Chemical modification of polymers: 17. Dyeing of sulphonated polystyrene films by ion exchange with cationic dyes*

Harry W. Gibson and F. C. Bailey
Webster Research Center, Xerox Corporation, Webster, NY 14580, *USA*

(*Received* 26 *August* 1980*; revised* 20 *October* 1980)

Heterogeneous dyeing of free-standing films of surface sulphonated polystyrene by ion exchange with aqueous cationic dyes has been studied. Studies of (1) the optical density of films with a given extent of sulphonation as a function of dyeing times, (2) the optical density for constant dyeing time as a function of extent of sulphonation and (3) the thickness of dye sulphonate layers as a function of both dyeing time and extent of sulphonation have been used to establish times for complete dyeing. Using the thickness measurements, estimates of equivalent volumes of the dye sulphonates were made. Displacement of one dye by another was also studied; use of previously derived analytical techniques for this sort of displacement must be used with care due to differences in degree of aggregation, as demonstrated for methylene blue.

INTRODUCTION

Manipulation of the physical and chemical properties of polymers by chemical modification is becoming increasingly important[2–7]. Application of this technique to the surfaces of polymers has been utilized for the variation of properties such as adhesion[8], dyefastness[9–11], wettability[12], weatherability[13], permeation[14], friction[15], electrostatic charging[15,16], and biocompatibility[17]. The details of these modifications are unknown in most, but not all[18], cases.

We have reported a detailed systematic study of the sulphonation of polystyrene surfaces[1a] as the introductory paper in a series aimed at providing a more detailed picture of surface modification and its effect upon physical properties. Our general objectives are: (1) establishment of techniques for quantitative analysis of surface modified polymers; (2) development of conditions for reproducible, controlled modification; (3) understanding the kinetics of modification; (4) analysis of the structure of the surface vs. bulk of resultant solids; and (5) relating surface and bulk structure to physical properties.

Our efforts focussed[1a] on objectives (1) to (3). In other papers[19,20] objectives (4) and (5) have been considered. Here the primary aims are objectives (1) and (2) for the ion exchange of sulphonated polystyrene surfaces with cationic dyes. Later reports will describe a study of the dyed sulphonated films produced.

Interactions of polymers with various cationic dyes in solution have been the subject of many reports, concerned with the extent of binding[21], metachromasia (the shift of dye absorption in presence of polyanions) and state of dye aggregation[22–24], use as fluorescent probes[25] and end-group analysis[26].

In contrast the interaction of cationic dye solutions with polyanionic solids has received little attention. The interaction of methylene blue solutions with ion exchange resins[27,28], with montmorillonite (a mineral)[29] and with cellulose derivatives[30] have been reported. Dyeing of anionic fibres has, of course, been well studied for textile applications[31,32]. However, the study of heterogeneous reactions of a well-characterized sulphonated polystyrene surface with aqueous cationic dyes has not been reported. This subject is the basis of this report.

EXPERIMENTAL

Sulphonation

The polystyrene films, the reagents, reaction conditions and analytical procecures were fully described in an earlier publication[1a].

Cationic dyes

Acridine orange was used as received (Reagent Grade) from Aldrich Chemical Co. Brilliant green (93%) was obtained from Matheson, Coleman and Bell. Crystal violet was 95% pure as certified by Matheson, Coleman and Bell; it was recrystallized once prior to use. Methyl violet was purchased from Eastman Kodak and used as received. Rhodamine B was used as received from Matheson, Coleman and Bell.

Dyeing procedures

Sulphonated films were kept wet in deionized water until the start of dyeing and were immersed in the dye solution in a covered beaker. They were then removed and washed repeatedly with deionized water over a period of minutes. Films were then air dried or vacuum dried prior to absorbance and interferometric thickness determinations.

The replacement of acridine orange from a dyed (19 h in 250 ml, 4.07×10^{-2}M) sulphonated film ($\sim 4 \times 7$ in, 2.05 $\times 10^{-5}$ mol g^{-1}) involved use of 250 ml of 4.16×10^{-2}M methylene blue.

