# Chemical Modification of Polymers. 13. Sulfonation of Polystyrene Surfaces

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(21) For similar behavior of alkaloid catalysts, see H. Wynberg and R. Helder, *Tetrahedron Lett.*, 4057 (1975), and ref 3-6.
(22) The reaction conditions were the same as those employed for the polymer-catalyzed reaction (see the Experimental Section).
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# Chemical Modification of Polymers. 13.[1] Sulfonation of Polystyrene Surfaces

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ABSTRACT: Polystyrene surfaces are readily sulfonated by 100% sulfuric acid at room temperature. For reproducible results, the reaction must be carried out under anhydrous conditions. Controlled reaction from zero to more than 4000 monolayers is possible in times less than 1 h. Three analytical techniques for the extent of sulfonation were employed: (1) ion exchange of the films with methylene blue, a cationic dye, and subsequent visible light absorption measurement; (2) direct titration of the sulfonic acid groups; and (3) direct reaction depth measurement by interferometry. The reaction consists of two distinct processes: a rapid initial rate and a slower final rate. These are interpreted as being due to surface and "bulk" sulfonation, respectively, or alternatively the interplay of diffusion and reaction processes.

Chemical modification of polymeric surfaces is known to alter physicochemical properties [e.g., adhesion,[2] dyefastness,[3-5] wettability,[6] weatherability,[7] permeation,[8] friction,[9] electrostatic charging,[9] and biocompatibility[10]]. These modifications have generally been poorly understood due to lack of analytical procedures, kinetic data, and knowledge of the nature and distribution of the functional groups produced.

We undertook a systematic study of the sulfonation of free-standing polystyrene films as a prototypical surface modification with the following objectives: (1) establishment of techniques for quantitative analysis; (2) development of conditions for reproducible, controlled sulfonation; (3) determination of the kinetics of the reaction; and (4) analysis of the structure of the "surface" vis-à-vis the "bulk" of the resultant films. The present paper will focus upon the first three aspects.

## Results and Discussion

**A. Choice of Sulfonating Agent.** It was desirable that the reaction be carried out at room temperature for ease of handling and that the reaction take place on a useful time scale. On the basis of these two limitations, various sulfonating agents were screened. Immersion of the polystyrene (1) films for various periods of time in the medium, followed by quenching in a suitable bath and washing with water, produced sulfonated films (2). Chlorosulfonic acid proved to be too reactive; the films were physically destroyed. Concentrated sulfuric acid was too unreactive; only very slightly sulfonated films (equivalent to a few monolayers per side) resulted from treatment with concentrated sulfuric acid at room temperature for times as long as 16 h. However, approximately 100% sulfuric acid, made from concentrated sulfuric acid and fuming sulfuric acid, is a reagent which gives reasonable sulfonation rates at room temperature.

**B. Reagent Analysis.** The concentrations of $SO_3$/$H_2SO_4$ and "concentrated" sulfuric acid were estimated by the determination of density.[11] From these known concentrations, solutions of known nominal $SO_3$ concentration in $H_2SO_4$ could be prepared. Each of the sulfonating mixtures was in turn analyzed by titration with standard

**Scheme I**
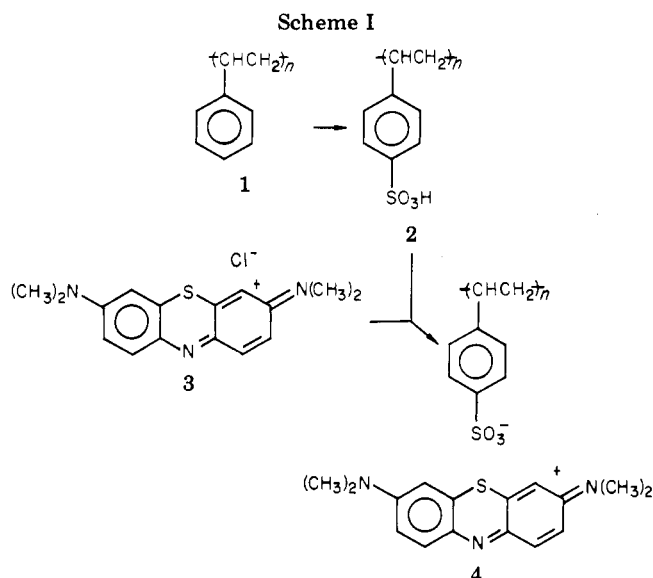
base. In terms of weight percent sulfuric acid wherein $SO_3$ is analyzed as $H_2SO_4$ after reaction with water, the measured concentrations ranged from 99.6–100.3%.

**C. Establishment of Analytical Techniques for the Extent of Sulfonation.** Analysis of the sulfonated surfaces of the polystyrene based upon the known ability of the sulfonic acid groups to exchange cations[12] could be accomplished in one of several ways. We chose to exchange the films with methylene blue.[13] This results in exchange of the proton on the sulfonic acid group (2) for a methylene blue cation (3), leading to a film with ionically bound blue dye (4). This technique allows some judgments based on visual inspection and allows use of spectrophotometry, a rapid technique of high accuracy and precision.

**1. Dyed Film Spectrophotometric Assay Reproducibility.** The first objective was to determine if the spectrophotometric assay of the films was reproducible. The results for several sets of films prepared and dyed simultaneously are given in Table I. The intense absorption of these films makes measurement of the absor-

Table I
Reproducibility of the Spectrophotometric Assay
of Films Identically Sulfonated and Dyed
with Methylene Blue[a]

| set no. | film no. | $A_{780}$ | av $A_{780}$ ± stand dev |
|---|---|---|---|
| a | 1 | 0.786 | 0.789 ± 0.047 (6.0%) |
|   | 2 | 0.777 | |
|   | 3 | 0.863 | |
|   | 4 | 0.731 | |
| b | 1 | 0.503 | 0.478 ± 0.016 (3.3%) |
|   | 2 | 0.480 | |
|   | 3 | 0.463 | |
|   | 4 | 0.465 | |
| c | 1 | 0.393 | 0.372 ± 0.012 (3.2%) |
|   | 2 | 0.365 | |
|   | 3 | 0.371 | |
|   | 4 | 0.365 | |
| d | 1 | 0.266 | 0.270 ± 0.007 (2.6%) |
|   | 2 | 0.268 | |
|   | 3 | 0.281 | |
|   | 4 | 0.264 | |

[a] 100.1 wt % $H_2SO_4$, 60 s reaction. Set (a) was sulfonated immediately after bath preparation, set (b) 10 min later, set (c) 20 min later, and set (d) 60 min later. Variation in the extent of the reaction with the time elapsed after the bath preparation is due to cooling of the bath; it warms due to exothermic heat of mixing. Dyeing was carried out over a 30-min period.

