

# Modeling VLE and GLE of Systems Involving Polymers by Using SRK Equation of State\*

JI Weirong(计伟荣)\*\*

College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310032, China

**Abstract** A simple extension of cubic equations of state (EOS) to polymer systems has been proposed. The Soave-Redlich-Kwong (SRK) EOS was taken as a prototype to be used to describe the  $PVT$  behavior of polymer melts in a wide temperature and pressure range. Combined with a modified Huron-Vidal  $g^E$ -mixing rule it was applied for modeling vapor-liquid equilibria of polymer-solvent solutions and the solubility of supercritical gases in polymer melts. Satisfactory results are obtained.

**Keywords** SRK equation of state, polymer, phase equilibrium,  $PVT$  behavior.

## 1 INTRODUCTION

Equations of state have been widely used in the engineering calculations for modeling thermodynamic properties and phase behaviors of systems involving not only normal substances but also heavy compounds. In the past decades equations of state (EOS) suitable for polymer systems was investigated with immense efforts. Many new EOS were proposed and they can be roughly categorized into two, namely, the lattice and the continuum models[1]. The lattice models[2—4] of either the hole or the cell type are on the basis of the classic Flory-Huggins theory[5]. They can be used to describe incompressible polymers as well as the Flory-Huggins type of activity coefficient models, and are better in the description of compressible ones, which are often of importance in the polymer processing at elevated pressures. The continuum models originate from the generalized van der Waals theory[6]. They are advantageous over the lattice ones in that they can satisfy the ideal gas limit and can, therefore, possibly be suitable for substances with low molecular weights as well. For example, the SAFT-equations[7—9] have been successfully applied to systems composed of polymers and small compounds. However, they are not always reliable for conventional substances and problems such as the satisfaction of critical conditions are still to solve. In addition, the complexity of these kinds of EOS leads to a very long computation time, which should be avoided in the engineering calculations. For these reasons, the extension of the cubic EOS to polymer systems has been paid much attention in the past, particularly for the phase equilibrium calculation of polymer-solvent systems[10—17]. In the literature, the cubic EOS was applied directly to polymer molecules by using model parameters estimated from the  $PVT$  properties of polymer melts. But this often leads to calculation problems because of the strong asymmetry of the systems studied. As an example, an extremely larger binary interactive parameter is needed in the calculation of phase equilibria for poly-

mer-solvent systems by using the classic van der Waals mixing rule[13,17] or the Huron-Vidal  $g^E$ -mixing rule (HVMR)[11] and in many cases its value is larger than 40, which is obviously physically meaningless and leads to further problems by the extension of the model to multicomponent systems.

In this study, a simple extension of conventional cubic EOS to polymer melts and polymer mixtures by taking the SRK EOS as a prototype is presented, in which the polymer segment rather than the polymer molecule is focused. The vapor-liquid equilibria (VLE) of polymer-solvent solutions and the solubility of supercritical gases in polymer melts (GLE) are investigated.

## 2 EXTENSION OF THE SRK EOS TO PURE POLYMERS

The starting point of this method is on the basis of the equality of the specific volumes of the polymer and its segment ( $v_{sp, polymer} = v_{sp, segment}$ ), *i.e.*

$$v_{sp} = \frac{v_{polymer}}{M_{polymer}} = \frac{rv_{segment}}{M_{polymer}} = \frac{v_{segment}}{M_{segment}} \quad (1)$$

where,  $r$  is the segment number of the polymer molecule that is usually estimated by the ratio of their molecular weights ( $r = M_{polymer}/M_{segment}$ ) and the molar volume of the polymer is related to that of the segment through the segment number by  $v_{polymer} = rv_{segment}$ . This means that molar volume of the polymer segments can be calculated from the specific volume of the polymer without the knowledge of its molecular weight and the molecular weight distribution, which are often not reliable or available. This quantity can be described by using a cubic EOS. Here the SRK EOS is taken as a prototype:

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (2)$$

Received 2006-01-19, accepted 2006-04-28.

\* Supported by the Zhejiang Provincial Foundation for Returned Scholars and the Scientific Research Foundation of the State Human Resource Ministry.

