

# PREDICTION OF PVT BEHAVIOR OF POLYMER MELTS BY THE GROUP-CONTRIBUTION LATTICE-FLUID EQUATION OF STATE

Byung-Chul Lee<sup>†</sup>

Department of Chemical Engineering, Hannam University, 133 Ojung-dong, Taeduk-gu, Taejon 306-791, Korea  
(Received 11 July 1997 • accepted 29 December 1997)

**Abstract** – The group-contribution lattice-fluid equation of state (GCLF-EOS), which is capable of predicting equilibrium behavior in polymer systems, was developed by establishing group contributions of the lattice-fluid EOS using the PVT properties of low molecular weight compounds only. This model was used to predict the PVT behavior of common polymers over a wide temperature range in the melt region and over a wide range of pressures up to about 2,000 bar. The GCLF-EOS predicted accurately the effect of pressure and temperature on the specific volumes of the polymer melts. Prediction results by the GCLF-EOS were compared with those by the group-contribution volume (GCVOL) method. The GCLF-EOS requires only the structure of the polymer repeat unit in terms of their functional groups as input information. No other polymer properties are needed. The GCLF-EOS is the only model that is capable of predicting the specific volumes of polymer melts as a function of temperature and pressure.

*Key words:* Prediction of PVT, Polymers, Group Contribution, Equation of State

## INTRODUCTION

The PVT properties of a polymer are essential information required either directly in the design of polymer processing operations or as an input parameter to obtain various other design variables. For example, in injection molding and extrusion processes, since operations are carried out at high pressures, compressibility and thermal expansion coefficients are required over wide regions of pressure, volume, and temperature. Here the accurate estimation of the properties of polymers is crucial.

Empirical models or correlative equations of state are often used to describe the PVT behavior of polymers [Zoller, 1989]. Such correlations are useful in the interpolation and extrapolation of data to the conditions of interest. A number of models have been developed and applied for the correlation of polymer PVT behavior. One of the first was the purely empirical Tait equation. Originally developed to describe the compressibility of ordinary liquids, this equation has been shown to work well for a wide variety of liquids ranging from water to long-chain hydrocarbon compounds [Nanda and Simha, 1964]. This approach has also been successfully applied to polymers [Zoller, 1989]. For most polymers, the average error with the Tait model was found to be within the reported experimental error—approximately 0.1% [Zoller et al., 1976]. To select a recommended PVT correlation, Zoller [1989] evaluated the Tait correlation, the Flory equation of state [Flory et al., 1964], the Simha-Somcynsky equation of state [Simha and Somcynsky, 1969], and the Sanchez-Lacombe equation of state

[Sanchez and Lacombe, 1976]. The Tait form yielded errors which were generally an order of magnitude lower than that found with the other models.

When the experimental PVT data of a polymer are not available, a method of predicting the PVT behavior of the polymer is needed. Van Krevelen and Hoftyzer [1972] proposed a group contribution approach for predicting the density of amorphous polymers. Elbro et al. [1991] developed the group-contribution volume (GCVOL) method for the prediction of liquid densities of both solvents and polymers. This method, however, considered only the effect of temperature on the densities of polymer melts, ignoring the pressure effect. The specific volume increases as temperature increases, while it decreases as pressure increases. A good predictive method must be able to take into account the effect of both temperature and pressure on the specific volume of the polymer melt.

Lee [1995] and Lee and Danner [1996a, b] have developed a group-contribution lattice-fluid equation of state (GCLF-EOS) that is capable of predicting pure component and mixture properties of low and high molecular weight compounds. The molecular parameters in the EOS based on the lattice-fluid theory of Panayiotou and Vera [1982a, b] were calculated from group contributions. Yoo et al. [1995a, b] also developed an equation of state based on the lattice-fluid theory for phase equilibria of complex mixtures.

In this work the specific volumes of a variety of polymer melts were predicted by the GCLF-EOS as functions of temperature and pressure. The GCLF-EOS can take into account the effect of pressure as well as that of temperature on the specific volumes of polymer melts, since it is based on an EOS. Prediction results by the GCLF-EOS were compared

<sup>†</sup>To whom all correspondence should be addressed.  
E-mail: bcllee@eve.hannam.ac.kr

with those by the GCVOL method.

### GROUP-CONTRIBUTION LATTICE-FLUID EQUATION OF STATE (GCLF-EOS)

The GCLF-EOS is a group-contribution method of the lattice-fluid EOS by Panayiotou and Vera [1982a, b]. Using the lattice statistics and quasichemical theory of Guggenheim [1952], Panayiotou and Vera [1982a, b] derived the lattice-fluid EOS which corrects for the nonrandom mixing arising from the interaction energies between molecules. A detailed derivation of the GCLF-EOS is available from Lee [1995] and Lee and Danner [1996a]. In this article the model for a pure component is briefly described. The EOS in terms of reduced variables for a pure component  $i$  is

$$\frac{\tilde{P}_i}{\tilde{T}_i} = \ln \left( \frac{\tilde{v}_i}{\tilde{v}_i - 1} \right) + \frac{z}{2} \ln \left( \frac{\tilde{v}_i + (q_i/r_i) - 1}{\tilde{v}_i} \right) - \frac{\theta_i^2}{\tilde{T}_i} \quad (1)$$