---

[*] Reference 1 gives details of other parts of this series in press

0032–3861/81/081068–05$02.00

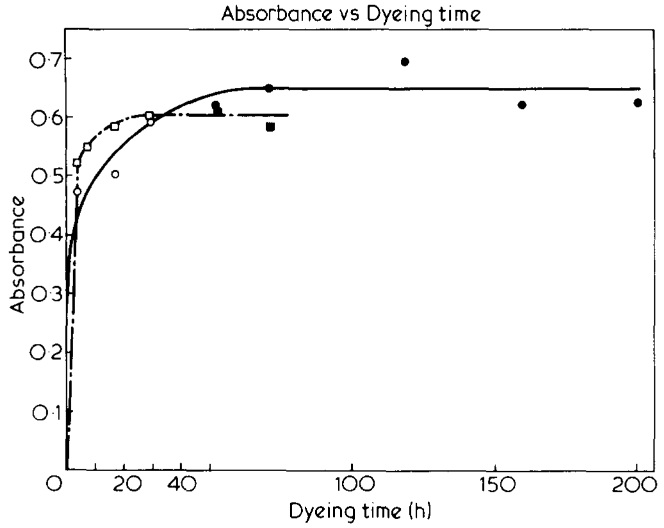


Figure 1 Absorbance of sulphonated polystyrene films vs. dyeing time in methyl violet and crystal violet. Polystyrene films 2.0 x 0.75 in; Sulphonated 2.74 x 10^{-4} mol g^{-1}; Methyl Violet (9.71 x 10^{-2} M) ○, 50 ml; ●, 100 ml; A_{715nm}. Crystal Violet (1.91 x 10^{-2}), □, 50 ml, ■, 100 ml; A_{710nm}

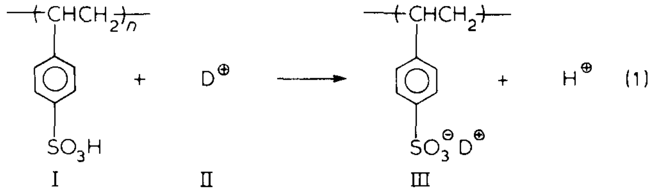
DISCUSSION

As mentioned above, one of our aims is to relate the physical behaviour of chemically modified polymer surfaces to the chemical and physical structures involved. In order to achieve this goal it is necessary that the chemical modification be reproducible and measurable by standard analytical techniques. Specifically, the incorporation of cationic dyes into sulfonated polystyrene films (equation 1) is of concern. The dyeing must reach completion [i.e. a large fraction (>0.95) of the sulphonate groups must be exchanged] in each case in order to be able to compare the physical properties of the resultant films. Here, the emphasis is on the development of methods for determination of the times required for complete dyeing, estimation of molar volumes of the dyed sulphonate and study of replacement of one dye by another. All of the present studies involve free-standing polystyrene films sulphonated and analysed as reported earlier[1a].

Time dependence of dyeing

A film sulphonated to the extent of 8.54 x 10^{-5} mol g^{-1} (1280 ideal monolayers per side) was shown to be fully dyed within 10 min in 2.18 wt % aqueous methylene blue[1a]. Less highly sulphonated films were also shown to be completely dyed in less than 10 min under these conditions. A more highly sulphonated film (3.05 x 10^{-4} mol g^{-1}, 2290 ideal monolayers) required between 0.5 and 4.5 h for complete methylene blue dyeing[1a].

In the same manner we have examined dyeing with other cationic dyes to ascertain minimum times for complete dyeing. Representative curves are given in *Figure 1*. It can be seen that under the stated conditions, 20 h is required to dye with methyl violet, while crystal violet requires about 75 h.



$$K = \frac{[\overset{+}{H}][III]}{[I][II]} \qquad (2)$$

Yet another way to examine the kinetics of dyeing is to monitor film absorbance as a function of extent of sulphonation for a given dyeing time. The point at which the plot changes from the initial slope to a line of different (lesser) slope is the extent of reaction beyond which the dyeing period is insufficient for saturation dyeing. This represents the depth of sulphonation beyond which the time is insufficient to allow diffusion of a number of dye cations equal to the number of sulphonic acid moieties. The diffusion of the protons out of the film is much more rapid and therefore is not rate limiting (*Figure 2*). This is borne out by the observation of an immediate drop in the pH of deionized water upon immersion of a sulphonated film and the immediate return to pH7 upon film withdrawal.

Thus, in *Figure 3* it can be seen that 1 h dyeing with 2.05 x 10^{-2}M brilliant green allows diffusion of the dye only through about 6 x 10^{-5} mol g^{-1} (~0.6μm of sulphonated polystyrene) and then the absorbance reaches a plateau level at $A_{700} = 0.92$.

