Table III
The Effect of the Parameter ω on Calculated Values of the Characteristic Ratio and Dipole Moment Ratio, and Their Temperature Coefficients, for the PDMSM Chain[a]

ω	$\langle r^2\rangle_0/nl^2$	$\langle \mu^2\rangle_0/nm^2$	$10^3 d \ln \langle r^2\rangle_0/dT$	$10^3 d \ln \langle \mu^2\rangle_0/dT$
1.00	3.60	0.430	0.00	0.00
0.86	3.83	0.442	−0.18	−0.09
0.71	4.09	0.456	−0.35	−0.16
0.57	4.40	0.470	−0.49	−0.22
0.29	5.14	0.500	−0.58	−0.23
0.10	5.75	0.520	−0.41	−0.12
0.00	6.21	0.531	0.00	0.00

[a] $\theta' = 65°$ throughout.

of 60°C, are included in the complete set of results shown in Table III. Careful comparisons between these calculated results and the corresponding experimental results[1] indicate that for this model, possibly still somewhat oversimplified, $\omega = 0.75$ gives the best presently attainable agreement between theory and experiment. Further refinements of the chain model for PDMSM must await more definitive information on the Si–C–Si bond angle and the charge distributions in appropriate small molecules. Also of great utility would be reliable interatomic potential functions for interactions involving Si atoms since this would permit direct semiempirical calculations of conformational energies of the PDMSM chain.

Conclusions

In summary, the best model for the PDMSM chain at the present time is one in which most conformational sequences are of identical energy. The only conformational states not of this type are $g^{\pm}g^{\mp}$ states about C–Si–C bond pairs which are totally suppressed because of interferences between very bulky $Si(CH_3)_2$ groups, and $g^{\pm}g^{\mp}$ states about Si–C–Si bond pairs which are partially suppressed, possibly because of Coulombic repulsions between relatively highly charged skeletal CH_2 groups. This model, although rather simplified, is at least semiquantitatively successful in that it explains the most striking configurational characteristics of the PDMSM chain.

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A Generalized van der Waals Equation for Polymers and Other Fluids

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ABSTRACT: A generalized van der Waals partition function is used to derive an equation of state for fluids containing small or large molecules. The derivation uses Prigogine's approximation that at liquid-like densities all external degrees of freedom can be considered as equivalent translational degrees of freedom. The new equation of state is therefore similar to Flory's but differs in three important respects: first, the equation is not restricted to high densities but goes to the ideal-gas limit as the density goes to zero; second, the free volume is given by the Carnahan–Starling expression; and third, the potential field is calculated from Alder's molecular-dynamics results using a square-well potential. The new equation of state represents well volumetric data of liquid polymers at high pressures. Characteristic parameters are given for 14 common polymers.

To obtain an equation of state for real fluids, including polymers, the most successful statistical-thermodynamic treatments are those based on the fundamental ideas of van der Waals: (1) the microstructure of the fluid is determined by the molecules' repulsive forces leading to the concept of free volume; (2) the contribution of attractive forces can be calculated by assuming that the molecules are situated in a homogeneous and isotropic field of force determined by the (attractive) intermolecular potential.

Numerous articles have presented detailed van der Waals type theories for fluids containing small, spherical molecules.[1,2] Only a few authors[3,4] have applied these ideas to fluids containing large molecules because, for such molecules, consideration must be given to external rotational and vibrational degrees of freedom in addition to translational degrees of freedom. An approximation for doing so was suggested by Prigogine,[5] but since this approximation is valid only at high (liquid-like) densities, previous van der Waals type equations of state using Prigogine's approximation are limited to high densities; as pointed out by Scott and van Konynenburg,[6] such equations are qualitatively incorrect at low densities.

In this paper we use generalized van der Waals theory, coupled with Prigogine's assumption, to derive an equation of state for fluids containing large or small molecules which, however, is not limited to high densities. For the free volume we use an expression obtained by Carnahan and Starling;[7,8] the contribution from attractive forces is found using the molecular-dynamics studies of Adler et al.[9] based on a square-well potential. In another publication[10] we have illustrated the applicability of our equation of state to fluids of normal molecular weight. Here we indicate application to polymers.

