Application of a New Cell Model for the Equation of State to 20 Polymer Melts and a Blend Melt

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(Received December 14, 2004; Accepted February 22, 2005; Published May 15, 2005)

ABSTRACT: In a previous publication, we reported a new cell model for the equation of state of polymer melts. The equation contains external degrees of freedom explicitly as a function of molecular weight of repeating unit. In this paper, we apply the theory to 20 polymer melts and a blend melt. The linear lengths of the coarse-grained particle (CGP) of several polymers coincide with those obtained by scattering experiments. In addition, we estimated the characteristic quantity T^* of the equation of state per repeating unit using van der Waals constants and the critical temperature of the repeating unit or monomer. The values, T^* , agreed with those from our result per repeating unit. This result suggests the quantitative validity of our theory. We strongly suggest that our theory must be related to the conformer model by Matsuoka and the helical wormlike chain model by Yamakawa, because T^* must be dependent on the chemical structure and stiffness of the polymers. [DOI 10.1295/polymj.37.363]

KEY WORDS Polymer Melt / Blend Melt / Equation of State / Coarse-grained Particle (CGP) / Characteristic Quantity T^* of the Equation of State / New Cell Model / Degrees of Freedom /

Our new cell model for the equation of state¹ is based on the classical cell model by Lennard-Jones and Devonshire theory.² A new definition of the integral limit^{1,3} for estimating the free volume of the cell results in the equation of state being similar to van der Waals equation of state.⁴ If we assume that the potential between coarse-grained particles (CGPs) is the only excluded volume in the free volume term, the equation coincides with van der Waals equation of state.⁴ Though van der Waals equation of state⁴ implicitly contains external degrees of freedom, our theory¹ contains the external degrees of freedom explicitly as a function of molecular weight of repeating unit in the free volume term, because of the consideration of the potential between the CGPs using the Sutherland potential. As a result, van der Waals equation of state⁴ is the approximate theory of our theory.¹ It should be noted that our theory¹ is rigorous and the only theory in history which explicitly contains the external degrees of freedom and only our theory can quantitatively discuss the characteristic quantities per CGP or per repeating unit of the polymer. In addition, we suggest that by considering the temperature dependence of the core volume, our theory⁵ is very successful.

In this paper, we apply our theory to 20 polymer melts and a blend melt, and discuss the quantitative validity of our theory for application to any polymer or blend melt.

We estimate the coefficient of thermal expansion of the polymers using the same definition in our previous paper.¹ We estimate the dimensions of the CGP, whose external degrees of freedom are equal to

$c = 1$, of 20 polymers and a blend using PVT data of these polymers and a blend. In addition, we estimated the characteristic quantity of the equation of state T^* per repeating unit by using van der Waals constants and the critical temperature of the repeating unit or monomer.

OUTLINE OF THE NEW CELL MODEL OF THE EQUATION OF STATE

In a previous publication,¹ we reported a new cell model for the equation of state. The theory is based on the classical cell model by Lennard-Jones and Devonshire.² We use the Sutherland potential instead of the Lennard-Jones potential. Because of the connectivity of successive segments in the polymer, the segments in a polymer are more compact between successive segments than those in simple liquids, while the distance between the intermolecular segments are similar to those in simple liquids. Combined with these two situations, the cell model can be applicable to polymer systems. In addition considering the temperature dependence of the core volume is one of the reasons for success of our theory.

Following Sanchez *et al.*,^{3,6} we estimated the coordination number of the classical cell model being equal to $4\pi/3$.

