Molecular Weight Dependence of Surface Tension of Polystyrene as Studied by the Corresponding States Principle

K. K. CHEE

Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

ABSTRACT: The corresponding states correlation with the surface tension (γ) of polymers after Patterson et al. has been modified by considering the molecular weight (M) dependence of the equation-of-state parameters, which may be estimated by either the Flory-Orwoll-Vrij (FOV) theory or the cell model (CEM). It has been found that the corresponding states principle-cum-FOV predicts the γs of polystyrene melts over a wide range of M satisfactorily. However, its CEM counterpart is rather irrelevant to the present system of interest. Indeed, the three classical linear equations proposed for the variations of γ with M are intimately correlated with the foregoing models, and hence, facilitating the predictions of the γs of polymer end groups. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 697–703, 1998

Key words: polystyrene; surface tension; number-average molecular weight; corresponding states principle; equation-of-state theories

INTRODUCTION

Temperature, T, and molecular weight, M, are the two important factors that would affect the surface tension, γ, of polymers. Specifically, the γ decreases linearly with T, but increases with increasing M. Two distinct semiempirical equations have been invoked to depict the latter relationship for a homogeneous series of polymers at constant T,[1] i.e.:

$$\gamma = \gamma_\infty - k_1/M_n^{2/3} \qquad (1)$$

$$\gamma^{1/4} = \gamma_\infty^{1/4} - k_2/M_n \qquad (2)$$

where γ_∞ is the surface tension at the infinite number-average molecular weight, M_n, and k_1,

and k_2 are the constants. According to eq. (1), a plot of γ against $M_n^{-2/3}$ would result in a straight line with the intercept and gradient equal to γ_∞ and k_1, respectively. Analogously, eq. (2) may be used to derive γ_∞ and k_2 from a linear plot of $\gamma^{1/4}$ against M_n^{-1}.

On the basis of the random distribution of the end groups and simple packing of polymer molecules in cubic lattice,[2,3] it has been shown that

$$k_1 = (\gamma_\infty - \gamma_e)(2m_r v_e/v_r)^{2/3} \qquad (3)$$

where m_r is the molecular weight of the repeat unit with molar volume v_r, and γ_e is the surface tension of the end group with molar volume v_e.

MacLeod equation leads to $\gamma^{1/n} = P_a/V$, where n is a positive constant independent of T, and P_a and V are the molar parachor and molar volume of the polymer, respectively. For linear polymers, we assume $M = rm_r + 2m_e$, $V = rv_r + 2v_e$, and $P_a = rP_r + 2P_e$, where r is the number of repeat units with molar parachor P_r, m_e, and P_e are the molec-

ular weight and molar parachor of the end group, respectively. It follows that

$$k_2 = (\gamma_\infty^{1/4} - \gamma_e^{1/4})(2m_r v_e/v_r) \tag{4}$$

by setting $n = 4$. A similar endeavour was made by Wu, who had implicitly assumed $2\,m_e \ll rm_r$.[3] The difference between the predictions on k_2 after Wu and the foregoing analysis [i.e., eq. (4)] is found to be $2m_e\gamma_\infty^{1/4}$.

Although eqs. (3) and (4) provide the rational of the molecular weight dependence of surface tension, the parameter γ_e is usually not known *a priori*. The main objective of the present study is to address this shortcoming by developing a more practical interpretation of the foregoing relationships using the corresponding states principle (CSP).

Corresponding States Correlation with Surface Tension

Patterson et al. have found a common curve of reduced surface tension, $\tilde{\gamma}$, against reduced temperature, $\tilde{T}$, for various high molecular weight liquids including n-alkanes, polyethylene, polypropylene glycol, and a homogeneous series of polydimethylsiloxanes over a range of temperatures.[4,5] Applying the Prigogine's CSP to the above observation, they have obtained an empirical expression given by

$$\gamma = (kT^*)^{1/3}(P^*)^{2/3\sim} \tag{5}$$

where k is the Boltzmann constant, T^* and P^* are respectively the hard-core reduction parameters for T and pressure, P. According to the cell model, the reduced parameter