$$\tilde{P}_i = \frac{P}{P_i^*} = \frac{2 P v_h}{z \epsilon_{ii}} \quad (2)$$

$$\tilde{T}_i = \frac{T}{T_i^*} = \frac{2 R T}{z \epsilon_{ii}} \quad (3)$$

$$\tilde{v}_i = \frac{v}{v_i^*} = \frac{v_h (N_h + r_i N_i)}{v_i^* N_i} \quad (4)$$

where  $z$  is the coordination number fixed at 10,  $v_h$  is the volume of a lattice site ( $9.75 \times 10^{-3} \text{ m}^3/\text{kmol}$ ),  $\epsilon_{ii}$  is the interaction energy between like molecules of type  $i$ , and  $v_i^*$  is the molecular reference volume of a pure component  $i$ .

The derivation of the EOS is based on the following definition of the lattice structure. The total number of lattice sites ( $N_r$ ) is given by the number of sites occupied by holes ( $N_h$ ) and the number of sites occupied by the molecules of type  $i$ :

$$N_r = N_h + r_i N_i \quad (5)$$

The total number of external contact sites ( $zN_q$ ) is expressed as:

$$zN_q = zN_h + zq_i N_i \quad (6)$$

The number of contact sites available to a molecule of type  $i$  ( $zq_i$ ) is calculated from

$$zq_i = (z - 2)r_i + 2 \quad (7)$$

where  $r_i$  is the number of lattice sites occupied by a molecule  $i$ :

$$r_i = \frac{v_i^*}{v_h} \quad (8)$$

$\theta_i$  in Eq. (1) is the fraction of contacts which involve molecules of type  $i$ :

$$\theta_i = \frac{zq_i N_i}{z(N_h + q_i N_i)} \quad (9)$$

The pure component EOS contains two adjustable parameters: molecular interaction energy,  $\epsilon_{ii}$ , and molecular reference volume,  $v_i^*$ . To make the model predictive, the following group-

contribution mixing rules for these two parameters have been developed:

$$\epsilon_{ii} = \sum_k \sum_m \Theta_k^{(i)} \Theta_m^{(i)} (\epsilon_{kk} \epsilon_{mm})^{1/2} \quad (10)$$

$$v_i^* = \sum_k n_k^{(i)} R_k \quad (11)$$

where  $\epsilon_{kk}$  is the group interaction energy between like groups  $k$  and  $R_k$  is the group reference volume of group  $k$ .  $\Theta_k^{(i)}$  is the surface area fraction of group  $k$  in the pure component  $i$ :

$$\Theta_k^{(i)} = \frac{n_k^{(i)} Q_k}{\sum_p n_p^{(i)} Q_p} \quad (12)$$

where  $n_k^{(i)}$  is the number of group  $k$  in component  $i$  and  $Q_k$  is the surface area of group  $k$ , as used in the UNIFAC method [Fredenslund et al., 1977].

The characteristic parameters are also functions of temperature. A quadratic form with respect to temperature was found to be adequate:

$$\epsilon_{kk} = \epsilon_{0,k} + \epsilon_{1,k} \left( \frac{T}{T_0} \right) + \epsilon_{2,k} \left( \frac{T}{T_0} \right)^2 \quad (13)$$

$$R_k = \frac{1}{10^3} \left[ R_{0,k} + R_{1,k} \left( \frac{T}{T_0} \right) + R_{2,k} \left( \frac{T}{T_0} \right)^2 \right] \quad (14)$$

where  $\epsilon_{i,k}$  and  $R_{i,k}$  are constants,  $T$  is the system temperature in kelvin and  $T_0$  was arbitrarily set to 273.15 K.

The group parameters ( $\epsilon_{kk}$ ,  $R_k$ ) were estimated from properties of low molecular weight compounds only. First, the molecular parameters,  $\epsilon_{ii}$  and  $v_i^*$ , at various temperatures for each pure compound were simultaneously determined by fitting the experimental saturated vapor pressure and liquid density data [Daubert and Danner, extent 1994] to the EOS. Second,  $\epsilon_{kk}$  and  $R_k$  at each temperature were independently estimated from  $\epsilon_{ii}$  and  $v_i^*$  by nonlinear regression using the mixing rules, Eqs. (10) and (11). Finally, the parameter constants ( $\epsilon_{i,k}$  and  $R_{i,k}$ ) were determined by fitting the group parameters obtained at the various temperatures to Eqs. (13) and (14). Tables of the group parameters for a variety of functional groups are available from Lee [1995] and Lee and Danner [1996a].

### GROUP CONTRIBUTION VOLUME (GCVOL) METHOD

Most methods for estimating saturated liquid densities are based on corresponding states [Rackett, 1970; Spencer and Danner, 1972] or on group contributions [van Krevelen and Hof-tyzer, 1972; Fedors, 1974]. The estimation of density using the corresponding state principles requires knowledge of the critical properties. For polymers, however, the critical properties cannot be determined. The GCVOL method, developed by Elbro et al. [1991], is a group contribution method which is capable of predicting specific volumes of polymers and low molar mass solvents as a function of temperature.

