

Phase Equilibrium Characteristics of Supercritical CO₂/Poly(Ethylene Terephthalate) Binary System

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ABSTRACT: The solubility of carbon dioxide in poly(ethylene terephthalate) (PET) at high pressure and elevated temperature conditions was investigated for a better understanding of the phase equilibrium characteristics of supercritical CO₂/PET binary system and useful data for the process development of the supercritical fluid dyeing. Based on the principle of pressure decaying, a novel experimental apparatus suitable to high pressure and high temperature measurement was established. The solubilities of CO₂ in PET were measured with the apparatus at temperatures of 110, 120, and 130°C and pressures up to 30.0 MPa. The results show that the solubility of CO₂ in PET

increases with the increase of pressure and CO₂ density, respectively, at a constant temperature, whereas it decreases with the increase of temperature at a constant pressure. The Sanchez-Lacombe equation of state (S-L EOS) was used to correlate the experimental data. The calculated results are in good agreement with the experimental ones. The average absolute relative derivation (AARD) is less than 3.91%. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2836–2841, 2008

Key words: phase equilibrium; solubility; supercritical CO₂; poly(ethylene terephthalate); S-L EOS

INTRODUCTION

Because of the advantages of supercritical CO₂ as an environmentally benign solvent and as a swelling and plasticizing agent,¹ some promising applications of supercritical CO₂ in polymer have received much attention, such as the supercritical fluid dyeing (SFD),² the membrane preparation by phase separation,³ the polymerization in supercritical fluids,⁴ the generation of microcellular polymeric foams,⁵ the impregnation of polymers,⁶ and the supercritical fluid devolatilization.⁷ To develop and design these processes, it is very important to understand the phase equilibrium characteristics (solubility) of supercritical CO₂ in polymers.

In recent years, application of supercritical CO₂ to PET dyeing^{8–11} has attracted considerable attentions from the dyeing and finishing industry because of the possibility of dyeing without water and almost completely avoiding the problems of water pollution. For the fundamental research and the process development of SFD, it is very important to understand the solubility characteristics of CO₂ in PET. However, there are few papers published by far to investigate the solubility of CO₂ in the PET because

of the limitations of experimental apparatus and the challenges of theoretical research. Koros and Paul¹² studied the solubility of CO₂ in PET under low pressure (<3 MPa). Von Schnitzler and Eggers¹³ measured the solubility of CO₂ in PET under the temperatures of 80, 100, and 120°C and the pressures less than 35 MPa using a magnetic suspension balance method, by which the apparatus cost is quite expensive and the technology requirements is sophisticated. Park and Bae¹⁴ attempted to predict the solubility data of CO₂ in PET using the Sanchez-Lacombe equation. Because PET typically has a very compact structure and high crystallinity, it is difficult to correlate or predict the solubility of CO₂ in PET by a theory. The limited research achievements cannot meet the needs of the rapid development of supercritical CO₂ dyeing.

In this work, a novel experimental apparatus was established based on the principle of pressure decaying. The solubilities of CO₂ in PET matrix were measured with the apparatus at temperatures of 110, 120, and 130°C and pressures up to 30 MPa. The Sanchez-Lacombe equation of state (S-L EOS) was used to correlate the measured solubility data.

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EXPERIMENT

Apparatus and principle

At present, some apparatus^{13,15} have been used to measure the solubility of gas in polymer. However,

