

Solubility of Propylene in Semicrystalline Polypropylene

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ABSTRACT: Gas solubilities and polymer swelling in propylene and semicrystalline polypropylene system at temperatures of 323.2 and 348.2 K and pressures up to propylene's vapor pressure were measured. Pressure, specific volume, and temperature (*PVT*) measurements of polypropylene were carried out at temperatures from 313 to 573 K and pressures up to 200 MPa. Two kinds of polypropylenes, which had different stereoregularities, were used for both solubility and *PVT* measurements. The solubilities were correlated with the Sanchez–Lacombe equation of state (EOS) with temperature-dependent binary interaction parameters to within 5% average relative percentage deviation. Swelling ratios estimated with Sanchez–Lacombe EOS coupled with optimized interaction parameters were 20% lower than the experimental values. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1134–1143, 2001

Key words: solubility; swelling; *PVT*; crystallinity; equation of state

INTRODUCTION

Although vapor-phase polymerization has been widely used for the manufacture of polyolefins, the kinetics of polymerization is not well understood. Floyd et al.¹ proposed a multigrain particle model for propylene and ethylene polymerization in liquid and gas media. In this model, a polymer particle (macroparticle) consists of some fine polymer particles containing the catalysts. Monomer dissolves into the polymer particle and diffuses to the catalysts, to polymerize in the polymer phase. It is clear that properties such as solubility and diffusivity of monomer in the polymer are important in developing such models.

Solubility and diffusivity of gases in molten polymers were investigated by several authors.^{2–5} The solubility in semicrystalline polymers, however, is complicated because of crystallinity of the polymers. Kamiya et al.⁶ determined the solubility of CO₂ and N₂ in semicrystalline low-density polyethylene, although the researchers did not consider the crystallinity effect. The gas solubility in semicrystalline polymers has received only modest attention by researchers^{7–10} studying the organic vapor solubility.

The solubilities in molten polymer are usually correlated or predicted with an equation of state (EOS) or an activity coefficient model, whereas solubilities in semicrystalline polymer are correlated/predicted by incorporation of an elastic factor.¹¹ For the semicrystalline polymer, the polymeric chains in the amorphous region can be considered to be spatially constrained and elastically deformed by the crystallites so that the penetration of solvent molecules is depressed.⁷ Doon and Ho⁸ reported that solubilities of a series of aromatic compounds in semicrystalline polyethylene

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are fit well by the UNIFAC-FV group contribution method¹² in conjunction with the Michaels–Hauslein (M-H) theory.⁹ In this theory, a parameter f (the fraction of elastically effective chains in amorphous regions defined in the M-H theory) was treated as independent of temperature, concentration of solute, and solute species. However, application of M-H theory to correlate gas solubility is difficult because the activity model is not suitable for high-pressure vapor–liquid equilibria.

Braun and Guillet^{13,14} proposed a crystallinity determination method with a gas chromatographic technique. In the chromatographic method, temperature dependence of the crystallinity is obtained from temperature dependence of Henry's constant for solute. In other words, they assumed that the difference between Henry's constant extrapolated from above-melting temperature and that of the semicrystalline state at a given temperature corresponded to the crystallinity. Hence, they did not consider the elastic factor at all. It may be useful in engineering fields to determine the crystallinity and to correlate the solubility without the elastic factor.

For highly soluble and dense gases, the quantity of dissolved gas can be appreciable and usually leads to polymer swelling. The high-pressure gas solubility always needs a swelling correction.^{2,6,15,16} In semicrystalline polymers, if the crystallinity is different between solubility and swelling experiments, the specific volumes of crystalline and amorphous regions are needed to convert swelling value to that of the same crystallinity of the solubility measurements. Hence, it is necessary to study the volumetric property of semicrystalline polymer.

The objective of this study was to determine the solubility of propylene in polypropylene at similar conditions to its polymerization and to develop a method for its correlation.

EXPERIMENTAL

Materials

The propylene (purity > 99.5%) was purchased from Sumitomo Seika Chemicals (Osaka, Japan). The two kinds of polypropylene powder produced in a test plant of a vapor-phase polymerization were provided by Idemitsu Petrochemicals (Ichihara). In this study, the two polypropylenes are

