

Influence of Temperature, Molecular Weight, and Molecular Weight Dispersity on the Surface Tension of Polystyrene, Polypropylene, and Polyethylene.

II. Theoretical

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ABSTRACT: Experimental data for the surface tension of polystyrenes of different molecular weights (3400–200,000) and different molecular weight dispersities (1–3) and of different polyolefins are compared with the predictions of the Patterson–Rastogi and Dee–Sauer cell theories, which infer the surface tension from pressure–volume–temperature (PVT) data. PVT data for these polymers were obtained from the literature and experimentally and are fitted to the Flory–Orwoll–Vrij equation of state. Both theories predict that the surface tension will decrease linearly with increasing temperature and increase with molecular weight, thereby corroborating the experimental data. However, both theories underestimate the entropy change in the surface formation per unit area at a constant volume for low molecular weight and polydisperse systems and underestimate the effect of molecular weight dispersity on surface tension. Both theories feature two parameters, m and b , that quantify the enthalpic and entropic contributions to surface tension. The theoretical predictions are fitted to the experimental data for monodisperse polystyrene (with a molecular weight above the molecular weight of entanglement), polypropylene, and linear low-density polyethylene to quantify the enthalpic contribution to surface tension. b is then evaluated as a function of molecular weight and molecular weight dispersity and is found to decrease with increasing molecular weight and to increase with increasing molecular weight dispersity, showing that end-group excess at the surface has some effect on surface tension. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2201–2212, 2002

Key words: surface tension; polystyrene; polyethylene; polypropylene

INTRODUCTION

Knowledge of the surface tension of molten polymers is very important for plastics, inks,

films, textiles, and adhesion technology. However, very little experimental evidence concerning the surface tension of molten polymers has been published because of experimental difficulties encountered in the determination of this parameter.

Therefore, it would be interesting to be able to predict theoretically the surface tension of molten polymers.^{1–11} Several thermodynamic theories have been developed for that purpose. They basically can be divided into two groups: (1) theories based on the square-gradient theory first developed by Cahn and Hilliard that correlates the

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surface free energy to the density and square gradient of the density profile at the surface^{2-6,9,11} and (2) cell model theories that rely on the fact that surface tension follows a principle of corresponding states.^{1-2,7-10} The latter theories correlate the reduced surface tension, $\tilde{\gamma} = \gamma/\gamma^*$, to reduced parameters for pressure, $\tilde{P} = P/P^*$, volume, $\tilde{V} = \nu/\nu^*$, and temperature, $\tilde{T} = T/T^*$, where γ , P , ν , and T are the surface tension, pressure, specific volume, and temperature of the system, respectively. The asterisked quantities, reduction parameters, represent the hard-core values. The reduced parameters for pressure, volume, and temperature can be obtained from experimental pressure–volume–temperature (PVT) data via an equation of state.

Roe¹² and Patterson and Rastogi⁸ demonstrated the existence of a corresponding-state principle for the surface tension of small-molecule liquids and several polymers. They observed the existence of a universal curve when plotting the reduced surface tension as a function of reduced temperature for all these materials. The reduced surface tension was defined by Patterson and Rastogi as:

$$\tilde{\gamma} = \frac{\gamma}{\gamma^*} = \frac{\gamma}{(k/\alpha)^{1/3}\beta^{2/3}} \quad (1)$$

where $\tilde{\gamma}$ and γ^* are the reduced and reduction surface tension, γ is the measured surface tension, k is Boltzmann's constant, α is the thermal expansivity, and β is the isothermal compressibility. The reduced temperature is defined as αT .

In their study, Patterson and Rastogi⁸ used values of the surface tension and PVT data from different sources in the literature and observed a scatter of 7% about the universal curve. To study a possible deviation from universal scaling within a group of molecules with similar chemical structures but different molecular weights and architectures, Dee and Sauer^{1,2} used more accurate PVT and surface-tension data (available because of the development of new experimental methods) and generated a universal curve within each polymer series.

The existence of a corresponding-state principle enabled Patterson and Rastogi⁸ and Dee and Sauer^{1,2} to use a cell formalism to generate an equation to predict the reduced surface tension of a polymer as a function of the thermodynamic properties of that polymer. In both theories, a lattice of cells is thought to generate a partition

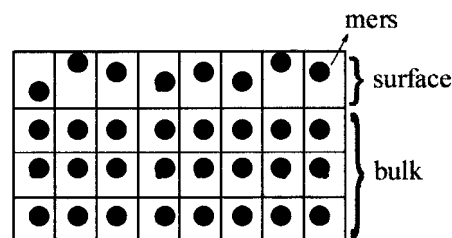


Figure 1 Cross section showing a cubic lattice model of a condensed state with a free surface at the top.

function that is used to calculate the free energy of the inhomogeneous system with a free surface, which is directly related to the surface tension of the system. An expression of the surface tension as a function of microscopic parameters is then obtained. The lattice considered has been described in detail in several references¹⁻³ and is based on the formalism developed by Lennard-Jones and Devonshire¹³ to describe the properties of small-molecule liquids. Figure 1 shows a two-dimensional cross section of the lattice considered in both models. Each black ball represents a polymer segment or mer that is allowed to wander within the walls of its own cell but not between cells. The connectivity of the polymer is taken into account with the assumption that each mer has $3c$ (where c is a constant smaller than 1) degrees of freedom. Each polymer segment has a hard-core volume ν^* . The volume unoccupied by the polymer segments corresponds to the free volume. In Figure 1, we see that the lattice can be divided into two zones, the bulk and the surface, and that the free volume associated with each segment differs with the location of the mer at the surface or in the bulk. To relate the microscopic parameter of the model to the properties of real systems, we use the Flory–Orwoll–Vrij¹⁴ equation of state in this article.