Following Prigogine,⁷ the degrees of freedom of a molecule in liquids can be separated into internal and external ones. As reported in a previous paper,¹ we introduce a CGP composed of $1/c$ repeating units (where c is the external degrees of freedom per repeat-

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ing unit), the external degrees of freedom of the particle are equal to 1; and the particle is a disconnected, freely and translationally movable particle. Flory *et al.*⁸ considered that the external degree of freedom depends only on the intermolecular interaction and corresponds to the translational motion in one direction. Since we use the definition of the integral limit $\rho_{\max}$ in a free volume, the equation is similar to van der Waals equation. The definition^{1,3} is $4\pi\rho_{\max}^3/3 = v - b$, where v and b are the volume of the cell per CGP and the van der Waals constant per CGP, respectively. Also, the b value has a temperature dependence.¹

It should be noted that by using the Sutherland potential, we have a correction term, $f(c, \tilde{V}, \tilde{T})$, which explicitly contain c , and the modified free volume in the van der Waals equation of state⁴ for the polymer liquids as follows:

$$V_f = \sigma_0^3 \tilde{V}_f = \sigma_0^3 [\tilde{V} - (1 + \tilde{\alpha} \tilde{T}/2)] + \sigma_0^3 f(c, \tilde{V}, \tilde{T}) \quad (1)$$

$$c = P^* v^*/(kT^*) = P^* V_0^* M/(kT^* N_A). \quad (2)$$

where P^* , V_0^* and T^* are the characteristic quantities in the equation of state defined at 0 K,^{9,10} and σ_0 , $\tilde{V} = V/V_0^*$, V , $\tilde{\alpha} = \alpha T^*$, α , $\tilde{T} = T/T^*$, T , v^* , k , M and N_A are the linear length of the CGP at 0 K, the reduced volume, the specific volume of the system, the reduced thermal expansion coefficient, the thermal expansion coefficient, reduced temperature, temperature, the core volume per CGP at 0 K, Boltzman's constant, molecular weight per repeating unit and Avogadro's constant, respectively.

cT^* is proportional to the depth of the Sutherland potential well per repeating unit. cRT^* is defined as the heat of vaporization of a hypothetical liquid at 0 K per repeating unit.⁹

THE THERMAL EXPANSION COEFFICIENTS

In the previous paper¹ we assumed that the specific volume of the CGP is the same as that of a single crystal, so we estimated the coefficient of thermal expansion, α , using the lattice constants of a single crystal of polyethylene (PE), and estimated the dimension of the CGP of PE.

We estimated α for polymers using the following equation¹¹ that is the same definition as discussed in our previous paper.¹

$$\alpha = (V_c^* - V_0^*)/(TV_0^*) = E_c/V_0^* \simeq E_g/V_0^* \quad (3)$$

where V_c^* and V_0^* are the molar volumes per repeating unit of crystal at 298 and 0 K, respectively, and $T = 298$ K. E_c and E_g are experimental data defined for the crystalline state and glassy state, respectively. According to Van Krevelen *et al.*¹¹ we assume

$E_c \simeq E_g$, and we used the relation; $V_0^* = 1.3V_w$ because we have no experimental data of V_0^* , where V_w is the van der Waals volume¹¹ per mole which is calculated using the van der Waals radii. We used the experimental values¹¹ of E_g , but for poly(ethylene oxide) (PEO) we used calculated value¹¹ of E_g . Though Van Krevelen *et al.*¹¹ showed two experimental data points of E_g for polystyrene (PS), poly(ethylene terephthalate) (PET), poly(vinyl acetate) (PVAC), polyisobutylene (PIB) and poly(vinyl chloride) (PVC), we used the lower data because E_c must be smaller than E_g . Since we have no data of E_g for poly(dimethyl siloxane) (PDMS), poly(vinyl methyl ether) (PVME) and poly(methacrylic acid) (PMA), we used the relation:¹¹ $V_0^* = 1.3V_w$ and $V_c^* = 1.435V_w$. In this case, $\alpha = 3.5 \times 10^{-4} \text{ K}^{-1}$. For PS/PVME (50/50 blend), we estimated α and M using the mole fraction. These results are shown in Table I.

