Influence of Temperature, Molecular Weight, and Molecular Weight Dispersity on the Surface Tension of PS, PP, and PE. I. Experimental

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ABSTRACT: In this work, the influence of temperature, molecular weight ($\bar{M}_n$), and molecular weight dispersity (MWD) on the surface tension of polystyrene (PS) was evaluated using the pendant drop method. The influence of temperature on the surface tension of isotatic polypropylene (i-PP) and of linear low-density polyethylene (LLDPE) was also studied here. It was shown that surface tension decreases linearly with increasing temperature for all the polymers studied. The temperature coefficient $-d\gamma/dT$ (where γ is the surface tension, and T, the temperature) was shown to decrease with increasing molecular weight and to increase with increasing MWD. 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 was shown to level off. The surface tension was shown to decrease with increasing molecular weight distribution. Contact angles formed by drops of diiomethane and water on films of PS with different molecular weights were measured at 20°C. The surface energies of those polymers were then evaluated using the values of the different pairs of contact angles obtained here using two different models: the harmonic mean equation and the geometric mean equation. It was shown that the values of the surface energy obtained are slightly less than are the ones extrapolated from surface-tension measurements in the rubbery state. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1907–1920, 2001

Key words: surface; molar mass; molar mass distribution; polystyrene; polyolefins

INTRODUCTION

The surface tension of molten polymers has received much experimental and theoretical attention.[1–7] It is fundamental to adhesion, coating, wetting, dewetting, foaming, and blending. For example, it has been shown that the morphology of a polymer blend depends on the interfacial tension between its molten components, which, in turn, depends on the surface tension of the individual polymers[8]; the adhesion or coatability of a polymer on a solid substrate is a function of the surface tension of that polymer.[9] Unfortunately, research in the field of surface tension of molten polymers has been limited because of experimental difficulties encountered in its determination.[7] Only a few methods can be used to measure the surface tension of molten polymers, because of shortcomings of the experimental techniques (e.g., inability to ascertain equilibrium and long equilibration times that would exceed the time for the melt to undergo degradation).

In particular, despite its importance, the influence of polydispersity on the surface tension of polymers has not been studied extensively. To our knowledge, only four studies of the influence of polydispersity on the surface and interfacial tension have been reported to date.[5,10–13] In those studies, the results seemed to indicate that interfacial tension decreases with increasing polydispersity. In spite of all the effort spent to study the influence of molecular weight and polydispersity on the interfacial tension between polymers, the data are still scarce in the literature. Also, few data have been published regarding the correlations that exist between the surface tension of polymers in the glassy and rubbery states. It has been shown that for amorphous polymers $[(d\gamma)/(dT)]_g$ (in the glassy state), where γ is the surface tension and T is the temperature, is related to the $[(d\gamma)/(dT)]_r$ (in the rubbery state) by the following equation[7]:

$$\left(\frac{d\gamma}{dT}\right)_g = \frac{\alpha_g}{\alpha_r}\left(\frac{d\gamma}{dT}\right)_r \tag{1}$$

where α_g and α_r are the isobaric volumetric thermal expansion coefficients in the glassy region and the rubbery region, respectively.

In this work, the effect of temperature, molecular weight, and molecular weight dispersity (MWD) on the surface tension of molten polystyrene (PS), polyethylene (PE), and polypropylene (PP) was evaluated experimentally using the pendant drop method. The experimental results of the surface tension of PS in the rubbery state were extrapolated to room temperature and compared to the ones obtained at room temperature inferred from contact-angle measurements.

EXPERIMENTAL

Materials

PS, isotatic polypropylene (i-PP), and linear low-density polyethylene (LLDPE) were used in this work to study the influence of temperature, molecular weight, and MWD on the surface tension of polymers. The characteristics of the resins are reported in Table I.

The polymers used to evaluate the influence of temperature and molecular weight on the surface tension had the following characteristics:

Table I Materials Used in This Work

Polymer	$\bar{M}_n$	$I = \bar{M}_w/\bar{M}_n$
PS1	2180	1.09
PS2	3400	1.09
PS3	12,400	1.06
PS4	18,100	1.07
PS5	29,100	1.08
PS6	41,200	1.07
PS7	107,200	1.07
PS8	200,600	1.11
PS9	339,500	1.16
PS10	678,000	1.12
i-PP$_1$	70,400	4.17
i-PP$_2$	80,100	4.32
LLDPE	91,800	4.42

1. PS: Monodisperse samples with molecular weight ranging from 3000 to 700,000 g/mol were used in this study.
2. PP: Two types of isotatic PP were used:
   - i-PP1: with $\bar{M}_n$ = 70,400 g/mol and $\bar{M}_w/\bar{M}_n$ = 4.17
   - i-PP2: with $\bar{M}_n$ = 80,100 g/mol and $\bar{M}_w/\bar{M}_n$ = 4.32.

   The difference between the two samples relied in the presence of additives
3. LLDPE: An LLDPE with $\bar{M}_n$ = 91,800 g/mol with $\bar{M}_w/\bar{M}_n$ = 4.42 was studied here.

The molecular weights of the PS, i-PP, and LLDPE used in this work were obtained by gel permeation chromatography (GPC). The following procedures were used in the determination of the molecular weight by GPC: The PS samples were dissolved in tetrahydrofuran (THF) at 30°C and the i-PP and LLDPE samples were dissolved in trichlorobenzene (TCB) at 140°C. The equipment used was a GPC 150 C from Waters Inc. In both cases, the GPC columns were calibrated with standard polymers.