$$\tilde{\gamma} = -\tilde{v}^{2/3}\{Q\tilde{u} - \tilde{T}\ln[(\tilde{v}^{1/3} - p/2)/(\tilde{v}^{1/3} - p)]\} \tag{6}$$

where $\tilde{v}$, $\tilde{u}$ are the reduced parameters for the specific volume, v, (or molar volume) and configuration energy respectively, p is the packing factor, and Q is the fraction of nearest neighbors that a polymer segment would lose when it moves from the bulk to the surface. Hence, $\tilde{\gamma}$ is readily estimated as a function of $\tilde{v}$ if Q is known. Least-square treatments of these data have revealed that eq. (6) can be conveniently approximated to

$$\tilde{\gamma} = \kappa\tilde{v}^{-m} \tag{7}$$

over a practical range of $\tilde{v}$, where κ and m are the empirical constants. In this connection, the parameter Q is predetermined by means of the least-squares method[6] based on eqs. (5) and (6) and the known qualities γ, P^*, T^*, and $\tilde{v}$.[7] To this end, two distinct equation-of-state theories are applied, namely the Flory-Orwoll-Vrij (FOV) theory[8] and the cell model (CEM)[9] characterized respectively by the configuration energy

$$\tilde{u} = -\tilde{v}^{-1} \tag{8}$$

$$\tilde{u} = \tilde{v}^{-4} - 2\tilde{v}^{-2} \tag{9}$$

and the packing factor $p = 1$ and 0.891, respectively. Their respective equations of state at $P = 0$ are

$$\tilde{v} = (1 - \tilde{T}\tilde{v})^{-3} \tag{10}$$

$$\tilde{T} = 2\tilde{v}^{-2}(1.2045 - 1.011\tilde{v}^{-2})[1 - (\sqrt{2}\tilde{v})^{-1/3}] \tag{11}$$

Perhaps, a striking feature of the partition function proposed for polymeric liquids and applied to obtain the reduced equation-of-state relevant to eq. (10) is the introduction of characteristic parameters[8] $T^* = \tilde{v}\epsilon^*/Ck$, and $P^* = \tilde{v}\epsilon^*/v_s^*$. Here, $-\epsilon^*$ is the intermolecular energy per segment, C is the mean number of external degrees of freedom per segment, v_s^* is the hard-core reduced volume per segment. Hence, it is possible to replace the parameter P^*, which may register large experimental error, by the ratio of the C to the molecular weight of polymer segment, M_0, given by

$$C/M_o = P^*v^*/RT^* \tag{12}$$

where v^* is the reduction parameter for specific volume, and R is the ideal gas constant. Combining eqs. (5), (7), and (12) yields

$$\gamma = \kappa k^{1/3}R^{2/3}v^{-m}(C/M_o)^{2/3}T^*(v^*)^{m-2/3} \tag{13}$$

Assuming

$$v = v_\infty + a/M_n, \ T^* = T_\infty^* - b/M_n,$$
$$v^* = v_\infty^* + d/M_n,$$

and

$$C/M_o = 1/3M_o + K/M_n,$$

Table I   Equation-of-State Parameters for Polystyrene Collected from the Literature

Model	P^*_∞ (MPa)	T^*_∞ (K)	v^*_∞ (ml g^{-1})	$b \times 10^{-5}$ (g mol^{-1} K)	d (mL mol^{-1})	K	M_o	
FOV	405.2	8118	0.8277	—	—	—	—	a
	477.4	8300	0.8296	—	—	—	—	b
	474.5	8105	0.8315	—	—	—	—	c
	461.0	7964	0.8277	7.28	15.6	0.86	57.6	d
CEM	608.2	5145	0.9228	—	—	—	—	a
	599.0	5167	0.9148	—	—	—	—	c
	623.0	4970	0.9120	3.44	23.2	1.78	23.9	d

[a] Ref. 13, valid conditions: 115–196°C, 0–200 MPa.
[b] Ref. 14. These are the average values derived from the data cited for 100–200°C at $P \to 0$. The datum of P^*_∞ was obtained by extrapolation.
[c] Ref. 15, valid conditions: 121–320°C, 0–180 MPa.
[d] Ref. 7, valid conditions: 100–230°C, 0–200 MPa.