An alternate method, using lattice-with-holes theory, has been briefly discussed by Bonner[11] and developed extensively by Simha and coworkers.[12]

In the following sections we summarize the essential steps in the statistical-mechanical derivation of our equation of state.

Partition Function

The generalized van der Waals partition function is conveniently written[3,13]

$$Q = \frac{1}{N!}\left[\frac{V_f}{\Lambda^3}\right]^N [q_{r,v}]^N [\exp(-\phi/2kT)]^N \qquad (1)$$

where V_f is the free volume, N is the number of molecules, ϕ is the potential field, k is Boltzmann's constant, T is the absolute temperature, and Λ is a constant depending only on temperature and molecular mass. The term $q_{r,v}$ represents the contribution (per molecule) from rotational and vibrational degrees of freedom. For simple (argon-like) molecules $q_{r,v}$ is independent of volume and therefore it does not contribute to the equation of state.

Following Prigogine,[5] we factor $q_{r,v}$ into an internal part and an external part

$$q_{r,v} = q_{int}(T) \cdot q_{ext}(V) \qquad (2)$$

At liquid-like densities we utilize Prigogine's approximation that external rotational and vibrational degrees of freedom can be considered as equivalent translational degrees of freedom; the total number of external degrees of freedom is designated by $3c$. For argon-like molecules $c = 1$ but for other molecules $c > 1$.

To find a suitable function for $[(V_f/\Lambda^3)q_{ext}]$, we note that there are four boundary conditions that must be satisfied: in the ideal gas limit,

$$(V_f/\Lambda^3)q_{ext} \rightarrow V/\Lambda^3 \quad \text{as } V \rightarrow \infty \qquad (3)$$

in the close-packed density limit

$$(V_f/\Lambda^3)q_{ext} \rightarrow 0 \quad \text{as } V \rightarrow V_0 \qquad (4)$$

where V_0 is the close-packed volume. For all fluid densities

$$\frac{V_f}{\Lambda^3}q_{ext} \rightarrow \frac{V}{\Lambda^3}\exp\left[\frac{(\tau/\tilde{v})(3\tau/\tilde{v} - 4)}{(1 - \tau/\tilde{v})^2}\right] \quad \text{as } c \rightarrow 1 \qquad (5)$$

where $\tau = \pi\sqrt{2}/6 = 0.7405$ and $\tilde{v}$ is a reduced volume defined by

$$\tilde{v} = \frac{V}{Nrv^*} = \frac{V}{V_0} \qquad (6)$$

where r = number of segments in the molecule, and v^* = close-packed volume per segment; finally, at liquid-like densities,

$$(V_f/\Lambda^3)q_{ext} \rightarrow [V_f/\Lambda^3]^c \quad \text{for } c \geq 1 \qquad (7)$$

Equation 3 is necessary not only to obtain the ideal gas law as the volume becomes very large, but also to obtain reasonable second, third, and higher virial coefficients. Equation 4 says that when the molecules are packed as densely as possible, all external degrees of freedom are locked in, i.e., the molecule cannot exercise any motions. Equation 5 is necessary to recover the free-volume expression for hard spheres given by Carnahan and Starling;[7,8] this expression is in excellent agreement with molecular-dynamics results for hard spheres with all fluid densities ($\tilde{v} > 1.5$).

Equation 7 expresses Prigogine's approximation: at liquid-like densities, all external degrees of freedom can be considered as equivalent translational degrees of freedom.

The simplest interpolation function which meets all four boundary conditions [eq 3, 4, 5, and 7] is

$$q_{ext} = (V_f/V)^{c-1} \qquad (8)$$

We therefore adopt eq 8 to represent the contribution of external rotations and vibrations to the partition function.

To calculate the potential field ϕ, we use the molecular-dynamics results of Alder[9] for molecules whose intermolecular forces are given by the square-well potential, with a well width equal to ½ the diameter of the molecule.

