Parameters for SL EOS

substance	P^*/MPa	$\rho^*/\text{kg}\cdot\text{m}^{-3}$	T^*/K	M_n	ref
propylene	379.0	0.755	346	42	9
iPP	300.7	0.886	689	46004	18

associating fluid theory equation of state) and SL EOS (Sanchez–Lacombe equation of state) are two well-known mathematical models which are used to predict the phase equilibrium of polymer–solvent systems.^{14,15} For a polymer–gas system, the SL EOS can predict the PVT of the gas–polymer well.^{16,17} In this work, the SL EOS was chosen to correlate the solubility of propylene in the amorphous regions of semicrystalline polypropylene and predict the PVT parameters. The SL EOS is given by:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right) \tilde{\rho} \right] = 0 \quad (5)$$

where:

$$\tilde{T} = \frac{T}{T^*}, \quad \tilde{P} = \frac{P}{P^*}, \quad \tilde{\rho} = \frac{\rho}{\rho^*}, \quad r = \frac{MWP^*}{RT^*\rho^*} \quad (6)$$

$$P^* = \sum_i \sum_j \phi_i \phi_j P_{ij}^* \quad (7)$$

For mixtures:

$$T^* = P^* \sum_i (\phi_i^\circ T_i^* / P_i^*) \quad (8)$$

$$1/r = \sum_i (\phi_i^\circ / r_i) \quad (9)$$

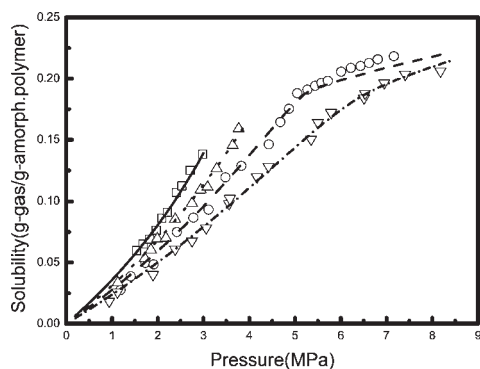


Figure 2. Solubility of propylene in iPP at different temperatures and pressures. \square , experimental data at 348.15 K; —, calculated by the SL EOS at $k_{12} = 0.019$, $T = 348.15$ K; \triangle , experimental data at 358.15 K; - - -, calculated by SL EOS at $k_{12} = 0.015$, $T = 358.15$ K; \circ , experimental data at 348.15 K; - · - ·, calculated by SL EOS at $k_{12} = 0.011$, $T = 368.15$ K; ∇ , experiment data at 348.15 K; · · · ·, calculated by SL EOS at $k_{12} = 0.004$, $T = 383.15$ K.

where:

$$P_{ij}^* = (1 - \kappa_{ij}) \sqrt{P_i^* P_j^*} \quad (10)$$

$$\phi_i = (w_i / \rho_i^*) / \sum_j (w_j / \rho_j^*) \quad (11)$$

$$\phi_i^\circ = (\phi_i T_i^* / P_i^*) / \sum_j (\phi_j T_j^* / P_j^*) \quad (12)$$

where T , P , and $\tilde{\rho}$ are the reduced temperature, pressure, and density, respectively. T^* , P^* , and ρ^* are characteristic parameters of the SL EOS, which are listed in Table 2. For a polymer chain, r is the number of sites occupied in the lattice, which can be related to its molecular weight. For mixture, the mixing rules are used with a temperature-dependent binary interaction parameter k_{ij} .

Solubility. Two regions are present in semicrystalline iPP samples: an amorphous region and a crystalline region. For the crystalline region, the crystal lamellae with folding structure resist solvents permeating. In this work, it is considered that propylene is only dissolved in the amorphous region.

The solubilities of propylene in polypropylene at four different temperatures and pressures are shown in Figure 2 and Table 3. The solubility was expressed in grams of propylene per gram of amorphous iPP. The operating temperatures in the gas-phase polymerization conditions are (348.15 and 358.15) K, while (368.15 and 383.15) K are the operating temperatures in the supercritical polymerization conditions. For propylene, the critical temperature is 365.57 K, while the critical pressure is 4.7 MPa. The saturated vapor pressures of propylene at (348.15 and 358.15) K are (3.4 and 4.1) MPa, respectively, which is the ceiling pressure in the measurement under these two temperatures. The solubility of propylene in polypropylene at 348.15 K was closed as the results of ref 9 around a similar pressure.

