

The Surface Orientation of Polystyrene Measured by Liquid Contact Angle

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Synopsis

The surface contact angle of glycerol and of water on polystyrene (PS) films has been found to depend on the extent of uniaxial draw for atactic PS. The contact angle depends on direction for the smooth films of PS drawn by solid state coextrusion. Results as a function of draw ratio to values over 4 on these noncrystalline PS samples, $M_w = 6 \times 10^5$, have also been interrelated with other measures of orientation such as the anisotropy of surface and bulk properties measured, respectively, by dichroic reflectance infrared spectroscopy and by birefringence.

INTRODUCTION

The contact angle of a liquid on a solid surface is determined mainly by the surface properties of the solid and by the surface tension of the liquid. This relationship has been described by the Young–Dupre equation

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (1)$$

where γ_{SV} is the solid–vapor surface tension, γ_{LV} is the liquid–vapor surface tension, γ_{SL} the solid–liquid interface tension (interaction forces), and θ is the contact angle.

The properties of an oriented polymer surface are inherently anisotropic. Thus for constant values of γ_{SV} and γ_{LV} , γ_{SL} in the parallel and perpendicular direction to a uniaxial draw may likely be different, resulting in a liquid contact angle of θ against the polymer that likely differs measurably with direction!

For evaluation of this concept of an anisotropic surface energy, we have utilized uniaxially drawn atactic polystyrene (PS) as prepared by the efficient and convenient method of solid state coextrusion to a draw ratio over four.^{1,2} The bulk properties and morphology of such efficiently drawn polystyrene have been reported. In these previous investigations, it has been found that the orientation of PS chains is high, with a dependence on PS molecular weight and temperature for coextrusion draw.^{3,4} As traditional, only the overall orientation features of the drawn PS were measured. Recently, however, there have been several studies by our group and by others on the surface orientation of drawn polymers,^{5–7} using a range of different techniques for the important characterization of polymer surface anisotropy.

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This present work concerns the observation that the liquid contact angle θ of water and glycerol differs with direction and extent of uniaxial drawn PS. Reflection infrared dichroism and birefringence have also been used to provide further surface and bulk orientation information, respectively, for interrelationships with this new measure of surface orientation by liquid contact angle.

EXPERIMENTAL

Used in this study was a single sample of pure amorphous, atactic polystyrene (PS) of narrow molecular weight distributions ($M_w = 6 \times 10^5$, $M_w/M_n = 1.10$). It was supplied by Pressure Chemical Co., Pittsburgh, Pa. Sample preparation and the drawing of the PS by solid state coextrusions were essentially as described earlier.^{3,4} The PS was compression molded at 180°C and 20,000 psi into films of ~0.6 mm thickness, followed by quenching in water at room temperature.

Split rods of high density polyethylene, diameter $\frac{3}{8}$ in., were used as the coextrudate; PS film was inserted between the billet halves that had previously been prepared by splitting the billet rod longitudinally. The consequent sandwich assembly was press fit into the barrel of an Instron rheometer of like barrel diameter. This assembly was then extruded through a conical brass die of 20° included entrance angle at 128°C, i.e., ~28°C above the ambient glass transition of the PS. The draw ratio λ was measured by displacement of ink marks placed on the PS film before coextrusion draw. Draw ratios to over 4 were studied here with considerably higher values attained for PS by these methods in separate studies.

The PS film thickness was calculated as the average of several micrometer measurements along the film before and after draw. Birefringence measurements were made on drawn PS samples, using a Zeiss polarizing microscope equipped with a tilting compensator.

The potential surface orientation of the drawn PS was studied by contact angle and by multiple-interval reflection infrared dichroism (MIR-IR). This measurement was performed in a Nicolet 7199 Fourier Transform Infrared Spectrometer equipped with a MIR accessory from Perkin-Elmer. A Quadruple Diamond Breaster's Single Polarizer was used. For enhanced sensitivity we used 200 IR scans at a resolution of 4 cm^{-1} . The reflection crystals of Ge, used at an incident angle of 45°, were purchased from Harrick Scientific Corp. For obtaining the dichroic ratio, the PS samples were rotated, rather than the polarizer.