\*\* To whom correspondence should be addressed. E-mail: weirong.ji@zjut.edu.cn

where the cohesive energy parameter  $a(T)$  and the volumetric parameter  $b$  of polymer segments can be expressed as

$$a(T) = a_c \alpha(T_r) \quad (3)$$

$$b = b_c \quad (4)$$

and an exponential  $\alpha(T_r)$ -function is proposed as

$$\alpha(T_r) = \exp(cT) \quad (5)$$

Because the critical properties of the polymer segments are unavailable, the  $a_c$  and  $b_c$  in Eqs.(3) and (4), together with the parameter  $c$  in Eq.(5), are estimated from the experimental  $PVT$  data of polymer melts.

For conventional substances the cohesive energy parameter  $a(T)$  and the volumetric parameter  $b$  of the SRK EOS are calculated as usual

$$a(T) = a_c \alpha(T_r) = 0.42748 \frac{R^2 T_c^2}{p_c} \alpha(T_r) \quad (6)$$

$$b = b_c = 0.08664 \frac{RT_c}{p_c} \quad (7)$$

where the three parameter  $\alpha(T_r)$ -function proposed by Mathias and Copeman[18] is used to represent the vapor pressures as accurate as possible

$$\alpha(T_r) = \left[ 1 + m_1 (1 - T_r^{0.5}) + m_2 (1 - T_r^{0.5})^2 + m_3 (1 - T_r^{0.5})^3 \right]^2 \quad (8)$$

The specific volumes of ten pure polymer melts in a wide temperature and pressure range including those at zero pressure have been calculated. The parameters of the EOS are correlated by using the following objective function

$$F_{\text{obj}} = \sum_m \left| \frac{v_{\text{sp,exp}} - v_{\text{sp,cal}}}{v_{\text{sp,exp}}} \right| \quad (9)$$

Two different methods have been used to calculate the zero pressure volumes of polymer melts during the correlation. In the first one (called method I), the zero pressure volumetric behavior is described by directly equating Eq.(2) to zero as done by Kontogeorgis *et al.*[12], and ignoring the isofugacity restraint. Fig.1 shows the  $PVT$  values of  $\alpha$ -polypropylene calculated by the extended SRK EOS in comparison with the experimental data. The agreement is very good in the whole temperature and pressure range studied. The overall average deviation for ten polymers amounts to only 0.2% (Table 1), which is already near the experimental uncertainty. However, as observed also by Kalospiros and Tassios[19], a disadvantage of this method is that it sometimes results in large vapor pressures (even of the order of  $10^{-1}$  kPa), which can lead to the prediction of a finite polymer solubility in the vapor phase. Because of this reason, the second method (method II) is used in which a very low fictitious vapor pressure ( $10^{-5}$  kPa) is assumed and the phase equilibrium condition is imposed during the calculation of the zero pressure volumes. The results of both methods are summarized in Table 1. For comparison, the results obtained by Sako *et al.*[10], Orbey

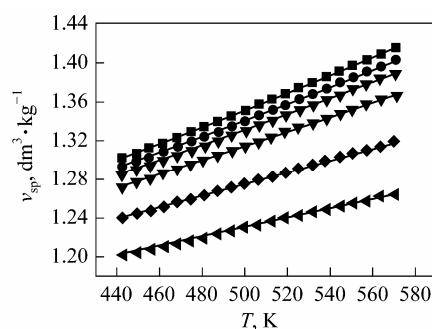


Figure 1  $PVT$  behavior of  $\alpha$ -polypropylene polymer melt represented by using SRK EOS with method I

■ 0; ● 5MPa; ▲ 10MPa; ▼ 20MPa; ◆ 50MPa; ◀ 100MPa; — calculated values

Table 1 Results of the calculation of specific volumes of polymer melts by using the extended SRK in comparison with PR, vdW and the Sako-Wu-Prausnitz EOS

Polymer	$\delta_{\text{rel}}(v)^{\text{①}}$				
	Method I	Method II	Peng-Robinson[11]	van der Waals[12]	Sako-Wu- Prausnitz[10]
polystyrene (PS)	0.122	1.590	18.87	—	4.11
LD-polyethylene (LDPE)	0.456	2.610	—	—	—
polybutadiene (PBD)	0.086	1.356	—	—	—
polyisobutylene (PIB)	0.130	1.621	6.01	7.22	0.59
polyvinylacetate (PVAc)	0.121	1.481	—	19.60	2.69
polyvinylchloride (PVC)	0.245	1.568	—	—	1.64
$\alpha$ -polypropylene ( $\alpha$ -PP)	0.082	3.518	—	—	—
polyethylmethacrylat (PEMA)	0.210	1.604	—	—	—
polybutylmethacrylate (PBMA)	0.407	1.746	—	—	—
polyvinylmethylether (PVME)	0.180	2.527	—	—	—
overall relative average deviation	0.204	1.962	12.44	13.41	2.26