Table I presents the expressions for reduced surface tension generated for both Patterson and Rastogi's⁸ and Dee and Sauer's^{1,2} theories. For both theories, the first term on the right-hand side of the equation [eqs. (2a) and (2b)] represents the enthalpic contribution to the surface tension, which is a function of the cohesive energy between the polymers, which in turn is independent of the molecular weight and molecular weight dispersity. The second term on the right-hand side of the equation [eqs. (2a) and (2b)] is a function of the ratio between the free volume at the surface and the free volume in the bulk. It represents the entropic contribution to surface tension.

Table I Expressions of Reduced Surface Tension for Patterson and Rastogi and Dee and Sauer's Theories

Patterson and Rastogi	Dee and Sauer
$\tilde{\gamma} = \frac{m}{\tilde{V}^{5/3}} - \frac{(1 - \tilde{V}^{-1/3})}{\tilde{V}^{5/3}} \ln \left[\frac{(\tilde{V}^{1/3} - 0.5b_{PR})}{(\tilde{V}^{1/3} - b_{PR})} \right] \quad (2a)$	$\tilde{\gamma} = \frac{\gamma}{\gamma^*} = \frac{m}{\tilde{V}^{5/3}} - \frac{\tilde{T}}{\tilde{V}^{2/3}} \ln \left[\frac{(b_{DS}\tilde{V}^{1/3})}{(\tilde{V}^{1/3} - 1)} \right] \quad (2b)$

$$\text{With } \tilde{\gamma} = \frac{\gamma}{\gamma^*} = \frac{\gamma}{P^{*2/3}T^{*1/3}(kc)^{1/3}} \quad (3)$$

Both theories feature three parameters, b , c , and m , which correspond to a packing factor, a lattice parameter representing the number of degrees of freedom of the mer in the lattice, and the number of nearest neighbors lost during diffusion from the bulk to the interface. The packing factors for the theories, b_{PR} and b_{DS} , differ in their definitions. For Patterson and Rastogi, b_{PR} is related to the potential used to model the interaction between the mers. Depending on the formalism used for the potential, b can be equal to 0.89 or 1. For Dee and Sauer, b_{DS} is a parameter that correlates the free volume of the mers of the surface layer to the free volume of the mers in the bulk. b_{DS} can be related to an interfacial layer thickness ϕ as follows:

$$b_{DS} = \frac{\phi}{(\nu^*\tilde{V})^{1/3}} \quad (4)$$

where ν^* is the mer hard-core volume.

Fitting their universal curve of $\tilde{\gamma} = f(\alpha T)$, Patterson and Rastogi⁸ found that m ranged from 0.25 to 0.52, depending on the form of the potential chosen to model the interaction between the mers. However, they recommended $m = 0.25$ because other values would lead to lower values of surface energy and entropy. Dee and Sauer^{1,2} fitted their theories to experimental data generated for various polymers to find the best values of m and b . In their theoretical predictions, they chose a value of c (0.11) such that the hard-core volume was of the order of the dimension of the chemical unit of polyethylene (PE).³ The values of b and m that produce the best fit to the experimental data are about 2 and 0.52, respectively. Because ν^* , the mer hard-core volume, has a volume close to the volume of the repeat unit, that is, a few angstroms, and \tilde{V} is about unity, they used eq. (4) to predict the interfacial dimension, which is about 10–15 Å.

These two theories relate surface tension to PVT data. Unfortunately, they have not yet been fully tested and compared with experimental data, especially with respect to the influence of the molecular weight and molecular weight dispersity on surface tension. It is interesting to evaluate these theories because PVT data are easily obtained because of developments in PVT apparatus^{15–17} and because of their mathematical simplicity in comparison with square-gradient theories. In this work, experimental data concerning the influence of temperature, molecular weight, and molecular weight dispersity on the surface tension of polystyrene (PS) and experimental data concerning the surface tension of linear low-density polyethylene (LLDPE) and isotactic polypropylene (iPP), as reported in part I of this series,¹⁸ are compared with the predictions of two cell model theories, those of Patterson and Rastogi⁸ and Dee and Sauer.^{1,2}

MATERIALS AND PROCEDURES

Materials

The influences of temperature, molecular weight, and molecular weight dispersity were studied experimentally for PS, polypropylene (PP), and PE. The polymers used in the study included the following:

1. PS. Monodisperse samples were used with molecular weights ranging from 3000 to 700,000 g/mol.
2. PP. Two types of iPP were used: iPP₁ [number-average molecular weight (M_n) = 70,400 g/mol and $I = 4.17$] and iPP₂ ($M_n = 80,100$ g/mol and $I = 4.32$). The difference between the two samples was dependent on the presence of additives.

Table II Polymers Used in this Work

Polymer	M_n	$I = M_w/M_n$
PS _{mono} ^{2,000}	2,180	1.03
PS _{mono} ^{3,400}	3,400	1.09
PS _{mono} ^{12,400}	12,400	1.06
PS _{mono} ^{18,100}	18,100	1.07
PS _{poli3} ^{18,100}	18,100	1.14
PS _{poli5} ^{18,100}	18,100	1.55
PS _{poli7} ^{18,100}	18,100	2.68
PS _{mono} ^{29,100}	29,100	1.08
PS _{mono} ^{41,200}	41,200	1.07
PS _{mono} ^{107,200}	107,200	1.07
PS _{poli3} ^{107,200}	107,200	1.40
PS _{poli5} ^{107,200}	107,200	1.93
PS _{poli7} ^{107,200}	107,200	2.98
PS _{mono} ^{200,600}	200,600	1.11
PS _{mono} ^{339,500}	339,500	1.16
PS _{mono} ^{678,000}	678,000	1.12
iPP ₁	70,400	4.17
iPP ₂	80,100	4.32
LLDPE	91,800	4.42

3. LLDPE. The LLDPE was characterized by $M_n = 91,800$ g/mol and $I = 4.42$.

To study the effect of the molecular weight dispersity of PS on the surface tension of PS, we mixed monodisperse PS samples in different weight proportions to obtain PS samples with various polydispersities and constant values of M_n ($\approx 18,100$ and $\approx 107,200$ g/mol).

