The Effect of Carriers on Drawn Poly(ethylene Terephthalate) Filaments

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Synopsis

The effect of various organic compounds on the birefringence equilibrium shrinkage and swelling of poly(ethylene terephthalate) filaments was studied. Evidence is presented that suggests the carrier action of the compounds is dominated by dispersion forces and that interaction between dye and the carrier in the fiber has been detected.

INTRODUCTION

It is convenient to divide the various explanations proposed to the mechanism of "carrier" dyeing[1–5] into two groups. One group deals with the explanations concerning the effect of the carriers on the fiber structure and the other, with those in which the possible interaction between the dyes and the carriers are considered.

Recent investigations concerned specifically with the effect of "carriers" on the kinetics of dyeing of poly(ethylene terephthalate) and polyacrylonitrile substrates[6,7] have emphasized the importance of the plasticizing action of carriers. A comparison of the respective solubility parameters of the fiber and dyebath additives is one way of anticipating when a compound will plasticize fibers and cause the associated changes in their physical properties.[8] For successful application of the solubility parameter concept account must be taken of the different intermolecular forces that contribute to the total cohesive energy density, from which the solubility parameter values are computed. When the appropriate results are interpreted in this way it is possible to show that polar forces are dominant in the plasticization of acrylic fibers.[8] More recently,[9] results have been produced that uphold the view that dispersion forces play a dominant role in the carrier dyeing of poly(ethylene terephthalate) fibers.[10] The work reported here provides further support for this suggestion.

Carriers also affect the equilibrium uptake of dyes. The effects have been considered before and related to the increased solubility of the dye in the dyebath phase caused by the presence of carriers.[29] This knowledge is extended here to demonstrate evidence of interaction between the carrier and dye in the fiber.

Journal of Applied Polymer Science, Vol. 22, 1583–1592 (1978)

0021-8995/78/0022-1583$01.00

EXPERIMENTAL

Materials

Dyes

CI Disperse Orange 3. The commercial dye powder was purified by extracting several times with hot water to remove water-soluble diluents, followed by successive recrystallizations from toluene until a constant melting point of 215°C was obtained.

Other dyes were supplied in a chromatographically pure form as follows: **4-aminoazobenzene,** with a melting point of 127°C, was supplied by BDH; **4-hydroxyazobenzene,** with a melting point of 156°C, was supplied by Aldrich Chemicals; **azobenzene,** with a melting point of 71°C, was supplied by BDH.

Carriers

The following BDH laboratory reagent-grade compounds were used as carriers: phenol, benzyl alcohol, *m*-cresol, aniline, and dichlorobenzene. The following laboratory reagent-grade compounds were supplied by Messrs Fisons Ltd.: nitrobenzene, *m*-toluidine, benzylamine, *n*-amyl alcohol, benzoic acid, and *n*-amylamine. *m*-Cresol, aniline, and toluidine were redistilled before use.

The values of the solubility parameters taken when comparing the activity of the different carriers are given in Table I. The contribution of the association solubility parameter δ_A and the dispersion solubility parameter δ_D[15] to the total solubility parameter δ are taken from the reference sources indicated. The presence of carrier caused swelling of the drawn (Fig. 2) but not the undrawn filaments.

TABLE I
Solubility Parameter Values

Compound	δ	δ_D	δ_A	Reference
Aniline	11.04	9.53	5.59	11
Benzoic acid	10.40	9.01	7.65	[b]
Benzyl alcohol	11.97	9.04	7.85	11
Benzylamine	10.30	8.69	5.53	11
o-Dichlorobenzene	9.98	9.43	2.95	11
m-Cresol	11.11	9.46	5.85	11
Nitrobenzene	10.62	9.73	4.26	11
Phenol	14.50	12.12	7.95	12
m-Toluidine	10.70	9.09	5.65	11
2-Phenoxyethanol	9.87	8.73	4.52	11
Poly(ethylene terephthalate)	10.70	9.54	4.80	13

[a] All in units of $cal^{0.5}\ cm^{-1.5}$.