Table II
Reproducibility of the Spectrophotometric Assay of
Single Films of Surface Sulfonated Polystyrene[a]

| film | elapsed time, days | $A_{780}$ | av $A_{780}$ ± stand dev |
|---|---|---|---|
| a3 | 0 | 0.863 | 0.856 ± 0.012 (1.41%) |
|   | 1 | 0.861 | |
|   | 5 | 0.835 | |
|   | 6 | 0.865 | |
| b1 | 0 | 0.503 | 0.502 ± 0.016 (3.2%) |
|   | 0.5 | 0.513 | |
|   | 4 | 0.513 | |
|   | 5 | 0.510 | |
|   | 740 | 0.472 | |

[a] Film preparation given in Table I.

bance at $\lambda_{max}$ impossible. Therefore, absorbance is given for a wavelength on the long wavelength tail. As can be seen, the standard deviation range is 2–6%.

To test the effects of film mounting and aging of the dyed films on the spectral analysis, a single film was studied by several independent mountings and determinations over a period of many days. The results in Table II show that the deviation is less than 4%. This is taken as evidence that film mounting and aging of this magnitude are not significant variables.

**2. Kinetics of Dyeing.** Next it was necessary to ascertain the point at which exchange of methylene blue with the sulfonated films had reached completion. Film strips were sulfonated simultaneously and identically in the same sulfonating bath. These films were then dyed by immersion for various lengths of time in an aqueous solution of methylene blue and examined spectrophotometrically. As can be seen in Figure 1, dyeing was essentially complete after 10 min. The results were corroborated by the dyeing of two other films which were identically sulfonated to a lesser extent. These results are taken to mean that the dyeing of films of absorbances up to $A_{780} < 1$ is complete within 10 min. For films with $1 < A_{780} < 2.5$, dyeing times of 4 h were found to be sufficient, using this technique.
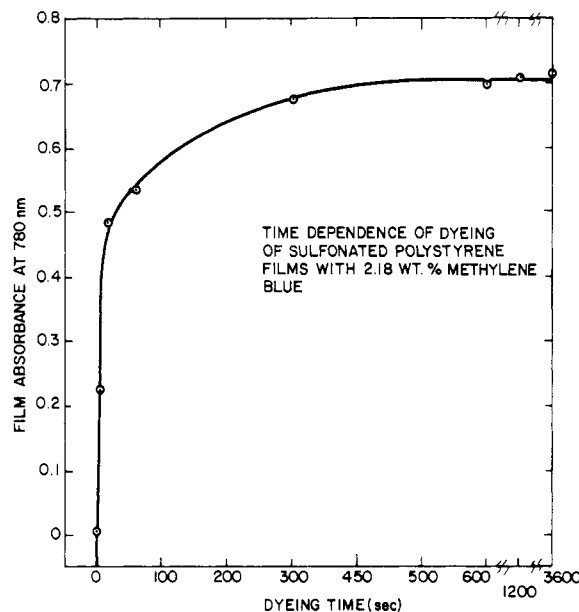


Figure 1. The film absorbance vs. the methylene blue dyeing time for sulfonated polystyrene films.

**3. Film Thickness.** The thickness of the commercial free-standing polystyrene films was determined from the interference fringes observed in the near infrared and visible regions of the spectra. The equation[14a]

$$d = \frac{n}{2}\left[\frac{\lambda_1\lambda_2}{\lambda_2 - \lambda_1}\right] \qquad (1)$$

where $d$ is the thickness, and $n$ is the number of interference fringes observed between wavelengths $\lambda_1$ and $\lambda_2$, enables a facile and accurate estimation of the thickness. The films in the present study were fairly uniform. The average thickness of 25 films was found to be 79 ± 1 $\mu$m.

This makes weight a convenient measure of the areas of the films. The area of the edges of the films is ignored throughout this report. Since films of 1 × 3 cm size (or larger) were employed for determination of absolute dye content, the area of the edges is 1.1% (or less) of the area of the larger faces. From the density[15] (1.05 g/cm$^3$) and the thickness, the weight per unit area can be calculated to be $W/A$ = 8.30 × 10$^{-3}$ g/cm$^2$.

**4. Absolute Dye Content of Films.** While the measurement of absorption of the films is very facile and precise, it does not lead to establishment of the absolute amount of dye present in the films. To do this there are several possibilities. The first and most obvious method is to dissolve a known amount of dyed film in a known volume of solvent, measure its absorption, and establish its absolute concentration by comparison with standard solutions. Only one solvent was found for the dyed sulfonated polystyrene films—dimethylformamide (DMF). These solutions unfortunately were rather rapidly (in some cases <1 h) bleached via a pink intermediate, making spectral analysis impractical.

The second method considered was the exchange of methylene blue cation from the film by metal ions. A number of metal salts in aqueous solutions were tested to bring about this displacement. Lead nitrate, $Pb(NO_3)_2$, was chosen because it rapidly replaced the methylene blue cation. The dyed sulfonated film of known weight was extracted with aqueous $Pb(NO_3)_2$ to yield a blue solution of methylene blue cation. The absorbances of the film and the solution were then determined. The amount of dye in the solution was estimated by use of a correlation curve
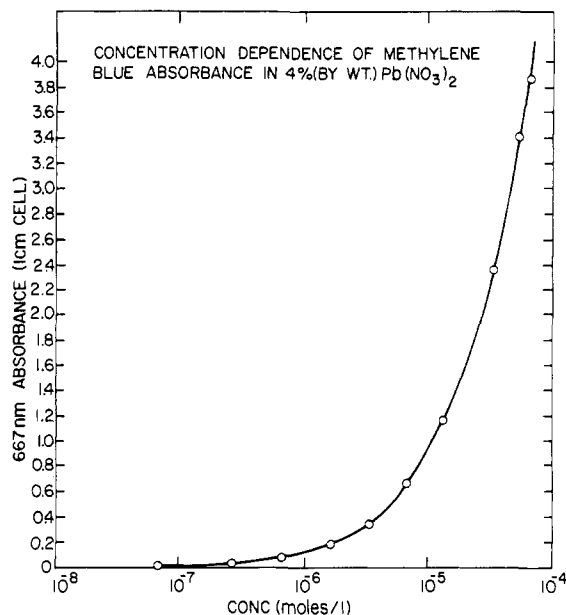
**Figure 2.** The absorbance vs. the concentration for methylene blue in 4% lead nitrate.