Alder's results are in the form:

$$\phi = \epsilon q W(\tilde{T},\tilde{v}) \qquad (9)$$

where ϵq = characteristic energy per molecule, energy parameter ϵ is per unit surface area, and parameter q is proportional to the external surface area of a molecule. Reduced temperature $\tilde{T}$ is defined by the ratio of kinetic energy to potential energy:

$$\tilde{T} = T/T^* = \frac{ckT}{\epsilon q} \qquad (10)$$

Details for W are given in Appendix I.

Equation of State

The equation of state is directly related to the partition function Q by

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \qquad (11)$$

where P is the pressure. Substitution into eq 11 gives the new equation of state:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = 1/c + \frac{4(\tau/\tilde{v}) - 2(\tau/\tilde{v})^2}{(1 - \tau/\tilde{v})^3} - \frac{\tilde{v}}{\tilde{T}}\left(\frac{\partial W}{\partial \tilde{v}}\right)_{\tilde{T}} \qquad (12)$$

where

$$\left(\frac{\partial W}{\partial \tilde{v}}\right)_{\tilde{T}} = -\sum_{n=1}^{4}\sum_{m=1}^{M}\left(\frac{mA_{nm}}{\tilde{v}^{m+1}}\right)\left(\frac{1}{\tilde{T}^{n-1}}\right) \qquad (13)$$

Table I
Characteristic Parameters of 14 Common Polymers[n]

Polymer[a]	v_{sp}*,[m] cm³/g	T*, °K	P*, bars	Range of PVT data used: Temp, °C	Range of PVT data used: Pressure, bars	Ref
PDMS	0.5438	369	975	0–150	1–1000	*b, c*
PIB	0.6013	473	1782	0–110	1–1000	*c*
PE						
(Branched)	0.6563	475	1229	140–200	1–1000	*c*
(Linear)	0.6519	458	1304	150–200	1–40	*d*
PVAC	0.4540	417	1983	60–120	1–1000	*c*
PS	0.5316	544	1691	120–200	1–2000	*e, f*
POMS	0.5391	542	1669	130–200	1–2000	*e*
NR	0.5854	399	2154	0–40	1–500	*g*
PTFE	0.2935	486	544	350–500	1–500	*h*
PP (atatic)	0.6289	415	2067	−10–30	1–700	*i*
PMMA	0.4623	510	1990	90–100	1–1000	*j*
PVC	0.3762	407	3028	90–100	1–100	*j*
PPO	0.5313	384	1606	60–75	1	*k*
PEO	0.4769	397	2197	60–70	1	*l*

[a] Abbreviations: PDMS, polydimethylsiloxane; PIB, polyisobutylene; PE, polyethylene; PVAC, poly(vinyl acetate); PS, polystyrene; POMS, poly(*o*-methylstyrene); NR, natural rubber; PTFE, polytetrafluoroethylene; PP, polypropylene; PMMA, poly(methyl methacrylate); PVC, poly(vinyl chloride); PPO, poly(propylene oxide); PEO, poly(ethylene oxide). [b] H. Shih and P. J. Flory, *Macromolecules*, 5, 758 (1972). [c] S. Beret and J. M. Prausnitz, *Macromolecules*, 8, 536 (1975). [d] R. A. Orwoll and P. J. Flory, *J. Am. Chem. Soc.*, **89**, 6814 (1967). [e] A. Quach and R. Simha, *J. Appl. Phys.*, 42, 4592 (1971). [f] H. Höcker, G. J. Blake, and P. J. Flory, *Trans. Faraday Soc.*, 67, 2251 (1971). [g] L. A. Wood and G. M. Martin, *J. Res. Natl. Bur. Stand., Sect. A*, 259 (1964). [h] C. A. Speratti and H. W. Starkweather, *Fortschr. Hochpolym.-Forsch.*, 2, 31 (1961). [i] B. Passaglia and G. M. Martin, *J. Res. Natl. Bur. Stand., Sect. A*, 273 (1964). [j] K. H. Hellwege, N. Knappe, and P. Lehmann, *Kolloid Z. Z. Polym.*, **183**, 110 (1962). [k] C. Booth and C. J. Devoy, *Polymer*, **12**, 320 (1971). [l] C. Booth and C. J. Devoy, *Polymer*, **12**, 309 (1971). [m] $M_w v_{sp}^* = rv^*$, where M_w is the molecular weight. [n] All data used are in the amorphous liquid state.