The specific molar volume of a liquid in  $\text{cm}^3/\text{mole}$  is expressed as:

**Table 1. Group assignment for polymers tested by the GCLF-EOS**

Polymers	Group assignments
BR	2 CH <sub>2</sub> , 1 CH=CH
HDPE	2 CH <sub>2</sub>
LDPE, LLDPE	2 CH <sub>2</sub>
<i>i</i> -PB	1 CH <sub>3</sub> , 2 CH <sub>2</sub> , 1 CH
PBMA	2 CH <sub>3</sub> , 4 CH <sub>2</sub> , 1 C, 1 COO
PCHMA	1 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 C, 5 cy-CH <sub>2</sub> , 1 cy-CH, 1 COO
PDMS	2 CH <sub>3</sub> , 1 SiO
PEG, PEO	1 CH <sub>2</sub> , 1 CH <sub>2</sub> O
PIB	2 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 C
PMMA	2 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 C, 1 COO
PMP	2 CH <sub>3</sub> , 2 CH <sub>2</sub> , 2 CH
POM	1 CH <sub>2</sub> O
PoMS	1 CH <sub>2</sub> , 4 ACH, 1 ACCH <sub>3</sub> , 1 ACCH
<i>i</i> -PP	1 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CH
PS	1 CH <sub>2</sub> , 5 ACH, 1 ACCH
PT	3 CH <sub>2</sub> , 1 CH <sub>2</sub> O
PVAC	1 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CH, 1 COO
PVAL	1 CH <sub>2</sub> , 1 CH, 1 OH
PVC	1 CH <sub>2</sub> , 1 CHCl

$$v = \sum_i n_i \Delta v_i \quad (15)$$

where  $n_i$  is the number of group  $i$  and  $v_i$  is the molar volume of group  $i$  in  $\text{cm}^3/\text{mole}$ .  $v_i$  is a function of temperature and its temperature dependence is given by

$$\Delta v_i = A_i + B_i T + C_i T^2 \quad (16)$$

The temperature,  $T$ , can vary between the melting point and the normal boiling point if the model is used for low molar mass solvent, and between the glass transition temperature and the degradation temperature if used for amorphous polymers. For polymers, only groups present in the repeating unit of the polymer need to be included in Eq. (15). Elbro et al. [1991] used liquid volume data of solvents below their normal boiling points to determine the group molar volumes ( $v_i$ ) at various temperatures, and then obtained the constants,  $A_i$ ,  $B_i$  and  $C_i$  by Eq. (16). The group molar volumes for various functional groups are available from Table 1 of Elbro et al. [1991]. This method, however, considers only the effect of temperature on the densities of polymer melts, not accounting for pressure effects.

### CALCULATION PROCEDURE

The liquid molar volume of a polymer melt by the GCLF-EOS was obtained by solving the pure component EOS [Eq. (1)] at a fixed temperature and pressure. The secant method was used to solve the equation of state. The molecular parameters,  $\epsilon_{ik}$  and  $v_i'$ , were calculated from the group parameters,  $e_{ik}$  and  $R_k$ , using the group contribution mixing rules, Eqs. (10) and (11). The group parameters,  $e_{ik}$  and  $R_k$ , were calculated by Eqs. (13) and (14) from the group constants,  $e_{ik}$  and  $R_{ik}$ . The group assignments for various common polymers are given in Table 1.

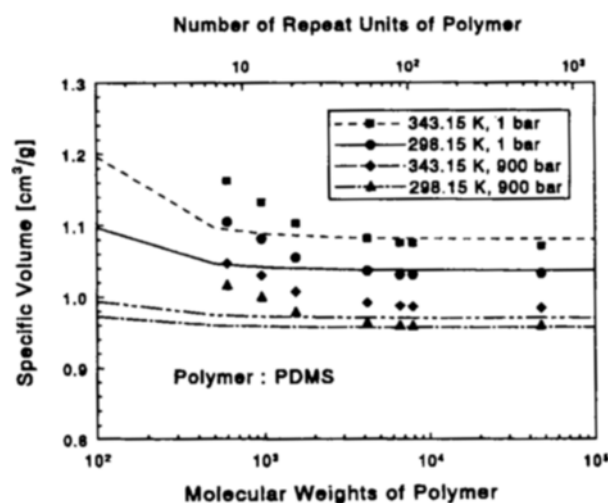
All the experimental data for the PVT properties of poly-

mers were obtained from the data bank of Danner and High [1993], and the original sources of the experimental data are shown in the title of each figure in the next section. In this work, the PVT properties of polymer melts only were tested. Therefore, all the temperatures were above the glass transition temperature for the glassy polymers and the melting temperature for the semi-crystalline polymers. Pressures ranged from zero or 1 bar up to 2,000 bar or higher.

### RESULTS AND DISCUSSION

Fig. 1 shows the influence of the polymer molecular weight on the specific volumes predicted by the model at several temperatures and pressures for poly(dimethyl siloxane), as an example. The experimental PVT data at various polymer molecular weights were available for poly(dimethyl siloxane), as shown in Table 2. The specific volumes decreased rapidly with increasing molecular weight only at very small molecular weights. However, they were constant above the number of repeat units of 100 or the molecular weight of 7,000, regardless of the system temperature and pressure. While the model gave poor predictions at low molecular weights of the polymer, it gave excellent agreement with the experimental data at high molecular weights of the polymer. Therefore, when the molecular weight was not available in experimental data, the number of the polymer repeat units of 200 was used in the model calculations to exclude the effect of the polymer molecular weight on the specific volumes of the polymers.