To study the effect of the MWD of PS on the surface tension of PS, monodisperse PS samples were mixed in different weight proportions to obtain PS samples with varying polydispersity and a constant number-average molecular weight ($\approx$18,100 and $\approx$107,200 g/mol). The polydisperse PS samples were prepared by solution blending to ensure proper mixing. The weighted proportions of the PS were mixed and dissolved in THF. After dissolution, the samples were allowed to dry in a vacuum oven at a temperature of 60°C for 72 h. It was checked by Fourier transform infrared spec-

Table II   Composition of Polydisperse PS for $\bar{M}_n$ = 18,100 g/mol

		Weight Ratio of the Different PS Used in the Blend						
Abbreviation	$I = \bar{M}_w/\bar{M}_n$	PS1	PS2	PS3	PS5	PS6	PS7	PS8
PS11	1.14	—	—	33.8	25.0	41.2	—	—
PS12	1.55	—	5.2	18.6	13.8	22.6	39.8	—
PS13	2.68	3.1	3.6	13.0	9.6	15.8	27.9	26.9

troscopy (FTIR) that such a procedure was adequate for complete removal of the solvent and lack of thermal degradation. The two molecular weights of PS ($\approx$18,100 and $\approx$107,200 g/mol) were chosen to study the effect of the MWD of PS on the surface tension below and above the molecular weight of entanglement. The polydispersities of the PS mixtures were calculated from the mixing ratios. Tables II and III list the composition, polydispersities, and abbreviations used for the polydisperse samples of PS with molecular weights of 18,100 and 107,200 g/mol, respectively.

Evaluation of Surface Tension in the Rubbery or Molten State

The surface tension in the rubbery or molten state of the polymers used in this work was measured with an apparatus based on the pendant drop method. The pendant drop method involves the determination of the profile of a pendant drop of one liquid at mechanical equilibrium. The profile of the drop is determined by a balance between gravity and surface forces. The equation of Bashforth and Adams,[14] which is based on Laplace's equation, relates the drop profile to the surface tension through a nonlinear differential equation which is given below:

$$\frac{1}{\frac{R_1}{a}} + \frac{\sin \Phi}{\frac{x}{a}} = B\frac{z}{a} + 2 \qquad (2)$$

where B is given by

$$B = \frac{a^2 g \rho}{\gamma} \qquad (3)$$

with

$$R_1 = \frac{ds}{d\Phi} = \frac{\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{3/2}}{\left(\frac{dz}{dx}\right)^2} \qquad (4)$$

$$\sin \Phi = \frac{\frac{dz}{dx}}{\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{1/2}} \qquad (5)$$

where ρ is the density of the liquid; g, the gravitational constant; γ, the surface tension; a, the radius of curvature at the apex of the drop; x, z, and Θ, the coordinates defined as in Figure 1; and R_1, the radius of curvature at the point with coordinates (x, z).

The apparatus used in this work was very similar to the one used by Demarquette and Kamal.[15] It consisted 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 PC Pentium microcomputer to compute the surface tension

Table III   Composition of Polydisperse PS for $\bar{M}_n$ = 107,200 g/mol

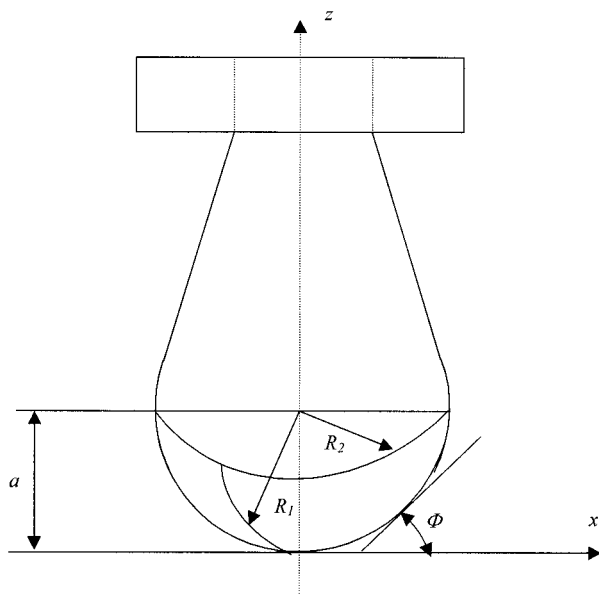|		Weight Ratio of the Different PS Used in the Blend						
Abbreviation	$I = \bar{M}_w/\bar{M}_n$	PS4	PS5	PS6	PS7	PS8	PS9	PS10
PS14	1.40	—	—	16.9	25	58.1	—	—
PS15	1.93	—	9.1	9.3	13.8	32.0	35.9	—
PS16	2.98	4.4	6.4	6.5	9.6	22.4	25.1	25.6

Figure 1 Pendant drop geometry.

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 PC microcomputer and analyzed online for surface-tension measurement. The drop analysis of the experiments conducted here was done using algorithms based on the ones developed by Anastasiadis et al.[16] (which are based on robust shape analysis). These algorithms were described elsewhere.[17] Other digitization procedures have been developed to measure the evolution of the contact angle and surface tension as a function of time.[18–24] They have been successfully used to study protein solutions[25] and polymer melts.[20,26]

Evaluation of Surface Energy in the Solid State

When a drop of a liquid rests on a solid surface, it forms an angle θ with the surface, called the contact angle. In thermodynamical equilibrium conditions, Young[27] showed that

$$\gamma_S = \gamma_{SL} + \gamma_{LV}\cos\theta \tag{6}$$

where γ_S is the surface energy of the solid; γ_{SL}, the interfacial tension between the solid and the liquid; and γ_{LV}, the surface tension of the liquid.

It was proposed by Wu[28] and it is widely accepted that the intermolecular energy between two materials results from the summation of a dispersion component and a polar component. Since surface tension is proportional to intermolecular energy, the surface tension, γ, itself can be considered as a sum of a dispersion component, γ^d, and a polar component γ^p.