**Figure 3.** The methylene blue content vs. the absorbance of methylene blue dyed sulfonated polystyrene films.
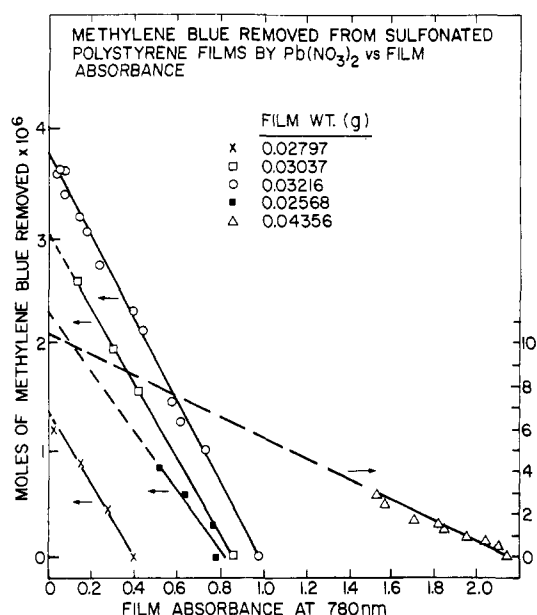


**Figure 4.** The methylene blue content vs. the absorbance of methylene blue dyed sulfonated polystyrene films.

(Figure 2) generated with known concentrations of methylene blue in $Pb(NO_3)_2$. By such repeated incremental extractions a curve of film absorbance at an arbitrary wavelength (780 nm) on the tail vs. moles of dye removed was constructed (Figure 3). By extrapolation of these plots to zero film absorbance, the amount of dye initially on the film was determined. Then for any given film the correspondence between the initial absorbance and the amount of dye initially present was known. Moreover, the same correspondence was known for any given increment of the extraction procedure. Thus by constructing a plot of moles of dye per gram of film vs. film absorbance a correlation curve was obtained. This is shown in Figure 4.

A similar procedure for lightly sulfonated and dyed films involving the absorption maxima at about 600 nm and the shoulder at 670 nm was precluded for the following reason. The 670-nm band is known to be due to the dye monomer, while the ~640-nm band is known to be due to aggregate or dimer dye structures, and higher aggregate structures
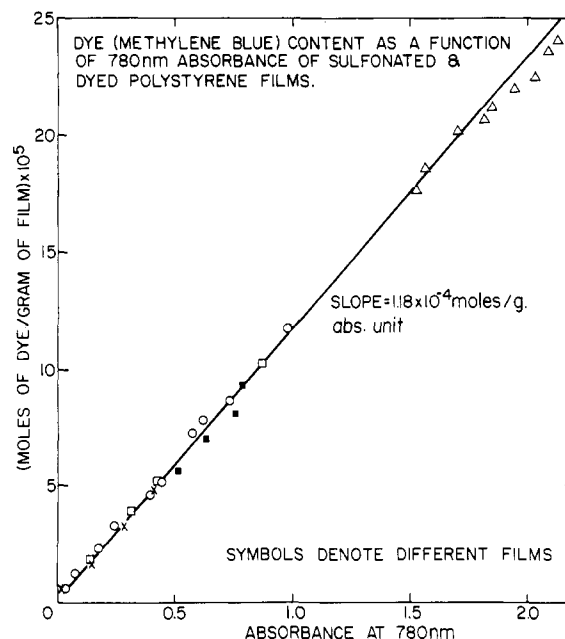
can appear at 545 nm.[16,17] However, when the dye is incrementally extracted from the polymer film by $Pb(NO_3)_2$, the state of aggregation of the residual dye on the polymer changes as evidenced by the shift in $\lambda_{max}$ with a 670-nm shoulder, followed by the 670-nm band becoming $\lambda_{max}$ with the 620-nm band as a shoulder. This change in aggregation is due to the presence of excess sulfonate sites liberated as dye is removed. Thus, this calibration procedure was impractical. A successful alternative was developed (see below). Selection of a nonaggregating cationic dye would have allowed the successful application of the extraction technique.

**5. Direct Determination of Sulfonic Acid Groups by Titration.** While the above procedure established the linear relationship between the film absorbance and the dye content of the film, there existed the possibility that not all of the sulfonic acid groups formed become dyed. If this were the case, the dye content would not completely reflect the extent of sulfonation. We thus sought an independent analytical technique for the sulfonic acid groups. We chose to titrate the sulfonated films with standard base. Sulfonated films covering a range of two orders of magnitude in acid content were examined. The absorptions of companion pieces of the sulfonated films dyed with methylene blue were measured. The absorbances ranged from very low values so that $\lambda_{max}$ (~600 nm) could be observed to intensely dyed films with which only the long wavelength tail was measurable.

The results are plotted in Figure 5. As can be seen, the acid content and the film absorbances are linear functions of one another; moreover, the intercepts are zero. The identity of the slopes of Figures 4 and 5a within experimental error is taken as evidence that the dyeing of the films with methylene blue results in essentially complete exchange of the available sulfonic acid groups, i.e., reaction 2 → 4 is complete. Thus the extent of reaction, $E$, in moles per gram of film is related to the 780 nm absorbance by eq 2 and to the ~600 nm absorbance by eq 3.