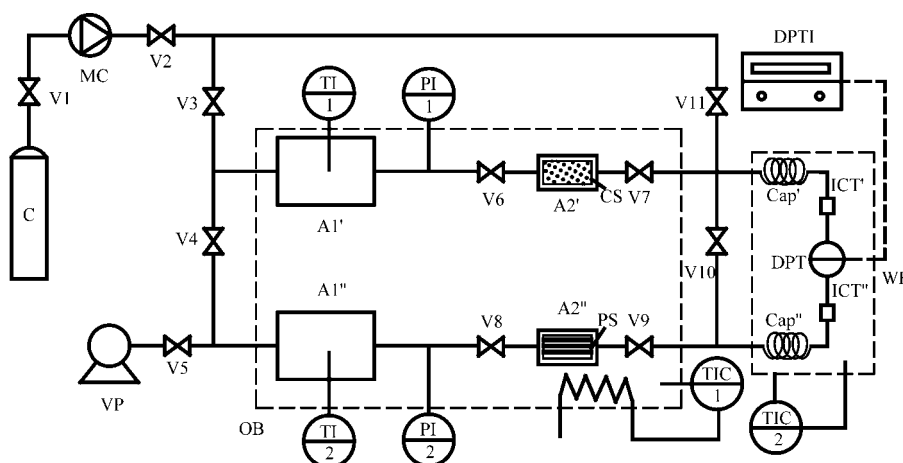


Figure 1 Schematic diagram of experimental apparatus: A1', A2', A1'', A2'', autoclave; C, CO₂ cylinder; Cap', Cap'', capillary; CS, contrast sample; DPT, differential pressure transmitter; DPTI, differential pressure transmitter indicator; ICT', ICT'', inner cavity of transmitter; MC, membrane compressor; OB, oil-bath; PI, pressure indicator; PS, polymer sample; TI, temperature indicator; TIC, temperature indicator and controller; V1-11, valve; VP, vacuum pump; WB, water-bath.

their applications are limited because of measuring accuracy, apparatus cost, or sophisticated technology requirements. In this study, a novel experimental apparatus (Fig. 1) suitable to high pressure and high temperature measurement was established based on the pressure decaying principle.^{16,17}

The apparatus mainly consists of two units (sorption unit and contrast unit). The two units have the same structure except that autoclave A2'' is filled with polymer sample, whereas autoclave A2' is filled with steel beads (~ ϕ = 2 mm) as contrast sample, which has the same volume of the original polymer sample and does not absorb any gas. The contrast unit provides a constant pressure (P') that is equal to the initial pressure in sorption unit. The pressure in the sorption unit (p'') decreases with the increase of gas sorption and a pressure difference (P' - p'') between sorption unit and contrast unit is formed. By measuring this pressure difference, the total amount of gas (Δn, mol) adsorbed by polymer sample can be calculated as follows:

$$\Delta n_1 = \frac{(P' - P'') \cdot (V_1'' + V_2'' - V_{ps})}{Z_1 RT_1} \quad (1)$$

$$\Delta n_2 = \frac{(P' - P'') V_t}{Z_2 RT_2} \quad (2)$$

$$\Delta n = \Delta n_1 + \Delta n_2 \quad (3)$$

where the prime and double prime superscripts denote the variables of contrast unit and sorption unit, respectively. Δn₁ denotes the difference between the amount of gas initially contacted with the polymer and the amount remaining in the gas phase in autoclaves A1'' and A2'' after equilibration. Δn₂ shows the decrease of the amount of gas in the

inner cavity of transmitter ICT'' as the sorption process goes on. Both Δn₁ and Δn₂ result from the gas sorption. R is the universal gas constant. T₁ and T₂ are the temperatures of the gas in the autoclaves A1'' and A2'' and in the differential pressure transmitter DPT, respectively. Z₁ and Z₂ are the compressibility factors of the gas in autoclaves A1'' and A2'' and in the inner cavity of transmitter ICT'', respectively. Z₁ and Z₂ are all regarded as constant values, because the pressure change in sorption unit due to CO₂ sorption is very small (<0.25 MPa). V₁' and V₂' are the volumes of autoclaves A1'' and A2'', respectively. V_t is the inner volume of single-side cavity of the differential pressure transmitter. V_{ps} is the volume of the polymer sample and is influenced by the static pressure, the thermal expansion, and the CO₂ swelling. The effect of the static pressure is relatively small and it was considered to be negligible. The effect of thermal expansion was predicted with the data in Ref. 18. The swollen volume of PET sample results from CO₂ swelling was approximately predicted with the data in Ref. 13.