ESTIMATION OF cT^*

Van der Waals constants a and b are related to the critical temperature (T_c) and critical volume (V_c).

$$a = 27RT_c b/8 \quad b = V_c/3 \quad (4)$$

For gas, a and b per mole are derived by using the Sutherland potential, $(\phi(r))$, of a hard core with attractive tail, as follows

$$a = -2\pi N_A^2 \int_0^\infty \phi(r) r^2 dr = \frac{2\pi}{3} N_A^2 \sigma^3 \varepsilon_0 \quad (5)$$

$$b = \frac{2\pi}{3} N_A \sigma^3 \quad (6)$$

where $\varepsilon_0 (= 4\varepsilon_{LJ})$ is the depth of the potential well of the Sutherland potential and ε_{LJ} is that of Lennard-Jones potential, and σ is the diameter of the gas molecules.

$$T^* = \frac{2\pi}{3} \frac{\varepsilon_0}{k} = \frac{9\pi}{4} T_c \quad (7)$$

We evaluated T_m^* and T_r^* (T^* per monomer and repeating unit, respectively) using eq 7. We estimated $T_{LJ}^* = 8\pi\varepsilon_{LJ}/(3k)$ of ethylene and propylene using ε_{LJ}/k . We use T_c of the monomer as the reference.^{12,13} We estimated T_c of the repeating unit using Fedors method.¹² In Table III, we show T_m^* , T_{LJ}^* , T_r^* , cT^* (results of our theory per repeating unit) and cT^*/M .

RESULTS AND DISCUSSION

Utilizing a nonlinear least squares method,¹⁴ we fit the experimental PVT data of 18 polymer melts and a blend melt,¹⁵ i-poly(methyl methacrylate) (i-PMMA)¹⁶ and PVME¹⁷ with the equation of state to get the values of P^* , V_0^* and T^* after some trial and

Table I. The characteristic quantities of our equation of state for Polymers, dimension of coarse-grained particles, external degrees of freedom per repeating unit and α

Data no. —	S^2 (MPa ²)	P^* (MPa)	V_0^* (10 ⁻³ m ³ /kg)	T^* (K)	σ_0 (10 ⁻¹⁰ m)	c —	α (10 ⁻⁴ K ⁻¹)
PE	4.8	516.8	0.9398	2509	4.062	0.3265	2.073
PEO	5.0	720.0	0.5881	1472	3.045	1.524	3.5
POM	1.3	703.1	0.6026	2864	3.831	0.5343	3.0
PET	7.9	330.6	0.4169	358.8	2.465	8.878	3.5
PMA	11	648.5	0.4009	346.6	1.947	7.767	3.5
PMAC	7.5	530.5	0.5139	890.8	2.852	3.168	2.6
PMMA*	12	520.4	0.5165	968.2	2.951	3.343	3.2
PMMA**	13	521.1	0.5220	1010	2.991	3.245	3.2
i-PMMA	30	550.3	0.5113	982.0	2.910	3.450	3.2
a-PP	1.6	318.3	0.9573	2775	4.937	0.5558	2.3
i-PP	4.1	379.9	0.9239	2614	4.563	0.6796	2.3
PPMA	13	353.5	0.7045	3500	5.151	1.097	4.1
PS/PVME	5.4	463.3	0.7390	3368	4.647	0.9118	3.0
PVME	2.8	457.2	0.7490	3057	4.519	0.7826	3.5
PVAL	15	1214	0.3886	296.6	1.500	8.430	4.1
PVAC	7.2	504.8	0.5296	905.3	2.915	3.057	2.6
PVC	13	802.3	0.4376	913.8	2.505	2.888	2.3
PVF	10	730.4	0.4064	1500	3.050	1.523	2.3

PE (0–200 MPa, 199.7–240.6 °C, data 55 points); PEO (0–200 MPa, 159.1–198.7 °C, data 55 points); POM (0–196.1 MPa, 200.4–220.9 °C, data 33 points); PET (0–200 MPa, 298.7–340.6 °C, data 55 points); PMA (0–200 MPa, 252.2–277.0 °C, data 55 points); PMAC (0–196.1 MPa, 190.1–219.6 °C, data 55 points); PMMA* ($M = 10^5$) (0–196.1 MPa, 190.4–230.4 °C, data 55 points); PMMA** ($M = 10000$) (0–200 MPa, 190.9–230.8 °C, data 55 points); i-PMMA (0.1–200 MPa, 116.3–190.2 °C, data 60 points); a-PP (0–200 MPa, 257.9–306.6 °C, data 55 points); i-PP (0–196.13 MPa, 189.9–230.2 °C, data 55 points); PPMA (0–196.1 MPa, 178.8–205.8 °C, data 55 points); PS/PVME (0–200 MPa, 165.1–198.5 °C, data 55 points); PVME (0–200 MPa, 150.0–190.0 °C, data 55 points); PVAL (0–200 MPa, 228.9–237.2 °C, data 44 points); PVAC (0–200 MPa, 170.5–203.6 °C, data 55 points); PVC (0–196.1 MPa, 149.5–182.9 °C, data 55 points); PVF (0–200 MPa, 199.5–230.9 °C, data 44 points).

