

Electrical Conduction in Sulfonated Polystyrene Films

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Synopsis

The d.c. electrical conductivity of 14% (by weight) sulfonated polystyrene films was measured as a function of temperature from 20° to 60°C in a 25-micron vacuum. Sulfonated films in the silver, cadmium, and methylene blue sorbed forms were prepared for these electrical measurements. Plots of log specific conductance versus reciprocal temperature gave straight lines with activation energies of 0.49 eV for methylene blue, 0.60 eV for Ag, and 0.98 eV for Cd. Large conductivity anisotropies were also measured for the sulfonated polystyrene films in the Ag and methylene blue forms. Attempts with Hall-effect measurements to determine the sign and concentration of the charge carriers were unsuccessful. Photoconduction studies were also carried out with Ag-, Cd-, and methylene blue-doped sulfonated polystyrene films in the film lateral direction of highest photocurrent. Rise of photocurrent under d.c. illumination was found to be exponential with time constants of 29, 3.5, and 1.0 sec for Ag-, Cd-, and methylene blue-doped samples. The rise and decay of photocurrent in these films exhibited similar responses. Photocurrent was ohmic up to 400 V and varied linearly with light intensity up to 200 milliwatts.

INTRODUCTION

Electrical conduction in organic polymers has been investigated and extensively reviewed both from the theoretical as well as the experimental viewpoints by Rembaum and Landel,¹ Rembaum, Moacanin, and Pohl,² Gutmann and Lyons,³ and Pohl.⁴

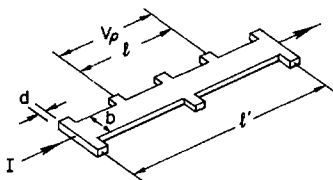
Seanor⁵ has reported that conduction anisotropy occurs in oriented nylon 66 films and confirmed that both electronic and protonic transfer are operative. He also has shown that a changeover from electronic to protonic conduction occurred below 50°C, the glass transition temperature of nylon 66. In our work, we also found a high degree of conduction anisotropy in partially sulfonated polystyrene films, containing 14% by weight of sulfonic acid content in both their ionic silver and sorbed methylene blue forms. The preparation and structural properties of these partially sulfonated polystyrene films have been recently reported by Wallace.⁶ Furthermore, the protonic transfer in these partially sulfonated polystyrene films has also been recently measured by Wallace.⁷ The hydrogen ion mobilities were computed below and above the glass transition temperature of several sulfonated polystyrene membranes having sulfonic acid contents from 2% to 14% by weight.

This paper presents the results of our d.c. conductivity and photo-conduction measurements of 14% sulfonated polystyrene films as a function of temperature between 20° and 60°C. These sulfonate films possessed a high degree of microscopic polarization and had an average dielectric constant of about 20 measured at 1 MHz and 25°C in the narrow or transverse film direction.⁸

EXPERIMENTAL

Film Preparation

Sulfonated polystyrene films each containing a 14% sulfonic acid content were prepared by casting a 20% solution of polystyrene (viscosity-average molecular weight of 125,000) in benzene followed by sulfonation by the method of Chen.⁹ The acid was readily removed from these films by washing with distilled water. Each sulfonated film was equilibrated overnight in individual aqueous 0.50 molar solutions of AgNO_3 , CdCl_2 , and



$l = 2.40 \text{ cm}$; $l' = 3.80 \text{ cm}$; $d = 2.67 \times 10^{-2} \text{ cm}$; $b = 0.50 \text{ cm}$;
 V_p = voltage across conductivity probes; I = current through sample.

Fig. 1. Sample shape of sulfonated polystyrene film.

methylene blue. After thorough washing with distilled water, each film was dried and cut into strips with a specially made die and stored under 3 microns of pressure at 25°C. The sample shape and dimensions were as shown in Figure 1. The electrode contact areas were painted with conductive Aquadag (carbon suspension in water) to reduce contact resistance.