①  $\delta_{\text{rel}}(v) = \left| 1 - v_{\text{sp,cal}}/v_{\text{sp,exp}} \right| \times 100\%$ .

and Sandler[11] and Kontogeorgis *et al.*[12] on the basis of the Sako-Wu-Prausnitz, Peng-Robinson and van der Waals EOS, respectively, are also listed. It is shown that keeping the low vapor pressure of a polymer melt is at the cost of some accuracy of its volume calculation. The overall average deviation becomes 2%, ten times bigger than that of the method I. But the results are still better than those given in the literature, and in addition, they are acceptable from the engineering point of view. The parameters obtained by using the method II, together with the temperature and pressure range of the experimental data, are summarized in Table 2.

### 3 EXTENSION OF THE SRK EOS TO POLYMER-SOLVENT MIXTURES

The polymer-solvent solution studied in this article is considered a mixture of polymer segments with a solvent. The mass fraction of the polymer in a mixture, which is often used for polymer systems, is equal to that of the corresponding polymer segment ( $w_{\text{polymer}} = w_{\text{segment}}$ ). Therefore, the use of the molecular weight of polymers can be avoided in transferring the mass fraction of the polymer into the mole fraction of polymer segments

$$x_{\text{segment}} = \frac{w_{\text{polymer}}}{M_{\text{segment}}} \left/ \left( \frac{w_{\text{polymer}}}{M_{\text{segment}}} + \frac{w_{\text{solvent}}}{M_{\text{solvent}}} \right) \right. \quad (10)$$

in which only the molecular weight of the polymer segment and that of the solvent are involved. Another advantage is that a flexible  $g^E$ -mixing rule can be easily incorporated into the polymer EOS. In this study, the modified HVMR proposed by Holderbaum and Gmehling[21] on the basis of zero pressure limit is used for estimating the cohesive energy parameter of the extended SRK EOS

$$a = b \left[ \sum_k x_k \frac{a_k}{b_k} - \frac{RT}{0.64663} \left( \sum_k x_k \ln \frac{b}{b_k} + \hat{g}_0^E \right) \right] \quad (11)$$

where the dimensionless excess free energy is calculated by the non-random two liquids (NRTL) equation.

$$\hat{g}^E = \frac{g^E}{RT} = \sum_k x_k \left[ \frac{\sum_l x_l G_{lk} \tau_{lk}}{\sum_l x_l G_{lk}} \right] \quad (12)$$

$$\tau_{ij} = \frac{\Delta g_{ij}/R}{T} = \frac{A_{ij}}{T} \quad G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad \alpha_{ij} = \alpha_{ji}$$

For the volumetric parameter of the EOS, a simple linear-combination mixing rule is used

$$b = \sum_k x_k b_k \quad (13)$$

Then the fugacity coefficient can be expressed by

$$\ln \phi_i^* = \frac{b_i}{b} \left( \frac{pv}{RT} - 1 \right) - \ln \left[ \frac{p(v-b)}{RT} \right] - \left[ \frac{1}{RT} \frac{\partial n(a/b)}{\partial n_i} \right]_{T,p,n_{j \neq i}} \ln \left( \frac{v+b}{v} \right) \quad (14)$$

and following equations are employed in the calculation of vapor-liquid and gas-liquid equilibria

$$x_i^V \phi_i^{*V} = x_i^L \phi_i^{*L} \quad (15)$$

$$x_i^G \phi_i^{*G} = x_i^L \phi_i^{*L} \quad (16)$$

### 4 CALCULATION OF VAPOR-LIQUID EQUILIBRIA OF POLYMER-SOLVENT SOLUTIONS

The knowledge of the phase equilibrium of polymer solutions is of importance not only for the industrial production but also for the processing of polymers. For example, the devolatilization of low molecular weight substances, such as unreacted monomers, plasticizers, and toxic additives, is essential for the product quality, environmental protection, and safety, and therefore an exact information about the equilibrium pressure as a function of the composition of polymer mixtures is necessary.