Table I Characteristics of Polypropylene

	Sample A	Sample B
Particle size (mm)	0.7 ~ 1.4	0.7 ~ 1.0
Specific surface area (m ² /g)	0.32	0.22
Weight-average molecular weight (g/mol)	2.2×10^5	1.0×10^6
Number-average molecular weight (g/mol)	5.2×10^4	2.0×10^5
Pentad fraction (mmmm) (mol %)	97	56
Pentad fraction (rrrr) (mol %)	0.3	12
Mass fraction crystallinity		
DSC (powder sample)	0.47	0.19
Density (bar sample)	0.66	0.33
DSC (sheet sample)	0.55	—

called samples A and B. The polypropylenes were used as received so that their original crystallinity could be maintained in solubility measurements. The powder sample was molded into bar and film for pressure, specific volume, temperature (PVT), and swelling measurements, respectively. Characteristics of the polypropylenes used in this work are given in Table I. Stereoregularity of the samples was obtained with a ¹³C–NMR from the supplier. Mass fraction crystallinities of samples were determined with a DSC (Perkin Elmer, DSC-7) and density. Thermophysical properties needed to calculate the crystallinity [such as heat of fusion of a perfect crystal ($\Delta H_m = 209$ J/g) and specific volume of the amorphous (v_{amo}) and crystalline (v_{cry}) phases ($v_{\text{amo}} = 1.174$ cm³/g; $v_{\text{cry}} = 1.067$ cm³/g)] were taken from Ref. 17. The crystallinity of sample B was lower than that of sample A, because of the lower stereoregularity of the sample. The isotactic fraction of sample B was 56 mol %, whereas sample A consisted almost entirely of isotactic polypropylene.

PVT Measurement

PVT of polypropylene was measured with a metal bellows method. The details of the experimental apparatus and procedures were described elsewhere.¹⁸ The uncertainty of pressure, specific volume, and temperature were less than 0.25 MPa, 0.2%, and 0.1 K, respectively.

Polymer Swelling

The polymer swelling with the dissolution of the propylene was determined by measuring the

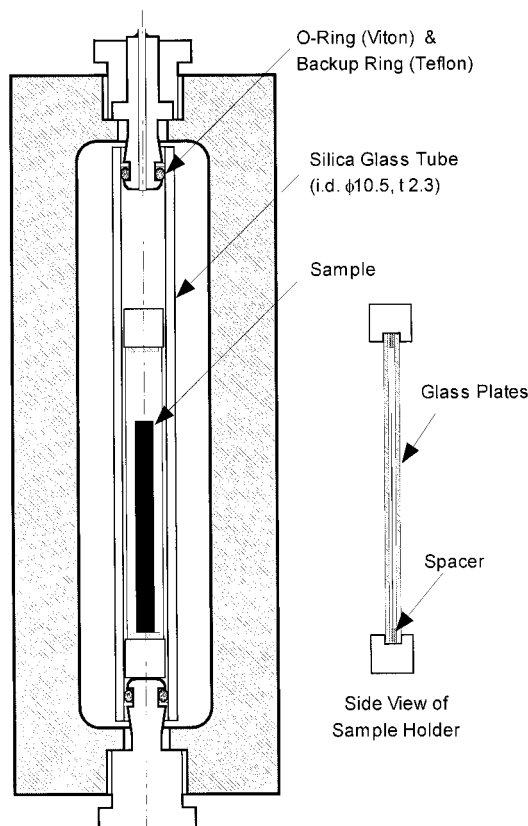


Figure 1 High-pressure view cell.

change in length of a thin polypropylene film. The film was prepared by stretching with a roller on a heated plate. The volume change ΔV of the polymer sheet was evaluated from the following relationship:

$$\text{Swelling (vol \%)} = (\Delta V/V_0) \times 100 = [(L_X/L_{X0}) \times (L_Y/L_{Y0})(L_Z/L_{Z0}) - 1] \times 100 \quad (1)$$

where the subscripts X , Y , and Z denote direction of the rolling, direction of perpendicular to the rolling direction, and direction of the sheet thickness, respectively. The L and L_0 are the measured lengths of the swollen and unswollen polymer film, respectively, and V_0 is the volume of the unswollen polymer.

The high-pressure view cell is shown in Figure 1. The view cell was similar to that used by Wissinger and Paulaitis¹⁶ and consisted of a silica glass tube (i.d. $\phi 10.5$ and t 2.3 mm) and a stainless steel O-frame. The sample dimension was approximately $50 \times 5 \times 2\text{--}4$ mm (length \times width

\times thickness). The sample was placed between two glass plates in a sample holder. A cathetometer (resolution: 0.01 mm) was used for measuring the length of the sample. Pressure was measured with a strain-gauge pressure sensor (PX-1A, accuracy: ± 2 kPa; Tsukasa Sokken, Tokyo, Japan) that had been calibrated against a deadweight tester (M2800; Pressurements Ltd., Bedfordshire, England). The view cell was immersed in a water bath and the temperature of the cell was controlled to within ± 0.05 K and was measured to ± 0.05 K with a standard mercury thermometer.