Conductivity Measurements

Each specimen was mounted on a six-point contact holder made of Teflon. This sample holder was constructed to mount the sample in three different orientations, as shown in Figure 2. Platinum-plated pressure-type contacts were used. The complete film holder was enclosed in a brass chamber evacuated to about 3 microns of pressure. Conductance measurements using the four-probe method were performed over a temperature range between 20° and 60°C. Low-noise Amphenol coaxial cables were used in making electrical connections to minimize stray effects. An attempt to determine the sign and concentration of the charge carriers by Hall measurements using the three-probe method was unsuccessful. No

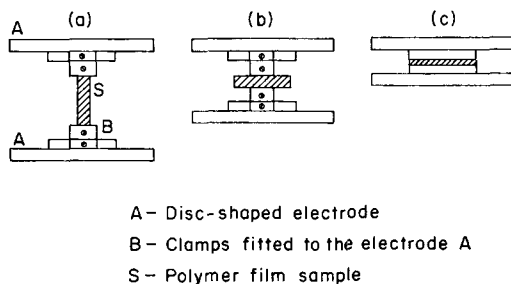


Fig. 2. Schematic photoconduction configurations of sample mountings.

detectable Hall voltage was observed in a 7.5 kilogauss magnetic field due to noise and drift problems. After the film strip was centered in the sample holder, the electrode assembly was placed in a silicone oil bath maintaining temperature within $\pm 0.2^\circ\text{C}$. It was then heated at a rate of $0.2\% \text{ C/min}$. Current was measured with a Keithley electrometer Model 610-Q. A Leeds and Northrup temperature potentiometer in conjunction with a Cu-Constantan thermocouple was used to measure temperature. Measurements were conducted at constant voltage, usually 6 volts supplied by a Trigon Electronics Model HR40-750 adjustable d.c. power supply.

The specific conductance of the sample was calculated from the equation

$$\sigma = \frac{Il}{V_p db} (\text{ohm cm})^{-1} \quad (1)$$

where I is conduction current, in amps; V_p is voltage drop across conductivity probes in volts; l is the length of sample between conductivity probes, in cm; b is the width of sample, in cm; and d is the sample thickness, in cm.

As the application of d.c. voltage to the film sample will give rise to decaying capacitive currents, a check was made of the duration of such currents to ensure that they introduced no significant error in our conductivity measurements. The time constant calculated with an experimental value of 30 as the approximate static dielectric constant for a dry sulfonated polystyrene film is approximately 10^{-4} sec. This value is small enough with respect to the measuring times involved (≥ 0.1 sec) that we can neglect capacitive currents.

In our measurements, the sample current decreased rapidly with time after the application of the voltage step, so we have chosen to report conductivity values corresponding to the maximum values of current registered on the electrometer before the decrease began. This choice minimized any errors due to sample polarization as well as eliminated the effect of capacitive currents. Our choice of a maximum sample current value was checked by comparison to a.c. measurements at 60 and 1000 Hz. The d.c., 60 Hz, and 1000 Hz conductivity values all agreed to within $\pm 5\%$. Our a.c. conductivity measurements also agreed with our maximum d.c. conductivity in all sample directions.

Photoconduction Measurements

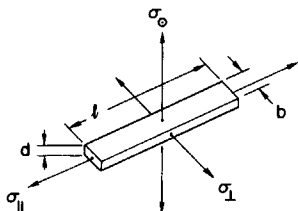
A different sample holder was constructed for the photoconductivity measurements. Two copper-disc electrodes were mounted on Teflon-insulated supports. Each disc could be heated individually by a 25-W, 10-ohm Silicohm resistor. By a set of clamps fitted to the discs, the film could be mounted in three different orientations. Referring to Figure 2, configuration (a) was used to measure photoconductivity and dark conductivity in the σ_{\parallel} lateral film direction. The electrode assembly was enclosed in a cylindrical outer case with windows and was evacuated to 25 microns. Illumination for the photoconduction experiments was provided by an AO No. 353 lamp with a focusing condensing system and a variable-voltage transformer to control the light intensity. Light intensity was measured with an Optics Technology Inc. power meter 610. An HP 711A power supply provided an applied voltage across the sample; current was measured with the Keithley 610B electrometer. To record the rise and decay of the photocurrent, the output of the electrometer was fed into a Nesco JY110 charge recorder.

RESULTS AND DISCUSSION

In Table I are shown the specific conductivities and activation energies of the substituent silver and cadmium ionic states and the sorbed methylene blue form. The values were measured along the parallel plane of the sample or along the σ_{\parallel} lateral direction as shown in Figure 3. Over the temperature range between 20° and 60°C, it is seen that film conductivity increases exponentially with temperature, as given by

$$\sigma = \sigma_0 \exp(-E/kT) \quad (2)$$

with σ_0 as the preexponential constant and E as the apparent activation energy of conduction.



