

Surface Properties of Fluorostyrene Polymers

It is known that the surface properties of macromolecular substances depend on the conformation of the polymeric chain. In fact, several reports have recently appeared in the literature¹ that demonstrate the possibility of the surface characterization and differentiation of macromolecular substances which differ from each other only in their steric configurations. On the other hand, some authors² have affirmed that the certain properties of bidimensional polymer films are a function of small segments that can even coincide with the monomeric unit.

The purpose of this communication is the surface characterization of two polymers which have the same tacticity and which differ only in the substitution isomerism of the monomeric unit.

The polymers, poly(*m*-fluorostyrene) (PMFS) and poly(*p*-fluorostyrene) (PPFS), were prepared, purified, and assayed by the Istituto di Chimica Industriale del Politecnico di Milano and were both found to be prevalently isotactic.³

The surface properties of polystyrene and its derivatives have not been studied in detail. In fact, Crisp⁴ and subsequently other authors⁵ have shown that bidimensional spreading films of these macromolecular substances at the W/A interface are not stable and do not have the characteristics of true monolayers. However, the adsorption films of polystyrene at the solid-liquid⁶ and liquid-air⁷ interfaces are stable.

After ascertaining that the polymers under examination do not, in fact, form stable spreading films at the W/A interface, we passed to a study of the W/O interface, since, as is known,^{4,8} the spreading at this interface is favored by the decrease of the strength of the interchain cohesive energies with respect to the W/A interface. We used toluene as the oil phase and xylene as solvent for both macromolecules. The surface pressure measurements were obtained by difference from the water/toluene interfacial tension values and the water/toluene interfacial tension values following the addition of solutions of the polymers in xylene.

The measurements were made with the ring method using a high-sensitivity bifilar tensiometer⁹ working under conditions that guaranteed the attainment of equilibrium (as reported in previous papers^{7,10}). The spreading isotherms of PMFS and PPFS are reported in Figures 1 and 2, respectively, and were obtained under identical conditions and at the same temperatures: 25°, 30°, and 35°C. It can be discovered from an examination of the graphs that all three isotherms of PMFS show a "step" that can be attributed to a first-order transition; since, as we stated above, surface equilibrium was guaranteed. The PPFS curves are continuous at all temperatures.

In order to characterize the bidimensional phases present from the experimental values of πA , the equations of bidimensional state $\pi A - \pi$ were obtained. For PMFS, it is necessary to give two equations of state for each temperature since two bidimensional phases are present at the surface: one equation for pressures less than the transition pressure and one for pressures greater than the transition pressure. For PPFS, on the contrary, only one equation of bidimensional state is necessary for each temperature since no phase transition is present:

For PMFS:

$$\begin{array}{l}
 25^{\circ}\text{C} \left\{ \begin{array}{l} \pi A = 0.034 + 2.200\pi - 0.524\pi^2 + 0.0490\pi^3 \\ \pi A = 1.000 + 0.384\pi - 0.015\pi^2 + 0.0004\pi^3 \end{array} \right. \\
 30^{\circ}\text{C} \left\{ \begin{array}{l} \pi A = 0.400 + 1.398\pi - 0.486\pi^2 + 0.1570\pi^3 \\ \pi A = 0.840 + 0.542\pi + 0.005\pi^2 - 0.0030\pi^3 \end{array} \right. \\
 35^{\circ}\text{C} \left\{ \begin{array}{l} \pi A = 0.295 + 1.323\pi \\ \pi A = 0.150 + 1.023\pi - 0.142\pi^2 + 0.0075\pi^3 \end{array} \right.
 \end{array}$$