The interfacial tension between a liquid and a solid polymer can then be evaluated either by the harmonic mean equation[28]:

$$\gamma_{SL} = \gamma_S + \gamma_{LV} - 4\left(\frac{\gamma_{LV}^d\gamma_S^d}{\gamma_{LV}^d + \gamma_S^d} + \frac{\gamma_{LV}^p\gamma_S^p}{\gamma_{LV}^p + \gamma_S^p}\right) \tag{7}$$

or the geometric mean equation[28]:

$$\gamma_{SL} = \gamma_S + \gamma_{LV} - 2[(\gamma_{LV}^d\gamma_S^d)^{1/2} + (\gamma_{LV}^p\gamma_S^p)^{1/2}] \tag{8}$$

where γ_S is the surface energy of the solid; γ_{SL} and γ_{LV}, the interfacial tension between the solid and the liquid and the surface tension of the liquid, respectively; γ_S^d and γ_S^S, the dispersion and polar components of the surface energy of the solid, respectively; and γ_{LV}^d and γ_{LV}^p, the disper-

Table IV Densities (g/cm³) of the Polymers Used in This Work

Polymer	180°C	190°C	200°C	210°C	220°C	240°C	260°C
PS2	0.9454	—	0.9338	—	0.9221	—	—
PS3	0.9586	—	0.9472	—	0.9357	—	—
PS4	0.9625	—	0.9511	—	0.9397	—	—
PS5	0.9674	—	0.9561	—	0.9448	—	—
PS6	0.9710	—	0.9598	—	0.9485	—	—
PS7	0.9810	—	0.9699	—	0.9588	—	—
PS8	0.9876	—	0.9766	—	0.9656	—	—
i-PP$_1$	0.6973	0.6902	0.6883	0.6763	0.6695	—	—
i-PP$_2$	0.6871	0.6792	0.6714	0.6636	0.6560	—	—
LLDPE	—	—	—	—	0.6693	0.6584	0.6476

Table V   Surface Energy (dyne/cm) of PS, i-PP, and LLDPE at 20°C Calculated with Harmonic and Geometric Mean Equations

Polymer	θ_{water} (degree)	$\theta_{diiodomethane}$ (degree)	$\gamma_{harmonic}$ (dyne/cm)	$\gamma_{geometric}$ (dyne/cm)
PS3	84.9 ± 4.0	22.4 ± 1.6	47.11	49.77
PS4	82.3 ± 2.6	20.1 ± 2.1	47.89	49.71
PS6	88.2 ± 3.9	26.8 ± 3.3	45.79	49.16
PS7	89.0 ± 1.3	25.1 ± 2.6	46.54	50.46
PS8	92.7 ± 2.7	23.9 ± 3.0	48.31	53.33
PS16	96.7 ± 1.9	30.1 ± 1.0	48.1	52.36
	(90.0 ± 0.5)[a]	(28.1 ± 0.5)[a]		
	(91)[a]	(35)[a]		
	(88.42 ± 0.28)[a]			
i-PP$_1$	92.7 ± 1.15	55.8 ± 4.16	32.7	31.7
i-PP$_2$	92.3 ± 1.1	50.1 ± 1.7	35.4	35.6
	(88.6 ± 0.7)[a]	(50.0)[a]		
	(100.3)[a]	(56.3)[a]		
LLDPE	96.7 ± 1.9	47.5 ± 3.7	36.6	37.2
	(100.3)[b]	(56)[b]		

[a] Ref. 29.
[b] Ref. 7.

sion and polar components of the surface tension of the liquid, respectively.

Using eq. (6), eqs. (7) and (8) transform in eqs. (9) and (10), respectively:

$$\gamma_{LV}(1 + \cos\theta) = 4\left(\frac{\gamma_{LV}^d \gamma_S^d}{\gamma_{LV}^d + \gamma_S^d} + \frac{\gamma_{LV}^p \gamma_S^p}{\gamma_{LV}^p + \gamma_S^p}\right) \quad (9)$$

$$\gamma_{LV}(1 + \cos\theta) = 2[(\gamma_{LV}^d \gamma_S^d)^{1/2} + (\gamma_{LV}^p \gamma_S^p)^{1/2}] \quad (10)$$

If the contact angles formed by drops of two liquids of known and γ^d and γ^p are measured, it is possible to solve eq. (9) (harmonic mean) or (10) (geometric mean) and infer γ_d^S and γ_p^S and, therefore, the surface energy of the solid.

To evaluate the surface energy of the polymers studied here in the solid state, contact angles formed by drops of diiodomethane and water on the surface of the solids polymers were measured.

Table VI   Surface Tension of PS in the Rubbery State

Polymer	$I = \bar{M}_w/\bar{M}_n$	Surface Tension (dyne/cm)		
		180°C	200°C	220°C
PS2	1.09	31.88 ± 0.2	30.22 ± 0.2	28.05 ± 0.2
PS3	1.06	31.59 ± 0.2	30.39 ± 0.2	28.54 ± 0.2
PS4	1.07	33.33 ± 0.1	31.93 ± 0.1	30.21 ± 0.1
PS5	1.08	35.10 ± 0.2	34.46 ± 0.2	32.14 ± 0.2
PS6	1.07	35.28 ± 0.1	34.71 ± 0.1	32.68 ± 0.1
PS7	1.07	35.87 ± 0.2	34.76 ± 0.2	32.33 ± 0.2
PS8	1.11	35.51 ± 0.2	34.30 ± 0.2	32.18 ± 0.2
PS11	1.14	32.22 ± 0.2	30.44 ± 0.1	27.82 ± 0.1
PS12	1.55	31.26 ± 0.1	28.74 ± 0.2	27.15 ± 0.1
PS13	2.68	29.93 ± 0.2	26.31 ± 0.1	24.58 ± 0.1
PS14	1.40	33.64 ± 0.1	31.68 ± 0.2	29.06 ± 0.1
PS15	1.93	32.47 ± 0.1	30.20 ± 0.1	28.38 ± 0.2
PS16	2.98	31.45 ± 0.1	29.79 ± 0.2	27.19 ± 0.1

Table VII   Surface Tension of i-PP in the Molten State

Polymer	$\bar{M}_n$	$I = \bar{M}_w/\bar{M}_n$	Surface Tension (dyne/cm)				
			180°C	190°C	200°C	210°C	220°C
i-PP$_1$	70,400	4.17	25.79 ± 0.1	24.62 ± 0.1	23.71 ± 0.1	22.96 ± 0.2	21.43 ± 0.1
i-PP$_2$	80,100	4.32	24.30 ± 0.1	23.32 ± 0.1	21.93 ± 0.2	20.99 ± 0.1	20.27 ± 0.1

It was shown previously[29] that this pair of liquids is adequate for surface-energy measurements of solid polymers. The values of the dispersion (γ^d) and the polar (γ^p) component of the surface tension for water and diiodomethane used in the calculation were 44.1 and 6.7 and 22.1 and 50.7, respectively. The contact angles made by the drops of liquids were measured using a Ramé–Hart contact-angle goniometer, Model 100-10. The experiments were performed at a temperature of 20°C.