Solubility

The solubilities of propylene in polypropylene were measured with a pressure-decay method. A schematic diagram of an apparatus is shown in Figure 2. The polypropylene powder was placed in sorption cell 2 and the apparatus was evacuated. Propylene gas was then introduced into sorption cell 1 and the temperature and pressure were measured to determine the amount of the propylene introduced. A valve between cells 1 and 2 was opened to start the dissolution of the gas into the polymer. The pressure decay resulting from gas dissolution was measured with a strain-gauge pressure sensor (PX-1A, accuracy: ± 2 kPa; Tsukasa Sokken). The temperature of the cell was controlled to within ± 0.05 K in the water bath and was measured to within ± 0.05 K with a standard mercury thermometer. The amount of the propylene dissolved into the polypropylene, n_P , was determined using the following equation:

$$n_P = \frac{P_i V_1}{Z_i R T} - \frac{P_f (V_1 + V_2 - V_P)}{Z_f R T} \quad (2)$$

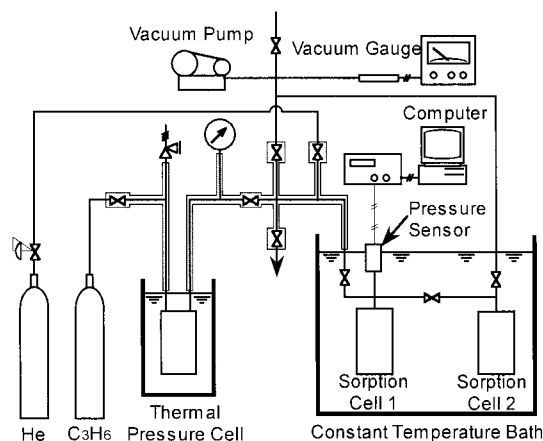


Figure 2 Schematic diagram of high-pressure sorption apparatus.

where V_1 and V_2 are the inner volume of the sorption cells 1 and 2, respectively; R and V_P are gas constant and the volume of the polymer, respectively; P_i and P_f are the initial and final pressure of the gas in sorption cell 1; and Z_i and Z_f are the compressibility factor of propylene at temperature T and pressures P_i and P_f , respectively. The V_P was determined from helium expansion experiments [in eq. (2), assuming $n_P = 0$] and the swelling data with dissolution of propylene were used to correct V_P . Gas compressibility factors Z were obtained from Angus et al.¹⁹ In this work, this procedure for measurement is called the sorption method.

It is hard to measure the solubility near the saturated vapor pressure of propylene with the sorption method because of the possibility of propylene condensation. Therefore, a desorption method was used to measure the solubility near the vapor pressure. The desorption method consisted of two steps. After dissolution equilibrium was reached at pressure P_i in cell 2, the gas in cell 2 was expanded to the evacuated cell 1. Then, the solubility was determined using the following equation:

$$n_P = n_{Pf} + \frac{P_f(V_1 + V_2 - V_P)}{Z_f RT} - \frac{P_i(V_2 - V_P)}{Z_i RT} \quad (3)$$

where n_{Pf} is the amount of gas in polymer at pressure P_f determined with the sorption method.

A repeated sorption method was also used to obtain the solubility near the saturation pressure. The repeated sorption method consisted of two steps. After dissolution equilibrium was reached in cell 2 at pressure P_{i1} , the gas refilled cell 1 at P_{i2} and was reintroduced to cell 2. After equilibrium at pressure P_f , the solubility was determined using the following equation:

$$n_P = n_{Pi} + \frac{P_{i1}(V_2 - V_P)}{Z_{i1} RT} + \frac{P_{i2} V_1}{Z_{i2} RT} - \frac{P_f(V_1 + V_2 - V_P)}{Z_f RT} \quad (4)$$

where n_{Pi} is the amount of gas in polymer at pressure P_{i1} that was obtained with the sorption method. Repeated times were limited to three to reduce accumulation of errors.

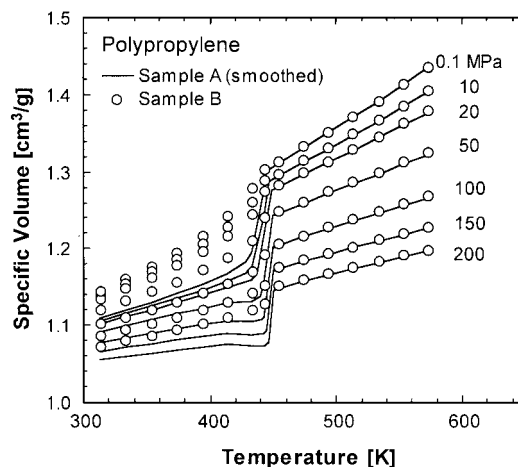


Figure 3 PVT results for polypropylenes.