$$E = (1.22 \times 10^{-4})A_{780} \qquad (2)$$

$$E = (8.33 \times 10^{-6})(A_{\sim 600}) \qquad (3)$$

From the results of Figures 4 and 5, a direct and absolute correlation between the dyed film absorbance and the
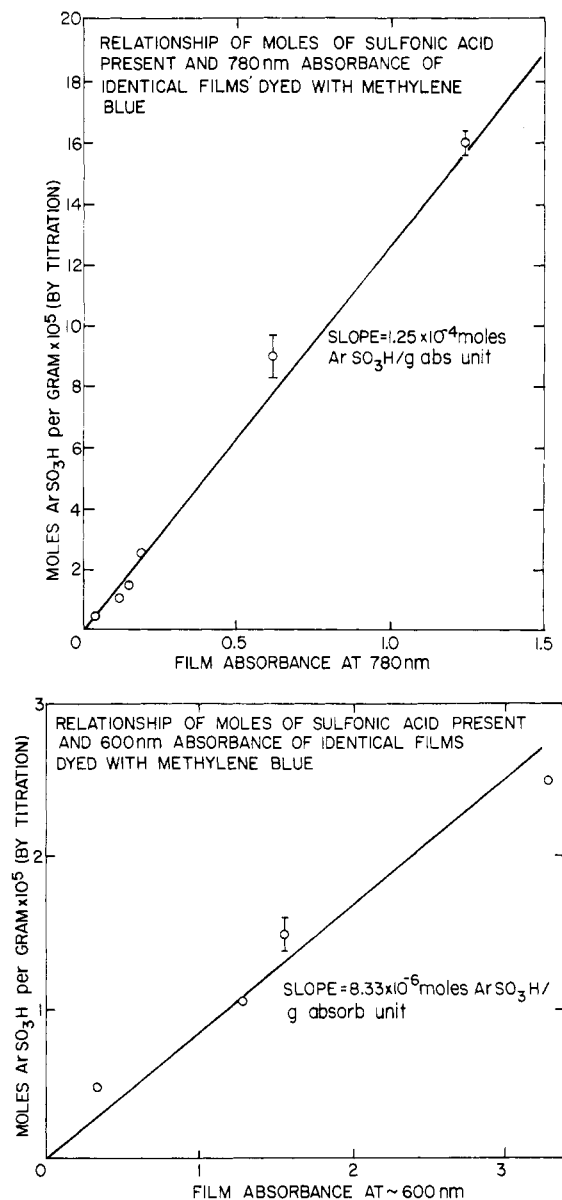
**Figure 5.** The sulfonic acid content of sulfonated polystyrene films by titration vs. the absorbance of the identical films dyed with methylene blue: (a, top) film absorbance at 780 nm; (b, bottom) film absorbance at ~600 nm.

extent of sulfonation is established. Dyeing is the method of choice over titration because it requires smaller samples of film, is easier, and is much more rapid than titration.

**6. Number of Monolayers Reacted.** With the knowledge of the number of sulfonate groups on the polystyrene film, the depth of sulfonation can be estimated in the following manner from the absolute amount of dye on a given weight of film.

The volume of 1 equiv of styrene units, $\bar{V}$, can be calculated from the density[15] to be $\bar{V} = 99.0$ cm$^3$/equiv. From Avagadro's number and the number of styryl units per equivalent, $N$, the volume per styryl unit can be calculated to be

$$V_m = \bar{V}/N = 1.64 \times 10^{-22} \text{ cm}^3/\text{unit}$$

From $V_m$, if one assumes a cubic shape, one can calculate the unit dimension $r_m$, the length of one side or unit thickness

$$r_m = V_m^{1/3} = 5.47 \times 10^{-8} \text{ cm/unit}$$

Therefore the effective exposed area per styryl unit, $\bar{A}_m$,
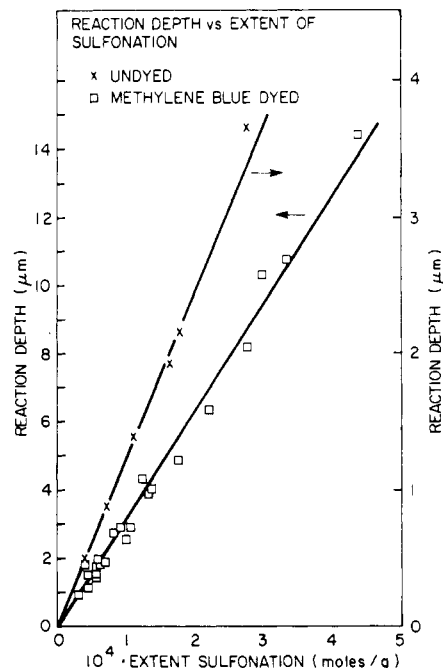


**Figure 6.** The thickness of the reacted layer vs. the extent of sulfonation for sulfonated polystyrene (X) and methylene blue dyed sulfonated (□) polystyrene films.

at the surface layer and at each succeeding layer can be calculated:

$$\bar{A}_m = r_m^2 = 2.99 \times 10^{-15}/\text{cm}^2$$

Thus an ideal planar film 1 × 1 cm would expose 3.34 × 10$^{14}$ styryl units or 5.54 × 10$^{-10}$ equiv of styryl units at the top monolayer and every succeeding monolayer. On a more readily determined weight basis, there are 6.67 × 10$^{-8}$ equiv of styrene per monolayer per gram.

Since the absorbance of the film is correlated to the amount of dye (eq 2 and 3), the film absorbance can be converted directly to the depth of sulfonation $R$ (eq 4 and 5). The total number of monolayers reacted per side is $R/2$, since the sides were shown to be equal in reactivity.

$$R = \frac{\text{mol of dye/g}}{\text{equiv of PS/layer/g}} =$$

$$\frac{\text{mol of dye/g}}{6.67 \times 10^{-8} \text{ equiv of PS/layer/g}}$$

$$R = (1.83 \times 10^3)A_{780} \qquad (4)$$

$$R = 125A_{600} \qquad (5)$$

**7. Interferometric Measurement of Reaction Depth.** Interference fringes of two distinct frequencies were observed. The high-frequency pattern corresponds to the total film thickness. The low-frequency signal corresponds to the reaction depth per side, $d_R$. The number of cycles observed over a given wavelength range is related to the depth by eq 1.

This technique was applied to both undyed sulfonated and methylene blue dyed sulfonated films. In the latter case, it was not possible to measure $d_R$ values less than 1.8 μm due to absorption. The results for both series are plotted in Figure 6 as a function of the extent of reaction determined by means of absorbance measurements (eq 1 and 2). As can be seen, the reaction depth, $d_R$, is directly proportional to the extent of reaction in both cases. This is taken as evidence that the reaction is essentially diffusion controlled, so that each monolayer is completely sulfonated before the next deeper monolayer reacts. If this

were not the case, as the reaction proceeded the diffusion front would move progressively further ahead of the reaction front, which would have a progressively increasing spatial distribution, leading to a measured reaction depth $d_R$ that increased super-linearly with absorbance. In other words, not all of the styryl units in the measured depth $d_R$ would have been reacted, and the percentage of unreacted groups in $d_R$ would have increased as the reaction proceeded.

A confirmation of this depth measurement was provided by scanning electron microscopy.[18] A sulfonated undyed film with $E = 7.0 \times 10^{-5}$ mol/g was abraded while wet. This caused removal of the sulfonated surface "skin". By examining the profile of this abrasion at 3000×, it was possible to estimate the reaction depth at $1.0 \pm 0.3$ μm. As can be seen, this point fits on the straight line plot of Figure 6 for sulfonated undyed films.