Figs. 2 through 4 show the prediction of the specific volumes as a function of temperature at various pressures, for butadiene rubber, poly(dimethyl siloxane), and high density polyethylene. The specific volumes of a polymer increased as temperature increased, while they decreased as pressure increased. The model represented well the variation in the specific volumes over a wide range of temperatures. The predicted values by the model always increased as temperature increased. As shown in the slopes of the curves, the temperature dependence decreased as pressure increased. The devia-



**Fig. 1. Effect of polymer molecular weight on the specific volumes of polymer melts. The experimental data were obtained from Lichtenthaler et al. [1978].**

**Table 2. Summary of predictions of specific volumes of polymer melts by the GCLF-EOS and the GCVOL method**

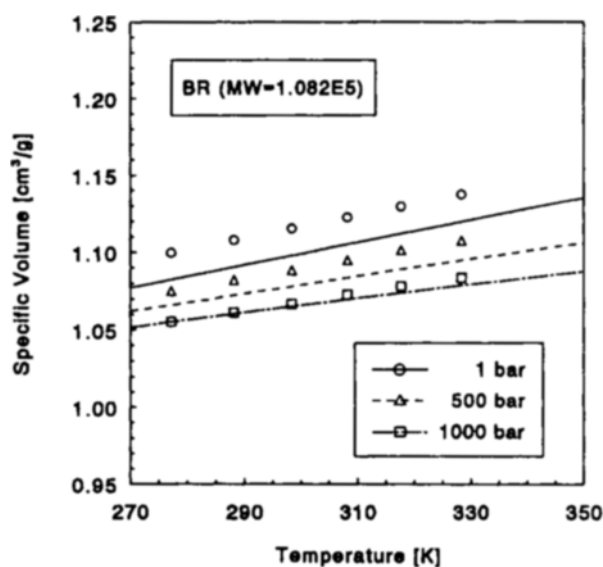
Polymer	Molecular weight	Temperature range [K]	GCLF-EOS			GCVOL method				
			P[bar]	N <sup>1)</sup>	$\delta v$ <sup>2)</sup>	s <sup>3)</sup>	P [bar]	N	$\delta v$	s
BR	N.A. <sup>4)</sup>	277-328	1-2830	156	1.0	0.59	1	6	1.0	0.70
HDPE	5.200E+04	415-473	1-2000	67	2.6	0.60	1	7	0.3	0.15
<i>i</i> -PB	1.800E+06	407-514	0-1960	45	4.9	1.53	0	9	0.2	0.07
<i>i</i> -PP	5.700E+05	447-572	0-1960	45	9.2	2.00	0	9	1.6	0.16
LDPE	N.A.	398-471	1-2000	78	2.5	0.61	1	8	0.1	0.06
LDPE	2.500E+04	413-473	0-1000	42	2.3	0.54	0	4	0.4	0.08
LLDPE	N.A.	410-473	1-2000	61	4.1	0.78	1	7	0.8	0.31
PBMA	N.A.	295-473	1-2000	168	2.1	1.38	1	15	2.1	0.22
PCHMA	N.A.	383-472	1-2000	90	2.2	0.73	1	9	13.9	0.60
PDMS	4.720E+04	298-343	0-1000	64	0.7	0.38	0	6	0.8	0.12
PDMS	5.940E+02	298-343	0-900	49	6.3	0.48	0	5	8.0	0.36
PDMS	9.580E+02	298-343	0-900	40	4.7	0.49	0	4	5.6	0.26
PDMS	1.540E+03	298-343	0-900	40	2.6	0.55	0	4	3.2	0.19
PDMS	4.170E+03	298-343	0-900	40	1.1	0.57	0	4	1.4	0.14
PDMS	6.560E+03	298-343	0-900	40	0.7	0.44	0	4	0.8	0.11
PDMS	7.860E+03	298-343	0-900	40	0.7	0.42	0	4	0.8	0.09
PDMS	5.000E+03	303-497	0-2000	126	3.7	2.22	0	6	2.3	1.10
PEG	7.500E+03	336-466	0-686	61	0.9	0.60	0	8	2.4	1.00
PIB	3.600E+04	326-383	0-1000	55	3.0	0.62	0	5	6.8	0.26
PMMA	N.A.	387-432	1-2000	41	0.8	0.50	1	5	1.2	0.13
PMP	N.A.	514-592	0-1960	126	12.6	1.74	0	6	3.5	0.41
POM	N.A.	462-492	0-1960	24	1.0	0.65	0	4	7.6	0.42
PoMS	N.A.	413-471	1-1800	50	3.0	0.30	1	7	2.4	0.21
PS	9.070E+04	389-469	1-2000	69	3.8	0.65	1	8	3.7	0.47
PT	4.000E+04	337-444	0-686	47	1.6	0.55	0	6	0.6	0.40
PVAC	8.400E+04	337-393	0-1000	63	4.5	0.84	0	6	4.1	0.99
PVAL	N.A.	431-469	0-2000	105	12.2	1.54	0	5	4.9	3.00
PVC	N.A.	355-370	0-1570	18	0.8	0.32	0	3	3.0	0.26
Total				1850	3.9	0.95		174	3.0	0.43

1) Number of data points.