RESULTS AND DISCUSSION

PVT Results

PVT results of polypropylene B (crystallinity: 0.33) are shown in Figure 3 and Table II. In this figure, solid lines denote the results of polypropylene A (crystallinity: 0.66) previously reported.¹⁸ The specific volume of sample B at 313.2 K and 0.1 MPa was 3.2% higher than that of sample A. The specific volume data of sample B increased more with temperature in comparison with those of sample A in a rubbery state, whereas volume change at the melting point temperature of sample B was less than that of sample A. These differences in *PVT* behavior were attributed to a difference in crystallinity between the two samples. Above the melting point temperature, the *PVT* of the two samples gave a good agreement to within 0.35%. Although the specific volume of sample B (isotactic fraction: 56 mol %) was slightly higher (0.28% average) than that of isotactic polypropylene (sample A), a difference in the specific volume between the two samples will not be significant. The *PVT* dependence on stereoregularity was small in the molten state as shown in Figure 3. Wilski²⁰ reported that the specific volume of atactic polypropylene was in good agreement with that of molten polypropylene at atmospheric pressure.

The specific volume of crystalline polypropylene was determined from *PVT* data of sample A (crystallinity: 0.66) previously reported.¹⁸ The specific volume of the crystalline fraction was defined as follows:

Table II Experimental Specific Volume ($10^{-3} \text{ m}^3/\text{kg}$) Results for Polypropylene B

Temperature (K)	Pressure (MPa)						
	0.1	10	20	50	100	150	200
313.2	1.1449 ^a	1.1409	1.1353	1.1209	1.1016	1.0859	1.0727
333.6	1.1615 ^b	1.1548	1.1485	1.1323	1.1110	1.0940	1.0797
353.6	1.1776 ^b	1.1699	1.1627	1.1445	1.1208	1.1022	1.0868
373.7	1.1950 ^b	1.1860	1.1778	1.1572	1.1308	1.1109	1.0943
393.9	1.2170 ^b	1.2060	1.1958	1.1719	1.1420	1.1200	1.1021
413.9	1.2432 ^b	1.2295	1.2174	1.1889	1.1546	1.1304	1.1107
433.8	1.2797 ^b	1.2612	1.2457	1.2103	1.1699	1.1421	1.1205
443.8	1.3035 ^b	1.2888	1.2744	1.2402	1.1920	1.1523	1.1278
453.6	1.3140 ^b	1.2977	1.2832	1.2483	1.2070	1.1771	1.1517
473.5	1.3329 ^b	1.3148	1.2988	1.2614	1.2176	1.1862	1.1609
493.4	1.3520 ^b	1.3319	1.3142	1.2742	1.2282	1.1949	1.1689
513.3	1.3718 ^b	1.3495	1.3300	1.2869	1.2381	1.2038	1.1766
533.5	1.3921 ^b	1.3674	1.3463	1.2999	1.2488	1.2126	1.1842
553.6	1.4134 ^b	1.3858	1.3625	1.3129	1.2588	1.2212	1.1918
573.4	1.4363 ^b	1.4052	1.3792	1.3261	1.2690	1.2299	1.1996

^a Hydrostatic weighing method.^b Extrapolated.

$$v_{\text{cry}} = v_{\text{amo}} + (v - v_{\text{amo}})/X_m \quad (5)$$

where v_{cry} and v_{amo} are the specific volumes of crystalline and amorphous, respectively, v is the specific volume of polymer in a rubbery state, and X_m is mass fraction crystallinity of the polymer. The v_{amo} was obtained from extrapolation below the melting point temperature with the Simha–Somcynsky equation of state (S-S EOS)²¹ ($P^* = 547.9 \text{ MPa}$, $V^* = 1.1867 \text{ cm}^3/\text{g}$, and $T^* = 10,924 \text{ K}$).¹⁸ The specific volume of the crystalline $v_{\text{cry}}(T, P)$ was represented by the Tait equation:

$$v_{\text{cry}}(T, P) = v_{\text{cry}}(T, P_0) \times \left\{ 1 - c \ln \left(\frac{P + B_0 \exp(-B_1 T)}{P_0 + B_0 \exp(-B_1 T)} \right) \right\} \quad (6)$$