[b] Calculated according to references 14 and 15.

Birefringence

The birefringence was measured using a Vickers interference microscope coupled with a Senormont compensator.[17] Filament samples were cut at 45° to the main axis in a brass block constructed for the purpose. The oblique edge was mounted in tritolyl phosphate and the birefringence measured using the "wedge method."[18] Carriers caused a significant change in the birefringence of the drawn (Fig. 3) but not the undrawn filaments. The birefringence value for the latter was very low (0.004).

Equilibrium Shrinkage

Shrinkage of the filaments occurs when they are pretreated in a relaxed state. The magnitude of the shrinkage depends upon the draw ratio of the filament and on the temperature and the concentration of carrier in solution. The values presented are those observed when the rate of shrinkage became too small to be measured accurately. The measurements were carried out in the apparatus described elsewhere,[19] which has also been used in recent investigations concerning acrylic fibers.[6,8]

Dyeing Experiments

The apparatus used is described elsewhere.[28]

Diffusion Coefficient of the Dyes

Preparation of the Dyebath. Sufficient dye to give a dyebath concentration of 10 mg/l. was weighed and dissolved in a small volume of acetone. Sufficient water to occupy about 75% of the total dyebath volume was heated to 50°C and the dye solution added. After driving off the acetone by boiling the aqueous solution, water was added to bulk up the dyebath to the required volume. The solution was filered through a No. 3 sintered glass crucible into the preheated dyebath vessel. Carrier was added at this stage. When the dyebath reached the required temperature the samples of polyester filament were inserted. The total liquor-to-goods ratio was about 5000:1. Samples were removed after the requisite time, dried, and the dye extracted using chlorobenzene. The optical density of the extract was determined using a spectrophotometer.

Calculation of the Diffusion Coefficient of the Dyes. The slope of the

TABLE II
Partition Coefficient for Carriers Between Water and Poly(ethylene Terephthalate) Filaments of Draw Ratio 5:1 at 95°C

Carrier	Partition coefficient
Benzoic acid	2.03
Benzyl alcohol	1.57
Benzylamine	1.30
m-Cresol	3.52
Nitrobenzene	17.51
Phenol	2.06
m-Toluidine	3.38
2-Phenoxy ethanol	1.65

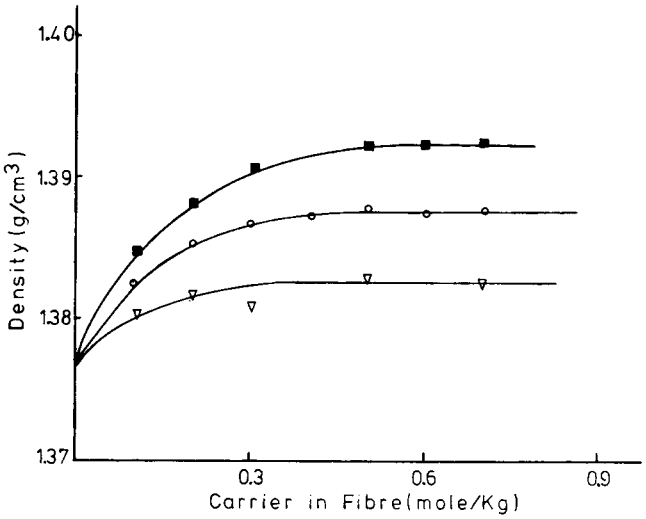

Fig. 1. Effect of carriers on density of poly(ethylene terephthalate) filaments (D.R. 5:1): (■) *m*-cresol; (○) phenol; (▽) benzyl alcohol.

linear plot of C_t/C_∞ against $t^{1/2}$ was measured and the diffusion coefficient D calculated according to the equation below[20]:

$$D = \frac{\pi r^2}{16t}\left(\frac{C_t}{C_\infty}\right)^2$$

where r = radius of the filament, t = dyeing time, C_t = dye on fiber at time t, and C_∞ = dye on fiber at equilibrium.