RESULTS

Material Characterization: Density

To measure the surface tension of a liquid using the pendant drop method, it is necessary to know the density of the liquid. The densities of the polymers used here were inferred from PVT data published in the literature (PS)[30] and reported in the second part of this article (polyolefins). Table IV shows the values of the density of the polymers used in surface-tension calculations.

Surface Energy in the Solid State

Table V presents the values of contact angles formed by drops of diiodomethane and water on the solid surface of the polymers as well as the surface energy of PS, i-PP, and LLDPE in the solid state at 20°C evaluated using contact angle values.

Surface Tension in the Rubbery State or Molten State

The surface tension for the polymers PS, i-PP, and LLDPE in the rubbery or molten state was determined using drop profiles obtained experimentally using a pendant drop apparatus. The experimental results are presented in Tables VI–VIII.

DISCUSSION

Influence of Temperature

Figure 2 shows the surface tension of PS as a function temperature. For the sake of clarity of Figure 2, not all the data of the surface tension of PS were plotted here. They are all reported in Table VI. They were plotted only for five types of PS: three monodisperse samples with three different molecular weights and two polydisperse samples. The different symbols represent the experimental data for the different PS samples and the straight lines represent the best fit obtained by linear regression. It can be seen that for all PS samples studied here the surface tension decreases linearly as a function of temperature, which is expected thermodynamically. This has been well reported in the literature for different polymers.[1–7]

Figure 3 shows the surface tension for i-PP$_1$, i-PP$_2$, and LLDPE and the surface tension data of i-PP obtained by Menke et al.[31] as a function of temperature. The different symbols represent the

Table VIII   Surface Tension of LLDPE in the Molten State

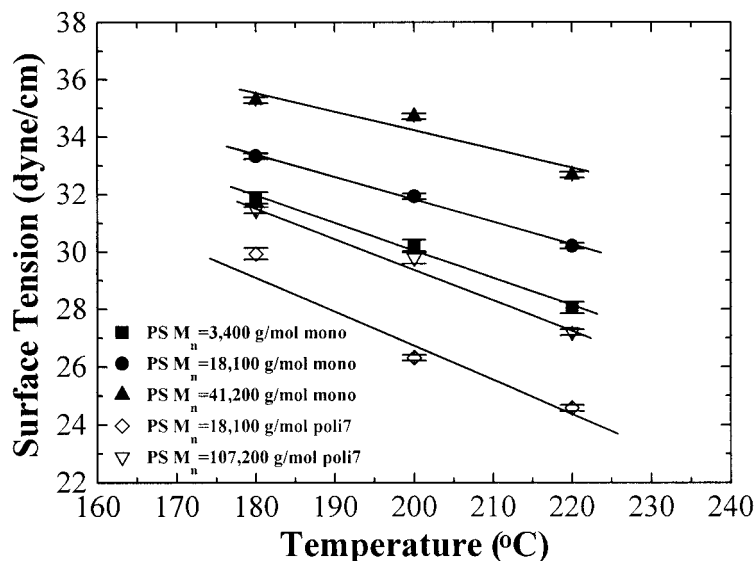| Polymer	$\bar{M}_n$	$I = \bar{M}_w/\bar{M}_n$	Surface Tension (dyne/cm)		
			220°C	240°C	260°C
LLDPE	91,800	4.42	23.05 ± 0.1	21.75 ± 0.1	20.15 ± 0.1

Figure 2 Surface tension of PS as a function of temperature for five different samples.

experimental data and the straight lines represent the best fit obtained by linear regression. It can be seen that the surface tension for the polymers of i-PP$_1$, i-PP$_2$, and LLDPE decreases linearly as a function of temperature.

The surface-tension results obtained for monodisperse PS and PE corroborate with the surface-tension data obtained by Dee and Sauer.[1–6] However, Dee and Sauer[1–6] only worked with lower molecular weights of PE. Here, we studied the influence of temperature on the surface tension of LLDPE. It can be seen from Figure 3 that there is a difference between the surface tension of the i-PP samples studied here and the value obtained

by Menke et al.[31] This discrepancy could be due to the difference between the MWD of our samples and the one used by Menke et al. This will be explained later in the article.

Table IX shows the surface-tension coefficients in the rubbery state of the lines obtained by fitting the surface tension as a function of temperature; a represents an extrapolation of the surface tension at 0°C and b represents the surface-tension coefficient in the rubbery state. The
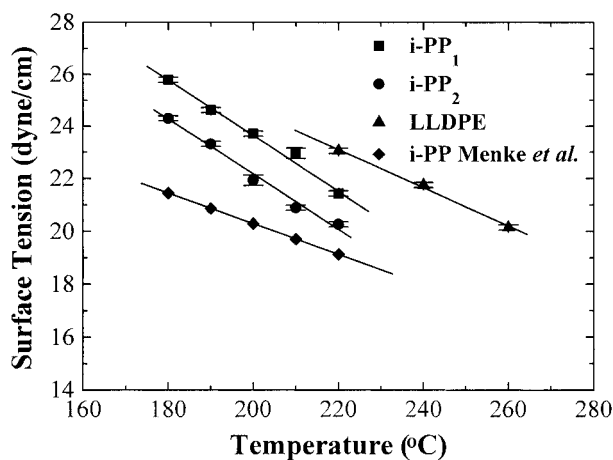

Figure 3 Surface tension of LLDPE and i-PP as a function of temperature.