Table II. The characteristic quantities of our equation of state for PS, PDMS and PIB, dimension of coarse-grained particles, external degrees of freedom per repeating unit and α

Data no. —	S^2 (MPa ²)	P^* (MPa)	V_0^* (10 ⁻³ m ³ /kg)	T^* (K)	σ_0 (10 ⁻¹⁰ m)	c —	α (10 ⁻⁴ K ⁻¹)
PS*	5.3	451.4	0.7505	4238	5.061	1.001	2.2
PS**	6.7	404.6	0.7608	4179	5.225	0.9226	2.2
PDMS*	2.5	250.9	0.7781	2170	4.925	0.8022	3.5
PDMS**	2.0	228.1	0.7845	2107	5.034	0.7574	3.5
PIB*	11.4	404.0	0.9153	3887	5.103	0.6418	1.7
PIB**	11.7	368.1	0.9195	3653	5.156	0.6251	1.7

PS* (0–200 MPa, 179.8–209.7 °C, data 44 points); PS** (0–200 MPa, 219.4–251.3 °C, data 44 points); PDMS* (0–200 MPa, 150.7–197.5 °C, data 55 points); PDMS** (0–200 MPa, 209.4–258.3 °C, data 55 points); PIB* (0–200 MPa, 198.3–246.7 °C, data 55 points); PIB** (0–200 MPa, 258.7–305.6 °C, data 55 points).

error. In Tables I and II, we show the final results of S^2 (the fitting goodness to P), P^* , V_0^* , T^* , σ_0 (linear length of CGP at 0 K), c and α . Especially, in Table II, we examine the temperature dependence of the results.

$$\sigma_0^3 = v^*/c = V_0^*M/(cN_A) = kT^*/P^* \quad (8)$$

We insist that σ_0 , v^* ($= V_0^*M/N_A$), c and V_0^* in eq 8 should be defined¹⁰ at 0 K.

In a previous paper,¹ we reported that the linear

length of the CGP of polyethylene at 443 K (σ_c) agrees with the scattering experiments¹⁸ (4.34 Å); at that time our average result is $\sigma_c = 4.21$ Å. The new results are $\sigma_c = 5.22$ Å for PS and $\sigma_c = 2.95$ Å for PMMA*, $\sigma_c = 3.02$ Å for PVAC and $\sigma_c = 1.58$ Å for poly(vinyl alcohol) (PVAL) at 443 K, respectively. If we observe Figure 10a in reference¹⁹ to the total correlation function, we have peaks around 5, 10, 15 Å for PS. Bjørnhaug *et al.*²⁰ also reported a radial electric distribution function of several polymers in

Table III. T^* for monomer (T_m^*), T^* obtained by using Lennard-Jones parameter of monomer (T_{LJ}^*), T^* obtained by using T_c of repeating unit (T_r^*) and our result cT^* and cT^*/M