Table II provides details regarding the materials and their molecular characteristics for the sake of clarity in the remaining graphs and figures. Details of the polymer characterization and obtention of blends can be found elsewhere.¹⁸

Experimental Procedures

Surface Tension

The experimental results were obtained with a pendant drop apparatus described elsewhere.^{18–20} It consisted essentially of a heated sample holder in which the pendant drop was formed, an optical system to capture the image of the pendant drop, and a data acquisition system resident in a Pentium personal microcomputer to compute the surface tension from the drop profile. An automatic digitization procedure was used in our surface-tension measurement. The image of the pendant drop was digitized by a frame grabber resident in a personal microcomputer and

analyzed online for surface-tension measurements. The drop analysis of the experiments conducted here was done with algorithms based on the ones developed by Anastasiadis et al.²¹ (which are based on robust shape analysis). These algorithms and experimental procedures have been described elsewhere.¹⁹

PVT Data

The PVT data for the monodisperse PS were obtained from the literature,¹⁶ and the ones for the polyolefins were obtained with a dilatometer manufactured by Gnomix (Denver, CO). The data were measured in the isothermal mode. The measurements consisted of volumes being recorded along isotherms with increasing pressure from 10 to 200 MPa in increments of 10 MPa. A typical experiment started at room temperature under 10 MPa. The sample was then heated to the desired temperature. After temperature stabilization, around 20 min, the pressure was increased to 200 MPa in increments of 10 MPa. The holding time, which was the time for which the program paused at each pressure point requested, was set at a compromise value of 20 s, with a compromise between accuracy and thermal degradation taken into account. After 200 MPa was reached, the pressure was released, and the sample was heated to the next isotherm. The details of the apparatus and the different modes of operation were already described in 1976 by Zoller et al.¹⁵ and Capt and Kamal.²²

EXPERIMENTAL DATA

PVT Data

Figure 2 shows the PVT (volume–temperature) data for the iPP used in this work (iPP₁). The uncertainty of the results is 0.003 cm³/g.²² The PVT (volume–temperature) data for the other iPP (iPP₂) and PE followed the same type of behavior.

Surface-Tension Data

The following summary outlines relevant experimental results regarding the dependence of the surface tension on temperature, molecular weight, and molecular weight dispersity. The results are reported in greater detail in another article.¹⁸

For all the polymers, the surface tension decreased linearly with temperature. The tempera-

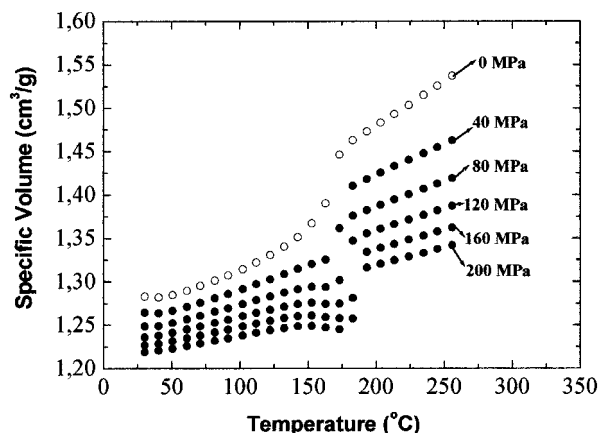


Figure 2 Volume versus temperature for PP₁. Values extrapolated to zero pressure are indicated by open circles.

ture coefficient $-\partial\gamma/\partial T$ (where γ is the surface tension and T is the temperature) increased when the molecular weight of the sample decreased and with increasing polydispersity. The surface tension of PS increased when the molecular weight was varied from 3400 to 41,200 g/mol. When the molecular weight of PS was further increased, the surface tension leveled off. The experimental results appeared to follow the following power-law relationship:

$$\gamma = \gamma_{\infty} - CM_n^{-z} \quad (5)$$

where γ is the surface tension and γ_{∞} , C , and z are constants. γ_{∞} refers to the limiting value of the surface tension for infinite molecular weight, and C reflects the dependence of the surface tension on molecular weight. For PS, z could be varied from 0.5 to 1 without the quality of the fit changing. The surface tension of PS decreased as a function of the molecular weight dispersity of PS when M_n was kept constant.

COMPARISON WITH THEORY

Obtention of Reduced and Reduction Parameters from PVT Data

To evaluate theoretically the surface tension of the different samples of PS, PE, and PP with the Patterson–Rastogi and Dee–Sauer theories, we had to evaluate the reduced volume and temperature and reduction temperature and pressure for those polymers. These parameters were allowed

to be a function of temperature and were correlated to the thermodynamic properties of the polymer with the Flory–Orwoll–Vrij equation of state according to the procedures adopted by Dee and Sauer.³ In the first step, the PVT data were extrapolated to atmospheric pressure with polynomial expressions. $\alpha = -(\partial \ln V / \partial T)$ was then inferred for atmospheric pressure for temperatures ranging from 180 to 220°C. \tilde{T} , \tilde{V} , T^* , and P^* were then obtained from¹⁴

$$\tilde{V} = \frac{v_{sp}}{v_{sp}^*} = \left[\frac{1 + T\alpha}{1 + 4T\alpha/3} \right]^{-3} \quad (6a)$$

$$\tilde{P} = P/P^* = P/(\tilde{V}^2 T \alpha / \beta) = P/(\tilde{V}^2 T \lambda) \quad (6b)$$

$$\tilde{T} = T/T^* = T\tilde{V}^{4/3}/(\tilde{V}^{1/3} - 1) \quad (6c)$$

where $\alpha = \partial \ln V / \partial T|_P$ is the thermal expansion coefficient, $\lambda = \partial p / \partial T|_v$ is the thermal pressure coefficient, and $\beta = -\partial \ln V / \partial p|_T$ is the isothermal compressibility. The values of β were found with $\ln V = f(P)$ fit to a straight line at a constant temperature for pressures ranging from 0 to 40 MPa.