Table IX   Linear Regression Coefficients of the Dependence of Surface Tension on Temperature $\gamma = a - bt$

Polymer	a (dyne/cm)	b (dyne/cm°C)	r^2
PS2	49.17	0.0956	0.9940
PS3	45.42	0.0763	0.9851
PS4	47.42	0.0780	0.9965
PS5	47.44	0.0673	0.9161
PS6	47.22	0.065	0.9049
PS7	52.02	0.0885	0.9557
PS8	50.65	0.0833	0.9757
PS11	52.18	0.1101	0.9878
PS12	49.58	0.1026	0.9831
PS13	53.70	0.1338	0.9602
PS14	54.36	0.1145	0.9966
PS15	50.80	0.1023	0.9980
PS16	50.78	0.1065	0.9920
i-PP$_1$	44.46	0.1038	0.9935
i-PP$_2$	42.94	0.1039	0.9943
LLDPE	39.05	0.0725	0.9982

Table X   Molecular Weight of PS Before and After a Pendant Drop Experiment

	Before a Pendant Drop Experiment			After a Pendant Drop Experiment		
Polymer	$\bar{M}_w$	$\bar{M}_n$	$I = \bar{M}_w/\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$I = \bar{M}_w/\bar{M}_n$
PS7	115,700	107,200	1.08	47,100	12,600	3.70

surface-tension coefficients in the rubbery state obtained are of the same order of magnitude as are the ones reported in the literature.[3,7]

It can be seen from the values presented in Table IX that the surface-tension coefficients in the rubbery state obtained for polydisperse systems are higher than are the ones for monodisperse systems. Also, the surface tension coefficients in the rubbery state seem to decrease with increasing molecular weight. This phenomenon can be explained thermodynamically: The surface tension coefficients in the rubbery state correspond to the entropy change of interface formation (polymer–air) per unit area at a constant volume. When the molecular weight decreases or the polydispersity increases, the conformations restrictions of the polymer decrease, increasing, therefore, the entropy change of interface formation. Similar behavior was observed by Kamal et al.,[11] Arashiro and Demarquette,[12] and Nam and Jo,[10] who studied the influence of temperature on the interfacial tension between PS and PP, PS and PE, and PS and polybutadiene, respectively. All these researchers saw that the interfacial tension temperature coefficients in the rubbery state for polydisperse systems were much higher than the interfacial tension temperature coefficients in the rubbery state for monodisperse systems.

It can be seen that for molecular weights of PS of 107,200 and 200,600 g/mol the surface-tension coefficient in the rubbery state is higher than is the surface-tension coefficient in the rubbery state for a lower molecular weight of PS, contradicting the observation made above. This cannot be explained thermodynamically. It was suspected that this result could be due to a possible degradation of the PS sample. It was verified by FTIR that no oxidation of the sample occurred. Table X shows the number-average molecular weight of PS 107,200 g/mol before and after a determination of the surface tension using the pendant drop method. It can be seen that after surface-tension determination the MWD increased. This is probably the reason why the surface-tension coefficient in the rubbery state for PS

with a number-average molecular weight of 107,200 g/mol is lower than for a lower molecular weight of PS. Similar behavior is expected for PS with a number-average molecular weight of 200,600 g/mol. In that aspect, due to long equilibration times, the pendant drop method may be limited for measurement of the surface tension of a polymer with a higher molecular weight.

It can be seen from Figure 3 that for each temperature studied the surface tension of i-PP$_1$ is higher than is the surface tension of i-PP$_2$.
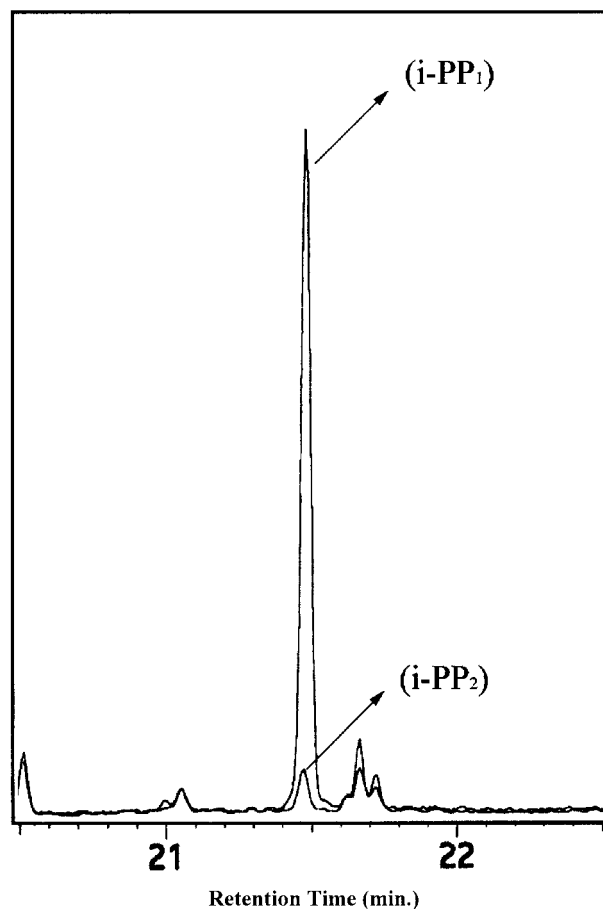

Figure 4   Chromatograms of the samples of i-PP$_1$ and i-PP$_2$. The peaks represent the quantity of additives (dibutyl phthalate).
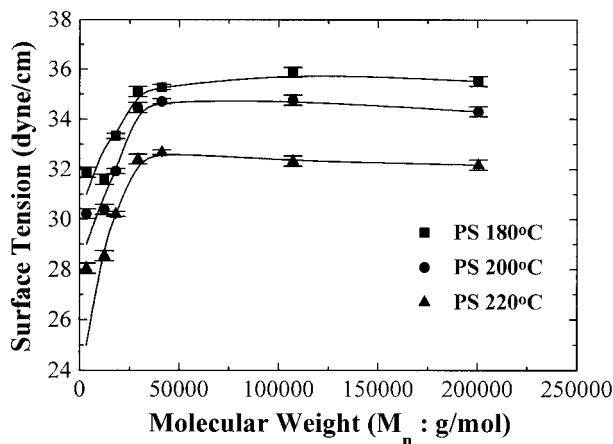
Figure 5 Surface tension of PS as a function molecular weight.