For the purpose of surface analyses, the drawn PS was carefully polished with "Hydrocurve," buffed with toothpaste, cleaned with a detergent solution, washed with distilled water, and finally dried. This procedure caused no apparent reaction, minimized surface disorientation, and provided a PS surface free of striations that could, of themselves, give an apparent directional dependence of liquid contact angle.

Contact angle measurements were performed only at ambient, ~30°C in air, and with a contact angle analyser marketed by Imass Corp., Accord, Mass. Deionized distillation water and glycerol were the two liquids used for contact angle analyses on the oriented surfaces of the drawn PS.

RESULTS AND DISCUSSION

The drawn PS films were characterized by several techniques including bulk birefringence and the surface analyses of contact angle, with water and glycerol, and by reflectance infrared. It is assumed that the extrusion draw direction is the x -axis with the y - and z -axes parallel and normal to the film plane, respectively. In MIR-IR dichroism measurements, for the x -axis normal to the plane of incidence beam, according to Fluornoy and Schaffers,⁸ the absorbances on rotating the polarizer by 90° can be expressed as follows:

$$A_{TE_x} = kA_x \quad (2)$$

$$A_{TM_x} = k'A_y + k''A_z \quad (3)$$

where A_{TE_x} and A_{TM_x} are the absorbances for the plane of polarization parallel and perpendicular, respectively, to the reflecting surface. k , k' , and k'' are constants related to the refractive indices of the atactic polystyrene and the IR crystal element. A_x , A_y , and A_z are three optical constants which are related to the reflectivities for the transverse electric (TE) and transverse magnetic (TM) waves. By rotating the sample 90° about the z -axis, two additional equations will be employed:

$$A_{TE_y} = kA_y \quad (4)$$

$$A_{TM_y} = k'A_x + k''A_z \quad (5)$$

The dichroic ratio R can be calculated from eqs. (2) and (4), i.e.,

$$R = A_x/A_y \quad (6)$$

It is well known that, for polarized infrared, the measurement of dichroic ratio is related to the second moment of the orientation function as follows:

$$\langle P_2(\cos \theta) \rangle_{av} = \frac{3 \overline{\cos^2 \theta} - 1}{2} = \frac{R - 1}{R + 2} \cdot \frac{R_0 + 2}{R_0 - 1} \quad (7)$$

with $R_0 = 2 \cot^2 \alpha$, where α is the angle for the dipole moment vector of the vibration. For polystyrene the vector is perpendicular to the plane of the phenyl ring and the chain axis; θ is the angle between the chain axis and the stretch direction. The mean value of α measured by Jasse and Koenig⁹ is 36. An orientation function of the drawn PS can thus be readily obtained from infrared dichroism measurements.

For PS the 1028 cm^{-1} and 906 cm^{-1} infrared bands are conformationally insensitive, and their dichroic ratio can thus be used to characterize the overall chain orientation. The dichroic ratio change with draw ratio observed for the PS is shown in Figure 1. To compare the orientation of the surface with that of the bulk, the orientation function calculated from birefringence and surface infrared dichroisms are both shown in Figure 2 as a function of extrusion draw ratio. The orientation function f is defined in terms of the average alignment angle of the chains, with the limits of 0.0–1.0, i.e., for zero to perfect uniaxial orientation. In our previous study, it was found that the orientation of coextrusion-drawn PS, as measured by three bulk methods, i.e., transmission infrared dichroism, birefringence, and by thermal expansivity, gave internally consistent results. In this investigation, however, the different orientation techniques