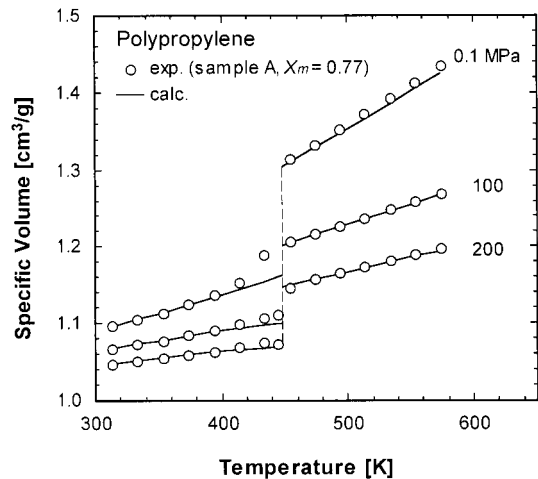
where $P_0 = 0.1 \text{ MPa}$, $c = 0.04467$, $B_0 = 4479.7 \text{ MPa}$, and $B_1 = 9.609 \times 10^{-3} \text{ K}^{-1}$. The $v_{\text{cry}}(T, P_0)$ was the specific volume of the crystalline at atmospheric pressure and was represented by a constant thermal expansivity α :

$$v_{\text{cry}}(T, P_0) = v_1 \exp(\alpha T) \quad (7)$$

where $v_1 = 0.9430 \text{ cm}^3/\text{g}$ and $\alpha = 3.774 \times 10^{-4} \text{ K}^{-1}$. These parameters were determined by fitting the data at temperatures from 313 to a maximum of 353 K, where the crystallinity remained constant.

imum of 353 K, where the crystallinity remained constant.

Specific volumes of polypropylenes in a rubbery state were compared with those of estimation from v_{cry} , v_{amo} , and the constant crystallinity value at room temperature, to confirm its applicability. Since PVT data of 0.66 crystallinity were used to determine v_{cry} , PVT data of samples B ($X_m = 0.33$) and A ($X_m = 0.77$, PVT data from Ref. 18) were used in the comparison.

**Figure 4** Estimated PVT for polypropylene (sample A, $X_m = 0.77$).

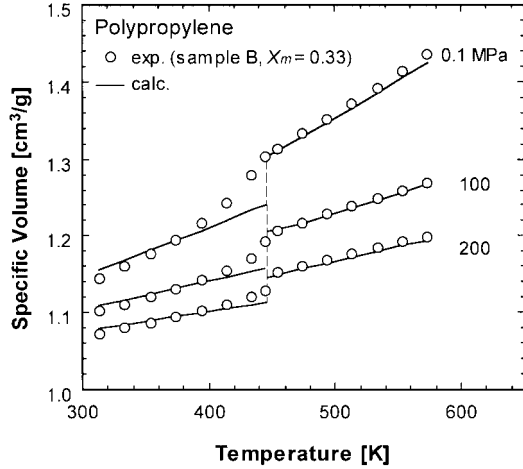


Figure 5 Estimated PVT for polypropylene (sample B, $X_m = 0.33$).

Estimation results are shown in Figures 4 and 5. Below 400 K, at which temperature the crystallinity seemed to be almost constant, estimation results agreed with experimental data to within 0.1 and 0.4% average relative deviation of specific volume for samples A and B, respectively. Whereas the specific volume values of crystalline and amorphous at 25°C and 0.1 MPa deviated by about 1% from literature values,¹⁷ they are important for solubility and swelling evaluations described below. Furthermore, they are useful for polypropylene processing, such as a simulation of shrinkage in an injection molding.

Swelling Results

The experimental elongation results (L/L_0) of the X and Y directions of the polypropylene sheet (sample A, $X_m = 0.55$) are shown in Figure 6. The elongation increased with pressure, with the effect of pressure being more pronounced at elevated pressures. The data showed a nonisotropic elongation between the X and Y directions. Because the polymer film was too thin to be measured, L_Y was substituted for L_Z . The swelling results evaluated using eq. (1) are shown in Figure 7. Dashed lines in the figure denote estimations that assume additivity ($V^E = 0$) of saturation liquid volume for propylene and polymer volume. In the estimation, the swelling was obtained as follows:

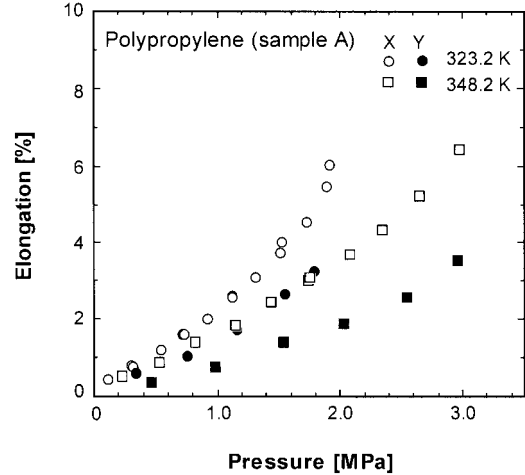


Figure 6 Elongation of polypropylene (sample A) in the presence of propylene.