The compressibility factors of CO₂ at different conditions can be calculated using the Peng–Robinson equation of state (P–R EOS). Two special “capillary” and a water-bath were introduced to keep the differential pressure transmitter operating at a relatively low temperature. The inner volume of autoclaves (including pipeline) was measured by a drain method. The autoclaves were first evacuated, and then the water was injected into it with a flow of 0.01 mL/min by means of a high-precision steady-flow pump (model LB-10, Beijing Xingda Technology Development, Beijing, China). Because compressibility of water is very small, the pressure of water started to rise as long as the autoclave was filled with water. The vol-

ume of the water injected into autoclave is equal to the inner volume of the measured autoclave. After three repeated measurements, the average value of the inner volume of each autoclave was obtained and the maximum measuring error is less than 1 mL. A smart differential pressure transmitter (model 1151HP, accuracy $\pm 0.075\%$ of span, Rosemount) was used to measure the pressure difference between sorption unit and contrast unit. The sorption unit and contrast unit were heated by means of an oil-bath whose temperature was controlled within 0.1 K. The temperatures of gas in high-pressure autoclaves were measured with a thermocouple. The pressures of gas in high-pressure autoclaves were measured with a pressure indicator within 0.1 MPa. The total error resulted from the measurement of various parameters in experimental process was evaluated within 2.01%.

The features of this apparatus are as follows: (1) The pressure difference is directly measured by a differential pressure transmitter instead of an absolute pressure transmitter. Therefore, the measuring accuracy of pressure difference is greatly improved. (2) Because the sorption unit and contrast unit are in the same environment, the effect of external conditions (e.g., operating temperature, equilibrium of heat) can be greatly eliminated. (3) The apparatus can be applied for real-time monitoring of experimental process. (4) The apparatus is simple and low in cost.

MATERIALS

A PET film with the thickness of 0.15-mm was supplied by Taicang Changfa Mapping Materials (China) and used without further purification. The crystallinity of PET sample is 35.39%, which was measured by means of differential scanning calorimetry (DSC) analysis (NETZSCH DSC 204, Germany). Carbon dioxide (>99.5% purity) was provided by Dalian University of Technology.

EXPERIMENTAL PROCEDURES

The experimental procedures are as follows:

1. The PET film sample (about 30 g) was placed in the autoclave A2". The steel beads as contrast sample were placed in autoclave A2'.
2. The apparatus was evacuated with a vacuum pump (model SHZ-C, Yuhua Instrument, China). After closing valves 5, 6, 7, 8, and 9, carbon dioxide was compressed and delivered to autoclaves A1' and A1" using a membrane compressor (MC). To protect the differential pressure transmitter from damaging, a small amount of CO₂ was simultaneously injected into the two inner cavities of the differential pressure transmitter.

3. The valves 3 and 11 were closed and the sorption autoclaves were preheated and maintained at expected values for about an hour.
4. After opening valves 6, 7, 8, and 9, and closing valves 4 and 10, CO₂ began to diffuse into PET matrix. At the same time, the pressure difference was built and recorded. After more than 2 h, the sorption reached equilibrium completely.

THEORETICAL CORRELATIONS

Sanchez-Lacombe equation of state

For the calculation of solubility of gas in polymers, the S-L EOS¹⁹⁻²¹ have received considerable attentions because it can be used to describe mixtures as well as pure substances and is suited for glass polymers as well as rubbery polymers with few characteristic parameters and adjustable parameters.

To describe the solubility of CO₂ in PET with S-L EOS, the following hypotheses should be assumed first: (1) The CO₂ sorption can reach equilibrium at the end of the sorption experiment. (2) The solubility of PET in gas phase is zero. (3) The PET can be modeled as a liquid under the present experimental conditions. Because the sorption time is long enough (>2 h) and the PET film sample is quite thin (0.15 mm), the sorption equilibrium can be fairly achieved. The solubility of polymer in gas phase is quite low, so the second hypothesis can approximately be satisfied. The glass transition temperature (T_g) of PET can be substantially lowered due to the sorption of CO₂, as discussed in our previous work.²² The experimental temperatures in this work are far above the T_g of PET, so the PET polymer can be regarded as in rubber state and treated as a liquid.