This same phenomenon can be detected by interferometric measurement of the thicknesses of sulphonated and dyed films as a function of extent of sulphonation for constant dyeing time. Such plots are shown in *Figure 4* for rhodamine B and brilliant green, for dyeing times of 1 and 4 h. Note that in each case, 1 h dyeing leads to a break in the curve (at ~1.75 x 10^{-4} mol g^{-1} for rhodamine B and

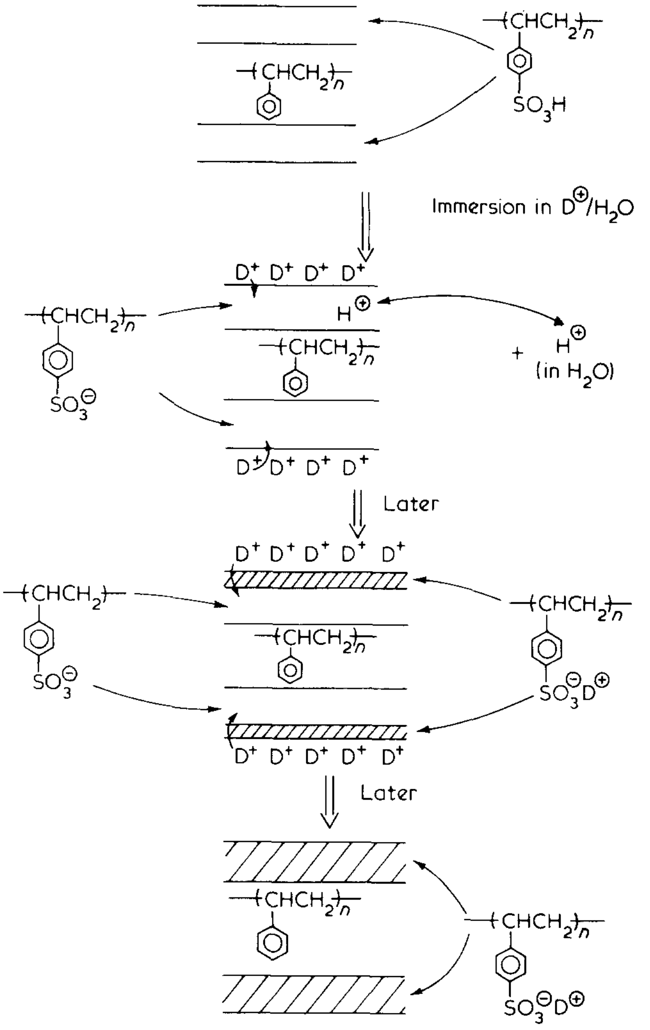


Figure 2 Schematic representation of diffusion of protons out of, and dye cations into, sulphonated polystyrene films

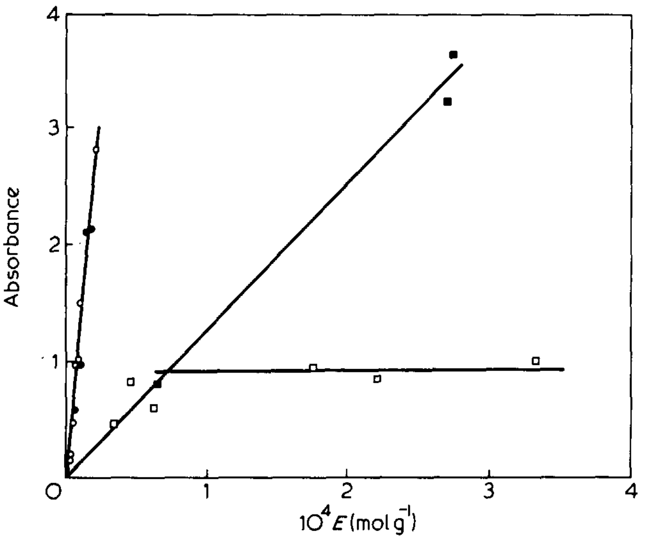


Figure 3 Absorbance of brilliant green dyed sulphonated polystyrene films as a function of extent of sulphonation. 2.05×10^{-2} M Brilliant green 1 litre per 4 x 7 inch film. ○, $A_{\lambda max(645 nm)}$ □, A(700nm). Open symbols, 1 h; closed symbols, 4 h