Swelling (vol %)

$$= \left[\frac{v_{\text{cry}}(T, P)X_m + v_{\text{amo}}(T, P)(1 - X_m) + v_{\text{sol}}S(1 - X_m)}{v_{\text{cry}}(T, 0)X_m + v_{\text{amo}}(T, 0)(1 - X_m)} - 1 \right] \times 100 \quad (8)$$

where v_{sol} is saturated liquid volume [cm^3/g] of propylene and S is solubility [g-gas/g-amorphous]. The average relative deviations between the estimated and experimental values were 4.6 and 12.4% at temperatures of 323.2 and 348.2 K, respectively.

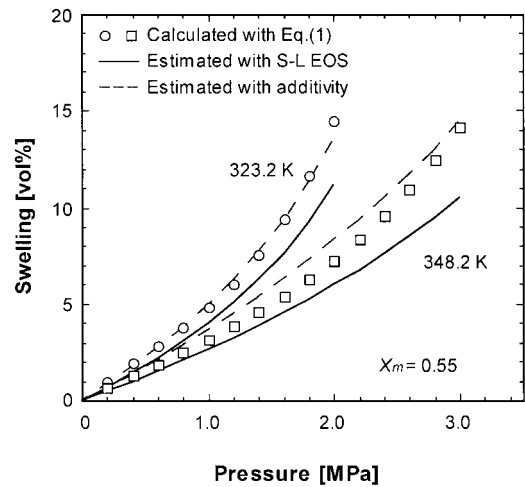


Figure 7 Swelling of polypropylene (sample A) in the presence of propylene.

Table III Characteristic Parameters for Sanchez–Lacombe EOS

	T^* (K)	ρ^* (kg/m ³)	P^* (MPa)	Error (%)		
				Vapor Pressure ^a	Liquid Volume ^b	Vapor Volume ^b
Propylene	345.4	755.0	378.8	6.6	5.3	6.7
Polypropylene	690.6	885.6	300.7		0.42	

^a Error = 100 ($\sum |P_{\text{cat}} - P_{\text{exp}}|/P_{\text{exp}}$) n^{-1} .

^b Error = 100($\sum |\nu_{\text{cat}} - \nu_{\text{exp}}|/\nu_{\text{exp}}$) n^{-1} .

Solid lines in the figure denote estimations with the Sanchez–Lacombe equation of state (S-L EOS).^{22,23}

$$\tilde{P} = -\tilde{\rho}^2 - \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] \quad (9)$$

$$\tilde{P} = P/P^*, \quad \tilde{\rho} = \rho/\rho^*, \quad \tilde{T} = T/T^*,$$

$$r = MP^*/RT^*\rho^* \quad (10)$$

where P^* , ρ^* , and T^* are characteristic parameters of the S-L EOS. The mixing rules reported by Sanchez and Lacombe²³ were used with binary interaction parameter k_{ij} as follows:

$$P^* = \sum_i \sum_j \phi_i \phi_j (1 - k_{ij}) \sqrt{P_i^* P_j^*} \quad (11)$$

The values of the characteristic parameters P^* , ρ^* , and T^* for propylene were determined by correlation of vapor pressure, saturated vapor, and saturated liquid volume at 21 temperatures from 210 K up to the critical point obtained from IUPAC tables.¹⁹ The parameters for polypropylene were determined from fitting the experimental PVT data of sample A¹⁸ in the molten state. The characteristic parameters of the S-L EOS are listed in Table III. The swelling values were estimated using S-L EOS with k_{ij} determined from the correlation of solubilities, described below. The swelling was obtained as follows:

Swelling (vol %)

$$= \left[\frac{v_{\text{cry}}(T, P)X_m + (1 + S)(1 - X_m)v_{\text{SL}}(T, P, S)}{v_{\text{cry}}(T, 0)X_m + (1 - X_m)v_{\text{SL}}(T, 0, 0)} - 1 \right] \times 100 \quad (12)$$

where v_{SL} is specific volume estimated with the S-L EOS and S is the solubility of gas in a unit mass of amorphous region. The estimated swelling was smaller than the experimental values by about 20% overall. For this system, underestimation by the model was observed, whereas in another study it was found that the S-L EOS could estimate the swelling of carbon dioxide and the molten poly(vinyl acetate) system to within an average relative deviation of 3.5%.¹⁵ The reason for the larger error is not clear but must be attributed to the elastic contribution, underestimation of crystallinity, or to some extent, the equation of state.