2) Percentage average absolute deviation for a system, %, as defined in Eq. (17).

3) Standard deviation of  $\delta v$ , as defined in Eq. (18).

4) The molecular weight of the polymer is not available in the literature.



**Fig. 2. Prediction of specific volumes of butadiene rubber as a function of temperature at various pressures. The experimental data were obtained from Barlow [1978].**

tions between the predicted and experimental values at different temperatures were found to be similar. For butadiene rubber, as shown in Fig. 2, the higher the pressure, the better the model predicted. For poly(dimethyl siloxane), as shown in Fig. 3, the best agreement between the predicted and experimental values was obtained at 100 bar. The model over-predicted at 0 bar, while it under-predicted at 500 and 1,000 bar. For high-density polyethylene, as shown in Fig. 4, the model under-predicted at all pressures, giving relatively poor prediction results. Normally polyethylene may have branches in its molecular structure, but the model assumes in the calculations that there are no branches in the polymer. Therefore, the large deviation in polyethylene is considered to be due to the fact that the model cannot take into account the branching effect of polyethylene.

Figs. 5 and 6 illustrate the prediction of the specific volumes as a function of pressure at fixed temperatures, for poly(ethylene glycol) and poly(*n*-butyl methacrylate). Fig. 7 shows the predicted specific volumes for three different polymers as a function of pressure at a given temperature. As expected, the predicted specific volumes always decreased as

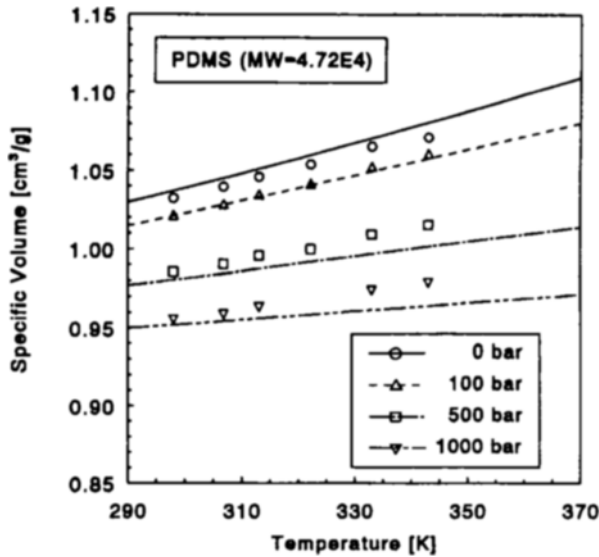


Fig. 3. Prediction of specific volumes of poly(dimethyl siloxane) as a function of temperature at various pressures. The experimental data were obtained from Beret and Prausnitz [1975].

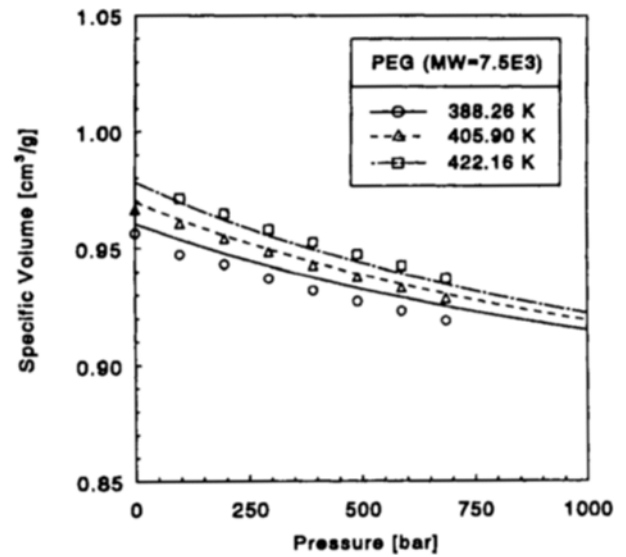


Fig. 5. Prediction of specific volumes of poly(ethylene glycol) as a function of pressure at various temperatures. The experimental data were obtained from Tsujita et al. [1973].

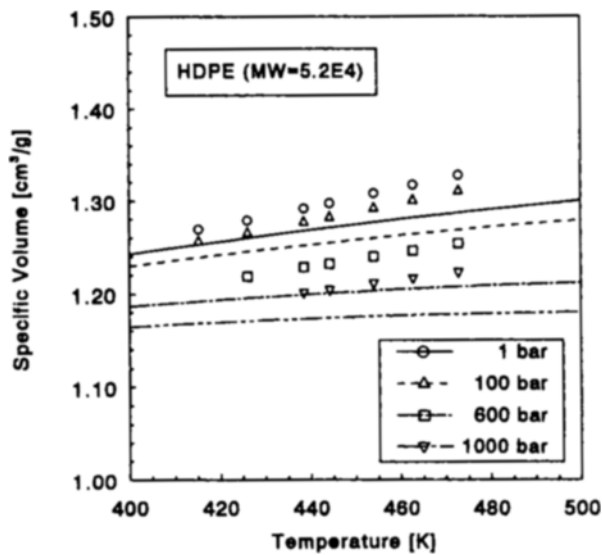


Fig. 4. Prediction of specific volumes of high density polyethylene as a function of temperature at various pressures. The experimental data were obtained from Olabisi and Simha [1975].