where the subscript ∞ is appended to v, T^*, and v^* at the infinite M_n, and a, b, d and K are the empirical coefficients, eq. (13) becomes

$$\gamma/\gamma_\infty = (1 + a/v_\infty M_n)^{-m}(1 + 3M_oK/M_n)^{2/3}$$
$$(1 - b/T^*_\infty M_n)(1 + d/v^*_\infty M_n)^{m-2/3} \quad (14)$$

Equation (14) is the basic equation for the present analysis. More importantly, it reveals the origin of molecular weight dependence of surface tension in that the four coefficients in eq. (14) are solely responsible for this striking effect. Here, γ_∞ is readily accessible by combining eqs. (5) and (7), which would lead to

$$\gamma_\infty = \kappa(kT^*_\infty)^{1/3}(P^*_\infty)^{2/3}(v^*_\infty/v_\infty)^m \quad (15)$$

To explore the explicit expressions for $\gamma(M_n)$ from CSP, eq. (14) is expanded to a series in powers of $1/M_n$, which can be truncated to give a cubic polynomial

$$\gamma/\gamma_\infty - 1 = \beta_1/M_n + \beta_2/M_n^2 + \beta_3/M_n^3 \quad (16)$$

where

$$\beta_1 = -[ma/v_\infty - 2M_oK + b/T^*_\infty$$
$$- (m - 2/3)d/v^*_\infty] \quad (16a)$$

$$\beta_2 = \beta_1^2/2 + [m(a/v_\infty)^2/2 - 3(M_oK)^2 - (b/T^*_\infty)^2/2$$
$$- (m - 2/3)(d/v^*_\infty)^2/2] \quad (16b)$$

$$\beta_3 = -\beta_1^3/3 + \beta_1\beta_2 - [m(a/v_\infty)^3/3 - 6(M_oK)^3$$
$$+ (b/T^*_\infty)^3/3 - (m - 2/3)(d/v^*_\infty)^3/3] \quad (16c)$$

A Taylor series expansion is applied to the right-hand side of eq. (16) about $M_n^{-2/3} = M_r^{-2/3}$, where M_r is a reference M_n, to yield a polynomial $P'(M_n^{-2/3})$. If both sides of eq. (16) are raised to the one-fourth powers, one would readily obtain a new polynomial $P''(M_n^{-1})$. Considering the ratios of the second term to the first term of the three polynomials, namely eq. (16), P' and P'', designated by θ, θ', and θ'' respectively, we have

$$\theta = \beta_2/\beta_1 M_n \quad (17)$$

Table II   Estimated Volume Characteristics of Polystyrene at the Atmospheric Pressure and Various Temperatures from Two Equation-of-State Models [eqs. (10) and (11)]

Model	Parameter	Temperature, t (°C)			
		120	148	176	200
FOV	v_∞ (ml g^{-1})	0.9938	1.0108	1.0288	1.0453
	a (ml mol^{-1})	43.7	47.6	52.3	56.7
CEM	v_∞ (ml g^{-1})	0.9891	1.0033	1.0187	1.0329
	a (mL mol^{-1})	42.3	45.2	48.4	51.4

Table III Temperature Dependence of Surface Tension (γ) for Various Polystyrene Samples Characterized by Number-Average Molecular Weight, M_n

| | $\gamma = A - Bt$ (°C) | | |
| | | $B \times 10^2$ | |
$M_n \times 10^{-3}$	A (mN m^{-1})	(mN m^{-1} °C^{-1})	Ref.
∞	42.3	7.1	16
60	41.3	6.7	12
21.4	41.5	6.7	12
9.29	40.5	6.4	16
2.91	40.4	6.8	16
1.79	40.5	7.0	12
1.68	40.8	7.7	16
0.70	37.1	6.8	12

$$\theta' = (1 + 9\phi^2/35)\phi^{2/3}/(1 - 3\phi^2/7) \quad (18)$$

$$\theta'' = (\beta_2/\beta_1 - 3\beta_1/8)/M_n \quad (19)$$

where $\phi = M_r/M_n$ with $M_r = (-35\beta_3/\beta_1)^{1/2}$. Clearly, P' and P'' are reduced respectively to eqs. (1) and (2) if $|\theta'|$ and $|\theta''| \ll 1$, with