Sanchez and Lacombe¹⁹ derived a dimensionless equation of state for classical fluids based on the Ising (lattice) fluid theory. Subsequently, Sanchez-Lacombe lattice fluid theory was successfully extended to fluid mixtures²⁰ and polymer solutions.²¹ The basic equation of state is as follows:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left(\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r} \right) \tilde{\rho} \right) = 0 \quad (4)$$

where \tilde{P} , \tilde{T} , and $\tilde{\rho}$ are the reduced pressure, reduced temperature, and reduced density, respectively. r represents the number of lattice sites occupied by a molecule. The reduced parameters for a pure component are defined as follows:

$$\tilde{P} = P/P^*, \tilde{T} = T/T^*, \tilde{\rho} = \rho/\rho^*, \text{ and } r = MP^*/RT^*\rho^* \quad (5)$$

where M is the molecular weight and R is the universal gas constant. P^* , T^* , and ρ^* are the characteris-

tic pressure, characteristic temperature, and close-packed mass density. Generally, these characteristic parameters are determined by any pure-component thermodynamic property.

Mixing rules

For describing a mixture with the Sanchez-Lacombe lattice fluid theory, the following mixing rules²³ are required.

1. The characteristic pressure P^* for the mixture is assumed to be pairwise additive as follows:

$$P^* = \sum_j \sum_i \phi_i \phi_j P_{ij}^* \tag{6}$$

where ϕ_i represents the close-packed volume fraction of component i in the mixture given by

$$\phi_i = \frac{m_i/\rho_i^*}{\sum_j m_j/\rho_j^*} \tag{7}$$

The cross-term P_{ij}^* is defined as

$$P_{ij}^* = (P_i^* P_j^*)^{1/2} (1 - \delta_{ij}) \tag{8}$$

where δ_{ij} is the binary interaction parameter obtained by fitting the experimental data.

2. The mixing rule for v^* is based on the assumption that the close-packed molecular volume of each component is conserved. Therefore,

$$v^* = \phi_i^0 v_i^* + \phi_j^0 v_j^* \tag{9}$$

where

$$\phi_i^0 = \frac{m_i/(\rho_i^* v_i^*)}{\sum_j m_j/(\rho_j^* v_j^*)} \tag{10}$$

$$v_i^* = \frac{RT_i^*}{P_i^*} \tag{11}$$

3. The characteristic temperature for mixture is given by

$$\frac{T^*}{T} = \frac{\phi_i/\tilde{T}_i + \eta\phi_j/\tilde{T}_j}{\phi_i + \eta\phi_j} - \phi_i\phi_j \frac{(P_i^* + P_j^* - 2P_{ij}^*)v^*}{RT} \tag{12}$$

where

$$\eta = \frac{v_i^*}{v_j^*} \tag{13}$$

4. The number of lattice sites occupied by an r -mer in the mixture is

$$r = \frac{r_i^0 x_i v_i^* + r_j^0 x_j v_j^*}{v^*} \tag{14}$$

where

$$r_i^0 = \frac{M_i P_i^*}{RT_i^* \rho_i^*} \tag{15}$$

r_i^0 is the number of lattice sites occupied by component i in the pure state, whereas r_i represent the number of sites occupied by component i in the mixture, given by

$$r_i = r_i^0 (v_i^*/v^*) \tag{16}$$

Solubility calculation

At equilibrium, the chemical potential of gas in the pure gas phase is equal to the chemical potential of gas in the gas/polymer mixture, that is,

$$\mu_1^g = \mu_1^p \tag{17}$$

Using the S-L EOS, the chemical potentials of the gas in the pure gas phase and in the gas/polymer mixture can be obtained.