Solubility Results

Experimental results for solubilities of propylene in polypropylene A are shown in Figure 8. The solubilities were corrected for polymer swelling by considering crystallinity in each sample. The swelling correction was less than 19% of the sol-

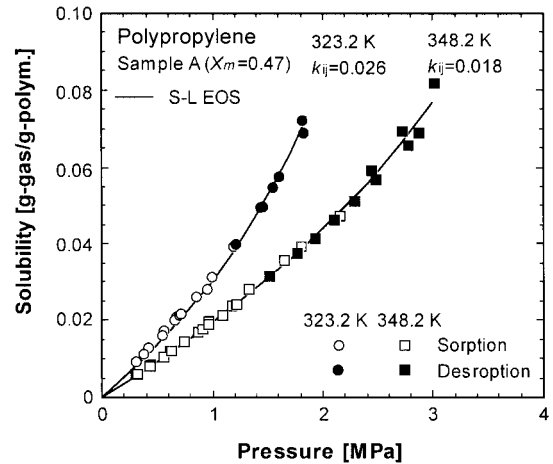


Figure 8 Solubility of propylene in polypropylene (sample A).

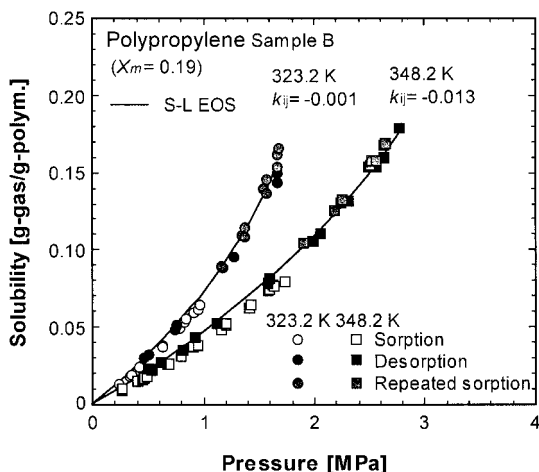


Figure 9 Solubility of propylene in polypropylene (sample B).

ubility. The typical time required to reach equilibrium was within 15 min, which was considered to be too fast for the mean diameter of the powder. The reason for this fast equilibration was probably caused by the sample porosity. The solubility was almost linear with pressure, and the slope gradually increased at elevated pressure. The solubility decreased with increasing temperature, a tendency that has been generally observed in many organic vapor + polymer and organic vapor + solvent systems. The experimental data obtained from the sorption and the desorption methods did not show an appreciable difference.

Experimental results for solubilities of propylene in polypropylene B are shown in Figure 9. The swelling for the sample B system could not be measured because a sample suitable for the measurements could not be prepared. Hence, the solubilities were corrected for polymer swelling, assuming the additivity as described earlier. For this case, the swelling correction was less than 29% of the solubility. Although the experimental data were obtained from three methods—the sorption method, the desorption method, and repeated sorption method—no significant difference among the methods was observed.

The solid lines in Figures 8 and 9 show correlated results with the S-L EOS. It is usually considered that the solute dissolved in semicrystalline polymer is present only in the amorphous region. Therefore, the interaction parameter k_{ij} was determined by fitting the solubility based on unit mass of amorphous region. The solubilities could be correlated the S-L EOS with the temper-

ature-dependent binary interaction parameter k_{ij} to within 5% average relative percentage deviation.