$$k_1 = -(9/16)\gamma_\infty\beta_1 M_r^{-1/3}(1 - 15\beta_3/\beta_1/\beta_1 M_r^2) \quad (20)$$

$$k_2 = -\gamma_\infty^{1/4}\beta_1/4 \quad (21)$$

for a practical range of M_n, over which the other pertinent M_n terms are virtually unimportant. Analogously, eq. (16) becomes

$$\gamma = \gamma_\infty - k_3/M_n \quad (22)$$

where

$$k_3 = -\beta_1\gamma_\infty \quad (22a)$$

if $|\theta| \ll 1$. In fact, eq. (22) has been applied by the other workers[10–12] for polymers with sufficiently large M_n.

Recently, Dee and Sauer have resorted to Cahn-Hilliard density gradient-cum-FOV method to predict the surface tensions of various polymeric liquids.[11,12] However, this particular approach is rather involved, and offers no direct γ-M relationships.

RESULTS AND DISCUSSION

Table I lists the values of the reduction parameters collected for polystyrene (PS) from the reliable sources.[7,13–15] Clearly, both FOV and CEM models generate self-consistent results in that the ratios of standard deviation to mean for P_∞^*, T_∞^*, and v_∞^* are, respectively, equal to 0.064, 0.015, and 0.0019 for FOV, and 0.016, 0.017, and 0.0050 for CEM. As noted earlier, the parameter P_∞^* sustains the highest uncertainty, which may be con-

Table IV Comparison of the Results on γ_∞ Obtained from Different Methods, at the Atmospheric Pressure and Various Temperatures for Polystyrene
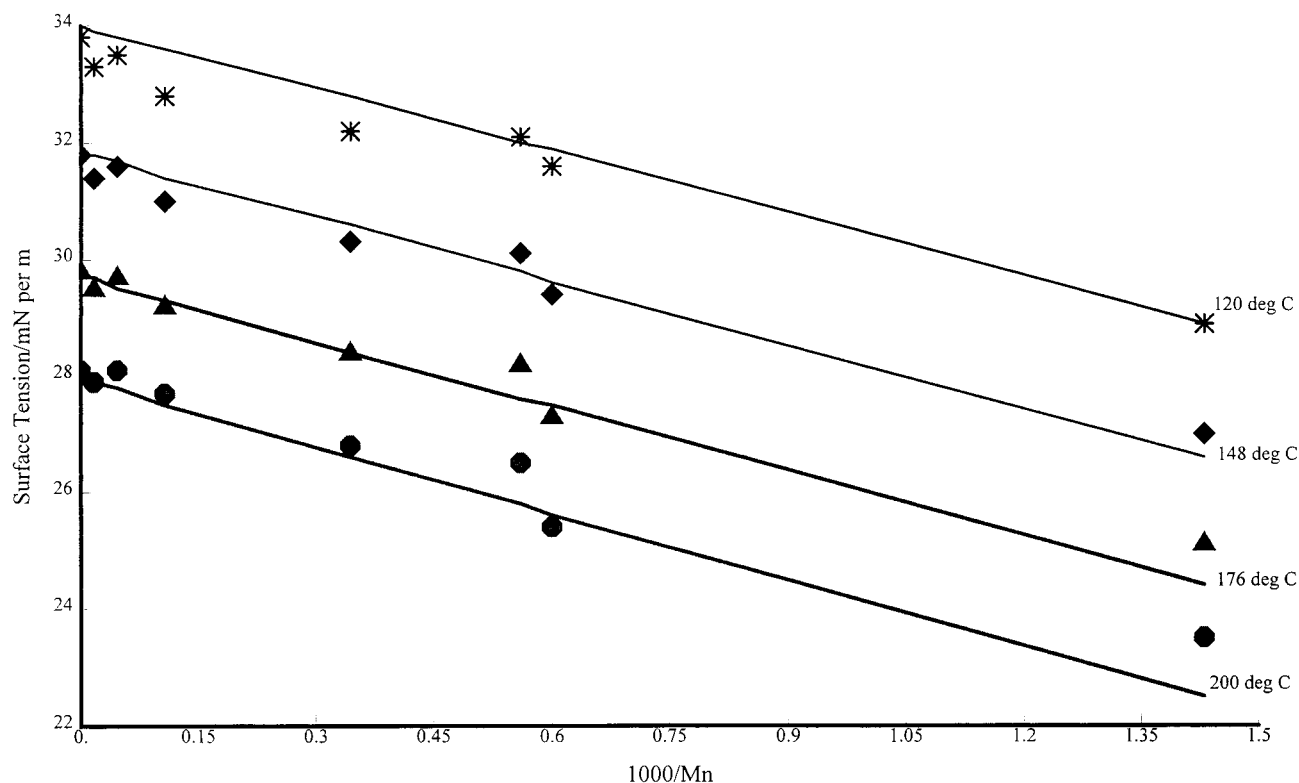
| | γ_∞/mN m^{-1} | | | | |
Method	120°C	148°C	176°C	200°C	σ_∞[a]/mN m^{-1}
EXPT[b]	33.8	31.8	29.8	28.1	—
CFOV	34.0	31.8	29.7	27.9	0.17
CCEM	34.4	31.7	28.1	26.9	1.25