However, the difference in molecular weight is too small to justify such a discrepancy between the results. To justify this discrepancy, gas chromatography coupled with mass spectroscopy was performed for both samples of i-PP. It was observed that both samples of i-PP contained dibutyl phthalate. However, the quantity of dibutyl phthalate found in of i-PP$_1$ was much higher than that found in i-PP$_2$, as can be seen in Figure 4. This could explain the difference of the surface-tension values observed here.

Influence of Molecular Weight

The influence of the molecular weight of PS on the surface tension of PS was studied at temperatures of 180, 200, and 220°C. The molecular weight of PS varied from 3400 to 200,600 g/mol. Figure 5 shows the surface tension of PS as a function of the number-average molecular weight of PS. The different symbols represent the data points; the continuous lines are just a guide for the eyes.

It can be seen that for all temperatures the surface tension increases as a function of the molecular weight of PS. Figure 5 suggests also that the influence of the molecular weight on the surface tension decreases significantly when the molecular weight of PS exceeds 41,200 g/mol (the value at which entanglements occur for PS[32]). Similar behavior was observed by Kamal et al.,[11] Ellingson et al.,[33] and Arashiro and Demarquette,[12] who studied the effect of molecular weight of PS on the interfacial tension between PS and PP, PS and PMMA, and PS and PE, respectively.

The results seem to indicate that for higher molecular weight ($\bar{M}_n > 107,200$ g/mol) the sur-
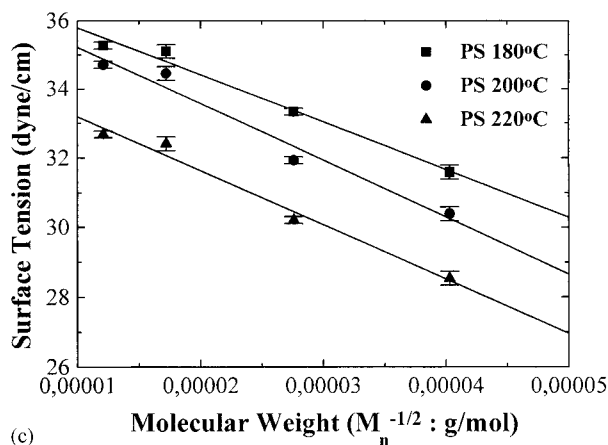
face tension decreases when the molecular weight increases. This phenomenon is most likely due to the thermal degradation as shown above. The equilibration time of a pendant drop of PS with a molecular weight of 200,600 g/mol is higher than 6 h because of the high viscosity of the polymer.
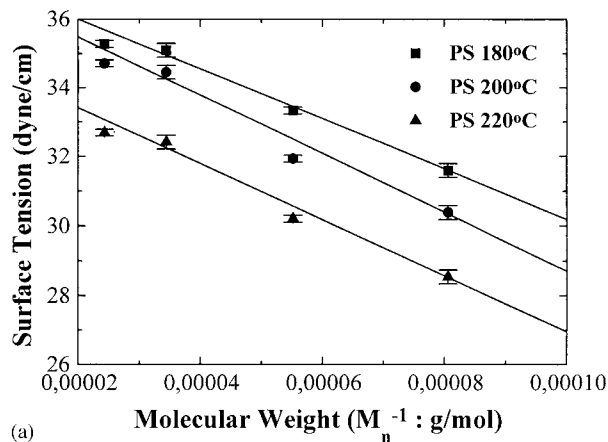
(a)
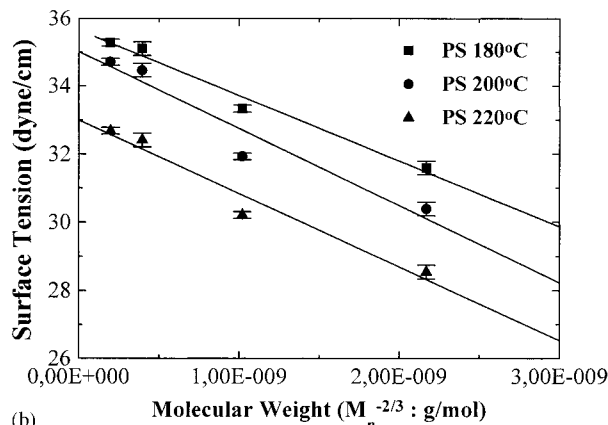
(b)

(c)

Figure 6 (a) Surface tension of PS as a function of $\bar{M}_n^{-1}$; (b) surface tension of PS as a function of $\bar{M}_n^{-(2/3)}$; (c) surface tension of PS as a function of $M_n^{-(1/2)}$.

Table XI   Effect of Molecular Weight on Surface Tension of PS: Parameters for Eq. (11)

z	Range of Molecular Weight ($\bar{M}_n$: g/mol)	Temperature (°C)	γ_∞	C_1	r^2
1/2	12,400–41,200	180	37.17	137,714	0.9847
		200	36.86	164,151	0.976
		220	34.74	155,469	0.9820
2/3	12,400–41,200	180	35.65	2.0×10^9	0.9793
		200	35.01	2.0×10^9	0.9364
		220	33.00	2.0×10^9	0.9583
1	12,400–41,200	180	37.17	68,857	0.9847
		200	36.86	82,075	0.9706
		220	34.74	77,734	0.9820

Although the experiments are performed in an argon atmosphere, thermal degradation is likely to occur, as shown in Table X. This thermal degradation involves an increase of the MWD of the sample, which, in turn, reduces the surface tension. Such degradation was observed only for samples with molecular weight above 100,000 g/mol.

All the reported studies on the effect of the molecular weight on the surface tension between polymers showed a dependence of the surface tension on the molecular weight as given by the following equation:

$$\gamma = \gamma_\infty - C_1(\bar{M}_n)^{-z} \qquad (11)$$

where γ is the surface tension; γ_∞, C_1, and z are constants; and $\bar{M}_n$ is the average molecular weight number of the polymer. γ_∞ refers to the limiting value of surface tension for infinite molecular weight, and C_1 reflects the dependence of the surface tension on the molecular weight.