The tendency of the solubility in sample B, however, was similar to that in sample A, and the amount of gas in sample B was larger than that of sample A. Since the sorbent molecules probably lie almost exclusively in the amorphous regions, specific solubility has to be considered (i.e., the amount sorbed per unit mass of the amorphous component), to make any meaningful comparison between samples. This comparison is shown in Figure 10(a). The solubility [g-gas/g-amorphous] in sample B ($X_m = 0.19$) is about twofold greater than that in sample A ($X_m = 0.47$). This disagreement may be attributed to three reasons. First, the true crystallinity is not known and varies according to the technique used. Akiba et al.²⁴ pointed out that the crys-

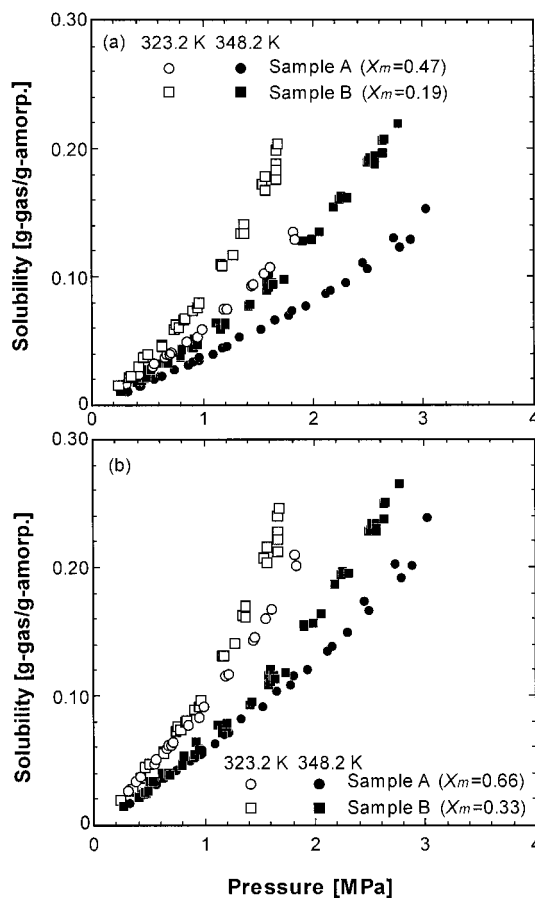


Figure 10 Comparison of propylene solubility in amorphous region of polypropylene. (a) Crystallinities determined with DSC; (b) crystallinities assumed similar to those of PVT measurements

tallinity of polypropylene determined with DSC is smaller than that obtained with gas chromatography. In the chromatographic method, crystallinity was evaluated from Henry's constant for solute in polymer above and below the melting temperature of polymer.^{13,14} Hence, the crystallinity obtained from the chromatographic method should be suitable for evaluation of the solubility. Guillet and coworkers^{13,25} reported that the crystallinity obtained with the chromatographic method was in good agreement with that obtained with X-ray diffraction and a density method. If the crystallinities of samples for the solubility measurement obtained with the DSC were similar to those for *PVT* measurement obtained with the density method, the solubility difference between two samples would be about half that shown in Figure 10(b). The second reason is an effect of the elastic contribution. Ochiai et al.⁷ reported that the elastic contributions resulting from the inhibition of chain deformations in the amorphous region from crystalline domains lower the solubility. They also mentioned that the concentration of sorbed carbon tetrachloride and hexane in polypropylene decreased with increasing crystallinity because of increasing elastic contributions. Therefore, the solubilities in sample A with higher crystallinity were smaller than those in sample B. The third possible reason for the difference between sample solubilities is a crystallinity change resulting from dissolution of gas. Mizoguchi et al.²⁶ reported that CO₂ induced crystallization of poly(ethylene terephthalate), whereas Zhang and Handa²⁷ reported that the melting point temperature decreased for dissolution of CO₂ in syndiotactic polystyrene and poly(ethylene terephthalate). However, the crystallinity change is not a major effect in this work, because the solubility showed good reproducibility. If crystallinity of the sample largely changed as a result of dissolution of gas, the solubility measurement would not be reproducible. It would be hard to consider the difference in gas solubilities between samples A and B in the molten state because interaction between propylene and any isotactic fraction polypropylene would be constant. Any combination of these factors, especially crystallinity evaluation, will influence the solubility of the gas in the polymer samples studied.

CONCLUSIONS

The gas solubilities and polymer swelling in propylene and semicrystalline polypropylene system at temperatures of 323.2 and 348.2 K, and pressures up to the vapor pressure of propylene were measured. *PVT* measurements of polypropylene were carried out to correct the solubility data. Polypropylenes having different stereoregularities were used in both solubility and *PVT* measurements. The *PVT* properties of both molten polypropylene samples gave a good agreement to within an average relative deviation of 0.28%. *PVT* dependence on the stereoregularity is negligibly small in the molten state. Gas solubility was lower in the polypropylene sample with higher stereoregularity, even when the crystallinity was considered. The solubilities measured were correlated by the Sanchez–Lacombe equation of state to within 5% average relative deviation. The Sanchez–Lacombe equation of state, coupled with the optimized interaction parameter, was able to estimate the polymer swelling to within 20% average relative deviation.

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