$$\mu_1^g = RT \left(r_1^0 \left(\frac{-\tilde{p}_1 + \tilde{P}_1 \tilde{v}_1}{\tilde{T}_1 + (\tilde{v}_1 - 1) \ln(1 - \tilde{p}_1) + \frac{1}{r_1^0} \ln \tilde{p}_1} \right) \right) \tag{18}$$

$$\begin{aligned} \mu_1^p = RT & \left(\ln \phi_1 + \left(1 - \frac{r_1}{r_2} \right) \phi_2 + r_1^0 \tilde{p} X_1 \phi_2^2 \right) \\ & + r_1^0 RT \left(-\frac{\tilde{p}}{\tilde{T}_1} + \frac{\tilde{P}_1 \tilde{v}}{\tilde{T}_1} + \tilde{v} \left((1 - \tilde{p}) \ln(1 - \tilde{p}) + \frac{\tilde{p}}{r_1^0} \ln \tilde{p} \right) \right) \end{aligned} \tag{19}$$

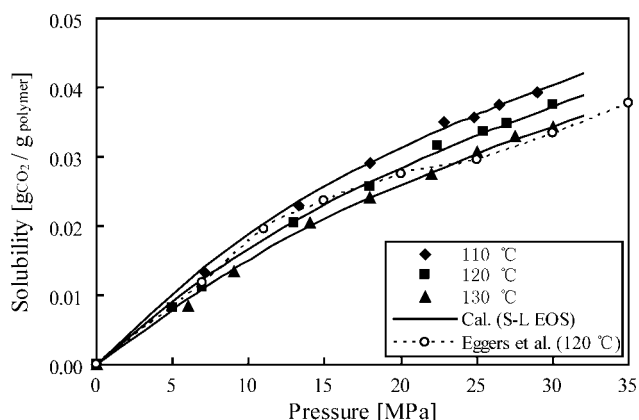


Figure 2 The relation of solubility of CO₂ in PET and operating pressure at different temperatures.

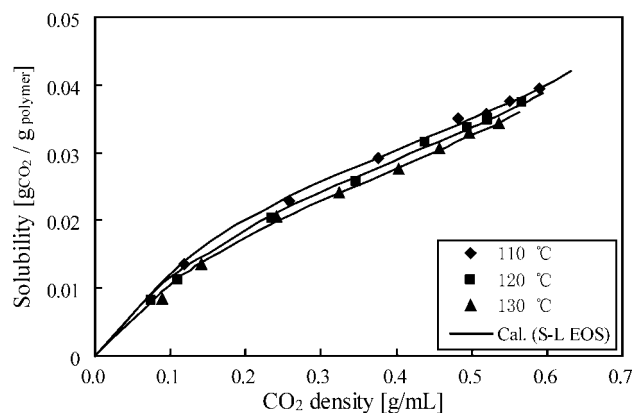


Figure 3 The relation of solubility of CO₂ in PET and CO₂ density at different temperatures.

with

$$X_1 = \frac{(P_1^* + P_2^* - 2(P_1^*P_2^*)^{1/2}(1 - \delta_{12}))v_1^*}{RT} \quad (20)$$

where the superscripts “g” and “p” represent the gas phase and gas/polymer mixture phase, respectively, subscript “1” and “2” represent gas and polymer, respectively. The adjustable binary interaction parameter δ_{ij} is determined by minimizing the following objective function.

$$F = \sum_i \left(\frac{x_i^{\text{cal}} - x_i^{\text{exp}}}{x_i^{\text{exp}}} \right)^2 \quad (21)$$

With the obtained binary interaction parameter δ_{ij} , the solubility of gas in polymer can be calculated by means of eqs. (17)–(20).