The VLE data of twenty-one systems with totally twenty-seven isotherms involving seven different polymers have been calculated by using the SRK EOS. For polymer segments, the parameters obtained by method II in Table 2 are used. The relative average deviations of vapor pressures are given in the Table 3. Satisfactory results are obtained. The overall relative average deviation is less than 2%. Figs.2(a)—2(d) show the VLE of some example systems. The calculated  $p$ - $x$  curves reproduce the experimental data very well. The system water+polyvinylacetate (PVAc), which has the largest relative average deviation (5.16%) of systems studied, is shown in Fig.2(d). As

Table 2 Parameters fitted by using experimental densities[20] of pure polymer melts

Polymer	$\rho$ -range, °C	$p$ -range, MPa	$c$ , K <sup>-1</sup>	$a_c$ , Pa·m <sup>6</sup> ·mol <sup>-2</sup>	$b_c$ , dm <sup>3</sup> ·mol <sup>-1</sup>
PS	115—196	0—100	-0.00244	33.213	0.09705
LDPE	142—200	0—100	-0.00393	26.420	0.03354
PBD	4—55	0—100	-0.00346	14.246	0.05622
PIB	53—110	0—100	-0.00195	11.963	0.05837
PVAc	35—100	0—100	-0.00447	31.432	0.06917
PVC	100—150	0—100	-0.00160	9.871	0.04357
$\alpha$ -PP	80—120	0—100	-0.00260	29.186	0.05181
PEMA	114—159	0—100	-0.00149	21.533	0.09828
PBMA	45—200	0—100	-0.00308	44.245	0.13030
PVME	30—198	0—100	-0.00339	21.741	0.05523

Table 3 Results of VLE calculations for polymer-solvent solutions by using the extended SRK EOS

System	$T, K$	$\alpha_{12}$	$A_{12}$	$A_{21}$	$\delta_{rel}(p)^{\text{①}}$
nonane+PBD[22]	353.15	-46.169	23.074	719.993	4.825
	373.15	-7.6492	88.585	534.584	4.287
	403.15	-0.7492	319.270	438.172	1.895
ethylbenzene+PBD[22]	353.15	0.4933	1264.692	546.94	3.613
	373.15	0.4382	1683.512	476.340	1.738
	403.15	0.01439	7536.49	-5114.03	3.924
chloroform+PBD[22]	298.15	0.6337	713.724	161.494	0.484
hexane+PE[22]	273.15	0.6765	507.664	598.314	1.687
methylbromide+PE[22]	273.15	0.8093	412.283	568.907	0.706
benzene+PE[22]	273.15	-3.0053	166.076	-272.993	0.228
pentane+PIB[23]	298.15	0.7038	176.389	329.495	0.631
benzene+PIB[23]	298.15	0.6537	415.413	363.762	0.827
cyclohexane+PIB[23]	298.15	0.7379	371.502	246.809	0.519
tetrachloromethane+PP[23]	298.15	-0.1977	-317.836	720.826	1.237
acetone+PS[22,23]	298.15	0.9370	260.872	227.716	0.714
	323.15	0.9454	255.960	237.337	0.431
benzene+PS[22]	318.15	1.1998	629.374	185.530	0.279
	333.15	1.3209	489.149	258.381	0.783
butan-2-one+PS[22]	321.65	0.8181	281.656	136.545	1.275
chloroform+PS[22]	298.15	-6.1812	55.296	75.364	0.869
tetrachloromethane+PS[22]	293.15	6.4149	147.908	9.125	0.166
toluene+PS[22]	298.15	0.8148	555.191	103.098	1.551
benzene+PVAc[23]	303.15	0.5107	1688.30	179.419	3.388
water+PVAc[22]	313.15	-4.1971	103.033	326.300	5.155
dibutylether+PVC[22]	315.35	0.5020	1019.139	495.381	2.472
tetrahydrofuran+PVC[22]	315.65	-0.1624	-776.963	777.010	1.923
toluene+PVC[22]	316.35	-1.0457	129.795	262.974	0.872
overall relative average deviation					1.72