The reduced pressure $\tilde{P}$ is defined by

$$\tilde{P} = Prv^*/\epsilon q = P/P^* \tag{14}$$

The coefficients A_{nm} are dimensionless constants given in Appendix I.

For long-chain molecules, $c \gg 1$ and $1/c \rightarrow 0$. Therefore the new equation of state reduces to a form similar to that suggested by Prigogine, a corresponding-states equation:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{4(\tau/\tilde{v}) - 2(\tau/\tilde{v})^2}{(1-\tau/\tilde{v})^3} - \frac{\tilde{v}}{\tilde{T}}\left(\frac{\partial W}{\partial \tilde{v}}\right)_{\tilde{T}} \tag{15}$$

Data Reduction

Reduced volume $\tilde{v}$, as given by eq 6, can also be defined by

$$\tilde{v} = v_{sp}/v_{sp}^* \tag{16}$$

where subscript sp (specific) designates that the volumes are per unit mass. The two quantities v_{sp}^* and v^* are related through

$$M_w v_{sp}^* = rv^* \tag{17}$$

where M_w is the molecular weight. It is advantageous to work with v_{sp}^* rather than rv^* because for the former we do not have to specify the segmental unit.

Equation 15 has three adjustable parameters: P^*, T^*, and v_{sp}^*. For polymer liquids they can be determined from volumetric data in various ways. One method is to determine them from data at (essentially) zero pressure for density, thermal expansion coefficient α, and thermal pressure coefficient γ. This is the method used by Flory and coworkers.[14]

Table II
Calculated and Measured Specific Volumes, Thermal Expansion Coefficients, and Thermal Pressure Coefficients at 1 bar for Polyisobutylene, Polydimethylsiloxane, and Polystyrene

Polymer	Temp, °C	Specific vol, cm³/g: Exptl	Specific vol, cm³/g: Calcd	Thermal expansion coefficient × 10⁴, deg⁻¹: Exptl	Thermal expansion coefficient × 10⁴, deg⁻¹: Calcd	Thermal pressure coefficient, bar/deg: Exptl	Thermal pressure coefficient, bar/deg: Calcd
PIB[a]	50	1.1059	1.1063	5.6	5.2	10.2	9.1
	100	1.1376	1.1375	5.7	5.9	8.2	9.3
	150	1.1706	1.1732	5.8	6.5	6.8	8.8
PDMS[b]	50	1.0549	1.0550	9.1	8.2	6.6	6.3
	80	1.0844	1.0821	9.2	8.7	5.5	6.0
	100	1.1046	1.1016	9.3	9.1	4.9	5.7
PS[c,d]	150	1.0032	1.0026	5.8	5.1	8.2	7.7
	200	1.0329	1.0295	5.9	5.5	7.5	7.4

[a] Experimental data from: B. E. Eichinger and P. J. Flory, *Macromolecules*, 1, 285 (1968). [b] Experimental data from: H. Shih and P. J. Flory, *ibid.*, 5, 758 (1972). [c] Experimental data from: H. Höcker, G. J. Blake, and P. J. Flory, *Trans. Faraday Soc.*, **67**, 2251 (1971). [d] Experimental data from: A. Quach and R. Simha, *J. Appl. Phys.*, **42**, 4592 (1971).