The reason there are two lines in Figure 6 is of course the difference in density of sulfonated and sulfonated dyed polystyrenes. From the knowledge of the number of equivalents of sulfonated styryl units and the reaction depth, the molar volume can be caluclated from the equation:

$$\bar{V}_m = \frac{2(A/W)d_R}{E} = 2(121 \text{ cm}^2/\text{g})(\text{slope})$$

The factor of 2 is to take into account both sides of the film. For the undyed sulfonated polymer, $d_R/E = 1.29$ μm/equiv/g, and, therefore,

$$\bar{V} = 315 \text{ cm}^3/\text{equiv}$$

Likewise for sulfonated methylene blue dyed polymer, since $d_R/E = 3.21$ μm/equiv/g,

$$\bar{V} = 783 \text{ cm}^3/\text{equiv}$$

These values are high relative to most polymers.[19a] The parachor calculated[19b] value for sulfonated polystyrene is 132 cm³/equiv, and for sulfonated methylene blue dyed polystyrene it is 379 cm³/equiv.

However, this discrepancy is readily accommodated by the known hygroscopicity of poly(styrenesulfonate)[14,34] and methylene blue[21] and the swelling effect of the water on these ion exchange polymers.[14] For Dowex 50 styrenesulfonic acid ion exchange resin prepared using 8% divinylbenzene, the volumes dry and wet of 1-g samples (initial dry weight) have been reported.[22] From the dry volume (0.696 cm³), we calculate $\bar{V} = 129$ cm³/equiv. This is in excellent agreement with the 132 cm³/equiv calculated above from parachors.[19b] From the wet volume (1.524 cm³) on the basis of $EW = 185$, i.e., an effective "solvated" equivalent, $\bar{V} = 282$ cm³/equiv. This agrees well with the value (315 cm³/equiv) derived from $d_R$ measurements made under ambient conditions. Values are not available for specific volumes of the methylene blue exchanged resin, but a value for the wet trimethylanilinium ion resin (1.666 cm³)[22] yields $\bar{V} = 533$ cm³/equiv. This value is less than the value calculated from $d_R$ for the methylene blue sulfonate, but the unit weight of the latter is greater. Correction for this on a direct proportion basis gives a predicted $\bar{V} = 780$ cm³/equiv if the hygroscopicity of the methylene blue sulfonate were the same as the trimethylanilinium sulfonate vs. the observed 783 cm³/equiv. Exhaustive drying of a methylene blue film of $d_R = 8.13$ μm over $P_2O_5$ in vacuo led to a decrease in $d_R$ that corresponds to $\bar{V} = 551$ cm³/equiv.

A plot of total film thickness vs. extent of reaction yields for $E = 0$ a thickness value within experimental error of the measured value of the starting films. This suggests

Table III
Sulfonation Bath Consistency Under Dry Conditions

| time elapsed after bath preparation | sulfonation time, min | $A_{610}{}^a$ | $A_{780}{}^a$ |
|---|---|---|---|
| 18 h[b] | 1 | 0.0406[c] | |
| | 3 | 0.119[c] | |
| | 5 | 0.175[c] | |
| 64 h[b] | 1 | 0.038[d] | |
| | 3 | 0.143[d] | |
| | 5 | 0.197[d] | |
| 18 h[e] | 10 | | 1.188[c] |
| 16.5 days[e] | 10 | | 1.169[c] |

$^a$ Dyed 30 min in 2.18 wt % methylene blue. $^b$ 99.65 wt % $H_2SO_4$. $^c$ Average of three or four films. $^d$ Single film. $^e$ 100.11 wt % $H_2SO_4$.
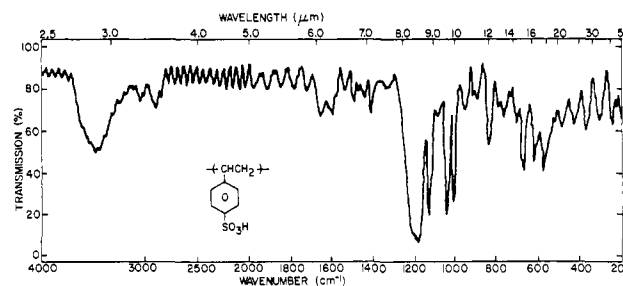


**Figure 7.** The infrared difference spectrum of the sulfonated polystyrene film vs. the polystyrene film.

that little sulfonated polymer is lost in the reaction washing and drying processes.

**D. Reaction Conditions.** To eliminate water absorption by the reagents, the sulfonations were carried out in a drybox containing open dishes of phosphorus pentoxide. As an added precaution, the sulfonation reactions were carried out in a desiccator containing $P_2O_5$.

To assure that bath deterioration by water absorption had been eliminated, several films were sulfonated at an arbitrary zero time and some 2 to 16 days later. As can be seen from Table III within experimental error the absorbance of the films is identical. The bath does not deteriorate within the time scale of the experiments.

**E. Spectral Verification of Sulfonation. 1. Infrared Characterization.** Use of the differential spectroscopy technique led to the infrared spectrum shown in Figure 7. There are a number of pertinent features. First there is a strong peak at 1190 cm⁻¹ (asymmetric $SO_2$ stretching absorption, 1150–1260 cm⁻¹).[14b] The symmetric $SO_2$ stretching absorptions appear at 1010 and 1040 cm⁻¹ (reported[14b] 1010–1080 cm⁻¹). The two peaks at 620 and 670 cm⁻¹ are considered to be due to the C–S and S–OH stretching absorptions which are reported[14b] to lie between 600 and 800 cm⁻¹ and 600 and 700 cm⁻¹, respectively. The spectrum lacks the signal associated with the sulfone moiety at 1310–1350 cm⁻¹ (asymmetric $SO_2$ stretch[14b]) but does possess a signal at 1130 cm⁻¹ that falls into the 1120–1160 cm⁻¹ range quoted for the symmetric $SO_2$ stretching absorption.[14b] However, this latter peak corresponds very nicely with an absorption of poly(m- and p-styrenesulfonic acids) prepared by polymerization.[23] Inasmuch as direct polymerization should not cause sulfone formation, the 1130-cm⁻¹ absorption is believed not to be due to the presence of sulfone linkages. Thus we believe that little sulfone formation occurs under our reaction conditions. However, the thickness measurements (above) and the linearity of the kinetic results (below) suggest that some cross-linking, presumably of the sulfone type, does occur. Moreover, the films do swell in aqueous solutions.
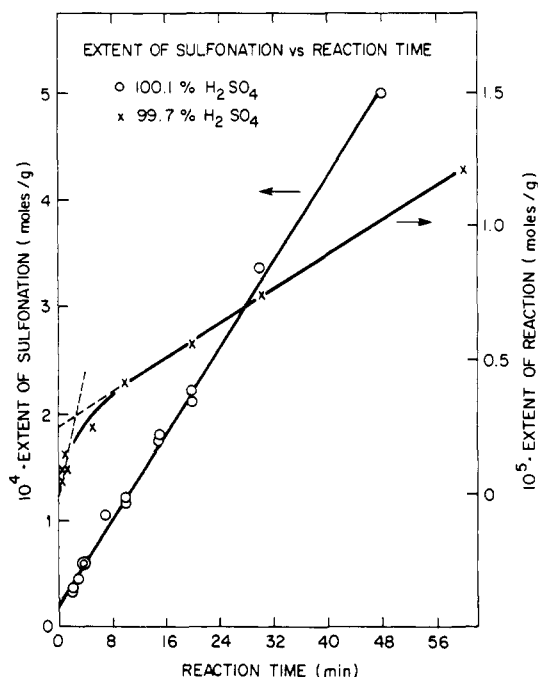
**Figure 8.** The extent of reaction vs. the reaction time for the sulfonation of polystyrene films.