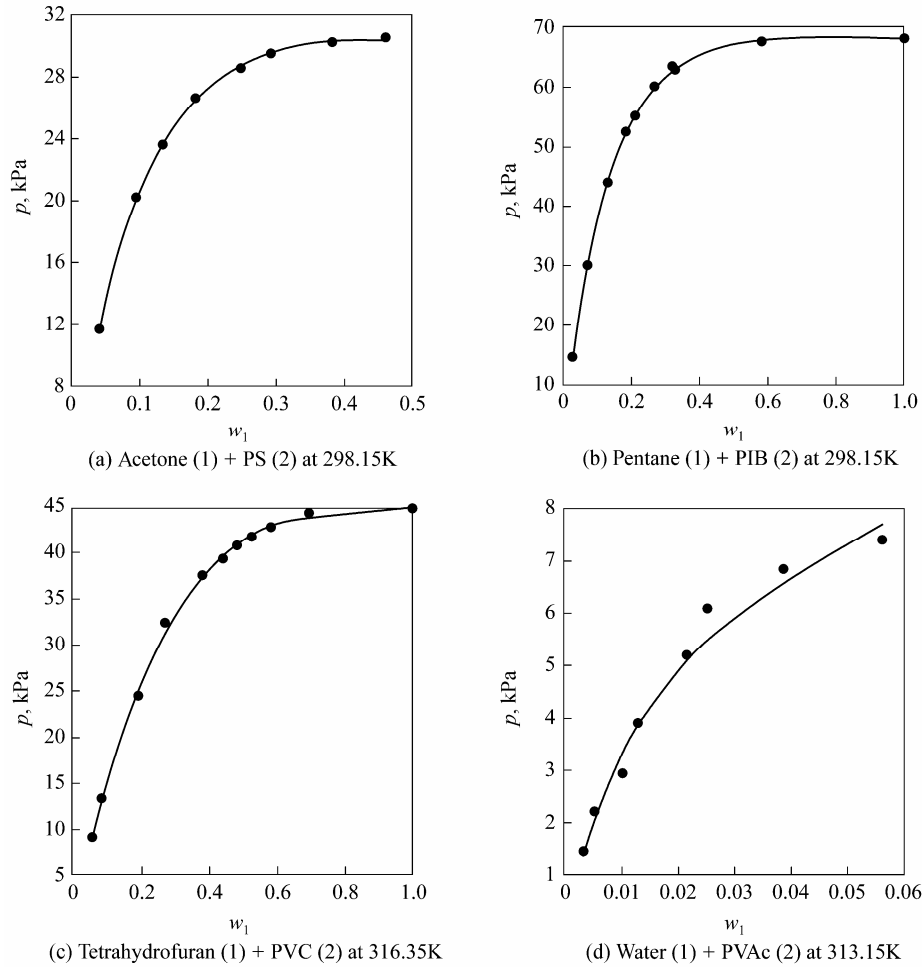
$$\text{① } \delta_{rel}(p) = \left| 1 - p_{cal}/p_{exp} \right| \times 100\% .$$

far as the poor quality of the experimental data of this system is concerned, the results are satisfactory.

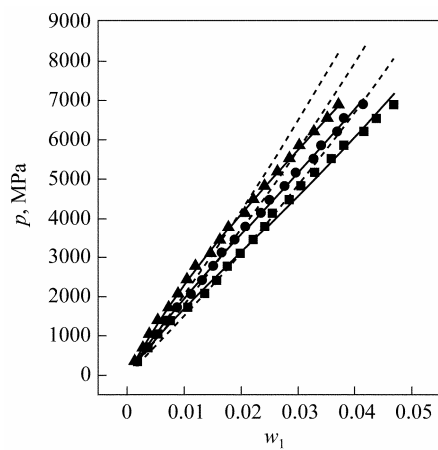
## 5 CALCULATION OF THE SOLUBILITY OF SUPERCRITICAL GASES IN POLYMER MELTS

Supercritical gases are often used as reactants, solvents, inflating agents or anti-solvents in polymer manufacturing and processing. Therefore, the description of the high-pressure phase equilibria for systems involving polymers is also needed. Here, the extended SRK EOS in combination with the HVMR introduced above is applied to the calculation of the solubility of supercritical gases in polymer melts. Five systems, each of which has three isotherms, have been calculated. To show the importance of the flexibility of mixing rules for polymer systems, parallel calculations have been carried out by using a simple vdW mixing rule (see Appendix). The results together with