Data no.	T_m^* (K)	T_{LJ}^* (K)	T_r^* (K)	cT^* (K)	cT^*/M (K/g)
—	—	—	—	—	—
PE	998	941	810	808.8	57.7
i-PP	2578	2504	2095	1776	42.2
a-PP	2578	—	2095	1542	36.7
PIB*	2954 ^a	—	2542	2495	44.5
PS*	4578	—	4245	4244	40.8
PVAC	3711	—	3590	2768	32.2
PVC	3037	—	2940	2639	42.2
PMMA*	3981	—	3785	3237	32.3
PMMA**	3981	—	3785	3276	32.7
i-PMMA	3981	—	3785	3388	33.8
PMAC	3789	—	3590	2823	32.8
PVME	3082	—	2689	2392	41.2
PEO	—	—	2372	2243	50.9
POM	—	—	1749	1530	51.0
PET	—	—	5273	3186	16.6
PVAL	—	—	3292	2500	56.8
PMA	—	—	4290	2692	31.3
PPMA	—	—	4174	3839	30.0
PDMS*	—	—	—	1741	23.5
PVF	—	—	2745	2286	35.7
PS/PVME	—	—	—	3071	41.2

^aWe use the datum T_c in ref 13.

Figure 2 of their paper. The figure shows that PS has peaks around 5 and 10 Å, PMMA has peaks around 2.7, 5 and 7 Å, PVAC has peaks around 2.5 and 5 Å and PVAL has peaks around 1.5 and 2.7 Å. The result must approximately agree with the peaks of the radial distribution function of hard sphere. The linear length of CGP of PE, PS, PMMA, PVAC and PVAL evaluated by our theory must be the smallest size of CGP and the blob of melt version, that is, hard spheres having an attractive force. It should be noted that the mean field approximation²¹ almost perfectly holds for the melt of polymers, though the mean field approximation does not hold in a dilute polymer solution.

In Figure 1, we show the plot cT^* vs. M . This figure shows that cT^* seems to have a tendency in direct proportion to M , but the plot is somewhat wide. The dispersion of the plots must be related to the chemical structure of the polymers.

T_m^* and T_{LJ}^* for monomers(ethylene and propylene) almost agree with each other. Since T_m^* , T_{LJ}^* and T_r^* have good agreement with each other, the estimation of T_r^* per repeating unit has great validity. In addition T_r^* coincides with cT^* , the result of our theory per repeating unit. For PE, we use T_c of $(-\text{CH}_2\text{CH}_2-)$, and T_r^* and cT^* are per $(-\text{CH}_2-)$. These results suggest the quantitative validity of our theory.

cT^* per repeating unit agrees with T_r^* estimated by

Figure 1. The plot of cT^* vs. M .

the T_c of the repeating unit. The values of PE and polypropylene (PP) coincide with the T_{LJ}^* values. Generally, cT^* agrees with T_r^* , but the cT^* of a polymer having $(-\text{COO}-)$ or $(-\text{COOH})$ groups is somewhat smaller than T_r^* . In addition, since cT^*/M is not constant, we postulate that cT^* or cT^*/M must depend on the chemical structure and stiffness of a polymer. The conformer model²² suggests that cT^*/M is constant. Table II shows that T^* or cT^* of the polymer may have a temperature dependence. The unperturbed dimensions of the polymer in a Θ solvent have a temperature dependence.²³ These results suggested that the stiffness of the polymer molecule has a temperature dependence. Therefore, T^* or cT^* must have a temperature dependence. As concerns T^* or cT^* , we must relate with great precision our theory to the conformer model²² and the helical wormlike chain model.²⁴ Matsuoka²² concluded that molecular weight of one conformer is equal to 9.6 that is smaller than that of repeating unit of PE $(-\text{CH}_2-)$. The validity of our result that c of several polymers are larger than 1 is supported by or agreed with the conformer model by Matsuoka. In the future, we hope that we can evaluate cT^* based on the chemical structure of the polymer, just the same as T_c was reviewed by Reid *et al.*¹² If we can estimate the cT^* based on the chemical structure of the polymer cT^* must reflect the change of conformation. The conformation (or stiffness) of polymer must change with temperature and the stiffness of polymer melt is represented by the parameters contained in the helical wormlike chain model.²⁴

Acknowledgment. The author would like to acknowledge the continuing guidance and encouragement of Dr. F. Hamada. We would like to thank Professors K. Yamada, H. Miyaji, T. Kanaya and Y. Tsunashima, Dr. Y. Yoshimura of Kyoto University, Japan, and Professor S. Suehiro of Kurashiki City College, Japan for their helpful advice on my work.

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