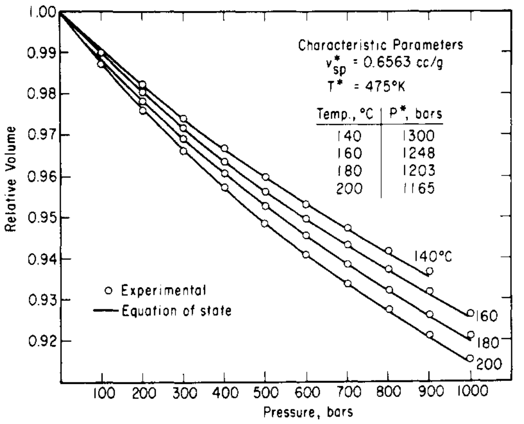

Figure 1. Calculated and observed densities of polyethylene.

The advantage of Flory's method is that only atmospheric-pressure data are required. However, accurate values of α and γ data are necessary and these are often not available. When determined by this method, the parameters are temperature dependent.

We fitted all available PVT data to eq 15 to determine the three parameters. We used Flory's method for polymers for which only atmospheric pressure data exist. (Equations for α and γ at 1 bar are given in Appendix II.)

Table I shows the three parameters v_{sp}^*, T^*, and P^* for 14 common polymers. Also shown are the temperature and pressure range of the data used for data reduction.

Results and Discussion

Figure 1 shows some calculated and observed densities for low-density (branched) polyethylene.

For low-density polyethylene, extensive PVT data have recently become available.[15] Therefore, in Figure 1, a sepa-

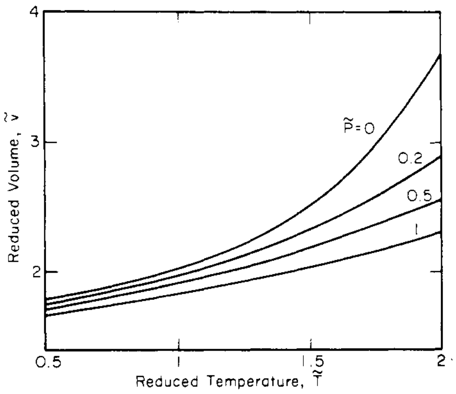

Figure 2. Reduced volume as a function of reduced temperature at selected reduced pressures.

rate P^* is calculated for each isotherm while v_{sp}^* and T^* are fixed. The calculated relative volumes agree with the observed relative volumes within ±0.1%. If constant P^* (reported in Table I) is used, the deviation is about ±0.5%.

Table II compares experimental and calculated densities, thermal expansion coefficients, and thermal pressure coefficients at 1 bar for polyisobutylene, polydimethylsiloxane, and polystyrene. Experimental values reported for α and γ show considerable variation. For example, for polystyrene at 150°C, Quach and Simha[16] reported $\alpha = 5.3 \times 10^{-4}$ deg^{-1} and Flory and coworkers[14] reported $\alpha = 5.81 \times 10^{-4}$ deg^{-1}.

Figure 2 shows calculated reduced volumes as a function of reduced temperature at several reduced pressures. Most common industrial processes for polymers occur near a reduced temperature of 1 and at reduced pressures in the range 0–0.5.

As shown in Figure 3, parameter v^* (per repeating unit) is closely related to van der Waals volume V_w (per repeating unit) as calculated from the group-contribution method of Bondi.[17]

Comparison with Flory Equation of State

The equation of state presented here is a three-parameter equation. The well-known equation of state of Flory is also a three-parameter equation of state. However, Flory's equation of state is applicable only for dense liquids; it approaches a wrong limit as the density goes to zero. Equation 12, however, is applicable to both the dense liquid and the dilute gas phase and therefore, when extended to mixtures, it may be useful for vapor–liquid phase equilibrium calculations when the light component is near or above its critical temperature.

The results shown in Figure 4 suggest that eq 15 is somewhat better than Flory's for predicting densities of polystyrene at high pressures. All calculations in Figure 4 are based on characteristic parameters obtained from volumetric data at atmospheric pressure only: data by Höcker et al.[14] for the density and the thermal expansion coefficient, and data by Quach and Simha[16] for the isothermal compressibility. The data points shown are from Quach and Simha.[16]

For polyisobutylene and polydimethylsiloxane, the new equation of state also is a little better than Flory's for predicting densities at high pressures, but for these polymers the improvement is not as large as that observed for polystyrene. In all cases considered here, Flory's equation predicts compressibilities smaller than those observed.