[a] Average deviation of γ_∞. In general, the average deviation of x, σ, can be defined by

$$\sigma = \left[\frac{\sum_{i=1}^{q}(\Delta x_1)^2}{q - 1}\right]^{1/2},$$

where Δx_i is the difference between the experimental and estimated x_i, and q is the total number of data points, x_i.

[b] Experimental data.

Figure 1 Dependence of the surface tension (γ) on number-average molecular weight (M_n) for polystyrene at various temperatures. Lines are the predictions of the CFOV model, whereas the symbols indicate the experimental data: ($*$), 120°C; ($\blacklozenge$), 148°C; ($\blacktriangle$), 176°C; ($\bullet$), 200°C.

sidered as one of the major sources of error in the following predictions on γ_∞. The present study employs the work of Ougizawa et al. who have also provided the crucial data on the coefficients, a, b, d, K, and constant M_o.

Equations (10) and (11) are applied to compute the reduced volume $\tilde{v}$ at various temperatures via $\tilde{T} = T/T^*$, where T is in Kelvin. Hence, the specific volume v_∞ ($= \tilde{v} v_\infty^*$) and coefficient a are readily obtained with the aid of the information on T_∞^*, v_∞^*, b, and d tabulated in Table I. These results are included in Table II.

The surface tensions of PS melts have been reported by a number of workers, using mainly the pendent drop method[16,17] and the modified Wilhelmy method lately.[12] It has been shown that $\gamma = A - Bt$, where A and B are the empirical constants, and t is the temperature in °C. Table III exhibits the data of these constants for eight PS samples characterized by M_n. However, the γ data reported by Lau and Burns[17] are significantly higher than those selected in Table III by $\sim 6\%$ and, hence, not included herein.

The primary data on γ are computed from the equations in Table III for the eight samples at 120, 148, 176, and 200°C. Hence, a total of 32 data points are available to assess the model parameter Q. It turns out that $Q = 0.291$ and 0.241 for the FOV and CEM models, respectively. Incidently, Patterson and Rastogi[4] have cited $Q = 0.290$ for the former model based on the relevant data obtained from a series of normal alkanes, polyethylene, and selected dimethylsiloxane oligomers. The constants in eq. (7) are then

Table V   Comparison of the Predictive Powers on γ of PS of the Two CSP-cum-Equation-of-State Models at Various Temperatures

| Model | σ_γ/mN m^{-1} | | | |
	120°C	148°C	176°C	200°C
CFOV	0.48	0.32	0.38	0.50
CCEM	0.74	0.54	1.18	1.74

Table VI   Coefficients and Related Parameters of eq. (16) and Other Polynomials for PS at Various Temperatures

Coefficient/ Parameter	t/°C			
	120°C	148°C	176°C	200°C
$\beta_1 \times 10^{-2}$	−1.024	−1.145	−1.290	−1.422
$\beta_2 \times 10^{-3}$	−3.117	−1.253	1.225	3.708
$\beta_3 \times 10^{-6}$	1.049	0.991	0.870	0.707
$\lvert\theta\rvert$ [a]	0.044	0.016	0.014	0.037
$\lvert\theta'\rvert$ [a]	1.27	0.97	0.68	0.47
$\lvert\theta''\rvert$ [a]	0.098	0.077	0.056	0.039