Below 368.15 K, the solubility is increased almost linearly with the pressure. The slope of the curve is increased slowly with the elevated pressure. The results also show that the solubility is decreased with the increased temperature under the same pressure. At 368.15 K the slope of the curve is decreased around pressure of 5.5 MPa, which is close to the critical point of propylene. Meanwhile, the slope of the solubility curve at 383.15

Table 3. Solubility of Propylene in iPP at Different Temperatures and Pressures

temperature	pressure	solubility	pressure	solubility
K	MPa	g-gas/g-amorph. polymer	MPa	g-gas/g-amorph. iPP
348.15	1.54	0.0598	2.21	0.0910
	1.68	0.0651	2.41	0.1070
	1.82	0.069	2.53	0.1123
	1.97	0.0763	2.71	0.1251
	2.09	0.0862	2.98	0.1381
358.15	1.13	0.0336	2.75	0.0984
	1.72	0.0534	2.94	0.1090
	1.85	0.0604	3.09	0.1113
	1.99	0.0695	3.29	0.1264
	2.18	0.0700	3.64	0.1456
368.15	2.38	0.0854	3.77	0.1590
	1.19	0.0275	5.05	0.1881
	1.41	0.0387	5.27	0.1911
	1.73	0.0497	5.44	0.1941
	1.91	0.0484	5.58	0.1965
383.15	2.42	0.0750	5.72	0.1982
	2.78	0.0866	6.01	0.2056
	3.11	0.0932	6.22	0.2087
	3.48	0.1193	6.43	0.2103
	3.83	0.1287	6.62	0.2128
	4.43	0.1462	6.81	0.2157
	4.68	0.1645	7.16	0.2183
	4.87	0.1753		
	0.94	0.0184	4.42	0.1283
	1.12	0.0260	5.35	0.1505
1.90	0.0401	5.50	0.1641	
2.38	0.0609	5.79	0.1723	
2.75	0.0677	6.51	0.1841	
3.06	0.0782	6.53	0.1879	
3.56	0.0981	6.95	0.1967	
3.58	0.1020	7.41	0.2034	
4.17	0.1197	8.18	0.2061	

K is also decreased around 6 MPa. The reason for this may be due to the presence of the crystalline polymer phase, which hinders the swelling of amorphous polymer phase.⁷

The results were correlated using the SL EOS with temperature-dependent binary interaction parameters k_{ij} . The SL EOS can predict well the solubility of propylene in polypropylene over a wide range even above the critical temperature and pressure. The deviations between experimental data and calculated results were within 5 % as shown in Table 4. The binary interaction parameter k_{12} of the SL EOS was dependent on temperature, which was shown in Figure 3. It was interesting that k_{12} of the SL EOS varies almost linearly with respect to temperature. The relationship between k_{12} and temperature was obtained as:

$$k_{12} = -4.280 \cdot 10^{-4} T + 0.1682 \quad (13)$$

This indicated that the solubility of propylene in semicrystalline polypropylene in other conditions can be estimated.

Table 4. Binary Interaction Parameters and Correlation Results Obtained by the SL EOS^a

	T (K)	binary interaction parameter k_{ij}	AAD correlation error (%)
iPP	348.15	0.019	2.11
	358.15	0.015	3.20
	368.15	0.011	3.67
	383.15	0.004	4.21

$$AAD = \frac{1}{n_o} \sum_{i=1}^{n_o} \left| \frac{S_{exp} - S_{cal}}{S_{cal}} \right|_i \times 100$$

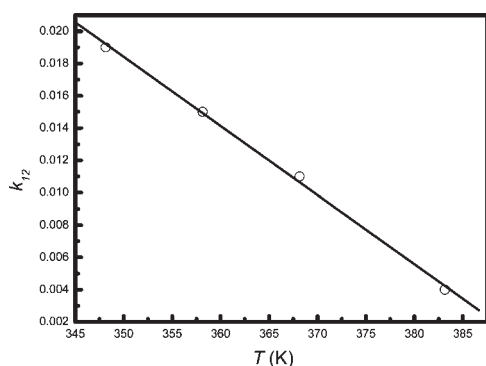


Figure 3. Variation of the interaction parameter k_{12} with respect to temperature. The relationship between k_{12} and temperature was $k_{12} = -4.280 \cdot 10^{-4}T + 0.1682$; the regression coefficient of the fitting equation (R^2) is 0.998.

CONCLUSIONS

In present work, the solubility of propylene in semicrystalline iPP was studied over temperatures of (348.15, 358.15, 368.15, and 383.15) K and pressures up to 8 MPa by a pressure-decay method. The results indicated that the solubility of propylene is increased with elevated pressure and decreased with elevated temperature. The results were correlated using the SL EOS with temperature-dependent binary interaction parameters k_{ij} . It has been shown that the SL EOS can predict well the solubility of propylene in polypropylene over a wide range even above the critical temperature and pressure. It is important to point out that the value of k_{ij} varies almost linearly with respect to temperature. According to the relationship between k_{ij} and temperature, the solubility of propylene in semicrystalline polypropylene in other conditions can be estimated.

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