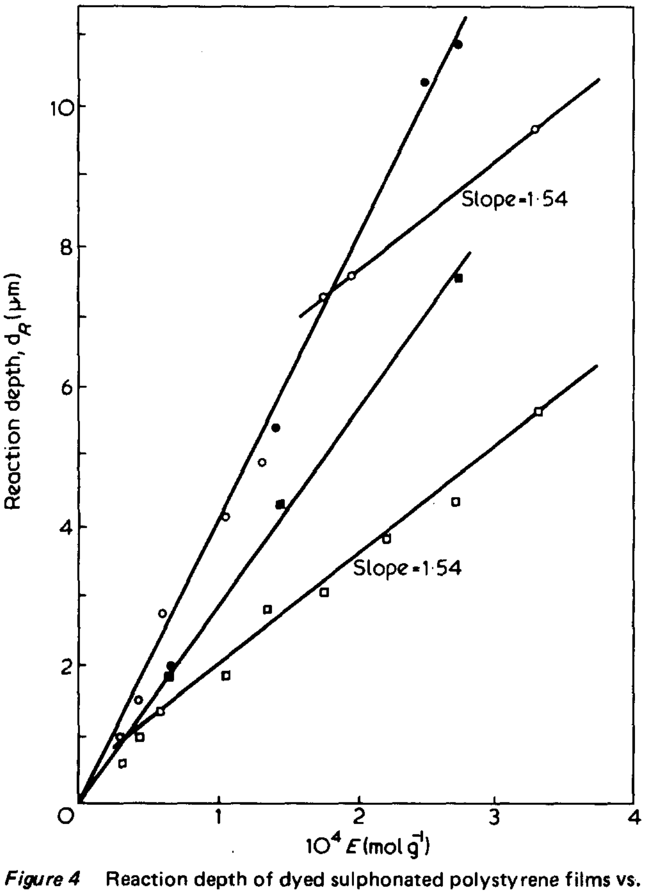


Figure 4 Reaction depth of dyed sulphonated polystyrene films vs. extent of sulphonation. ○, Rhodamine B; □, brilliant green; open symbols, 1 h; closed symbols 4 h

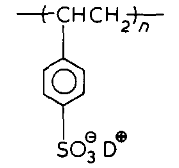
at 6×10^{-5} mol g^{-1} for brilliant green). The initial slopes for 1 h dyeing are representative of complete dyeing of the films. This is demonstrated by the points for 4 h dyeing, lying on these lines. Assuming that the spatial distribution of the dye is unchanged above the break point, the slope of the curves beyond the break point should be the same as that of sulphonated undyed polystyrene (1.29×10^4 μm.g mol^{-1})[1a]. The slopes of the lines of *Figure 4* are identical (1.54) and within 20% of this value.

Determination of equivalent volumes of dye-polystyrenesulphonate

The equivalent volume of the sulphonate unit can be calculated, as noted previously[1a], from the slopes of d_R vs. E in *Figure 4*. In *Table 1* slopes of such plots for various dyes and other cations are given. The calculated equivalent volumes, $\bar{V}_E$, are listed. These were calculated from the relationship[1a]:

$$\bar{V}_E = (244\ \text{cm}^2\ \text{g}^{-1})\ (d_R/E)$$

Table 1 Slopes of d_R vs E plots and resultant calculated equivalent volumes for sulphonated polystyrene films



$D^{\oplus}$	$10^4\ d_R/E^a$ (μm g mol^{-1})	V_E (cm^3 mol^{-1})	E.W.
H	1.29^b	315	185
Na	0.885^c	216	207
$N(C_2H_5)_4$	1.62^b	395	315
Methylene Blue	3.21^b (2.26^d)	783^b (551^d)	468
Brilliant Green	2.80^c	683	570
Rhodamine B	4.07^b	993	627

[a] Slope of plot of reaction depth vs. extent of reaction
[b] Dried under ambient conditions
[c] Dried at 25°C, 1 Torr for 2–4 weeks
[d] Dried at 78°C, 5×10^{-3} Torr over P_2O_5 for 24.5 h