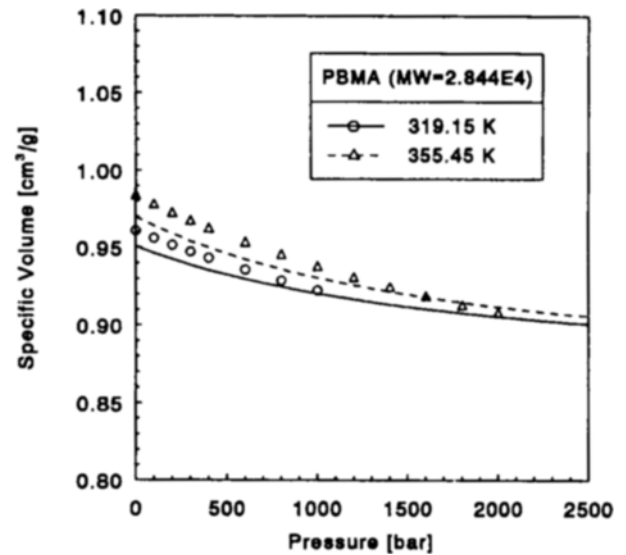


Fig. 6. Prediction of specific volumes of poly(n-butyl methacrylate) as a function of pressure at various temperatures. The experimental data were obtained from Olabisi and Simha [1975].

pressure increased. The model gave very good agreement with the experimental data over the entire range of pressures from atmospheric to high pressures. For most systems, the model gave better agreement with the experimental data at high pressures rather than at low pressures.

Table 2 shows the statistical summary of the prediction results of the specific volumes for various polymers by the GCLF-EOS. The prediction results by the GCVOL method are also given for comparison. This table includes the molecular weight of each polymer and the range of temperature and pressure. The entire range of temperature and pressure in the experi-

mental data was considered.  $\delta v$  is the percentage average absolute deviation between the predicted and experimental specific volumes, defined as:

$$\delta v = \frac{1}{N} \sum_i \frac{|v_i^{pred} - v_i^{exp}|}{v_i^{exp}} \times 100 \quad (17)$$

where  $N$  is the total number of data points,  $v_i^{pred}$  is the predicted value of the specific volume in  $\text{cm}^3/\text{g}$ , and  $v_i^{exp}$  is the experimental value of the specific volume.  $s$  is the standard deviation of the percentage average absolute deviations, expressed as:

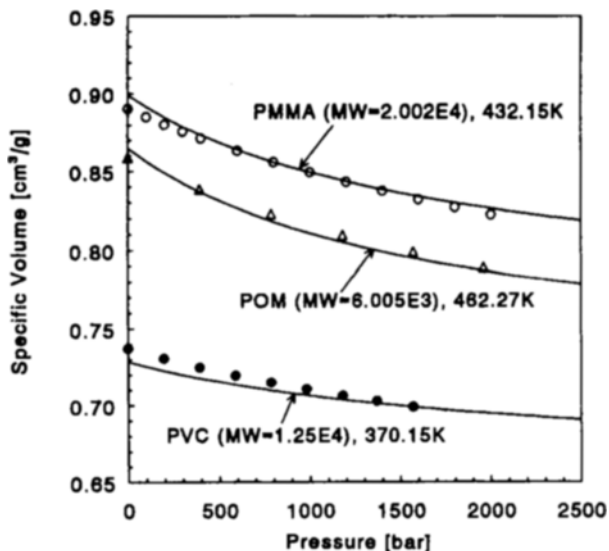


Fig. 7. Prediction of specific volumes of poly(methyl methacrylate), poly(oxyethylene) and poly(vinyl chloride) as a function of pressure. The experimental data were obtained from Olabisi and Simha [1975] for PMMA, Starkweather et al. [1988] for POM, Hellwege et al. [1962] for PVC.

$$s = \left[ \frac{1}{N-1} \sum_i^N (\delta v_i - \bar{\delta v})^2 \right]^{1/2} \quad (18)$$

where  $\delta v_i$  is the percentage absolute deviation between the predicted and experimental values for an individual point:

$$\delta v_i = \frac{|v_i^{pred} - v_i^{exp}|}{v_i^{exp}} \times 100 \quad (19)$$

For the GCLF-EOS, the total number of data points for the entire homopolymers tested was 1,850 and the total average error was 3.9%. None of the polymers, except poly(4-methyl-1-pentene) and poly(vinyl alcohol), showed an average error of more than 10%. Excluding these two polymers which gave large deviations reduced the total average error to 2.7% (1,619 data points). The GCVOL method cannot take into account the pressure effect on the specific volumes. Thus, it could be tested for only 174 low pressure data points, resulting in a total average error of 3.0%. For polymers such as polyethylene, polypropylene and poly(4-methyl-1-pentene) which may have branching, the GCLF-EOS gave relatively large errors. It may be that these errors result from assuming in the calculations that there is no branching. The large deviation in poly(vinyl alcohol) is considered to be due to the strong association. The GCLF-EOS is capable of predicting the PVT behavior of a wide variety of homopolymer melts with reasonable accuracy.