- σ_{\parallel} = Direction of highest conductivity
- σ_{\perp} = Direction of intermediate conductivity
- σ_0 = Direction of lowest conductivity

Fig. 3. Conductivity anisotropy.

TABLE I
Conductivity of Ionic Polystyrene Films^a

Form	$\sigma_{21^\circ\text{C}}$, (ohm cm) ⁻¹	σ_0 , (ohm cm) ⁻¹	E , eV
Ag	3.94×10^{-7}	3.3×10^3	0.60
Cd	1.05×10^{-9}	6.3×10^7	0.98
Methylene blue	1.04×10^{-6}	3.3×10^2	0.49

^a Specific conductivity measured along the $\sigma_{||}$ lateral direction or highest conductivity as shown in Figure 3.

The activation energy E in Table I was calculated from the slope of $\log \sigma$ versus reciprocal temperature plots, as given by

$$E = -1.98 \times 10^{-4} \left[\frac{\Delta \log \sigma}{\Delta(1/T)} \right]. \quad (3)$$

The preexponential constant σ_0 was calculated from eq. (2) by substituting in the computed value of E and the measured specific conductivity value of σ at a given temperature. Considering the preexponential constant σ_0 and experimental activation energy E_{act} results given in Table I, it is noted that $\log \sigma_0 = A + B E_{\text{act}}$ for the different ions. The constants A and B are computed to be -3.2 (ohm cm)⁻¹ and 11.3 (eV ohm cm)⁻¹.

Upon application of the applied voltage across a sulfonated polystyrene film in its substituent form, the measured conduction current initially decayed with time and thence approached a steady-state value. This time dependence of conduction current was more prominent for the film in its cadmium ionic form. Moreover, for the sample in either its silver or methylene blue form the initial conductance current also dropped by about an order of magnitude but thence remained fairly constant with time up to about 1000 min.

Sorbed methylene blue functions as an organic oxidation-reduction agent¹⁰ upon the sulfonated polystyrene substrate. The electronic behavior of these dye-sorbed films appears to resemble solid electron exchanges.¹¹ It is believed that the electron conduction process probably involves the formation of charge transfer complexes at the methylene blue-sulfonate sites within the film.

Conductivity anisotropies for the sulfonated polystyrene films at 21°C in their respective ionic silver and sorbed methylene blue forms are given in Table II. In these measurements, conductivity was highest in the $\sigma_{||}$ direction, intermediate or slightly lower in the σ_{\perp} direction, and markedly lower in the σ_0 direction. These conduction anisotropies appear to be caused by nonuniform sulfonic acid distribution across the film rather than differences in mobility. It is extremely unlikely that the sulfonic acid groups and consequently the diffused counterions are distributed uniformly across the film. Consequently, conduction anisotropy is to be expected. It is interesting to note that the minimum conductivity of the Ag and methylene blue is the same within 1%, suggesting that indeed this is the

TABLE II
Conductivity Anisotropies in Ionic Polystyrene Films

Current direction	Specific conductance at 21°C, (ohm cm) ⁻¹	
	Ag	Methylene blue
Lateral σ_{\parallel}	3.94×10^{-7}	1.04×10^{-6}
Lateral σ_{\perp}	2.44×10^{-7}	0.99×10^{-6}
Transverse σ_0	1.96×10^{-9}	1.95×10^{-9}

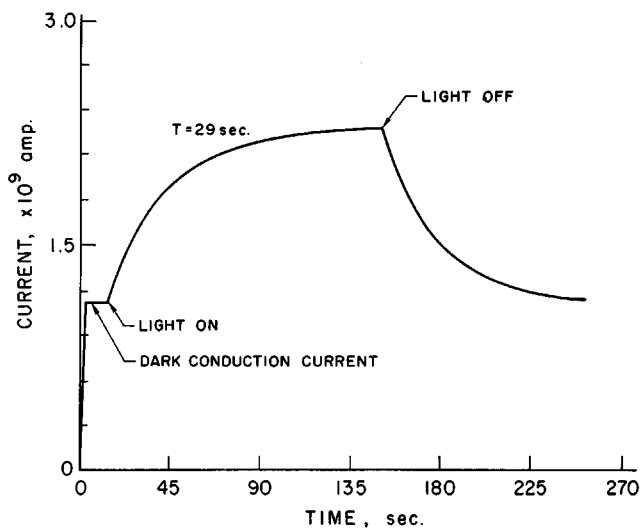


Fig. 4. Response of photocurrent in Ag-doped sulfonated polystyrene film under a d.c. illumination of 99 milliwatts and measured at 25°C in a 25-micron vacuum.