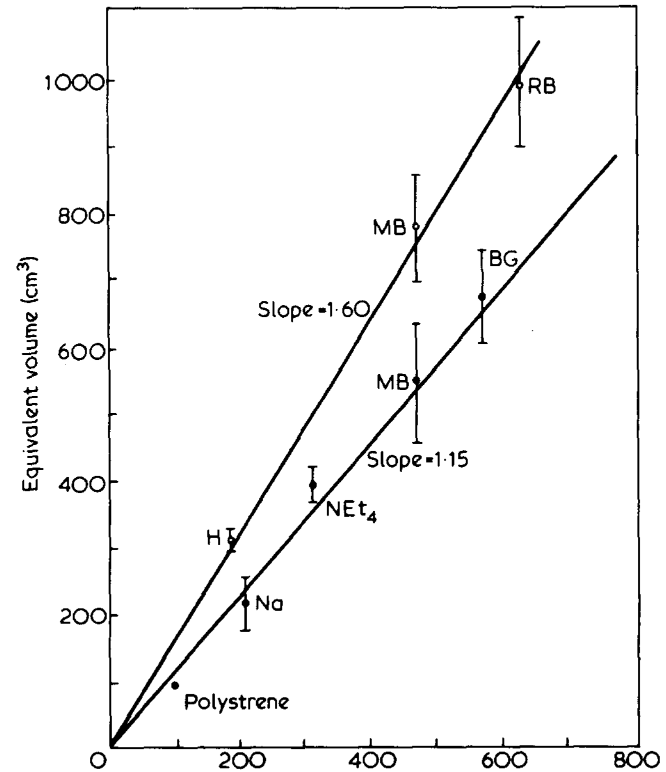


Figure 5 Experimental equivalent volume vs equivalent weight of polystyrene sulphonates. Closed symbols, vacuum dried; open symbols, ambient dried

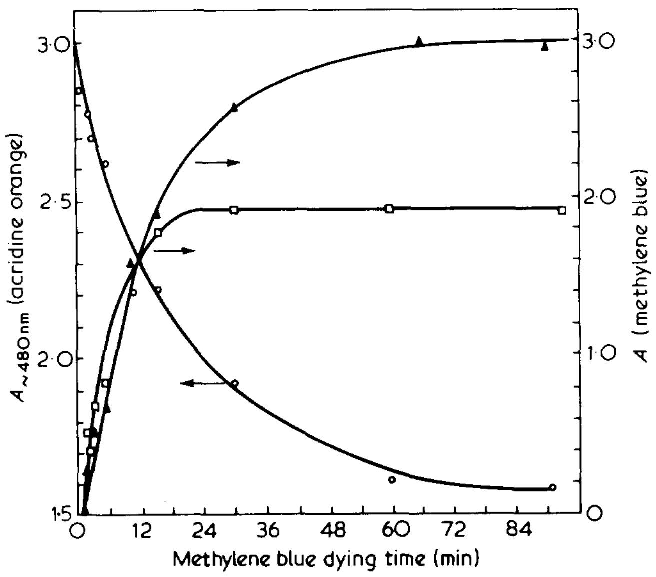


Figure 6 Acridine orange and methylene blue absorptions vs. methylene blue dyeing time for sulphonated polystyrene film initially completely dyed with acridine orange. Replacement of acridine orange by methylene blue (4.16 x 10^{-2} M) from film with 2.05 x 10^{-5} mol g^{-1} sulphonate functions. Methylene blue absorbances: ▲, $A_{aggregate(590-645\,nm)}$; □, $A_{monomer(673-685\,nm)}$

The relationship between V_E and equivalent weight (per unit) of the sulfonated polystyrenes is shown to be approximately linear in *Figure 5*. A value is also plotted for polystyrene. Two lines are shown: one for vacuum dried samples, the other for samples dried under ambient conditions. There is about 25% loss of reacted thickness upon vacuum drying on the average. It is worth noting that in each case there is a linear relationship between the equivalent volume calculated from the reacted depth and equivalent weight of the dye sulphonate. This fact corroborates the other evidence indicating essentially complete exchange of the sulphonic acid protons by the various cations. From the slopes, the average densities of the vacuum dried exchanged sulphonates can be calculated, assuming the complete absence of water, to be 0.88 g cm^{-3}. This number appears to be reasonable; for Dowex 50 resin exchanged with triethylammonium cations Gregor *et al.*[33] report a dry density of 0.89 g cm^{-3}. This corresponds to a specific volume (the slope of *Figure 5*) of 1.13, while completely wet the specific volume was 1.62[33]. These numbers are in excellent agreement with the slopes of *Figure 5*.

A peculiarity of these films is that once they have been vacuum dried the reacted thicknesses, d_R, increases only slowly upon re-exposure to ambient conditions. This observation is consistent with the fact that dried films are not wetted by brief immersion in water and the low surface energy of the sulphonic acid films themselves[19,20] and indicates that the sulphonate groups in the dry state aggregate in the bulk, leaving an essentially polyethylene-like surface structure due to the aliphatic backbone of the polymer. For this reason, films for dyeing were never allowed to dry, but were kept in deionized water. Films sulphonated to the extent of 2.26×10^{-5} to 1.40×10^{-4} mol g^{-1} took up to 13% less methylene blue dye when vacuum dried prior to dyeing.

Replacement of one dye cation by another

We had an interest in replacement of one dye from a completely dyed film by a second dye. At equilibrium the relative amount of the two dyes is controlled by the relative concentrations and the selectivity of the sulphonated polystyrene (equation 2)[34].