The presence of a peak at 835 cm$^{-1}$ is indicative of para substitution (810–840 cm$^{-1}$).[14c] The lack of peaks in the range 735–770 cm$^{-1}$ rules out ortho substitution,[14c] and the lack of a peak at 793 cm$^{-1}$ rules out meta substitution.[23] Therefore, as shown in other heterogeneous[24] and homogeneous[23] sulfonations, only para sulfonation occurs.

The broad absorption at 3500 cm$^{-1}$ and the weak absorption at 1655 cm$^{-1}$ are due to water (reported at the same positions[14d]) adsorbed by the hygroscopic sulfonic acid groups. (See also section C7.)

Another noteworthy feature of the spectrum is the interference pattern, especially from 3.5 to 5.0 $\mu$m. As noted above (section C3), this may be used to determine the total film thickness.

**2. X-ray Photoelectron Spectroscopy (XPS, ESCA).** XPS or ESCA provides a method of analysis of surfaces to a depth of about 50 Å.[25] The technique is capable of identifying elements present by means of the binding energy distribution of core level electrons displaced by the incident X-rays. The depth profile can also be probed by changing the "viewing" angle relative to the sample.[26] Examination of the sulfonated polystyrene films by XPS yielded spectra containing signals due to oxygen 1s electrons at 540 eV binding energy and sulfur 2p electrons at 180 eV binding energy, in addition to the carbon 1s signal at 295 eV binding energy (be).[27] The untreated polystyrene film of course has only the carbon 1s signal.[27] The angular dependence of the spectrum indicates that the sulfonic acid groups do not reside at the immediate surface (top ~2 Å).[27]

The XPS spectra of the films confirm the presence of sulfur and oxygen and, in conjunction with the exchange experiments, indicate an acidic surface. Taken with the infrared spectra, the XPS confirms the introduction of sulfonic acid groups into the polystyrene "surface".

**F. Kinetics of Sulfonation.** The kinetics of sulfonation of the free-standing polystyrene films in several compositions of sulfuric acid were examined. Plots of the extent of reaction vs. reaction time typically showed two distinct regimes: (1) a linear portion at very short times (in the more concentrated sulfuric acid solutions this was difficult to see), and (2) a second linear portion extending
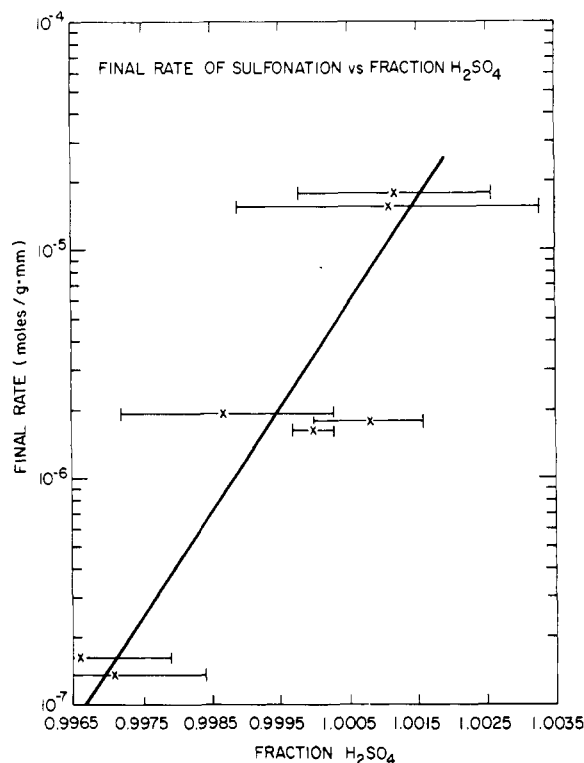


**Figure 9.** The rate of sulfonation of the polystyrene films vs. the logarithm of the sulfuric acid concentration.

to infinite times, apparently. (In more concentrated solutions this line extrapolated to finite extents of reaction at zero time.) Such plots are exemplified by those in Figure 8.

The break points in curves such as those in Figure 8 are conveniently expressed in terms of $R$. The initial slope is subject to significant error due to the short times involved, but nonetheless it can be seen that the break point occurs at $R = 20$ or less, i.e., ten or fewer monolayers per side. One interpretation of the kinetics is in terms of two distinct processes: (1) reaction of the top monolayer (the initial rate), and (2) reaction in the bulk (the final rate). The fact that the break does not occur at $R = 2$ could be attributed to the underestimation of the initial slope and the fact that the true surface area is not equivalent to the geometric area, as assumed (section C6), due to surface roughness. The greater rate of surface reaction could then be viewed as a consequence of its accessibility to the reagent. The bulk reaction is believed to be diffusion controlled in view of the linear dependence of reaction depth on conversion (Figure 6, section C7).

A second interpretation is that the reactive species is present at such low concentrations at the reaction front that both the diffusion and reaction processes play a role in the determination of the kinetics.[28] These two alternate interpretations will be discussed more fully in a subsequent report.

The rate of sulfonation very strongly depends upon the sulfuric acid concentration, as can be seen by reference to Figure 9. Two orders of magnitude in rate were observed over the narrow concentration range (0.5%) employed! This is related to the concentration of the active sulfonating species, which is believed to be $SO_3$, or compounds or ions of $SO_3$ such as $H_3SO_4^+$ or $H_2S_2O_7$.[29]

**G. Relationship to Other Work.** The only other study of surface sulfonation of polystyrene is that of Matsuda and Litt, who sulfonated polystyrene Petri dishes.[30] The reagent they employed was claimed to be

5% $SO_3/H_2SO_4$ prepared by mixing commercial 30% fuming sulfuric acid and sulfuric acid of specific gravity 1.84 (97–98 wt %[11a]). Matsuda and Litt detected by ESCA S and O on the surface of the dish after sulfonation. Attenuated total reflection infrared spectra also revealed "weak to medium" peaks at 1100 and 1200 cm$^{-1}$, which were attributed to the $SO_3H$ group.