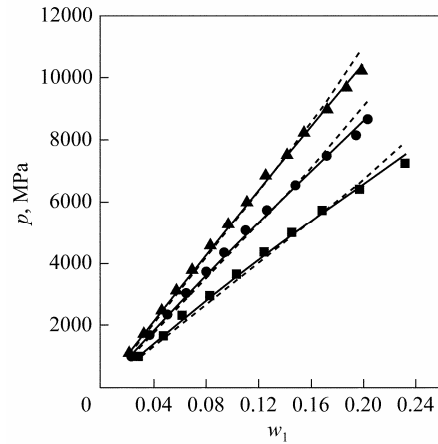
the parameter values obtained are given in Table 4. As illustrated by the systems ethylene+polyethylene (PE) and carbon dioxide + polybutylmethacrylate (PBMA) in Figs.3(a) and 3(b), the description of phase equilibria at high pressures by using the extended SRK EOS with HVMR is as good as that at low pressures. The calculated values are in good agreement with the experimental data. The overall relative average deviation for the five systems is about 2%. In addition, the use of a vdW mixing rule leads to reasonably good results. The overall average deviation amounts to less than 6%. But, as shown in Figs.3, 4, the vdW mixing rule is unable to describe the solubility satisfactorily when the gas concentration is relatively high. For comparison, the results of Zhong and Masouka[17] calculated by applying the Peng-Robinson EOS together with a van der Waals mixing rule (vdW1) and a new mixing rule proposed by them (New 1) (Appendix) directly to polymer molecules are also listed in Table 4. The



**Figure 2 VLE for the systems**  
 ● experimental data; — calculated values by using SRK EOS



**Figure 3 Solubility of supercritical ethylene (1) in LDPE (2) melt**  
 ■ 399.15K; ● 413.15K; ▲ 428.15K; — calculated values by using SRK EOS/HVMR; --- values calculated by using SRK EOS/vdW mixing rule



**Figure 4 Solubility of supercritical carbon dioxide (1) in PBMA (2) melt**  
 ■ 313.15K; ● 333.15K; ▲ 353.15K; — calculated values by using SRK EOS/HVMR; --- calculated values by using SRK EOS/vdW mixing rule

extended SRK EOS gives better results even with the simple vdW mixing rule. This means that the proposed treatment of polymer solutions works very well.

## 6 CONCLUSIONS

It is possible to represent phase equilibria and *PVT* behavior of polymer systems by applying cubic EOS directly to polymer segments. With one-parameter

**Table 4** Results of the calculation of the solubility of supercritical gases in polymer melts by using the extended SRK EOS

System	T, K	Extended SRK EOS					Zhong-Masuoka[17]		
		Huron-Vidal			vdW		vdW1	New-1	
		$\alpha_{12}$	$A_{21}$	$A_{21}$	$\delta_{rel}(p)$	$k_{ij}$	$\delta_{rel}(p)$	$\delta_{rel}(p)$	
ethylene+LDPE[24]	399.15	6.457	59.681	210.640	2.80	-0.405	8.19	50.9	5.7
	413.15	5.433	17.023	239.921	1.85	-0.402	12.25	49.8	6.2
	428.15	3.077	-53.264	371.635	1.62	0.400	12.38	48.6	6.2
carbon dioxide+PBMA[25]	313.2	11.937	-16.646	-34.355	2.25	0.657	3.75	44.5	6.1
	333.2	3.180	126.621	-126.622	2.25	0.655	3.98	55.5	4.0
	353.2	1.523	235.518	-235.605	1.97	0.650	3.20	56.7	3.8
carbon dioxide+PVAc[25]	313.2	3.710	188.733	-188.633	3.16	0.410	4.48	19.1	6.0
	333.2	2.300	238.780	-238.577	1.24	0.417	2.28	16.8	4.7
	353.2	1.167	358.421	-358.720	1.55	0.419	3.58	35.1	4.2
carbon dioxide+PS[26]	373.2	1.150	378.319	633.060	1.73	0.706	12.68	20.4	11.1
	413.2	0.967	364.862	714.977	2.01	0.726	7.07	19.2	7.2
	453.2	1.530	333.522	631.422	3.50	0.753	6.20	53.4	6.0
nitrogen+PS[26]	373.2	1.125	209.969	688.588	0.22	0.838	1.18	10.6	19.1
	413.2	1.101	279.263	747.730	3.37	0.844	3.25	19.7	13.8
	453.2	1.304	370.930	922.621	1.30	0.859	4.19	14.4	12.5
overall relative average deviation					2.05	5.91	34.3	7.8	

Note:  $\delta_{rel}(p) = |1 - p_{cal}/p_{exp}| \times 100\%$ .

$\alpha(T_r)$ -function the SRK EOS can describe the  $PVT$  data of different polymer melts in a wide temperature and pressure range satisfactorily. Combined with a modified HVMR, it can be successfully extended to polymer mixtures and gives satisfactory results in modeling vapour-liquid equilibria of polymer-solvent solutions, the solubility of supercritical gases in polymer melts. It is to mention that the method proposed can be extended to polymer-solvent mixture and copolymer-solvent systems. As an example, the correlation of the system PS + chloroform + carbon tetrachloride at 50°C [27] gives an average deviation of vapor pressures of 1.54% and that of vapor phase compositions of 2.11%. A detailed discussion will be given in the upcoming contribution.