A polystyrene film sulphonated to the extent of 2.05 $\times 10^{-5}$ mol g^{-1} was completely dyed with acridine orange. After being washed free of excess dye but while still wet, pieces of this film were immersed for various lengths of time in methylene blue solution. The changes in absorbances at various wavelengths are shown in *Figure 6*. As anticipated, $A_{\sim 480\,nm}$, the absorbance due to acridine orange, decreases smoothly to a constant value after about 60 min and $A_{\sim 600}$ and $A_{\sim 680}$, the absorbances due to methylene blue[24,29], increase smoothly to a constant value after 30 to 60 min. However, there are some differences between these spectra and the spectra of fully dyed films of varying extent of sulphonation (*Figure 8*). This is seen most clearly in the methylene blue spectra. Firstly, there are wavelength differences. The absorbance of fully dyed lightly sulphonated polystyrene films is a maximum at ~620 nm; with increasing extent of sulphonation λ_{max} shifts to ~580 nm (*Figure 8*). This is attributable to the formation of more of the higher order aggregates of the dye in the more heavily sulphonated films, which, under the aqueous dyeing conditions, allow more mobility of the sulphonate-dye moieties than the lightly dyed films. However, in the acridine orange–methylene blue films, λ_{max} (of MB) varies from 683 nm (monomer), at low dyeing times, to 590 nm (aggregate) at longer times (*Figure 7*). Due to the presence of greater amounts of monomer in the acridine orange–methylene blue dyed films, use of $A_{\sim 600\,nm}$[1a] to calculate the number of moles of methylene blue gives erroneously high results. The final A_{590} value gives a value of 2.48×10^{-5} mol g^{-1} of methylene blue, a factor of 1.2 times more than the total number of sulphonate groups. The $A_{\sim 480}$ absorbance (acridine orange) decreases by a factor of 1.93, indicating that 48% of the acridine orange was replaced by methylene blue, i.e., 9.84×10^{-6} mol g^{-1} of methylene blue were present at the final time. These results illustrate the danger of using absorbance to estimate dye levels in such mixed systems; use of appropriately integrated intensity data would presumably be viable.

Note that replacement of acridine orange by methylene blue is much slower (*Figure 6*) than displacement of a proton from the acid by methylene blue[1a] by a factor of about 100. Moreover the ratio of equilibrium constants (equation 2) K_{AO}/K_{MB} can be evaluated on the basis of the amount of acridine orange displaced, the amount of

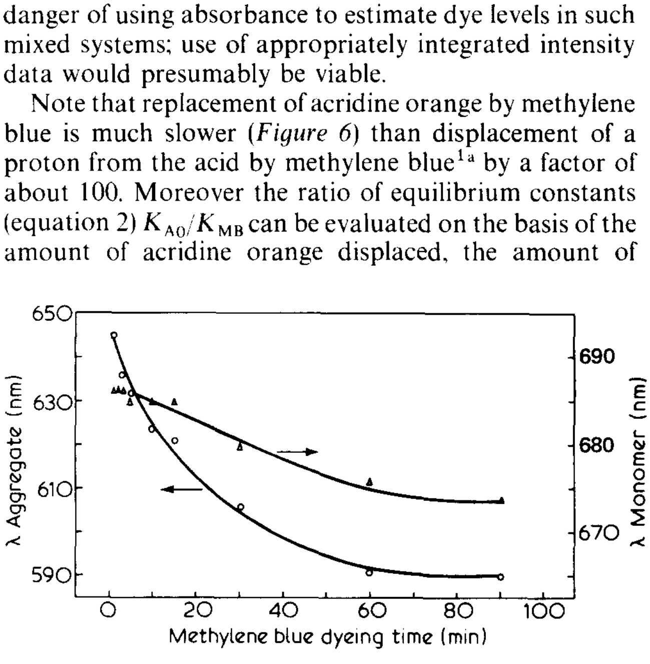


Figure 7 Wavelength of absorption maxima for aggregate and monomer peaks of methylene blue vs methylene blue dyeing time for a film completely dyed initially with acridine orange (see *Figure 6*)