At high densities, incorporation of eq 8 into the partition function has little effect. Also, at high densities, using Alder's function (eq 9) probably does not offer significant improvement. However, both eq 8 and eq 9 are necessary for good representation at low densities.[10] At high densities, the improved performance is probably due to the Carnahan–Starling formula (eq 5).

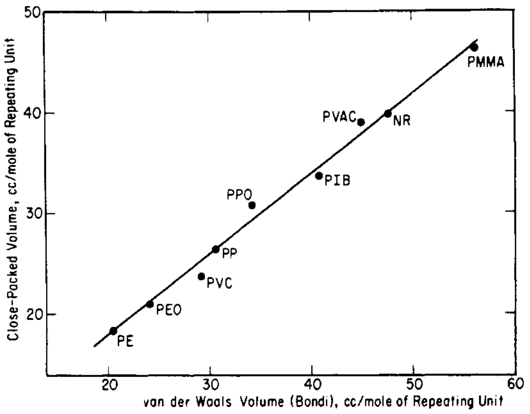

Figure 3. Relation between close-packed and van der Waals volumes.

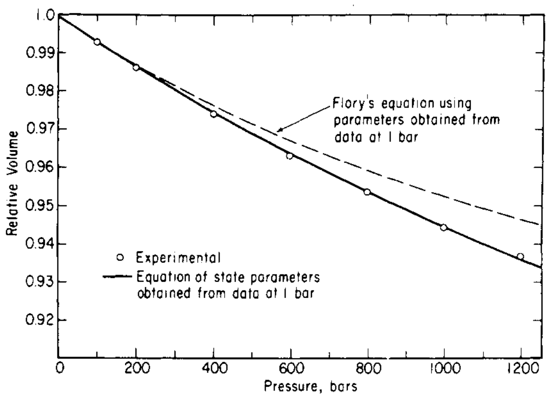

Figure 4. Predicted and observed densities of compressed polystyrene at 184.9°C.

Conclusion

A new partition function is presented for fluids containing either small or large molecules. The resulting equation of state is applicable throughout the entire fluid density range. It may, therefore, be particularly useful for those polymer mixtures where the solvent is already well dilated, that is, where the solvent's density is small.

The new equation of state accurately predicts the volumetric data for amorphous polymers at high pressures. Characteristic parameters v_{sp}^*, T^*, and P^* are given for 14 common polymers.

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Appendix I. Alder's Equation

The molecular-dynamic results of Alder are given in a form where the Helmholtz energy is the sum of a hard-sphere part and a perturbation part; the latter follows from attractive intermolecular forces. These are represented by a square-well potential where the diameter of the well is one-half that of the hard sphere. For the hard-sphere part we use the Carnahan–Starling equation. For the perturbation part we use Alder's results:

$$W(\tilde{T},\tilde{v}) = \sum_{n=1}^{4} \sum_{m=1}^{M} \left(\frac{A_{nm}}{\tilde{V}^m}\right) \left(\frac{1}{\tilde{T}^{n-1}}\right) \tag{I-1}$$

The dimensionless constants A_{nm} are

$A_{11} = -7.0346$
$A_{12} = -7.2736$
$A_{13} = -1.2520$
$A_{14} = 6.0825$
$A_{15} = 6.8$
$A_{16} = 1.7$

$A_{21} = -0.330\,155\,80 \times 10^1$
$A_{22} = -0.981\,557\,82 \times 10^0$
$A_{23} = +0.220\,221\,15 \times 10^3$
$A_{24} = -0.191\,214\,78 \times 10^4$
$A_{25} = +0.864\,131\,58 \times 10^4$
$A_{26} = -0.229\,114\,64 \times 10^5$
$A_{27} = +0.353\,888\,09 \times 10^5$
$A_{28} = -0.293\,436\,43 \times 10^5$
$A_{29} = +0.100\,904\,78 \times 10^5$