## CONCLUSIONS

The GCLF-EOS was developed by establishing group contributions of the lattice-fluid EOS using the saturated liquid density and vapor pressure data of low molecular weight com-

pounds only. The specific volumes of a number of common homopolymer melts were predicted by the GCLF-EOS over a wide temperature range in the melt region and over a wide range of pressures up to about 2,000 bar. The GCLF-EOS gave good predictions with the average absolute deviations of 3.9% between the predicted and experimental specific volumes for the entire polymers tested and represented well the effect of pressure and temperature on the specific volumes of the polymer melts.

The GCLF-EOS requires only the structure of the polymer repeat unit in terms of their functional groups as input information. No other polymer properties are needed. The GCLF-EOS is the only model that is capable of predicting the specific volumes of polymer melts as a function of temperature and pressure.

## ACKNOWLEDGMENT

This work was supported in part by a 1997 university research grant of Hannam University.

## NOMENCLATURE

- $e_{kk}$  : group interaction energy parameter between like groups k [J/mol]
- $e_{0,k}, e_{1,k}, e_{2,k}$  : constants in group interaction energy parameter
- $n_i$  : number of group i
- $n_k^{(i)}$  : number of group k in molecule i
- $N$  : number of data points
- $N_h$  : total number of holes in the lattice
- $N_i$  : number of molecules of type i
- $N_q$  : number of contact sites available in the lattice
- $N_r$  : total number of lattice sites
- $P$  : pressure
- $P_i^*$  : characteristic pressure of a pure component i
- $\bar{P}_i$  : reduced pressure of a pure component i [-]
- $q_i$  : surface area parameter of a component i
- $Q_k$  : group surface area parameter for group k
- $r_i$  : number of lattice sites occupied by the segments of a molecule i
- $R$  : gas constant
- $R_k$  : group reference volume parameter for group k [ $\text{m}^3/\text{kmol}$ ]
- $R_{0,k}, R_{1,k}, R_{2,k}$  : constants in group reference volume parameter
- $s$  : standard deviation of percentage average absolute deviation for a system
- $T$  : temperature [K]
- $T_0$  : reference temperature [=273.15 K]
- $T_i^*$  : characteristic temperature of a pure component i
- $\bar{T}_i$  : reduced temperature of a pure component i
- $v$  : molar volume [ $\text{m}^3/\text{kmol}$ ]
- $v_h$  : molar volume of a lattice site [=9.75  $\times 10^{-3}$   $\text{m}^3/\text{kmol}$ ]
- $v_i^{exp}, v_i^{pred}$  : experimental and predicted values of specific volume, respectively [ $\text{cm}^3/\text{gram}$ ]
- $v_i^*$  : molecular reference volume of a pure component i [ $\text{m}^3/\text{kmol}$ ]
- $\bar{v}_i$  : reduced volume of a pure component i
- $v_i$  : molar volume of group i [ $\text{cm}^3/\text{mole}$ ]

$z$  : coordination number [=10]

### Greek Letters

$\delta v$  : percentage average absolute deviation between predicted and experimental specific volumes for a system [%]

$\delta v_i$  : percentage absolute deviation between predicted and experimental specific volumes for an individual data point [%]

$\epsilon_{ii}$  : characteristic interaction energy between like molecules  $i$  [J/mol]

$\theta_i$  : molecular surface area fraction of component  $i$ , or fraction of contacts which involve molecules of type  $i$

$\Theta_k^{(i)}$  : surface area fraction of group  $k$  in component  $i$

### Subscripts and Superscripts

$i, ii, (i)$  : component  $i$  in the molecular parameters

$k, m, p$  : functional groups in a molecule

### Polymer Abbreviations

BR : butadiene rubber [polybutadiene]

HDPE : high density polyethylene

LDPE : low density polyethylene

LLDPE : linear low density polyethylene

$i$ -PB : *isotactic*-poly(1-butylene)

PBMA : poly(*n*-butyl methacrylate)

PCHMA : poly(cyclohexyl methacrylate)

PDMS : poly(dimethyl siloxane)

PEG : poly(ethylene glycol)

PIB : polyisobutylene

PMMA : poly(methyl methacrylate)

PMP : poly(4-methyl-1-pentene)

POM : poly(oxymethylene)

PoMS : poly(*o*-methylstyrene)

$i$ -PP : *isotactic*-polypropylene

PS : polystyrene

PT : polytetrahydrofuran

PVAC : poly(vinyl acetate)

PVAL : poly(vinyl alcohol)

PVC : poly(vinyl chloride)

ties as a Function of Temperature for Solvents, Oligomers, and Polymers", *Ind. Eng. Chem. Res.*, **30**, 2576 (1991).

Fedors, R. F., "A Method for Estimating Both the Solubility Parameter and Molar Volumes of Liquids", *Polym. Eng. Sci.*, **14**, 147 (1974).

Flory, P. J., Oriji, R. A. and Vrij, A., "Statistical Thermodynamics of Chain Molecule Liquids. I. An Equation of State for Normal Paraffin Hydrocarbons", *J. Am. Chem. Soc.*, **86**, 3507 (1964).

Fredenslund, Aa., Gmehling, J. and Rasmussen, P., "Vapor-Liquid Equilibria Using UNIFAC", Elsevier Scientific Publishing, New York, 1977.

Guggenheim, E. A., "Mixtures", Clarendon Press, Oxford, 1952.