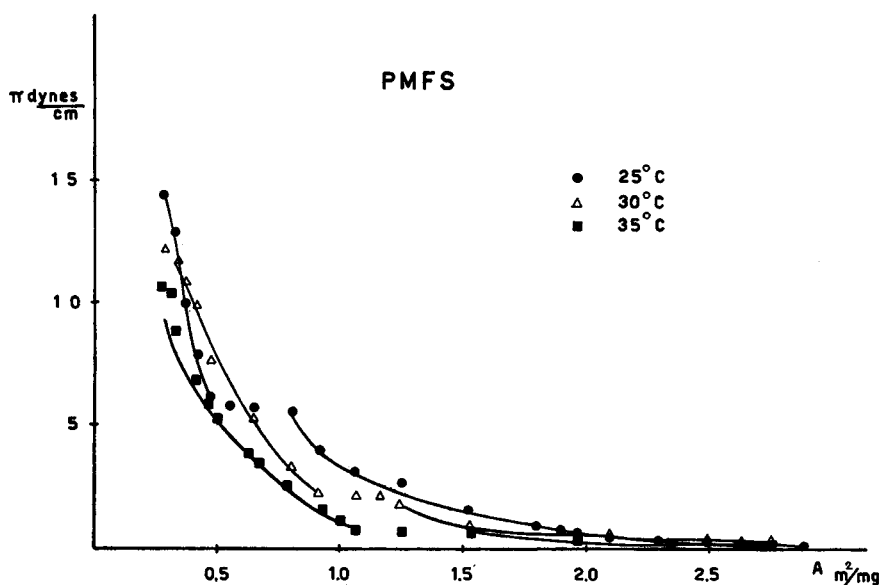


Fig. 1. Plot of surface pressure π (dynes/cm) vs. surface area A (m^2/mg) for PMFS.

For PFFS:

$$\begin{aligned} 25^\circ\text{C} \quad \pi A &= 0.052 + 1.817\pi - 0.310\pi^2 + 0.0210\pi^3 \\ 30^\circ\text{C} \quad \pi A &= 0.109 + 1.466\pi - 0.086\pi^2 + 0.0033\pi^3 \\ 35^\circ\text{C} \quad \pi A &= 0.798 + 1.091\pi - 0.016\pi^2 - 0.0023\pi^3 \end{aligned}$$

The maximum fitting error for the equations is about 4%. In Figures 1 and 2, the points represent the experimental values, while the continuous curves are derived from the equations.

From the equations it can be seen that for PMFS the most expanded phase could be considered to be gaseous, but nonideal, only at 35°C, whereas for PFFS all third-degree equations could represent bidimensional states that cannot be compared to gaseous phases. To further characterize these phases, we calculated the surface compressional modulus¹¹

$$C_S^{-1} = A_0 \left(\frac{\partial \pi}{\partial A} \right)_T$$

for each temperature: two for PMFS (one for the phase that exists at pressures lower than transition pressure and one for pressures higher than the transition pressure) and one for PFFS. These values, together with those for the limiting areas A_0 , are reported in Table I.

As can be deduced from this table, values of C_S^{-1} for PMFS at pressures lower than the transition pressure can be ascribed to a gaseous bidimensional phase, even if not ideal, whereas the C_S^{-1} values at pressures higher than the transition pressure are ascribable to a liquid bidimensional phase.^{12,13} The values of the heats of transition, obtained by applying the Clapeyron equation to the bidimensional state, are reported in Table I and are approximately of the order of magnitude of the first-order transition enthalpies of low molecular weight substances in the bidimensional phase.^{12,13} To further define the prevalent energies in the monolayers, we calculated the spreading entropy ΔS_s and the

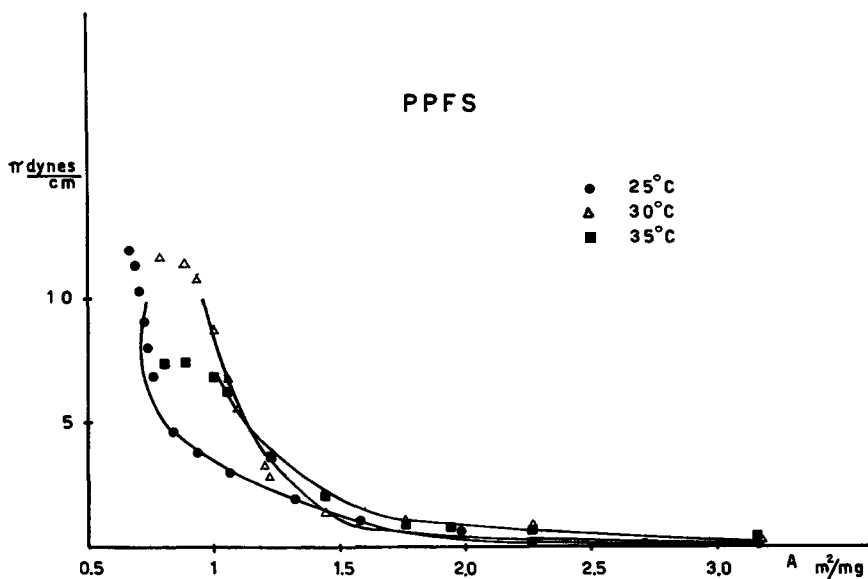


Fig. 2. Plot of surface pressure π (dynes/cm) vs. surface area A (m^2/mg) for PPFS.