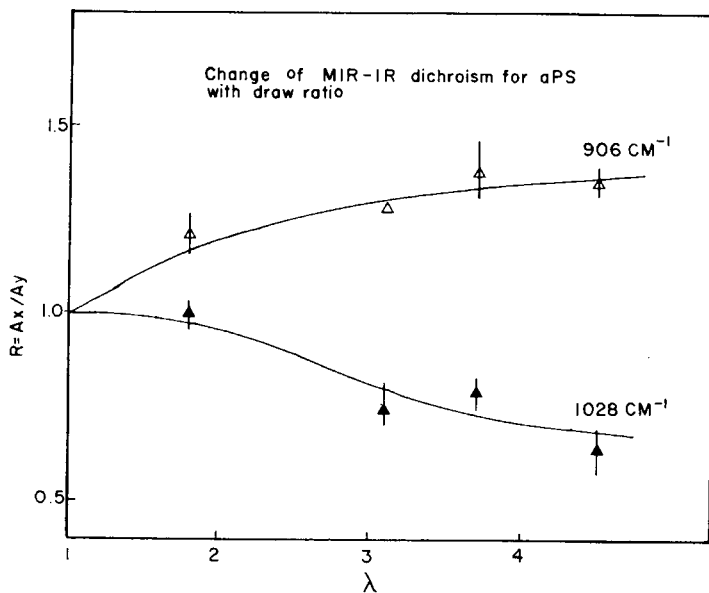


Fig. 1. Dichroic ratio from reflection infrared analyses on PS as a function of draw ratio λ at (Δ) 906 cm^{-1} and (\blacktriangle) 1028 cm^{-1} .

exhibit differences, particularly for bulk vs. surface measurements. It can be seen that, at low draw ratio, bulk orientation increases slowly relative to the apparent surface orientation. At high draw ratio, the bulk and surface orientations, however, are found to be both similar and high. The difference of surface

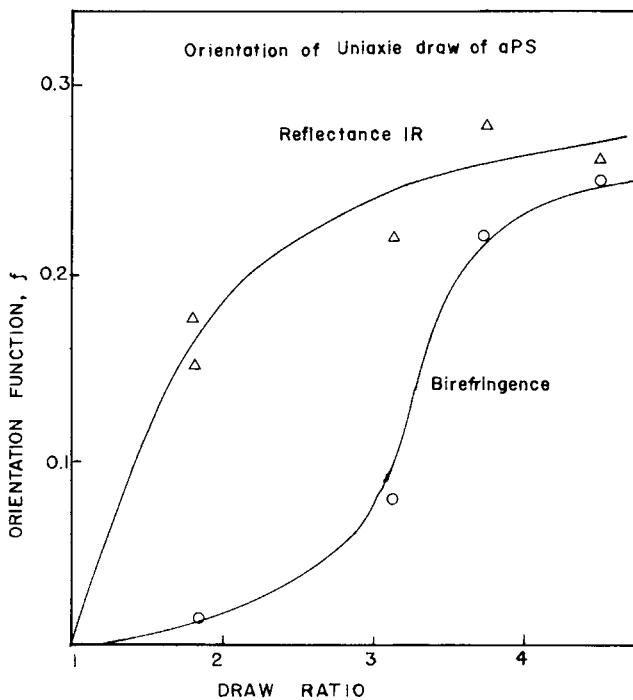


Fig. 2. Orientation function for PS vs. draw ratio: (Δ) from MIR-IR dichroism; (\circ) from birefringence.

and bulk orientation at low draw are likely caused by a change in the deformation profile on draw or possibly by analytical technique differences. The former is also suggested by the displacement of lateral lines at early stages of draw consistent with a shear component, in addition to extension, which will result in differences between surface and bulk orientation.

For the contact angle measurements, the smoothness and clarity of the PS surface are important. Consequently, considerable care was given to sample polishing and washing, as described above. The advancing contact angles for pure water and for glycerol on the unoriented PS surface were 90° and 79° , respectively. Both values are in excellent accord with the limited literature values for just these systems.¹⁰⁻¹² For PS oriented by coextrusion drawing, the liquid contact angle changed systematically with draw ratio. The contact angles for the direction parallel to draw decreased, and in the perpendicular direction it increased; see Figure 3. The consequent calculated changes in λ_{SL} with draw ratio are shown in Figure 4.

The surface tension, like electrical and optical properties of solids, is thus a vector quantity. For an anisotropic surface, surface tension should thus depend on the direction of measurement. From thermodynamics it is known that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (8)$$

and

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \frac{\alpha}{\beta} \quad (9)$$