To infer the reduced and reduction parameters of the polydisperse PS, we used a simple law of additivity, following Dee et al.,²³ and we assumed that

$$\tilde{V} = \sum x_i \tilde{V}_i \quad (7a)$$

$$\tilde{T} = \sum x_i \tilde{T}_i \quad (7b)$$

$$T^* = \sum x_i T_i^* \quad (7c)$$

$$P^* = \sum x_i P_i^* \quad (7d)$$

where P^* and T^* and \tilde{T} and \tilde{V} are the reduction and reduced parameters of the multicomponent system, respectively; \tilde{V}_i and \tilde{T}_i and P_i^* and T_i^* are the reduced and reduction parameters of the i th species, respectively; and x_i is the molar fraction of the i th species.

Tables III–VIII show the values of α and β , the reduced and reduction parameters for the different samples of PS, PP, and PE, respectively.

Does Surface Tension Follow the Corresponding-State Principle?

Figure 3 shows the reduced surface tension as a function of reduced temperature according to Dee

Table III Equation of State Parameters for Monodisperse Polystyrene

Panel A: Thermal Expansion Coefficient			
M_n	α (K ⁻¹)		
PS _{mono} ^{2,180}	6.664 × 10 ⁻⁴		
PS _{mono} ^{3,400}	6.549 × 10 ⁻⁴		
PS _{mono} ^{12,400}	6.226 × 10 ⁻⁴		
PS _{mono} ^{18,100}	6.134 × 10 ⁻⁴		
PS _{mono} ^{29,100}	6.021 × 10 ⁻⁴		
PS _{mono} ^{41,200}	5.940 × 10 ⁻⁴		
PS _{mono} ^{107,200}	5.722 × 10 ⁻⁴		
PS _{mono} ^{200,600}	5.584 × 10 ⁻⁴		
PS _{mono} ^{340,000}	5.470 × 10 ⁻⁴		
PS _{mono} ^{678,000}	5.324 × 10 ⁻⁴		

Panel B: Isothermal Compressibility β (MPa ⁻¹)			
M_n	180°C	200°C	220°C
PS _{mono} ^{2,180}	7.064 × 10 ⁻⁴	7.730 × 10 ⁻⁴	8.042 × 10 ⁻⁴
PS _{mono} ^{3,400}	6.966 × 10 ⁻⁴	7.615 × 10 ⁻⁴	8.300 × 10 ⁻⁴
PS _{mono} ^{12,400}	6.688 × 10 ⁻⁴	7.292 × 10 ⁻⁴	7.930 × 10 ⁻⁴
PS _{mono} ^{18,100}	6.609 × 10 ⁻⁴	7.201 × 10 ⁻⁴	7.830 × 10 ⁻⁴
PS _{mono} ^{29,100}	6.511 × 10 ⁻⁴	7.087 × 10 ⁻⁴	7.700 × 10 ⁻⁴
PS _{mono} ^{41,200}	6.440 × 10 ⁻⁴	7.005 × 10 ⁻⁴	7.610 × 10 ⁻⁴
PS _{mono} ^{107,200}	6.249 × 10 ⁻⁴	6.784 × 10 ⁻⁴	7.360 × 10 ⁻⁴
PS _{mono} ^{200,600}	6.127 × 10 ⁻⁴	6.643 × 10 ⁻⁴	7.200 × 10 ⁻⁴
PS _{mono} ^{340,000}	6.026 × 10 ⁻⁴	6.527 × 10 ⁻⁴	7.070 × 10 ⁻⁴
PS _{mono} ^{678,000}	5.896 × 10 ⁻⁴	6.378 × 10 ⁻⁴	6.900 × 10 ⁻⁴

Panel C: Reduction Parameters at a Temperature of 453 K			
M_n	T^* (K)	P^* (MPa)	V^* (cm ³ /g)
PS _{mono} ^{2,180}	7971	668	0.8504
PS _{mono} ^{3,400}	8048	662	0.8487
PS _{mono} ^{12,400}	8279	645	0.8440
PS _{mono} ^{18,100}	8349	640	0.8425
PS _{mono} ^{29,100}	8438	634	0.8407
PS _{mono} ^{41,200}	8505	629	0.8394
PS _{mono} ^{107,200}	8693	618	0.8357
PS _{mono} ^{200,600}	8820	610	0.8332
PS _{mono} ^{340,000}	8930	604	0.8311
PS _{mono} ^{678,000}	9078	596	0.8282

Panel D: Reduction Parameters at a Temperature of 473 K			
M_n	T^* (K)	P^* (MPa)	V^* (cm ³ /g)
PS _{mono} ^{2,180}	8130	647	0.8551
PS _{mono} ^{3,400}	8207	641	0.8533
PS _{mono} ^{12,400}	8437	626	0.8482
PS _{mono} ^{18,100}	8507	622	0.8467
PS _{mono} ^{29,100}	8596	616	0.8448
PS _{mono} ^{41,200}	8663	613	0.8434
PS _{mono} ^{107,200}	8850	602	0.8394
PS _{mono} ^{200,600}	8978	595	0.8368
PS _{mono} ^{340,000}	9087	590	0.8345
PS _{mono} ^{678,000}	9234	583	0.8316