RESULTS AND DISCUSSIONS

The solubilities of CO₂ in PET at temperatures 110, 120, and 130°C and pressures up to 30.0 MPa were measured. The results are shown in Figures 2 and 3 and Table I. In Figure 2, the CO₂ solubility increases with the increase of pressure at a constant temperature and decreases with the increase of temperature at a constant pressure. One of the temperatures, 120°C, was also studied by Von Schnitzler and Eggers.¹³ It can be seen from Figure 2 that the isotherm data points for 120°C obtained in this work are in a good agreement with those of Von Schnitzler and Eggers.¹³ The “S-bend” in sorption isotherms of Von Schnitzler and Eggers occur at lower temperature than used in this work, and thus would not be seen in Figure 2. In Figure 3, it can be seen that the CO₂ solubility increase with the increase of CO₂ density at a constant temperature. The effect of

TABLE I
Measured Solubilities Compared with Calculated Ones Using S-L EOS

T (°C)	P (MPa)	Densities (g/cm ³)	Solubility (exp.) (gCO ₂ /g _{polymer})	Solubility (cal.) (gCO ₂ /g _{polymer})	Relative deviation (%)	AARD ^a
110	7.1	0.118	0.0135	0.0141	-4.07	1.61
	13.3	0.258	0.0229	0.0235	-2.74	
	18.0	0.375	0.0291	0.0292	-0.35	
	22.8	0.481	0.0350	0.0341	2.70	
	24.8	0.520	0.0357	0.0359	-0.57	
	26.5	0.551	0.0376	0.0374	0.51	
	29.0	0.590	0.0394	0.0395	-0.35	
120	5.0	0.075	0.0082	0.0091	-10.98	3.91
	7.0	0.111	0.0111	0.0124	-11.27	
	13.0	0.234	0.0204	0.0208	-1.83	
	18.0	0.346	0.0256	0.0265	-3.39	
	22.4	0.439	0.0315	0.0308	2.32	
	25.4	0.494	0.0337	0.0334	0.83	
	27.0	0.521	0.0348	0.0348	0.09	
130	30.0	0.567	0.0374	0.0372	0.53	2.72
	6.0	0.089	0.0085	0.0096	-13.26	
	9.0	0.142	0.0135	0.0138	-2.29	
	14.0	0.240	0.0205	0.0199	2.94	
	18.0	0.323	0.0241	0.0241	0.01	
	22.0	0.402	0.0276	0.0278	-0.84	
	25.0	0.456	0.0307	0.0304	0.96	
27.5	0.497	0.0329	0.0324	1.41		
30.0	0.535	0.0344	0.0344	0.03		

^a AARD = $\frac{100}{N} \cdot \sum_i \left| \frac{\text{Solubility}^{\text{exp}} - \text{Solubility}^{\text{cal}}}{\text{Solubility}^{\text{exp}}} \right|$

TABLE II
Characteristic Parameters of CO₂ and PET Used in the S-L EOS

Substances	P^* (MPa)	ρ^* (g/cm ³)	T^* (K)	Binary interaction parameter		
				δ_{ij}		
				110°C	120°C	130°C
CO ₂	567.0	1.510	305.0	0.0109	0.0116	0.0125
PET	642.1	1.368	818.0			

temperature and pressure on CO₂ solubility depends on the free volume and molecular interaction energy of the CO₂ and polymer to a great extent. These temperature and pressure (including density) dependence can be described by the Sanchez-Lacombe lattice fluid theory.

The calculated results using the S-L EOS are also shown in Figures 2 and 3 and Table I. In the calculation, the characteristic parameters (P^* , T^* , and ρ^*) of CO₂ and PET are from the Refs. 23, 24, and are listed in Table II. The binary interaction parameter δ_{ij} was determined by fitting the calculated and experimental solubilities to minimize the objective function [eq. (21)], and the results are also listed in Table II. The calculated solubilities agree well with the experimental ones and the average absolute relative derivation (AARD) is less than 3.91%. From Table I, it can be seen that the relative deviation between experimental and calculated solubilities is somewhat large at lower pressure, which may be brought by a relatively larger measuring error under low pressure conditions.