## NOMENCLATURE

$A_{ij}$	energy parameters of the NRTL model in the HVMR
$a, b$	parameters in the SRK cubic EOS
$c$	parameter in the $\alpha(T_r)$ -function for polymer segments
$F$	objective function
$g^E$	molar excess free energy, $J \cdot mol^{-1}$
$\hat{g}^E$	dimensionless excess free energy [ $\hat{g}^E = g^E / (RT)$ ]
$M$	molecular weight
$m_1, m_2, m_3$	parameters in $\alpha(T_r)$ -function for normal substances
$p$	pressure, kPa
$R$	molar gas constant ( $= 8.314 J \cdot mol^{-1} \cdot K^{-1}$ )
$r$	segment number of polymers
$T$	thermodynamic temperature, K
$v$	molar volume, $dm^3 \cdot mol^{-1}$
$v_{sp}$	specific volume, $dm^3 \cdot kg^{-1}$
$w_i$	mass fraction of component $i$
$x_i$	mole fraction of component $i$

$\alpha(T_r)$  temperature function of cubic EOS parameter  $a$   
 $\alpha_{ij}$  non-random parameter of NRTL model  
 $\delta_{rel}$  relative average deviation

## Superscripts

E excess property  
 G supercritical gases  
 L liquid phase

## Subscripts

c critical  
 cal calculated value  
 exp experimental value  
 $i$  component  $i$   
 $j$  component  $j$   
 $k$  component  $k$   
 polymer properties of polymers  
 r reduced value  
 segment properties of polymer segments  
 solvent properties of solvents  
 sp specific properties  
 0 reference state

## REFERENCES

- Condo, P.D., Radosz, M., "Equations of state for monomers and polymers", *Fluid Phase Equilibria*, **117**, 1-10(1996).
- Sanchez, I.C., Lacombe, R.H., "Statistical thermodynamics of fluid mixtures", *J. Phys. Chem.*, **80**, 2568-2580(1976).
- Panayiotou, C.G., Vera, J.H., "Statistical thermodynamics of r-mer fluids and their mixtures", *Polymer J.*, **36**, 681-694(1982).
- High, M.S., Danner, R.P., "Application of the group contribution lattice-fluid EOS to polymer solutions", *AIChE J.*, **36**, 1625-1632 (1990).
- Flory, P.J., *Principle of Polymer Chemistry*, Cornell Univ. Press, Ithaca (1953).
- Beret, S., Prausnitz, J. M., "Perturbed hard-chain theory, an equation of state for fluids containing small or large