Figure 6(a–c) shows the surface tension of PS at temperatures of 180, 200, and 220°C as a function of $\bar{M}_n^{-1/2}$, $\bar{M}_n^{-2/3}$, and $\bar{M}_n^{-1}$. Since there is no variation of the surface tension with the molecular weight for PS samples above $\bar{M}_n = 41,200$ g/mol, only the PS samples with $\bar{M}_n \leq 41,200$ g/mol are considered here. The symbols represent the experimental data and the best-fitting lines (obtained by linear regression). It can be seen that for all the different values of z the power law fits the experimental data equally.

Table XI shows the parameters γ_∞ and C_1 for PS for a range of number-average molecular weights between 12,400 and 41,200 g/mol for z = 1/2, z = 2/3, and z = 1. It seems from Table XI that the quality of the fit is the same for the three values of z. It can be also seen that the values of γ_∞ decrease with an increase of the temperature, which is expected as surface tension is a decreasing function of temperature. It also can be seen that the dependence of the surface tension on the molecular weight does not seem to depend on the temperature for the polymers studied here (no trend is observed in the value of C_1).

Influence of MWD

The effect of MWD on the surface tension was studied for PS with values of MWD ranging from 1 to 3 for temperatures of 180, 200, and 220°C. Two molecular weights of PS were studied ($\bar{M}_n$ = 18,100 g/mol and $\bar{M}_n$ = 107,200 g/mol).

Figure 7(a,b) shows the surface tension for both molecular weights of PS as a function of the MWD of PS. The different symbols represent the data points; the continuous lines are just a guide for the eyes. It can be seen that the surface tension decreases with increasing MWD. This could be due to the migration of the short chains of the polydisperse systems to the interface (polymer–air), which results in a broadening of the thickness of the interface (polymer–air), lowering, therefore, the surface tension.

Table XII(a,b) shows the difference between the surface tension of monodisperse and polydisperse samples for molecular weights 18,100 and 107,200 g/mol, respectively. The values reported on the first line represent the absolute difference between the surface tension of the monodisperse and of the polydisperse sample, and the values
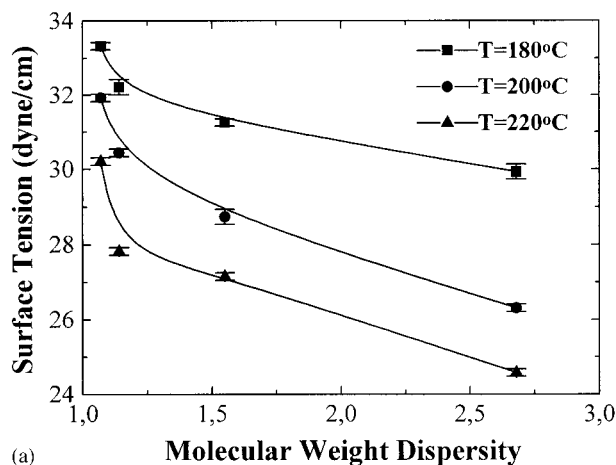
(a)
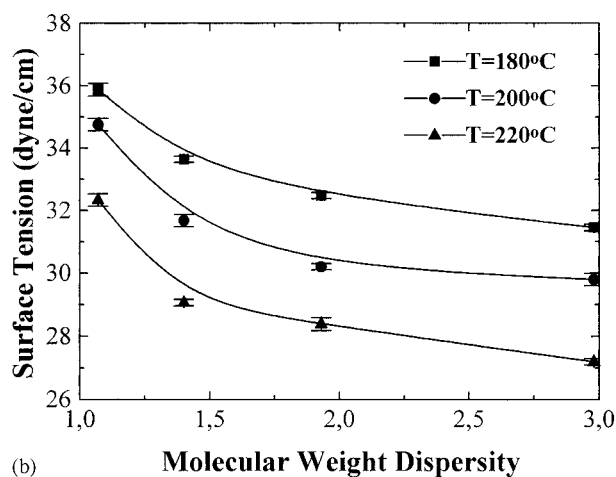
(b)

Figure 7 (a) Surface tension of PS as a function of molecular weight dispersity: $\bar{M}_n$ = 18,100 g/mol; (b) surface tension of PS as a function of molecular weight dispersity: $\bar{M}_n$ = 107,200 g/mol.

reported on the second line represent the difference in percentage. It can be seen from the data presented in Tables XII(a,b) that the difference of the surface tension between the monodisperse and polydisperse samples increases as a function of the temperature. This corroborates with the fact that the lower surface tension of the polydisperse sample could be due to the migration of short chains to the interface (polymer–air). The migration of short chains is a diffusion phenomenon which is faster when the temperature increases.

Figure 8(a,b) shows the difference between the surface tension of monodisperse and polydisperse samples for both the molecular weight of PS at temperatures of 180, 200, and 220°C. It can be seen that at 180°C the decrease of surface tension for the molecular weight of 107,200 g/mol is

greater than for the molecular weight of 18,100 g/mol. However, at temperatures of 200 and 220°C, the trend seems to be reverted: 18,100 g/mol corresponds to a molecular weight below the molecular weight of the entanglements. It is expected that the mobility of short chains of polydisperse systems will be higher than for 107,200 g/mol. However, this only happens for higher temperature, showing, once again, that the lower value of the surface tension for polydisperse samples is due to a migration difference of the short molecules to the interface (polymer–air). Similar results already have been shown by Kamal et al.[34]

Relation Between Surface Tension and Surface Energy

It can be seen from Table V that the values of the contact angle reported in this work corroborate the ones reported in the literature.[7,29] The surface energy of the solid polymers was evaluated using those values and they are also reported in Table V.

It can be seen that, within experimental error, the surface energy at room temperature does not vary with the molecular weight and MWD. This is expected as the mobility of the short chains is much less at temperatures below the T_g.

The values of the surface tension of PS in the rubbery state were extrapolated to calculate the surface energy of PS at 20°C using eq. (1). The values of the isobaric volumetric thermal expansion coefficient in both the glassy and rubbery regions used in the calculations are reported in Table XIII. They were inferred from PVT data published in the literature (PS)[30] and reported in the Materials subsection of this article (polyolefins). The glass transition temperatures (T_g) of PS were measured by differential scanning calorimetry (DSC).