where α is the thermoexpansivity and β the compressibility and the other terms

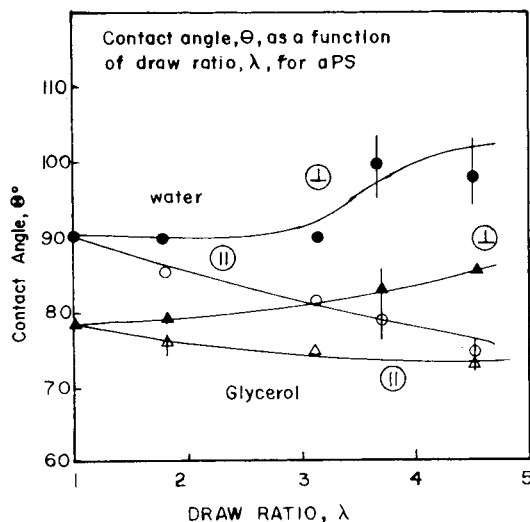


Fig. 3. Ambient contact angle as a function of draw ratio λ for PS from water in the (\bullet) perpendicular direction and (\circ) parallel direction and for glycerol in the (\blacktriangle) perpendicular direction and (\triangle) parallel direction.

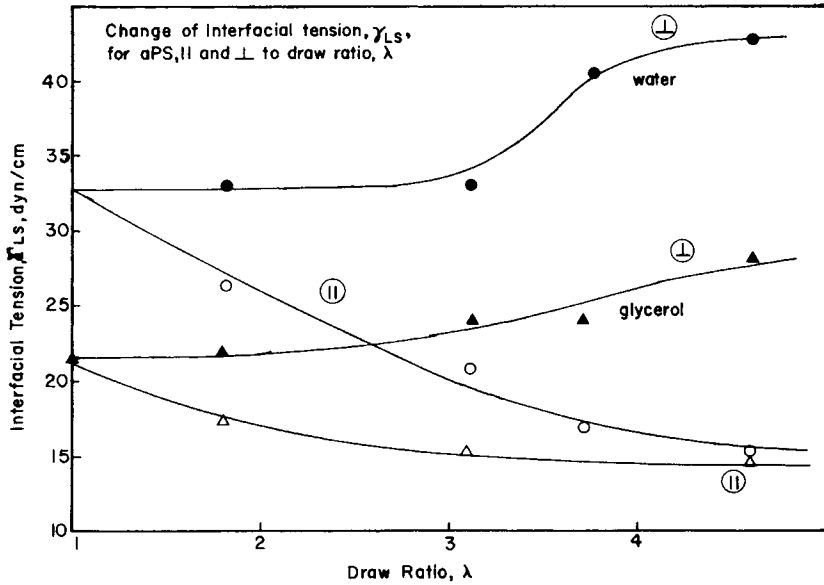


Fig. 4. The change of interfacial tension of PS with draw for (1) water (●) in the perpendicular direction and (○) in the parallel direction; (2) for glycerol (▲) in the perpendicular direction and (△) in the parallel direction.

have their usual meaning. The left side of eq. (8) can also be expressed as follows:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial S}{\partial A}\right)_T \left(\frac{\partial A}{\partial V}\right)_P \quad (10)$$

where A is the area and $\partial A/\partial V$ is the specific area of the object. From the definition of surface tension, the final result is

$$\gamma = \left(\frac{\partial H}{\partial A}\right)_{T,P} - \frac{\alpha \cdot T}{\beta \cdot K} \quad (11)$$

The first term to the right in eq. (10) is the specific enthalpy which depends on the polymer properties. By definition, β is negative. K is a constant. From eq. (11) it can be seen that the surface tension λ is proportional to α . In our previous thermal expansivity studies of ultradrawn PS,¹³ it was found that the α is highly anisotropic after deformation. We report here that the change of liquid contact angle with draw for PS follows the same pattern as the anisotropy observed in thermal expansivity. An added significance to these studies is that neutron scattering results have shown that the deformation is basically affine, i.e., the molecular draw ratio is virtually that measured macroscopically by the displacement on draw of lines on the PS film.¹⁴

CONCLUSIONS

As investigated by dichroic MIR-IR and by birefringence, the orientation of the surface and bulk for extrusion drawn PS differ at low draw ratio, suggesting

differences in the mode of deformation. The liquid contact angle also changes with drawn ratio, for both the parallel and for the perpendicular direction to draw, as an added and new measure of surface orientation. This new method has an appeal due to simplicity, yet requires caution in use for a reliable measure of surface orientation, as independently analyzed here by dichroic ratios from multiple internal reflection infrared spectroscopy.

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