Table III *Continued*

Panel D: Reduction Parameters at a Temperature of 473 K			
M_n	T^* (K)	P^* (MPa)	V^* (cm ³ /g)
PS _{mono} ^{2,180}	8130	647	0.8551
PS _{mono} ^{3,400}	8207	641	0.8533
PS _{mono} ^{12,400}	8437	626	0.8482
PS _{mono} ^{18,100}	8507	622	0.8467
PS _{mono} ^{29,100}	8596	616	0.8448
PS _{mono} ^{41,200}	8663	613	0.8434
PS _{mono} ^{107,200}	8850	602	0.8394
PS _{mono} ^{200,600}	8978	595	0.8368
PS _{mono} ^{340,000}	9087	590	0.8345
PS _{mono} ^{678,000}	9234	583	0.8316

Panel E: Reduction Parameters at a Temperature of 493 K			
M_n	T^* (K)	P^* (MPa)	V^* (cm ³ /g)
PS _{mono} ^{2,180}	8290	627	0.8599
PS _{mono} ^{3,400}	8366	622	0.8580
PS _{mono} ^{12,400}	8596	608	0.8526
PS _{mono} ^{18,100}	8666	604	0.8510
PS _{mono} ^{29,100}	8755	599	0.8490
PS _{mono} ^{41,200}	8821	596	0.8474
PS _{mono} ^{107,200}	9008	586	0.8433
PS _{mono} ^{200,600}	9135	580	0.8405
PS _{mono} ^{340,000}	9244	575	0.8381
PS _{mono} ^{678,000}	9391	568	0.8350

and Sauer¹ for all the polymers studied in this work, PS and polyolefins. Figure 3(b) is an amplification of Figure 3(a), showing the reduced surface tension as a function of reduced temperature for different types of monodisperse PS with molecular weights ranging from 3100 to 210,000 g/mol and the different polydisperse samples of PS studied here (see Table I). The data presented in Figure 3(a,b) seem to collapse on a universal curve [the scatter in Fig. 3(a) is $\pm 11\%$ and in Fig. 4(b) is $\pm 8\%$], showing the existence of an approximate corresponding-state principle for both oligomers and polymers. It seems from Figure 3(b) that the largest deviation, although small, is observed for the polydisperse samples. However, the deviations observed could be due to experimental imprecision in the surface-tension determination and due to the extrapolation of PVT data for the polydisperse sample [see eq. (7)].

The apparent existence of corresponding states implies that the surface tension of oligomers and polymers can be described equally well with their thermodynamic properties and that cell theories

can be used to predict the surface tension of polymers. Below our experimental data are compared the predictions of the Patterson–Rastogi and Dee–Sauer theories.

Comparison with Different Cell Theories

The experimental data presented in part I of this series were compared with the theoretical prediction of the Patterson–Rastogi and Dee–Sauer theories [eqs. 2(a) and 2(b), respectively]. The values of \tilde{V} , P^* , and T^* necessary for the calculations were inferred from Tables IV–VIII. The values of m , c , and b taken in the calculations were 0.25, 1, and 1 and 0.52, 1, and 2, respectively, according to the recommendations of Patterson and Rastogi and Dee and Sauer, respectively.

Figure 4(a,b) shows a comparison of the experimental data and theoretical predictions for the influence of temperature on the surface tension of two types of PS and both samples of PP. Figures 5 and 6 show the same comparisons for the influence of molecular weight and molecular weight

Table IV Equation of State Parameters for Polydisperse PS with a Molecular Weight of 18,100

Panel A: Reduction Parameters at a Temperature of 453 K			
PS 18100	T^* (K)	P^* (MPa)	V^* (cm ³ /g)
PS _{poli3} ^{18,100}	8337	641	0.8428
PS _{poli5} ^{18,100}	8287	645	0.8438
PS _{poli7} ^{18,100}	8226	649	0.8452
Panel B: Reduction Parameters at a Temperature of 473 K			
PS 18100	T^* (K)	P^* (MPa)	V^* (cm ³ /g)
PS _{poli3} ^{18,100}	8496	623	0.8470
PS _{poli5} ^{18,100}	8445	626	0.8481
PS _{poli7} ^{18,100}	8384	630	0.8496
Panel C: Reduction Parameters at a Temperature of 493 K			
PS 18100	T^* (K)	P^* (MPa)	V^* (cm ³ /g)
PS _{poli3} ^{18,100}	8654	605	0.8513
PS _{poli5} ^{18,100}	8604	608	0.8525
PS _{poli7} ^{18,100}	8544	612	0.8540

Table V Equation of State Parameters for Polydisperse PS with a Molecular Weight of 107,200

Panel A: Reduction Parameters at a Temperature of 453 K			
PS 107200	T^* (K)	P^* (MPa)	V^* (cm ³ /g)
PS _{poli3} ^{107,200}	8650	621	0.8365
PS _{poli5} ^{107,200}	8610	623	0.8378
PS _{poli7} ^{107,200}	8562	626	0.8384
Panel B: Reduction Parameters at a Temperature of 473 K			
PS 107200	T^* (K)	P^* (MPa)	V^* (cm ³ /g)
PS _{poli3} ^{107,200}	8807	605	0.8403
PS _{poli5} ^{107,200}	8768	607	0.8412
PS _{poli7} ^{107,200}	8720	610	0.8423
Panel C: Reduction Parameters at a Temperature of 493 K			
PS 107200	T^* (K)	P^* (MPa)	V^* (cm ³ /g)
PS _{poli3} ^{107,200}	8966	588	0.8442
PS _{poli5} ^{107,200}	8926	591	0.8451
PS _{poli7} ^{107,200}	8878	593	0.8463

dispersity. For the three figures, the different symbols represent the experimental data, and the lines represent the theoretical predictions.

It can be seen in Figures 4 and 5 that both the Patterson–Rastogi and Dee–Sauer theories predict that the surface tension of PS and PP decreases linearly with temperature and that the surface tension of PS increases with increasing molecular weight, corroborating the experimental results. However, Dee and Sauer's theory seems to overestimate surface tension, whereas Patterson and Rastogi's theory seems to underestimate surface tension. Similar behavior was observed for all the PS and polyolefin samples studied here. This discrepancy can be corrected by the adjustment of the parameters b and m inherent in the theory.