[a] Based on $M_n = 700$.

resolved, resulting in κ and m respectively equal to 0.241 and 3.88 for FOV, 0.182 and 5.67 for the CEM model. Substituting these two pairs of values into eq. (15) yields respectively $\gamma_\infty = 69.10 (v^*_\infty/v_\infty)^{3.88}$ and $\gamma_\infty = 54.45 (v^*_\infty/v_\infty)^{5.67}$ mN m^{-1}, which are T dependent. The results on γ_∞ thus obtained are shown in Table IV., which also includes the corresponding γ_∞s derived from the data given in Table III. In the present exercise, the reliability of a theoretical model is conveniently assessed by the average deviation between the estimated and measured variables designated by σ and defined in Table IV. On this basis, Table IV indicates that the CSP-cum-FOV (CFOV) method is convincingly more dependable in predicting the γ_∞ values than the CSP-cum-CEM (CCEM) method, which registers a disagreeably large $\sigma_\infty = 1.25$ mNm^{-1}.

Using eq. (14), the CFOV model results in the linear relationships between γ and M_n^{-1} shown in Figure 1, where the measured γs are also displayed. Again, the discrepancy between the theoretical and experimental γs is monitored in terms of the σ of γ, σ_γ, in Table V. It is observed that the CFOV model offers the acceptable estimates of γ in the sense that the σ_Y does not exceed 0.50 mNm^{-1} in any case. However, the CCEM theory seems to yield erratic results, particularly at high temperatures. Apparently eq. (14) would be less reliable at the temperatures near the lower and upper limits of their valid range cited in Table I, due to the increasing errors in the reduction parameters. Perhaps a more serious defect of the CCEM model is its rather unrealistic Q, which is smaller than the critical Q (= 0.250) for the hexagonal close packing. Hence, it is inappropriate for the present system of interest and will not be recalled again for the ensuing analysis.

Table VI includes the values of the coefficients β_1, β_2, and β_3, from which the parameters θ, θ', and θ'' are computed via eqs. (17)–(19). The performance of eqs. (1), (2), and (22), which are the

Table VII   Results on the Linear Least-Squares Regression Analyses Pertaining to the Predicted γs for PS Based on the CFOV Model

Equation	Parameter	t/°C			
		120°C	148°C	176°C	200°C
(1)	γ_∞/mN m^{-1}	34.36	32.31	30.12	28.41
	$k_1 \times 10^{-2}$/				
	mN m^{-1} g$^{2/3}$ mol$^{-2/3}$	3.93 (3.32)[b]	3.97 (3.57)[b]	3.96 (3.92)[b]	4.31 (4.27)[b]
	$\lvert r_c\rvert$ [a]	0.9817	0.9597	0.9618	0.9850
(2)	γ_∞/mN m^{-1}	34.01	31.86	29.74	27.97
	k_2/mN$^{1/4}$				
	$m^{-1/4}$ g mol^{-1}	67 (62)[c]	73 (68)[c]	78 (75)[c]	85 (82)[c]
	$\lvert r_c\rvert$ [a]	0.9996	0.9997	0.9998	0.9998
(22)	γ_∞/mN m^{-1}	33.99	31.83	29.71	27.93
	$k_3 \times 10^{-3}$/				
	mNm^{-1} g mol^{-1}	3.55 (3.48)[d]	3.67 (3.64)[d]	3.74 (3.83)[d]	3.82 (3.97)[d]
	$\lvert r_c\rvert$ [a]	0.9999	0.9998	0.9999	0.9998

[a] Correlation coefficient.
[b] Computed by eq. (20).
[c] Computed by eq. (21).
[d] Computed by eq. (22a).

simplified versions of eq. (14) under different conditions, is shown in Table VII. Herein, the foregoing linear equations are applied to fit the estimates of γ accessible from eq. (14). The results on θ, θ', and θ'' in Table VI imply that eqs. (2) and (22) but not eq. (1) are valid for PS. This is substantiated by the linear plots exhibited in Figure 1, and the correlation coefficient $|r_c|$ cited in Table VII. In addition, the σ_∞s for the predictions of γ_∞ from eqs. (1), (2), and (22) are respectively found to be 0.51, 0.15, and 0.16 mNm^{-1}. However, their respective slopes are reasonably reproduced by eqs. (20), (21), and (22a).