CONCLUSIONS

A novel experimental apparatus suitable to the high pressure and high temperature measurement was established based on the principle of pressure decaying. The solubilities of CO₂ in PET were measured with the apparatus at temperatures of 110, 120, and 130°C and pressures up to 30.0 MPa. The solubilities of CO₂ in PET increase with the increase of pressure and CO₂ density, respectively, at a constant temperature and decrease with the increase of temperature at a constant pressure.

The solubility data of CO₂ in PET were successfully correlated using the S-L EOS with only one adjustable parameter δ_{ij} . The calculated results are in good agreement with experimental ones and the

AARD between the experimental and calculated data is less than 3.91%.

The experimental apparatus can be used to measure the solubilities of other gases in polymers under high pressure and high temperature conditions. When the experimental temperature is above the T_g of PET, the S-L EOS is applicable to calculating the solubility of CO₂ in PET.

References

- Wang, Y.; Li, Z. Y.; Hu, D. P.; Liu, X. W.; Zhang, X. D.; Xia, Y. *J. J Chem Ind Eng (China)* 2004, 25, 23.
- Bach, E.; Cleve, E.; Schollmeyer, E. *Rev Prog Color* 2002, 32, 88.
- Tang, H. H.; Xia, Y. J.; Liu, X. W.; Li, Z. Y. *Chem Eng Oil Gas* 2007, 36, 106.
- Watkins, J. J.; Mccarthy, T. J. *Macromolecules* 1994, 27, 4845.
- Goel, S. K.; Beckman, E. *J Polym Eng Sci* 1994, 34, 1137.
- Berens, A. R.; Huvad, G. S.; Korsmeyer, R. W.; Kuning, F. W. *J Appl Polym Sci* 1992, 46, 231.
- Alsoy, S.; Duda, J. L. *AICHE J* 1998, 44, 582.
- Saus, W.; Knittel, D.; Schollmeyer, E. *Text Res J* 1993, 63, 135.
- Knittel, D.; Schollmeyer, E. *Int J Clothing Sci Technol* 1995, 7, 36.
- Chang, K. H.; Bae, H. K.; Shim, J. J.; *Korean J. Chem Eng* 1996, 13, 310.
- Rita, M.; Cadoni, E. D.; Piras, A. *Dye Pigment* 2000, 45, 75.
- Koros, W. J.; Paul, D. R. *J Polym Sci Part B: Polym Phys* 1947, 16, 16.
- Von Schnitzler, J.; Eggers, R. *J Supercrit Fluids* 1999, 16, 81.
- Park, M. W.; Bae, H. K. *J Supercrit Fluids* 2002, 22, 65.
- Wissinger, R. G.; Paulaitis, M. E. *J Polym Sci Part B: Polym Phys* 1987, 25, 2497.
- Vieth, W. R.; Tam, P. M.; Michaels, A. S. *J Colloid Interface Sci* 1966, 22, 360.
- Sato, Y.; Fujiwara, K.; Takikawa, T.; Sumarno Takishima, S.; Masuoka, H. *Fluid Phase Equilib* 1999, 162, 261.
- Zoller, P.; Bolli, P. *J Macromol Sci Phys* 1980, 18, 555.
- Sanchez, I. C.; Lacombe, R. H. *J Phys Chem* 1976, 80, 2352.
- Lacombe, R. H.; Sanchez, I. C. *J Phys Chem* 1976, 80, 2568.
- Sanchez, I. C.; Lacombe, R. H. *Macromolecules* 1978, 11, 1145.
- Li, Z. Y.; Meng, T. Y.; Liu, X. W.; Wang, Y.; Hu, D. P. *Chin J High Press Phys* 2006, 20, 243.
- Zhang, Y.; Gangwani, K. K.; Lemert, R. M. *J Supercrit Fluids* 1997, 11, 115.
- Patrick, A. R. *J Appl Polym Sci* 1993, 48, 1061.