They report that the maximum number of $SO_3H$ groups obtained after 60 min of sulfonation as measured by radioactive calcium ion exchange was 1 per 1800 Å$^2$ of surface. Note that in the present work the *surface* area per $SO_3H$ group for 2000 monolayers reacted ($6.2 \times 10^4$ mol of $SO_3H$ per g) is $1.29 \times 10^{-2}$ Å$^2$. In other words, the degree of sulfonation in the present work appears to be more than $5.58 \times 10^5$ as great as that in the work of Matsuda and Litt. In terms of number of monolayers, $R$, they reportedly sulfonated only 0.358% of the top monolayer while we sulfonated >2000 monolayers fully per side.

To test the possibility that the Petri dishes were less reactive than free-standing films, they were identically sulfonated. The extents of reaction were equal within experimental error.

It is believed that the discrepancy arises from the fact that the reagent used by Matsuda and Litt was much less than the nominal 5% value, inasmuch as the two components (50% fuming sulfuric and concentrated sulfuric acids) were from previously opened bottles.[31] In the present work it was found that the measured concentrations of the sulfonating mixtures were always much less than nominally calculated from the reagent concentrations. As can be seen from Figure 9, small changes in the reagent concentration have pronounced effects upon the reactivity.

## Summary and Conclusions

This study establishes procedures for the reproducible sulfonation and analysis of polystyrene films. Reaction of >2000 monolayers in depth per side is readily achieved. This corresponds to formation of a sulfonated layer of 3.5 μm thickness per side.

## Experimental Section

**Free-Standing Polystyrene.** All of the experiments described in this report were carried out with film from a single roll of Dow Trycite oriented polystyrene, Type 1000. Anal. Calcd: C, 92.26; H, 7.74. Found (Spang Microanalytical Laboratory): C, 92.26; H, 7.80. Gel permeation chromatography[32] in tetrahydrofuran through Stygragel columns gave $\bar{M}_w = 1.87 \times 10^5$, $\bar{M}_n = 3.93 \times 10^4$, and MWD = 4.75. The thickness as measured by interferometry on a Cary 17D spectrometer over the range 300 to 3000 nm using more than 25 samples was 79 ± 1 μm.

**Sulfonating Mixtures.** Commercial concentrated sulfuric acid and 30–33% fuming sulfuric acid were used as received. The density of the concentrated acid was 1.8350 g/mL at 23.2 °C (average of four determinations in a volumetric flask of 24.954 mL volume, standard deviation 0.0012 g/mL). The fuming acid likewise determined had a density of 1.9418 ± 0.0004 g/mL at 19.7 °C. From these densities, the concentrated sulfuric acid was determined to be 95.72 (range due to standard deviation 95.05 to 96.78) wt % $H_2SO_4$ and the fuming sulfuric 30.28 ± 0.14 wt % $SO_3$.[11] Sulfonating mixtures were prepared by weighing the two components. Each sulfonation mixture was analyzed by direct titration with 0.500 N KOH solution and a Beckman Research pH meter, using an ASTM method (Dely tube technique).[33] Three to five determinations were made on each solution. The solutions had the following compositions: 99.66 ± 0.13, 99.71 ± 0.15, 99.87 ± 0.16, 100.00 ± 0.03, 100.08 ± 0.08, 100.11 ± 0.22, 100.12 ± 0.14, and 100.34 ± 0.04 wt % $H_2SO_4$. These solutions were stored in sealed glass bottles in a drybox.

**Methylene Blue.** Commercial (J. T. Baker) dye was recrystallized three times from water to yield green-brown crystals. Anal. Calcd for $C_{16}H_{18}ClN_3S\cdot5.5H_2O$: O, 18.60; $H_2O$, 20.95. Found: O, 18.98, $H_2O$, 21.34 (Spang Microanalytic Lab.). This corresponds

to the sample equilibrated under ambient conditions and yields an equivalent weight of 473. The concentration dependence in 4 wt % $Pb(NO_3)_2$ is shown in Figure 2. The extinction coefficient (Cary 118 spectrometer) below $10^{-6}$ M is $10.7 \pm 0.2 \times 10^4$. Varying values have been quoted,[17] $9.5 \times 10^4$ being the highest, in aqueous solution due to effects of aggregation and adsorption on the glass cell walls at low concentrations. Another measure of purity is the peak (667 nm) to shoulder (~610 nm) ratio. The best reported value is 2.01 at $5.7 \times 10^{-6}$ M.[17] This sample gave 1.97 ± 0.11 (average of three values) between $10^{-6}$ and $10^{-5}$ M in 4% $Pb(NO_3)_2$.

**Sulfonation Procedure.** Strips of the free-standing polystyrene film about $2.5 \times 6.4$ cm were washed with hexane and methanol and dried. They were mounted in holders consisting of bottoms of polyethylene bottles that were slit with a knife. The films were placed in a drybox maintained at zero humidity by dry air purge and the presence of $P_2O_5$ in open dishes. The sulfonating mixture was transferred to a 100-mL beaker which was placed in a desiccator containing $P_2O_5$. The bath was stirred with a magnetic stirrer. The films were placed in the bath to a depth of about 4 cm for the requisite time of reaction and then quenched in a similar volume of commercial concentrated $H_2SO_4$ for ~2 min. Upon removal from the drybox, the films were rinsed by immersion into a beaker of deionized water several times.

**Dyeing Procedure.** The sulfonated films after rinsing were immersed without drying in 150-mL beakers full of 2.18 wt % ($4.16 \times 10^{-2}$M) aqueous methylene blue for 0.5 or 4 h (0.5 h was shown to be sufficient up to $A_{780} = 1.2$ (Figure 1); for $A_{780} = 2.5$, complete dyeing was achieved in less than 4 h). The films were rinsed with deionized water until no further dye solution was removed; this usually required only three to five 100-mL rinses. They were then air dried for several hours at room temperature.