Table IX shows the coefficients obtained by the fitting of the theoretical predictions of surface tension as a function of temperature to a straight line for all the polymers studied here; a repre-

sents an extrapolation of the surface tension at 0°C and b represents $-\partial\gamma/\partial T$. The coefficients obtained by the fitting of the experimental data are reported in Table IX as well for the sake of comparison. It can be seen from Table IX that $-\partial\gamma/\partial T$ obtained theoretically corroborates with $-\partial\gamma/\partial T$ obtained experimentally for monodisperse PS with a molecular weight above the mo-

Table VI Reduction Parameters for PP₁

Temperature (K)	β (MPa ⁻¹)	T^* (K)	P^* (MPa)	V^* (cm ³ /g)
453	1.072×10^{-3}	6486	937	1.0623
463	1.082×10^{-3}	6569	926	1.0686
473	1.091×10^{-3}	6651	914	1.0750
483	1.157×10^{-3}	6734	903	1.0820
493	1.111×10^{-3}	6817	891	1.0881

$$\alpha = 1.018 \times 10^{-3} \text{ K}^{-1}.$$

Table VII Reduction Parameters for PP₂

Temperature (K)	β (MPa ⁻¹)	T^* (K)	P^* (MPa)	V^* (cm ³ /g)
453	1.212×10^{-3}	6154	831	1.0506
463	1.219×10^{-3}	6238	853	1.0581
473	1.227×10^{-3}	6321	872	1.0658
483	1.237×10^{-3}	6405	892	1.0736
493	1.244×10^{-3}	6489	912	1.0815

$$\alpha = 1.072 \times 10^{-3} \text{ K}^{-1}.$$

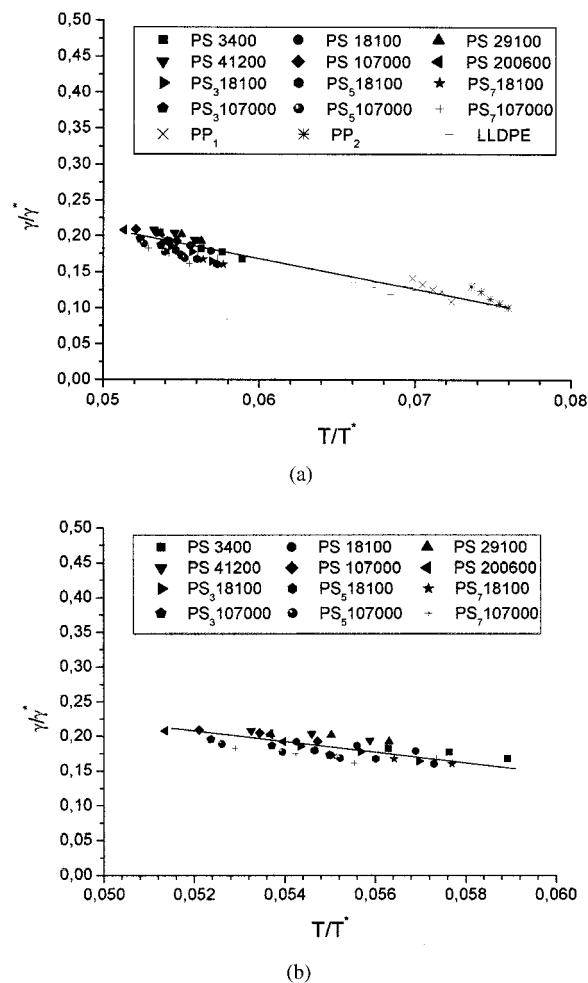
molecular weight of entanglement for PS. The two samples of PS with a molecular weight greater than 100,000 should not be considered because they suffered thermal degradation during surface-tension determination using the pendant drop method.¹⁸ This thermal degradation involved an increase in the polydispersity of the samples. It can be also seen from Table IX that the theoretical value of $-\partial\gamma/\partial T$ is constant as a function of molecular weight and as a function of molecular weight dispersity. This was not observed experimentally. The experimental value of $-\partial\gamma/\partial T$ increases with increasing polydispersity and decreases with increasing molecular weight. $-\partial\gamma/\partial T$ corresponds to the entropy change in surface formation (polymer air) per unit area at a constant volume. When the molecular weight decreases and the polydispersity increases, the conformation restrictions of the polymer decrease, increasing the entropy change in surface formation per unit area. It seems, therefore, that the theory is underestimating the entropy change in surface formation. The values of $-\partial\gamma/\partial T$ reported in Table IX for the polyolefins are smaller than the ones obtained experimentally. We believe that this is because the polyolefins samples were polydisperse and that the theory underestimates the entropy change in surface formation per unit area for polydisperse systems.

It has been shown experimentally that the surface tension of PS decreases with increasing poly-

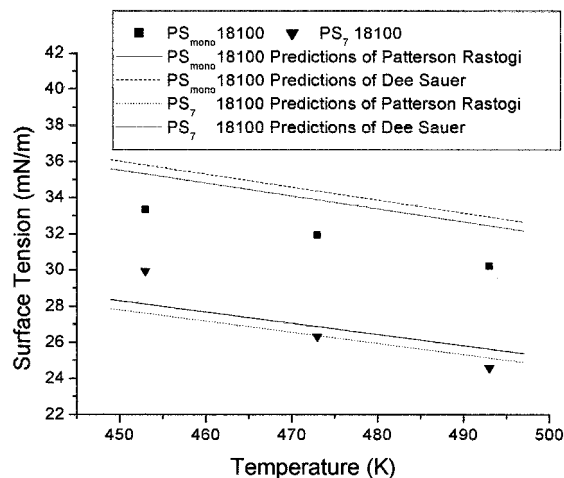
Table VIII Reduction Parameters for LLDPE