$A_{31} = -0.118\,687\,77 \times 10^1$
$A_{32} = +0.724\,475\,07 \times 10^1$
$A_{33} = -0.174\,324\,07 \times 10^2$
$A_{34} = +0.196\,662\,11 \times 10^2$
$A_{35} = -0.851\,451\,88 \times 10^1$

$A_{41} = -0.517\,390\,49 \times 10^0$
$A_{42} = +0.252\,598\,12 \times 10^1$
$A_{43} = -0.412\,468\,08 \times 10^1$
$A_{44} = +0.234\,345\,64 \times 10^1$

When $n = 1, M = 6; n = 2, M = 9; n = 3, M = 5; n = 4, M = 4$.

Appendix II. Limiting Forms as $1/c \rightarrow 0$

Equation of state at atmospheric pressure

$$\frac{(4\tau/\tilde{v}) - 2(\tau/\tilde{v})^2}{\tilde{v}(1 - \tau/\tilde{v})^3} = \frac{1}{\tilde{T}}\left(\frac{\partial W}{\partial \tilde{v}}\right)_{\tilde{T}} \tag{II-1}$$

Thermal expansion coefficient at atmospheric pressure

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P=1} \tag{II-2}$$

$$\alpha = \frac{\Omega(\tilde{T},\tilde{v}) - \frac{1}{\tilde{T}}\left(\frac{\partial W}{\partial \tilde{v}}\right)_{\tilde{T}}}{T\tilde{v}\left\{\left[\frac{2(\tau/\tilde{v})^2 - (8\tau/\tilde{v})}{(1 - \tau/\tilde{v})^4\tilde{v}^2}\right] - \frac{1}{\tilde{T}}\left(\frac{\partial^2 W}{\partial \tilde{v}^2}\right)_{\tilde{T}}\right\}} \tag{II-3}$$

where

$$\Omega(\tilde{T},\tilde{v}) = \frac{1}{\tilde{T}^2}\sum_{m=1}^{9}\frac{mA_{2m}}{\tilde{v}^{m+1}} + \frac{2}{\tilde{T}^3}\sum_{m=1}^{5}\frac{mA_{3m}}{\tilde{v}^{m+1}} + \frac{3}{\tilde{T}^4}\sum_{m=1}^{4}\frac{mA_{4m}}{\tilde{v}^{m+1}} \tag{II-4}$$

Thermal pressure coefficient at atmospheric pressure

$$\gamma \equiv (\partial P/\partial T)_V \tag{II-5}$$

$$\gamma = (P/T\tilde{P})[(\partial W/\partial v)_{\tilde{T}} - \tilde{T}\Omega(\tilde{T},\tilde{v})] \tag{II-6}$$

$$\tau = \pi\sqrt{2}/6 = 0.7405 \tag{II-7}$$

W is given in eq I-1 and $(\partial W/\partial \tilde{v})_{\tilde{T}}$ is given in eq 13.

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Studies of Polystyrene in the Region of the Glass Transition Temperature by Inverse Gas Chromatography

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ABSTRACT: The chromatographic behavior of polystyrene was investigated at temperatures encompassing its glass transition temperature (T_g) with packed columns ranging over three orders of magnitude of coating thickness. It is shown that the temperature of first deviation from the normal linear behavior due to surface adsorption is essentially unaffected by coating thickness and is to be identified with the glass transition temperature of the polymer as determined by other methods. A quantitative analysis of retention data measured under widely different conditions of surface to volume ratio of the stationary phase is given for both bulk retention and surface adsorption.

Anomalous behavior is frequently observed in gas–liquid chromatography in the temperature region associated with transitions in the stationary phase. For analytical purposes, such anomalies are undesirable, because they often alter the resolution of the column, and make interpretation of the retention time difficult due to changes in peak shape.