The pH of the dye solution was 3.2, i.e., $[H^+] = 6.3 = 10^{-4}$ M. For the equilibrium

$$PSSO_3H + MB^+ \overset{K}{\rightleftharpoons} PSSO_3^- \ MB^+ + H^+$$
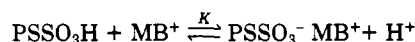
as $[MB^+] \rightarrow 0$, $K = 2200$.[34] $[PSSO_3^- \ MB^+]/[PSSO_3H] = 1.6 \times 10^6$ with the use of the $H^+$ and the dye concentrations of the present solutions. Since $K$ increases with $[MB^+]$,[34] this ratio is a minimum value and confirms complete exchange of the sulfonated films, especially since the maximum number of sulfonate sites used herein is ~$2.4 \times 10^{-5}$ equiv and the dye bath contains $7 \times 10^{-3}$ mol of methylene blue.

**Spectral Analysis.** The dyed films were examined by mounting them in the cell holder of a Cary 17D spectrophotometer, routinely scanning from 1200 nm downward. The reference beam contained an unreacted polystyrene film. The base line was taken as the lowest point between 1200 and 900 nm.

The infrared spectrum was recorded on a Perkin-Elmer 283 with a sulfonated film in the sample beam and an unsulfonated polystyrene film in the reference beam.

**Extraction of Dyed Films.** A dyed sulfonated film was trimmed to exclude all unreacted portions, weighed, and placed in a test tube. Then a known volume (usually two increments of 5.0 mL) of 10% (0.302 M) aqueous $Pb(NO_3)_2$ was delivered by pipet into the test tube, which was then shaken on a Vortex-genie mixer. The extract was decanted off into a volumetric flask (usually 25.0 mL). The test tube was rinsed incrementally with sufficient water (usually 15.0 mL) to bring the final concentration of $Pb(NO_3)_2$ to 4.00 wt %. The absorbance of this final extract was measured on a Cary 118 spectrometer, and by use of the calibration curve of Figure 2 the amount of methylene blue removed was determined. The absorbance of the film was also measured on a Cary 17D. Repetition of this process led to the curves of Figure 3. In some cases, to remove more dye per increment the 10% $Pb(NO_3)_2$ was heated prior to extraction.

**Titration of Sulfonated Films.** Sulfonation and quenching were carried out as described above on polystyrene films of $6 \times 11$ cm size. After the films were quenched in concentrated sulfuric acid, they were washed successively in 600 mL HCl solutions of 5, 4, 3, 2, and 1% concentrations to remove any $H_2SO_4$. This was tested by use of $BaCl_2$ on the final wash solution. Under the conditions used, a negative test meant that $[H_2SO_4]$ was less than $2 \times 10^{-8}$ M. They were then air dried and dried at 50 °C or less at 0.1 mmHg for 18 h to remove any residual HCl. Small ($2.5 \times 6.4$ cm) companion films for dyeing were similarly treated,

except that they were not dried prior to dyeing. The dried sulfonated films were trimmed to exclude the unreacted portion, cut into smaller ($1 \times 1$ cm) pieces, and weighed into a 150-mL beaker. The total weight was adjusted, depending on the extent of reaction, to obtain an appropriate acid concentration. Then 50.0 mL (except where noted) of standard KOH solution was pipetted into a beaker. Swelling of the films was observed. The covered beaker was placed in a desiccator containing Ascarite to exclude $CO_2$ and magnetically stirred for 18–72 h. With the use of a Beckman Research pH meter, the mixture was back-titrated with standard HCl using an argon purge. From the amount of KOH required to neutralize the film and its weight, the number of sulfonic acid groups per gram of film was calculated and plotted against the absorbance of the dyed analogue of an identically sulfonated film (Figure 5).

Titration of a film that when dyed gave $A_{780} = 1.25$ involved use of ~0.25 g of film, $2.00 \times 10^{-3}$ N KOH, and $2.00 \times 10^{-3}$ N HCl. The average of two separate determinations was $1.60 \pm 0.04 \times 10^{-4}$ mol of $ArSO_3H$ per g of film. A blank film that was carried through the quench, wash, dry, and titration cycles demonstrated that there was no acid carryover. Titration of film that when dyed gave $A_{780} = 0.621$ involved use of ~0.25 g, $1.00 \times 10^{-3}$ N KOH and $1.00 \times 10^{-3}$ N HCl; three determinations gave $9.01 \pm 0.71 \times 10^{-5}$ mol of $ArSO_3H$ per g. Titration of film that when dyed gave $A_{780} = 0.151$ and $A_{590} = 1.549$ involved use of ~0.25 g of film, $2.00 \times 10^{-4}$ N KOH and $2.00 \times 10^{-4}$ N HCl; two determinations gave $1.49 \pm 0.11 \times 10^{-5}$ mol of $ArSO_3H$ per g. Other values in Figure 5 involve single determinations. A film that when dyed gave $A_{610} = 0.331$ involved 2.3311 g of film, 60.0 mL of $2.00 \times 10^{-4}$ N KOH, and $1.00 \times 10^{-4}$ N HCl; it yielded a value of $4.93 \times 10^{-6}$ mol of $ArSO_3H$ per g of film.

**Depth of Reaction ($d_R$) Determination.** The reaction depth was determined in a number of cases by interferometry on a Cary 17D spectrometer. The film which was dried under ambient conditions was scanned from 3000 nm downward. The number of interference fringes was counted and used in eq 1. It was possible in the case of undyed sulfonated films to measure smaller depths, since there was no absorption above 300 nm. The results were directly proportional to the extent of sulfonation for both dyed and undyed films. In one instance a methylene blue dyed film of $d_R = 8.13$ $\mu$m was dried in vacuo at $5 \times 10^{-3}$ mm over $P_2O_5$ at 78 °C for 24.8 h and remeasured to give $d_R = 6.29$ $\mu$m. After 4 days under ambient conditions, $d_R = 7.34$.

**Relative Reactivity of the Two Sides.** Experiments to determine any difference between reactivities of the two sides of the film were carried out by mounting the film on a brush-grained Al plate, using General Electric M&R 10 silicone gasket cement. Two samples, one with the side taken from the inside of the film roll exposed and the other vice versa, were sulfonated simultaneously in the same bath for the same length of time in the usual manner. They were dyed simultaneously in the same bath for the same time period. The absorbances at 780 nm were 0.234, 0.229, and 0.465 for the films sulfonated on the "inside" surface, the "outside" surface, and both surfaces, respectively.

**Sulfonation of the Petri Dish.** The bottom of a Falcon 1006 polystyrene Petri dish was exposed for 6 min to ~11 mL of 100.11 ± 0.22 wt % $H_2SO_4$. Concurrently a film strip was sulfonated as usual for 6 min. The dish and film were quenched, washed, and dyed together as usual. The absorbances at 780 nm were 0.459 for the dish and 0.879 for the film. Since the film was reacted on both sides, the absorbance per side was 0.440. Thus, within experimental error, the dish and film are of equal reactivity.

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