Temperature (K)	β (MPa ⁻¹)	T^* (K)	P^* (MPa)	V^* (cm ³ /g)
493	1.071×10^{-3}	7462	658	1.1330
513	1.147×10^{-3}	7626	642	1.1426
533	1.225×10^{-3}	7790	626	1.1525

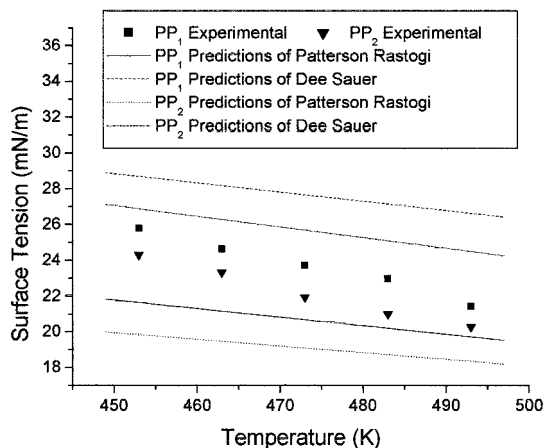
$$\alpha = 8.25 \times 10^{-4} \text{ K}^{-1}.$$

**Figure 3** Scaled surface tension versus reduced temperature for (a) all the polymers studied in this work and (b) the different types of PS studied in this work.

dispersity.¹⁸ For $M_n = 18,000$, the surface tension at 503 K decreased 18.7% when the polydispersity increased from 1.07 to 2.68. For $M_n = 107,200$, the surface tension at 503 K decreased 16% when the polydispersity increased from 1.07 to 2.98. It can be seen in Figure 6 that both cell theories predict that the surface tension will decrease linearly with increasing polydispersity, which is not the case experimentally. Also, the magnitude of the decrease in surface tension when the molecular weight dispersity increases is much lower theoretically than experimentally. The decrease in surface tension with increasing polydispersity is due to an increase in the entropy of surface formation when the molecular weight dispersity increases. Therefore, it seems once again from these results that the theory is underestimating the entropy of surface formation.



(a)



(b)

Figure 4 Surface tension versus temperature for (a) $PS_{mono}^{18,100}$ and $PS_{poly}^{18,100}$ and (b) PP_1 and PP_2 .

Because for both theories m is an adjustable parameter that quantifies the enthalpic part of surface tension, the theoretical predictions were fitted to the experimental data for monodisperse PS (with a molecular weight greater than the molecular weight of entanglement), PP, and LLDPE to find the best values of m , with b kept constant, so that the experimental and theoretical values of the surface tension would corroborate. The values of m for both theories are reported in Table X. If the end-group excess or depletion exhibits negligible effects on surface tension, with these values of m , the theories should corroborate the experimental data even for lower molecular weight and polydisperse samples. This was not the case. Therefore, in a second step, the theoretical predictions were fitted to the experimental

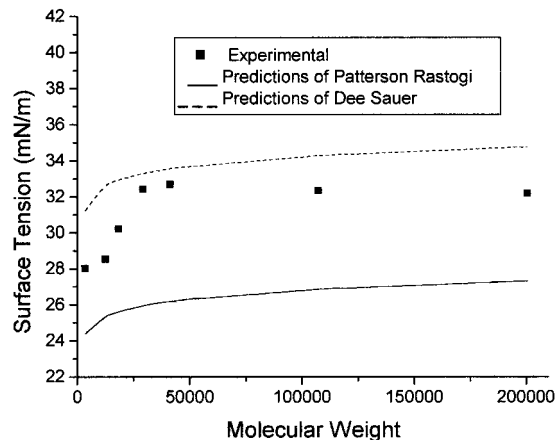


Figure 5 Surface tension versus molecular weight for PS.

data to find b for each type of polymer and temperature. b quantifies the entropic contribution to surface tension. This was not possible with the Patterson–Rastogi theory because b can only adopt two discrete values, 0.89 and 1. The values of b obtained are reported in Table XI. It can be seen from Table XI that b decreases with increasing molecular weight for molecular weights smaller than the molecular weight of entanglement for PS and that b increases with increasing polydispersity. In other words, the theoretical entropic contribution to surface tension should be a function of the number of end groups, which do not exhibit a negligible effect on surface tension. The effect of end groups on the surface tension of molten polymers was previously seen by Koberstein and coworkers,^{24,25} who studied the surface tension of poly(dimethyl siloxane) with modified

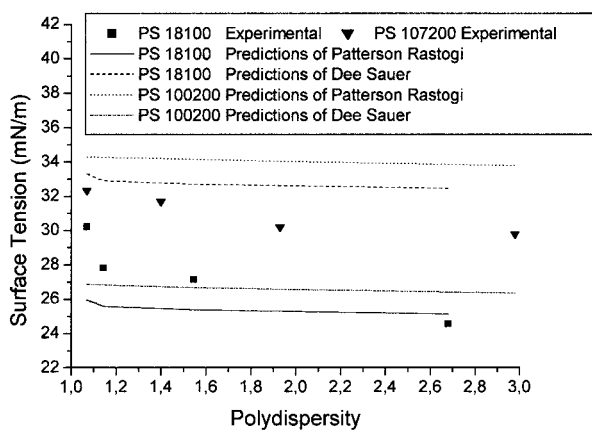


Figure 6 Surface tension versus polydispersity for PS.