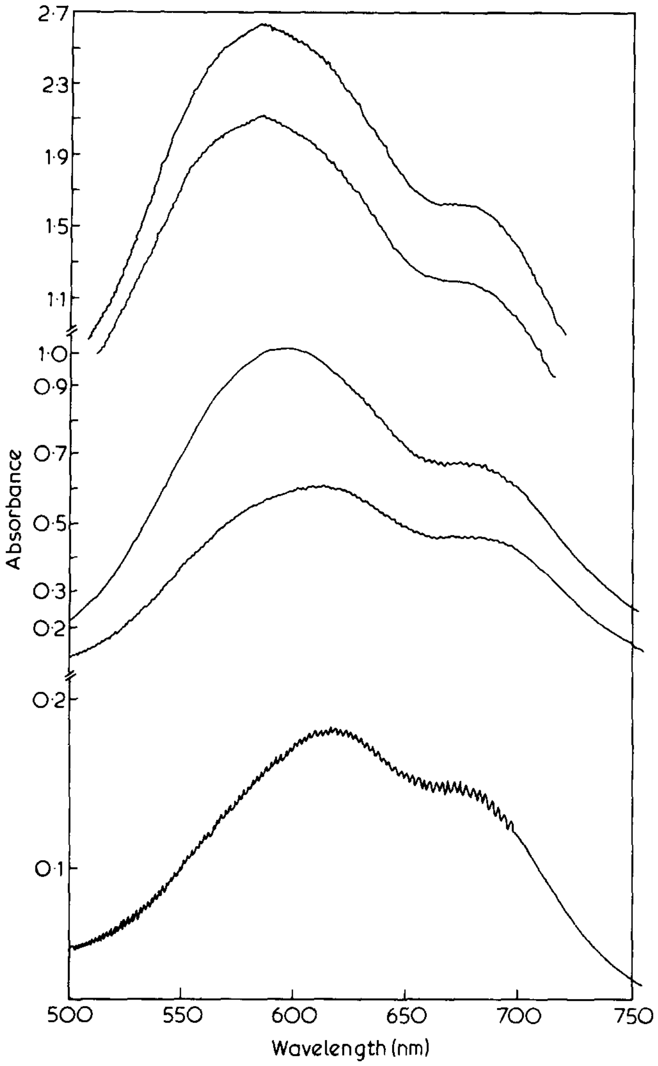


Figure 8 Absorption spectra of sulphonated polystyrene films completely dyed with methylene blue for several different extents of sulphonation

acridine orange remaining, the weight of the film and the volume of methylene blue solution (equation 3). $K_{\mathrm{AO}}/K_{\mathrm{MB}}$ is thus estimated to be 1.2×10^4. Since $K_{\mathrm{MB}}=2200$ as a minimum value[28] $K_{\mathrm{AO}}\geqslant 2.5\times10^7$. This calculation ignores any interactions between acridine orange and methylene blue that quantitatively effect $A_{\sim 480\,\mathrm{nm}}$[35].

$$\frac{K_{\mathrm{Ao}}}{K_{\mathrm{MB}}}=\frac{[\mathrm{MB}^+][\mathrm{IIIAO}]}{[\mathrm{AO}^+][\mathrm{IIIMB}]} \qquad (3)$$

CONCLUSION

In summary, heterogeneous cationic dyeing of free-standing films of polystyrene that have been sulphonated has been examined to establish minimum dyeing times. Several techniques were applied for the determination of total dyeing, including variation of dyeing time at constant extent of sulphonation, variation of extent of sulphonation of constant dyeing time and variation of reaction layer thickness with extent of reaction and dyeing time. Thickness measurements allow calculation of equivalent volumes of the dye sulphonates, which are directly proportional to equivalent weights.