cause of the measured anisotropy. These anisotropic effects can be incorporated into our conduction eq. (2) by including a geometric factor in the preexponential factor k_j in the preexponential term:

$$\sigma_j = k_j \sigma_0 \exp\left(\frac{-E}{RT}\right) \quad (4)$$

where $j = \parallel, \perp$, or 0.

Photoconduction characteristics of our doped films, using the configuration (a) orientation as given in Figure 2, were measured in a 25-micron vacuum and at 25°C. The response of conduction current under a d.c. illumination of, for example, 99 milliwatts for the Ag-doped film in the σ_{\parallel} lateral direction was as shown in Figure 4. When the light was turned on, the current rose exponentially with a time constant of 29 sec, and reached a steady state in about 150 sec. After the light was turned off, the photo-generated carriers recombined and the decay of conduction current was again exponential.

TABLE III
Photoconduction Characteristics of an Ag-Doped Sulfonated Polystyrene Film
Measured at 25°C in the σ_{\parallel} Lateral Direction

Light intensity, mW	Illuminated current, amp	Illuminated Conductivity, (ohm cm) ⁻¹
28	1.38×10^{-8}	3.18×10^{-8}
54	1.68×10^{-8}	3.87×10^{-8}
67	1.83×10^{-8}	4.21×10^{-8}
99	2.31×10^{-8}	5.31×10^{-8}

The rise of conduction current in the Ag-doped sulfonated polystyrene film under illumination was found to be

$$i(t) = I_D + I_{Ph} (1 - e^{-t/\tau}). \quad (5)$$

The decay of conduction current after the light was turned off followed the expression

$$i(t) = I_D + I_{Ph} e^{-t/\tau} \quad (6)$$

where I_D = steady-state dark conduction current, I_L = steady-state illuminated current; I_{Ph} = steady-state photocurrent = $I_L - I_D$, and τ = time constant.

For an illuminated intensity of 99 milliwatts, the constants in the conduction current and conductivity eqs. (5) and (6) are 1.11×10^{-8} amp for the steady-state dark conduction current I_D ; 2.56×10^{-8} (ohm cm)⁻¹ for the steady-state dark conductivity σ_D ; and 29 sec for the time constant. On substituting, eqs. (5) and (6) become

$$i(t) = 1.11 \times 10^{-8} + 1.20 \times 10^{-8} (i - e^{-t/29}) \quad (7)$$

$$\sigma(t) = 2.56 \times 10^{-8} + 3.1 \times 10^{-8} (i - e^{-t/29}). \quad (8)$$

The photoconduction characteristics of the Ag-doped film as a function of light intensity are shown in Table III. Photocurrent was found to vary linearly with light intensity. Both the dark and illuminated conduction currents as a function of applied voltage were found to be ohmic up to 400 volts in the σ_{\parallel} lateral film direction.

Photoconduction characteristics of the sulfonated polystyrene films in the cadmium and methylene blue forms in a 25-micron vacuum and at 25°C were also measured in the σ_{\parallel} direction using configuration (a) orientation as given in Figure 2. The rise in photocurrent under a d.c. light intensity of 54 milliwatts was found to be exponential but with faster time constants of 3.5 and 1.0 sec. The rise and decay of photocurrent in the Cd- and methylene blue-doped films exhibited similar responses to that in the Ag-doped form. Similarly, photocurrent was ohmic up to about 400 volts and varied linearly with light intensity up to 200 milliwatts. Comparatively, photoconduction in other photoconducting benzophenone-dyed polymer films,¹² measured under equivalent conditions of light intensity,

film direction, vacuum, and temperature, also showed macroscopic photoconductivity but to a much lower extent than observed in our methylene blue sulfonated polystyrene film.

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