The extrapolated values of the surface energy seem to indicate that the surface energy at room temperature does not vary with molecular weight and MWD. This corroborates with the experimental values reported in this work. However, it can be seen that the values obtained using the geometric and harmonic equations are slightly higher than are the ones obtained by extrapolating the values of the surface tension in the rubbery state. This could be due to approximations inherent to the empirical equation used to evaluate the surface energy from contact angles.[29]

Table XII   Difference Between the Surface Tension of Monodisperse and MWD Samples: (a) $\bar{M}_n$ = 18,100 g/mol; (b) $\bar{M}_n$ = 107,200 g/mol

(a)

Temperature (°C)	γ_{mono} (dyne/cm)	$\Delta\gamma_{1.07}$	$\Delta\gamma_{1.14}$	$\Delta\gamma_{1.55}$	$\Delta\gamma_{2.68}$
180	33.33	0 0%	1.11 3.33%	2.07 6.21%	3.40 10.21%
200	31.93	0 0%	1.49 4.67%	3.19 9.99%	5.62 17.60%
220	30.21	0 0%	2.39 7.91%	3.06 10.12%	5.63 18.63%

(b)

Temperature (°C)	γ_{mono} (dyne/cm)	$\Delta\gamma_{1.07}$	$\Delta\gamma_{1.40}$	$\Delta\gamma_{1.93}$	$\Delta\gamma_{2.98}$
180	35.87	0 0%	2.23 6.21%	3.40 9.47%	4.42 12.32%
200	34.76	0 0%	3.08 8.90%	4.56 13.11%	4.97 14.30%
220	32.33	0 0%	3.27 10.11%	3.85 11.90%	5.14 15.90%

CONCLUSIONS

It was shown that for all the polymers studied here the surface tension decreases linearly with the temperature. The temperature coefficient $d\gamma/dT$ (where γ is the surface tension, and T, the temperature) was shown to decrease with increasing molecular weight and to increase with increasing MWD. 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 was shown to level off. The experimental data of the surface tension as a function of the molecular weight could be fitted by a power law. Since there was no variation of the surface tension above the molecular weight of 41,200 g/mol, only the PS samples with molecular weight $\leq$ 41,200 g/mol were considered. It was shown that for all the different values of z the power law fitted the experimental data equally. The surface tension decreased as a function of the MWD of PS

Table XIII   Surface Energy of PS at 20°C: Comparison Between the Values Inferred from Contact-Angle Measurement and the Ones Extrapolated from the Rubbery State

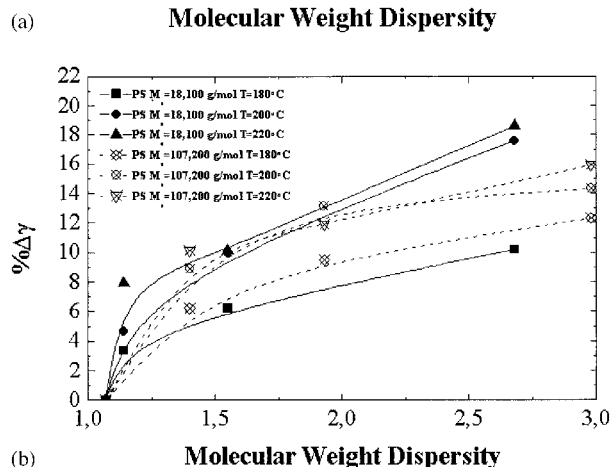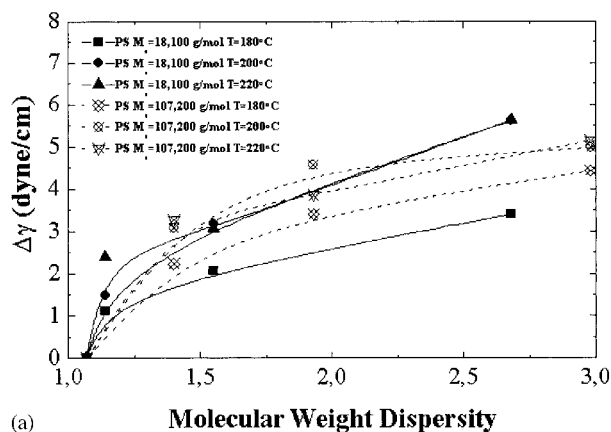| Polymer	α_g ($\times 10^4$ deg^{-1})	α_r ($\times 10^4$ deg^{-1})	T_g (°C)	γ at T_g (dyne/cm)	γ at 20°C (dyne/cm)	$\gamma_{geometric}$ (dyne/cm)	$\gamma_{harmonic}$ (dyne/cm)
PS3	3.710	6.003	90.4	38.53	41.85	47.11	49.77
PS4	3.403	6.011	99.3	39.67	43.17	47.89	49.71
PS6	2.747	6.039	104.9	40.40	42.91	45.79	49.16
PS7	1.974	6.077	107.4	42.52	45.03	46.54	50.46
PS8	1.470	6.098	107.1	41.73	43.48	48.31	53.33
PS16	1.441	6.101	89.5	41.24	42.99	48.10	52.36

Figure 8 (a) Difference between surface tension of monodisperse and molecular weight dispersity of PS at temperatures of 180, 200, and 220°C; (b) Difference between surface tension of monodisperse and molecular weight dispersity of PS at temperatures of 180, 200, and 220°C.

when the average molecular weight number was kept constant. The experimental results evidenced that the lower surface tension for polydisperse polymers was due to the migration of short chains to the surface.

The values of the surface tension of PS in the rubbery state were used to evaluate the surface energy of PS at 20°C using the relation that exists between $d\gamma/dT$ in the glassy and rubbery states. These values were compared to the experimental values of the surface energy evaluated using the values of contact angles of drops of diiodomethane and water. It was shown that the values of the surface energy obtained were slightly greater than were the ones extrapolated from the surface tension measurements in the rubbery state and also that they do not vary with the molecular weight and MWD.

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