REFERENCES

1a Part 13: Gibson, H. W. and Bailey, F. C. *Macromolecules* 1980, **13**, 34
b Part 14: Pochan, J. M., Gibson, H. W., Bailey, F. C. and Pochan, D. F. *Polymer* 1980, **21**, 250
c Part 15: Pochan, J. M., Gibson, H. W. and Bailey, F. C. *J. Polym. Sci. Polym. Lett. Edn.* 1980, **18**, 447
d Part 16: Pochan, J. M., Pochan, D. F., Rommelmann, H. and Gibson, H. W. *Macromolecules* 1980, **14**, 110
2 Okawara, M., Endo, T. and Kurusu, Y. *Prog. Polym. Sci., Jpn.* 1970, **4**, 105
3 More, J. A., 'Reactions on Polymers', D. Reidel Publishing Co., Boston, Mass. 1973
4 Leznoff, C. C. *Chem. Soc. Rev.* 1974, **3**, 65
5 Blossey, E. C. and Neckers, D. C., 'Solid Phase Synthesis', Dowden, Hutchinson and Ross, Stroudsburg, Pennsylvania, 1975
6 Ledwith, A. and Sherrington, D. C. *Mol. Behav. Dev. Polym. Mat.* 1975, 303; *Chem. Abstr.* 1975, **83**, 796316
7 Heitz, H. *Adv. in Polym. Sci.* 1977, **23**, 1
8 Wales, W. E., *U.S. Pat.* 3 779 840 (1973); *Chem. Abstr.* 1974, **80**, 13439w
9 Takabayaski, F. and Maeda, S. *Japanese Patent* 73–16, 1973, 709; *Chem. Abstr. 1974*, **80**, 3828n
10 Senda, K. and Nakajima, E. *Japanese Patent* 74–20, 1974, 827; *Chem. Abstr.* 1975, **82**, 44928f
11 Kissa, E. *Text. Res. J.* 1975, **45**, 488; Muller, H. *ibid.* 1977, **47**, 77, and references cited
12 Zisman, W. A. in 'Adhesion Science and Technology' (Ed. L. H. Lee), Plenum Publishing Co., New York, 1975, p 55
13 Carlsson, D. J. and Wiles, D. M. *J. Macromol. Sci. Rev. Macromol. Chem.* 1976, **14**, 65
14 Thomas, L. S., Clerrman, K. J., Parsons, C. P. and Ziemba, G. P. *Tech. Pap., Reg. Tech. Conf., Soc. Plast. Eng.* 1975, 111; *Chem. Abstr.* 1975, **83**, 148538r. Hartmann, F. and Hirschberg, H. G. *German Offen.* 1975, 2345971; *Chem. Abstr* 1975, **83**, 288644
15 Diggwa, A. D. S. *Plast. Polym.* 1974, **43**, 101
16 Gibson, H. W., Bailey, F. C., Mincer, J. L. and Gunther, W. H. H. *J. Polym. Sci. Polym. Chem. Edn.* 1979, **17**, 2961
17 Lyman, D. J. *Angew. Chem., Int. Ed., Engl.* 1974, **13**, 108
18 See, for example, Johnson, M. and Williams, M. E. *Eur. Polym. J.* 1976, **12**, 842; Rasmussen, J. R., Stedronsky, E. R. and Whitesides, G. M. *J. Am. Chem. Soc.* 1977, **99**, 4736; Rasmussen, J. R., Bergbreiter, D. E. and Whitesides, G. M. *J. Am. Chem. Soc.* 1977, **99**, 4746; Melby, L. R. *Macromolecules* 1978, **11**, 50
19 Salaneck, W. R., Gibson, H. W., Bailey, F. C., Pochan, J. M. and Thomas, H. R. *J. Polym. Sci. Polym. Lett. Edn.* 1978, **16**, 447
20 Bigelow, R. W., Pochan, J. M., Bailey, F. C., Salaneck, W. R., Thomas, H. R., Pochan, D. F. and Gibson, H. W. *Adv. Chem.* 1980, **187**, 295
21 Carroll, B. and Cheung, H. C. *J. Phys. Chem.* 1962, **66**, 2585
22 Pal, M. K. and Ash, K. *J. Phys. Chem.* 1974, **78**, 536
23 Smets, G. J. and Simionescu, B. *Makromol. Chem.* 1977, **178**, 2719
24 Shirai, M., Murakami, Y. and Tanoka, M. *J. Polym. Sci. Polym. Chem. Edn.* 1979, **17**, 2627
25 Cundall, R. B., Lawton, J. B., Murray, D., Rowlands, D. P. and Phillips, G. O. *Polymer* 1979, **20**, 389
26 Banthia, A. K., Mandal, B. M. and Palit, S. R. *J. Polym. Sci. Polym. Chem. Edn.* 1977, **15**, 945
27 Sansoni, B. *Naturwissenshaft* 1952, **39**, 281
28 Libinson, G. S. and Vagina, I. M. *Russ. J. Phys. Chem. (Engl. Transl.)* 1967, **41**, 1575
29 Bergmann, K. and O'Konski, C. T. *J. Phys. Chem.* 1963, **67**, 2169
30 Baugh, P. J., Lawton, J. B. and Phillips, G. O. *J. Phys. Chem.* 1972, **76**, 688
31 Müller, H. *Textile Res. J.* 1977, **47**, 77
32 Cegena, J. *J. Soc. Dyers Colour* 1971, **87**, 149
33 Gregor, H. P., Gutoff, F. and Bregman, J. I. *J. Colloid Sci.* 1951, **6**, 245
34 'Dowex: Ion Exchange', Dow Chemical Co., Midland, Mich., 1959, p 8
35 Pal, M. D. and Schubert, M. *J. Phys. Chem.* 1963, **67**, 1821