spreading enthalpy ΔH_s of the polymers. As proposed by Harkins,¹⁴ these thermodynamic spreading values can be determined from the following relations:

$$g_s = \left(\frac{\partial G}{\partial A} \right)_{T, p, n_i} \quad H_s = \left(\frac{\partial H}{\partial A} \right)_{T, p, n_i} \quad S_s = \left(\frac{\partial S}{\partial A} \right)_{T, p, n_i}$$

where T = absolute temperature; p = pressure; n_i = number of moles of the components; G = free energy. From these relations, the spreading entropy S_s and enthalpy H_s are expressed:

$$g_s = -\pi \quad S_s = \left(\frac{\partial \pi}{\partial T} \right)_A \quad H_s = T \left(\frac{\partial \pi}{\partial T} \right)_A - \pi$$

The mean values of these thermodynamic quantities are reported in Table II for the 25°–35°C temperature interval. It should be noted that two values appear in the table for PMFS: one for the gaseous phase and one for the liquid phase. As to PPFS, as is easily seen from Figure 2 for surface areas greater than 1.5 m^2/mg , the spreading entropy and the corresponding enthalpy can be considered negligible within the limits of experimental error. We have therefore calculated the thermodynamic spreading quantities only for areas smaller than 1.5 m^2/mg .

It can also be seen from the table that the spreading enthalpy is negative for PMFS and positive for PPFS. Since the enthalpic contribution is not negligible, the polymer interphase system cannot be considered athermal as in Singer's treatment.¹⁵ The positive or negative value of the spreading entropy means in general that the free energy of spreading for a given area is increased or decreased by the entropy term.

The positive value of the enthalpy term for PPFS means that the spreading process is endothermic, as previously noted.¹⁶ This means that intra- and intermolecular attractive forces prevail. The negative value in the case of PMFS means that, other enthalpic contributions being equal, the intra- and intermolecular repulsive forces prevail.

To validate this assumption, we calculated, as with other polymers,¹⁷ the factor η^2/z that appears in the equation of Motomura and Matuura¹⁸ and that represents the energy

TABLE I
Parameters of Fluorostyrene Polymers at W/O Interface

PMFS						
Parameter	25°C		30°C		35°C	
	Before transition	After transition	Before transition	After transition	Before transition	After transition
A_0 , m ² /mg	0.81	0.60	1.16	0.76	1.54	0.69
C_s^{-1} dynes/cm	7.84	26.40	0.70	17.50	0.75	16.90
λ_{trans} , cal/mole m.u.	1127		1063		2113	
PPFS						
Parameter	25°C		30°C		35°C	
	Before transition	After transition	Before transition	After transition	Before transition	After transition
A_0 , m ² /mg	0.90		1.30		1.50	
C_s^{-1} , dynes/cm	54.00		43.30		17.50	

TABLE II
Spreading Thermodynamic Properties

Parameter	PMFS		PPFS
	Gaseous phase	Liquid phase	
ΔS_s , cal/degree mole m.u.	-1.77	-12.3	+7.31
ΔH_s , cal/mole m.u.	-581	-3462	+2068

of interaction between rigid segments present at the interface. These values are calculated from the virial coefficients of the previously reported equations of bidimensional state.

The values of η^2/z are reported in Table III. They are positive for PMFS, indicating that the prevalent energies between macromolecular segments at the interface are repulsive, whereas the negative values of PPFS indicate the prevalence of intramolecular attractive energies.

TABLE III
Values of η^2/z at W/O Interface

Temp, °C	PMFS		PPFS
	Gaseous phase	Liquid phase	
25	+0.1 <i>KT</i>	+10.8 <i>KT</i>	-1.0 <i>KT</i>
30	+9.2 <i>KT</i>	+6.7 <i>KT</i>	-2.0
35	+2.2 <i>KT</i>	+2.1 <i>KT</i>	-4.3 <i>KT</i>

The previously reported experimental data could lead to the following conclusions:

1. Polystyrene and its derivatives do not form stable films at the W/A interface, whereas at the W/O interface PMFS and PPFS monolayers are stable and reproducible. The possibility of studying styrene derivatives at this interphase is thus foreseen.

2. It is possible to differentiate at the surface, at least in the cases examined, polymers that have the same steric configuration but whose monomeric units are position isomers.

In particular, the macromolecules studied differ not only in the different limiting areas, but also in the type of bidimensional phase and in the energies present in the monolayers, even though the steric conformation of the macromolecular chain remains constant.

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Received January 21, 1972
Revised April 4, 1972