Equation (1) is applicable for poly(dimethyl siloxane) and other polymers, as demonstrated elsewhere.[10,11] This is possible if the third power term of eq. (16) is discernible, indicating the irreconcilability of eqs. (1) and (22). Incidentally, the experimental data of γ have been applied to construct the linear plots according to eqs. (1) and (2) to obtain, respectively, $\gamma_\infty = 30.0$ mNm^{-1}, $k_1 = 373$ mNm^{-1} g$^{2/3}$ mol$^{-2/3}$, and $\gamma_\infty = 29.5$ mNm^{-1}, $k_2 = 75$ mNm^{-1} g mol^{-1} for PS at 176°C.[1] These findings are consistent with the corresponding estimates of CFOV cited in Table VII. However, an early work of Patterson et al. has cited $\gamma_\infty = \sim 33.8$ mNm^{-1} and $k = \sim 550$ mNm^{-1} g$^{2/3}$ mol$^{-2/3}$ for the same system, using the CFOV approach without considering the M effects on the P^* and T^*. This means that the coefficients of M_n^{-1} pertaining to eq. (14) play the crucial role for the present analysis.

Combining the foregoing classical and CSP models for the γ of polymers would facilitate the estimation of γ_e. For example, eqs. (4) and (21) result in $\gamma_e = 17.6$ mNm^{-1} for PS at 148°C by taking $m_r = 104$ and $v_e = v_r$.

In conclusion, eqs. (2) and (22) outperform eq. (1) in depicting the scaling behavior of surface tension with molecular weight for polystyrene melts. All these correlation equations are interpretable in terms of the corresponding states principle-cum-FOV equation-of-state theory. As a result, the surface tensions of polymers may be predicted from the pertinent equation-of-state parameters.

REFERENCES

1. S. Wu, *Polymer Interface and Adhesion,* Marcel Dekker, Inc., New York, 1982.
2. S. Jalbert, J. T. Koberstein, I. Yilgor, P. Gallagher, and V. Krukonis, *Macromolecules,* **26,** 3069 (1993).
3. S. Wu, in *Polymer Blends,* vol. 1, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978, p. 243.
4. D. Patterson and A. K. Rastogi, *J. Phys. Chem.,* **5,** 1067 (1970).
5. K. S. Siow and D. Patterson, *Macromolecules,* **4,** 26 (1971).
6. M. R. Spiegel, *Schaum's Outline of Theory and Problems of Probability and Statistics,* McGraw-Hill Book Company, New York, 1975.
7. T. Qugizawa, G. T. Dee, and D. J. Walsh, *Polymer,* **30,** 1675 (1989).
8. P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.,* **86,** 3507 (1964).
9. I. Prigogine, A. Bellemans, and A. Mathot, *The Molecular Theory of Solutions,* North-Holland, Amsterdam, 1957.
10. S. K. Kuma, M. Vacatello, and D. Y. Yoon, *Macromolecules,* **23,** 2189 (1990).
11. B. B. Sauer and G. T. Dee, *Macromolecules,* **24,** 2124 (1991).
12. G. T. Dee and B. B. Sauer, *J. Colloid Interface Sci.,* **152,** 85 (1992).
13. P. A. Rodgers, *J. Appl. Polym. Sci.,* **48,** 1061 (1993).
14. H. Hocker, G. J. Blake, and P. J. Flory, *Trans. Faraday Soc.,* **67,** 2251 (1971).
15. G. T. Dee and D. J. Walsh, *Macromolecules,* **21,** 811 (1988).
16. G. W. Bender and G. L. Gaines, Jr., *Macromolecules,* **3,** 128 (1970).
17. W. W. Y. Lau and C. M. Burns, *J. Polym. Sci., Polym. Phys. Ed.,* **12,** 431 (1974).