- molecules", *AIChE J.*, **21**, 1123—1132(1975)
- 7 Huang, S.H., Radosz, M., "Equation of state for small, large, polydisperse, and associating molecules, extension to fluid mixtures", *Ind. Eng. Chem. Res.*, **30**, 1994—2005(1991).
  - 8 Fu, Y.H., Sandler, S.I., "A simplified SAFT equation of state for associating compounds and mixtures", *Ind. Eng. Chem. Res.*, **34**, 1897—1909(1995).
  - 9 Gross, J., Sadowski, G., "Perturbed-chain SAFT, an equation of state based on a perturbation theory for chain molecules", *Ind. Eng. Chem. Res.*, **40**, 1244—1260(2001).
  - 10 Sako, T., Wu, A.H., Prausnitz, J.M., "A cubic equation of state for high-pressure phase equilibria of mixtures containing polymers and volatile fluids", *J. Appl. Polym. Sci.*, **38**, 1839—1858(1989).
  - 11 Orbey, H., Sandler, S.I., "Vapor-liquid equilibrium of polymer solutions using a cubic equation of state", *AIChE J.*, **40**, 1203—1209(1994).
  - 12 Kontogeorgis, G.M., Fredenslund, A., Economou, I.G., Tassios, D.P., "Equations of state and activity coefficient models for vapor-liquid equilibria of polymer solutions", *AIChE J.*, **40**, 1711—1727(1994).
  - 13 Kontogeorgis, G.M., Harismiadis, V.I., Fredenslund, A., Tassios, D.P., "Application of the van der Waals equation of state to polymers ( I ). Correlation", *Fluid Phase Equilibria*, **96**, 65—92(1994).
  - 14 Orbey, H., Bokis, C.P., Chen, C.C., "An extension of cubic equations of state to vapor-liquid equilibria in polymer-solvent mixtures", *Fluid Phase Equilibria*, **145**, 169—192(1998).
  - 15 Tork, T., Sadowski, G., Arlt, W., De Haan, A., Krooshof, G., "Modelling of high-pressure phase equilibria using the Sako-Wu-Prausnitz equation of state ( II ) Vapour-liquid equilibria and liquid-liquid equilibria in polyolefin systems", *Fluid Phase Equilibria*, **163**, 79—98(1999).
  - 16 Zhong, C., Masuoka, H., "A new mixing rule for cubic equations of state and its application to vapor-liquid equilibria of polymer solutions", *Fluid Phase Equilibria*, **123**, 59—69(1996).
  - 17 Zhong, C., Masuoka, H., "Modeling of gas solubilities in polymers with cubic equation of state", *Fluid Phase Equilibria*, **144**, 49—57(1998).
  - 18 Mathias, P.M., Copeman, T.W., "Extension of the Peng-Robinson equation of state to complex mixtures: Evaluation of the various forms of the local composition concept", *Fluid Phase Equilibria*, **13**, 91—108(1983).
  - 19 Kalospiros, N.S., Tassios, D.P., "Prediction of vapor-liquid equilibria in polymer solutions using an equation of state/excess gibbs free energy model", *Ind. Eng. Chem. Res.*, **34**, 2117—2124(1995).
  - 20 Rodgers, P.A., "Pressure-volume-temperature relationships for polymeric liquids, A review of equations of state and their characteristic parameters for 56 polymers", *J. Appl. Polym. Sci.*, **48**, 1061—1080(1993).
  - 21 Holderbaum, T., Gmehling, J., "PSRK: A group contribution equation of state based on UNIFAC", *Fluid Phase Equilibria*, **70**, 251—265(1991).
  - 22 Hao, W., Elbro, H.S., Alessi, P., Polymer Solution Data Collection: Vapor-Liquid Equilibrium, Chemistry Data Series (Vol. XIV, Part1), DECHMA, Frankfurt/Main (1992).
  - 23 Wohlfarth, C., Vapour-Liquid Equilibrium Data of Binary Polymer Solutions, Elsevier, Amsterdam (1994).
  - 24 Cheng, Y.L., Bonner, D.C., "Solubility of ethylene in liquid, low-density polyethylene to 69 atmospheres", *J. Polym. Sci.*, **15**, 593—603(1977).
  - 25 Wang, N.H., Takishima, S., Masuoka, H., "Measurement and correlation of solubility of a high pressure gas in a polymer by piezoelectric quartz sorption — CO<sub>2</sub>+PVAc and CO<sub>2</sub>+PBMA systems", *Int. Chem. Eng.*, **34**, 255—262(1994).
  - 26 Sato, Y., Yurugi, M., Fujiwara, K., Takishima, S., Masuoka, H., "Solubilities of carbon dioxide and nitrogen in polystyrene under high temperature and pressure", *Fluid Phase Equilibria*, **125**, 129—138(1996).
  - 27 Tanbonliang, J.O., Prausnitz, J.M., "Vapour-liquid equilibria for some binary and ternary polymer solutions", *Polymer*, **38**, 5775—5783(1997).

## APPENDIX

(1) The van der Waals mixing rule used with the extended SRK EOS

$$a = \sum \sum x_i x_j a_{ij} \quad a_{ij} = \frac{1}{2}(a_i + a_j)(1 - k_{ij}) \quad (\text{A1})$$

$$b = \sum x_i b_i \quad (\text{A1a})$$

(2) Mixing rules used by Zhong and Masouka[17] in modeling gas solubilities in polymers using the Peng-Robinson EOS:

The van der Waals mixing rule (vdW1)

$$a = \sum \sum x_i x_j a_{ij} \quad a_{ij} = \sqrt{a_i a_j} \frac{(b_i + b_j)}{\sqrt{b_i b_j}} (1 - k_{ij}) \quad (\text{A2})$$

$$b = \sum x_i b_i \quad (\text{A2a})$$

and the New-1

$$a = \sum \sum x_i x_j a_{ij} \quad a_{ij} = \sqrt{a_i a_j} \frac{(b_i + b_j)}{\sqrt{b_i b_j}} (1 - k_{ij}) \quad (\text{A3})$$

$$\frac{a}{b} = \sum x_i \frac{a_i}{b_i} \quad (\text{A4})$$