Table IX Linear Regression Coefficients of the Dependence of Surface Tension on Temperature

Polymer	Experimental			Patterson–Rastogi Theory			Dee–Sauer Theory		
	<i>a</i>	<i>b</i>	<i>r</i> ²	<i>a</i>	<i>b</i>	<i>r</i> ²	<i>a</i>	<i>b</i>	<i>r</i> ²
PS _{3,400} _{mono}	49.17	0.0956	0.9940	56.3	0.0643	1.000	73	0.0845	0.998
PS _{12,400} _{mono}	45.42	0.0763	0.9851	56.0	0.0623	1.000	68.1	0.0720	1.000
PS _{18,100} _{mono}	47.42	0.0780	0.9965	56.2	0.0620	1.000	68.3	0.0718	1.000
PS _{29,100} _{mono}	47.44	0.0673	0.9161	56.5	0.0620	1.000	68.5	0.0715	1.000
PS _{41,200} _{mono}	47.22	0.065	0.9049	56.3	0.0610	1.000	68.1	0.0700	1.000
PS _{107,200} _{mono}	52.02	0.0885	0.9557	57.4	0.0620	1.000	69.0	0.0705	1.000
PS _{200,600} _{mono}	50.65	0.0833	0.9757	57.4	0.0610	1.000	68.8	0.0690	1.000
PS _{18,100} _{poli3}	52.18	0.1101	0.9878	56.1	0.0620	1.000	68.3	0.0718	1.000
PS _{18,100} _{poli5}	49.58	0.1026	0.9831	56.1	0.0623	1.000	68.3	0.0723	1.000
PS _{18,100} _{poli7}	53.70	0.1338	0.9602	55.6	0.0618	1.000	67.7	0.0715	1.000
PS _{107,200} _{poli3}	54.36	0.1145	0.9966	33.3	0.0090	0.999	68.1	0.0688	1.000
PS _{107,200} _{poli5}	50.80	0.1023	0.9980	32.0	0.0090	0.998	66.6	0.0666	1.000
PS _{107,200} _{poli7}	50.78	0.1065	0.9920	30.4	0.00825	0.999	64.9	0.0630	1.000
iPP ₁	44.46	0.1038	0.9935	33.6	0.0277	0.899	51.9	0.0513	0.985
iPP ₂	42.94	0.1039	0.9943	36.7	0.0373	0.979	54.1	0.0600	1.000
LLDPE	39.05	0.0725	0.9982	37.9	0.0360	0.999	47.1	0.0417	1.000

$$\gamma = a - bt \quad (a \text{ [dyn/cm]}; b \text{ [dyn/cm } ^\circ\text{C]}).$$

end groups very high in surface energy relative to the main chain. It can be also seen from Table XI that *b* increases with increasing temperature for all the polymers. Dee and Sauer suggested that *b* is related to an interfacial layer thickness according to eq. (4). Therefore, a comparison of the experimental data with the theoretical data seems

to indicate that this interfacial layer thickness is a function of the number of end groups and temperature and is increasing when the molecular weight decreases and the molecular weight dispersity increases.

Table X Values of *m*

Polymer	Patterson–Rastogi	Dee–Sauer
PS	0.27	0.51
PP	0.26	0.49
LLDPE	0.26	0.48

Table XI Values of *b*

Polymer	453 K	473 K	493 K
PS _{3,400} _{mono}	2.4	2.4	2.5
PS _{12,400} _{mono}	2.8	2.7	2.9
PS _{18,100} _{mono}	2.2	2.3	2.4
PS _{29,100} _{mono}	2.0	2.0	2.0
PS _{18,100} _{poli3}	2.7	2.8	3.2
PS _{18,100} _{poli5}	2.9	3.3	3.4
PS _{18,100} _{poli7}	3.2	4.3	4.5
PS _{107,200} _{poli3}	2.6	2.8	3.1
PS _{107,200} _{poli5}	3.0	3.3	3.4
PS _{107,200} _{poli7}	3.3	3.4	3.9

CONCLUSIONS

With the scaling of the measured surface tension with thermodynamic properties obtained from PVT measurements for PS (with molecular weights of 3400–200,000 and polydispersities of 1–3), PP, and LLDPE, a universal curve can be obtained within 11%. The existence of this universal curve demonstrated the existence of an approximate corresponding-state principle for surface tension. The apparent existence of corresponding states implies that the surface tension of the polymers studied here can be predicted by cell theories that relate the surface tension to PVT data. Therefore, the experimental data for the influence of temperature (for temperatures ranging from 180 to 220°C), molecular weight (for molecular weights ranging from 3400 to 200,000), and molecular weight dispersity (for molecular weight dispersities ranging from 1 to 3) were compared to the predictions of the Patterson–Rastogi and Dee–Sauer theories.

The Patterson–Rastogi and Dee–Sauer theories feature two adjustable parameters, b and m , that quantify the entropic and enthalpic contributions to surface tension. For the Patterson–Rastogi theory, b can adopt only two values, 0.89 and 1. Patterson and Rastogi⁸ and Dee and Sauer¹ reported that when fitting the universal curve to their cell theories, they found the best values of m and b to be 0.25 and 1 and 0.52 and 2, respectively, and that these values do not depend on the molecular weight of the samples. We showed that when these values of m and b were used to evaluate the surface tension from PVT data, both theories predicted that the surface tension of PS, PP, and LLDPE would decrease linearly with increasing temperature and increase with molecular weight, corroborating the trends observed in the experimental results. However, both theories underestimated the entropy change in surface formation per unit area at a constant volume for low molecular weight and polydisperse PS and underestimated the effect of molecular weight dispersity on surface tension. Moreover, the Patterson–Rastogi and Dee–Sauer theories underestimated and overestimated, respectively, the surface tension. Because m quantifies the enthalpic contribution to the surface tension, the experimental data for the surface tension of PS (for monodisperse PS of a molecular weight greater than the molecular weight of entanglement), PP and LLDPE were fitted to the theories to backcalculate m with b kept constant. These values of m did not result in good agreement between the experimental data and theoretical predictions for low molecular weight and polydisperse samples. For good agreement between the experimental data and theoretical predictions, b had to be a function of the number of end group because b increased with decreasing molecular weight and increasing polydispersity. In other words, the theories should be modified to take into account the nonnegligible effects of end-group excess or depletion at the surface on the surface tension.

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