Hellwege, V. K. H., Knappe, W. and Lehmann, P., "Die isotherme Kompressibilität einiger amorpher und teilkristalliner Hochpolymerer im Temperaturbereich von 20-250 °C und bei Drucken bis zu 2,000 kg/cm<sup>2</sup>", *Kolloid-Z. Z. Polym.*, **183**, 110 (1962).

Lee, B.-C. and Danner, R. P., "Application of the Group-Contribution Lattice-Fluid Equation of State to Random Copolymer-Solvent Systems", *Fluid Phase Equilibria*, **117**, 33 (1996b).

Lee, B.-C. and Danner, R. P., "Prediction of Polymer-Solvent Phase Equilibria by a Modified Group-Contribution EOS", *AIChE J.*, **42**, 837 (1996a).

Lee, B.-C., "Prediction of Phase Equilibria in Polymer Solutions", Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1995.

Lichtenthaler, R. N., Liu, D. D. and Prausnitz, J. M., "Specific Volumes of Dimethylsiloxane Polymers to 900 bars", *Macromolecules*, **11**, 192 (1978).

Nanda, V. S. and Simha, R., "Equation of State of Polymer Liquids and Glasses at Elevated Pressures", *J. Chem. Phys.*, **41**, 3870 (1964).

Olabisi, O. and Simha, R., "Pressure-Volume-Temperature Studies of Amorphous and Crystallizable Polymers. I. Experimental", *Macromolecules*, **8**, 206 (1975).

Panayiotou, C. and Vera, J. H., "An Improved Lattice-Fluid Equation of State for Pure Component Polymeric Fluids", *Polym. Eng. Sci.*, **22**, 345 (1982a).

Panayiotou, C. and Vera, J. H., "Statistical Thermodynamics of *r*-Mer Fluids and Their Mixtures", *Polym. J.*, **14**, 681 (1982b).

Rackett, H. G., "Equation of State for Saturated Liquids", *J. Chem. Eng. Data*, **15**, 514 (1970).

Sanchez, I. C. and Lacombe, R. H., "An Elementary Molecular Theory of Classical Fluids: Pure Fluids", *J. Phys. Chem.*, **80**, 2352 (1976).

Simha, R. and Somcynsky, T., "On the Statistical Thermodynamics of Spherical and Chain Molecule Fluids", *Macromolecules*, **2**, 342 (1969).

Spencer, C. F. and Danner, R. P., "Improved Equation for Prediction of Saturated Liquid Density", *J. Chem. Eng. Data*, **17**, 236 (1972).

Starkweather, H. W. Jr., Jones, G. A. and Zoller, P., "The Pressure-Volume-Temperature Relationship and the Heat of Fusion of Polyoxymethylene", *J. Polym. Sci.*, **26**, 257 (1988).

### REFERENCES

Barlow, J. W., "Measurement of the PVT Behaviour of *cis*-1,4-Polybutadiene", *Polym. Eng. Sci.*, **18**, 238 (1978).

Beret, S. and Prausnitz, J. M., "Densities of Liquid Polymers at High Pressure. Pressure-Volume-Temperature Measurements for Polyethylene, Polyisobutylene, Poly(vinyl acetate), and Poly(dimethylsiloxane) to 1 kbar", *Macromolecules*, **8**, 536 (1975).

Danner, R. P. and High, M. S., "Handbook of Polymer Solution Thermodynamics", Design Institute for Physical Property Data, American Institute of Chemical Engineers, New York, 1993.

Daubert, T. E. and Danner, R. P., "Physical and Thermodynamic Properties of Pure Compounds: Data Compilation", Taylor and Francis, New York, extant 1994.

Elbro, H. S., Fredenslund, Aa. and Rasmussen, P., "A Group Contribution Method for the Prediction of Liquid Densi-

- Tsujita, Y., Nose, T. and Hata, T., "Thermodynamic Properties of Poly(ethyleneglycol) and Poly(tetrahydrofuran). I. P-V-T Relations and Internal Pressure", *Polym. J.*, **5**, 201 (1973).
- Van Krevelen, D. W. and Hoftyzer, P. J., "Properties of Polymers: Correlation with Chemical Structure", Elsevier Scientific, Amsterdam, 1972.
- Yoo, K.-P., Kim, H. and Lee, C. S., "Unified Equation of State Based on the Lattice Fluid Theory for Phase Equilibria of Complex Mixtures. Part I. Molecular Thermodynamic Framework", *Korean J. Chem. Eng.*, **12**(3), 277 (1995a).
- Yoo, K.-P., Kim, H. and Lee, C. S., "Unified Equation of State Based on the Lattice Fluid Theory for Phase Equilibria of Complex Mixtures. Part II. Application to Complex Mixtures", *Korean J. Chem. Eng.*, **12**(3), 289 (1995b).
- Zoller, P., Bolli, R., Pahud, V. and Ackermann, H., "Apparatus for Measuring Pressure-Volume-Temperature Relationships of Polymers to 350 °C and 220 kg/cm<sup>2</sup>", *Rev. Sci. Instrum.*, **47**, 948 (1976).
- Zoller, P., "PVT Relationships and Equations of State of Polymers", Chapter VI, *Polymer Handbook*, 3rd ed., Brandrup, J. and Immergut, E. H., eds., Wiley-Interscience, New York, 475 (1989).