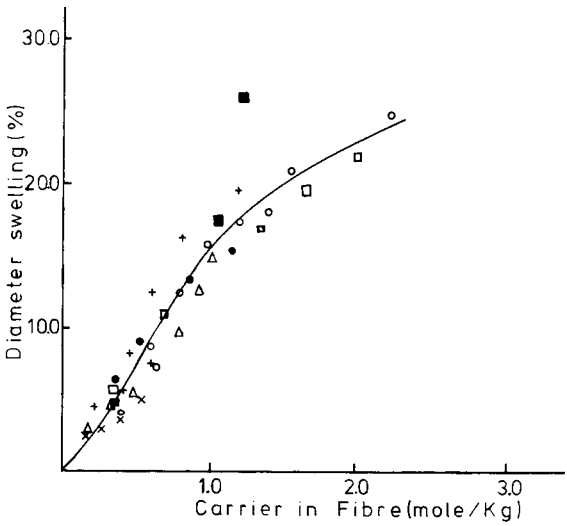

Fig. 2. Effect of carriers on diameter of poly(ethylene terephthalate) filaments (D.R. 5:1): (○) phenol; (□) *m*-toluidine; (■) *m*-cresol; (+) benzoic acid; (●) nitrobenzene; (×) benzylamine; (△) benzyl alcohol.

Partition Coefficient of the Carriers

Calculations of the concentration of the carrier in the filaments were carried out using the experimentally determined values of their partition coefficients. The experimental methods used are described elsewhere.[8] The values obtained for the drawn filaments are given in Table II.

RESULTS AND DISCUSSION

Effect of Carriers on the Physical Properties of PET Filaments

One effect caused by carriers that is important for dyeing is a reduction in the T_g of the fiber in the dyebath. The relationship between the T_g of the fiber and dyeing properties has been described elsewhere,[6,8] but in addition other associated effects can be interpreted in a way which expands further the understanding of the mechanism of carrier dyeing.

It is well known that some organic solvents or water will induce crystallization of amorphous poly(ethylene terephthalate),[21–23] and the same is true for carriers. The density of filaments of draw ratio 5:1 treated in aqueous solutions of carrier increases with increasing concentration of carrier, but significant changes in density are not apparent once the concentration of carrier has reached a certain level (Fig. 1), indicating that the crystallization is completed. The density of the undrawn filaments is initially lower than that of the drawn; and when benzyl alcohol was used as a carrier, the density increased with increasing concentration of carrier over the entire concentration range examined.[24] Further differences between the drawn and undrawn filaments are that the undrawn fiber does not

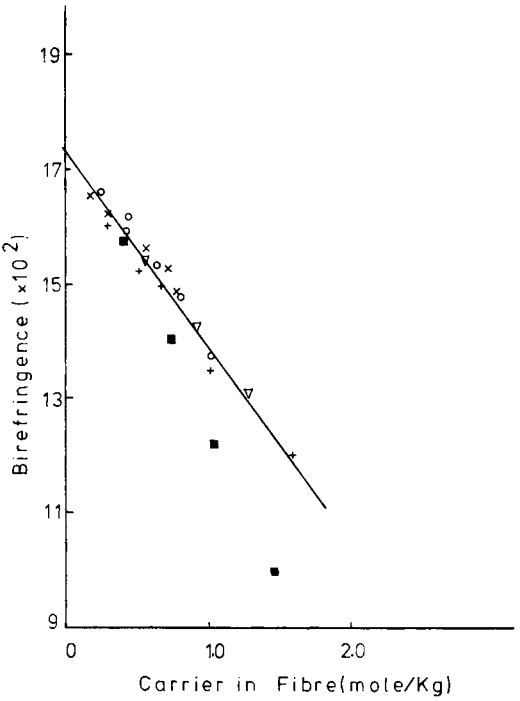

Fig. 3. Effect of carriers on birefringence of poly(ethylene terephthalate) filaments (D.R. 5:1): (○) phenol; (■) *m*-cresol; (+) benzoic acid; (×) benzylamine; (▽) benzyl alcohol.

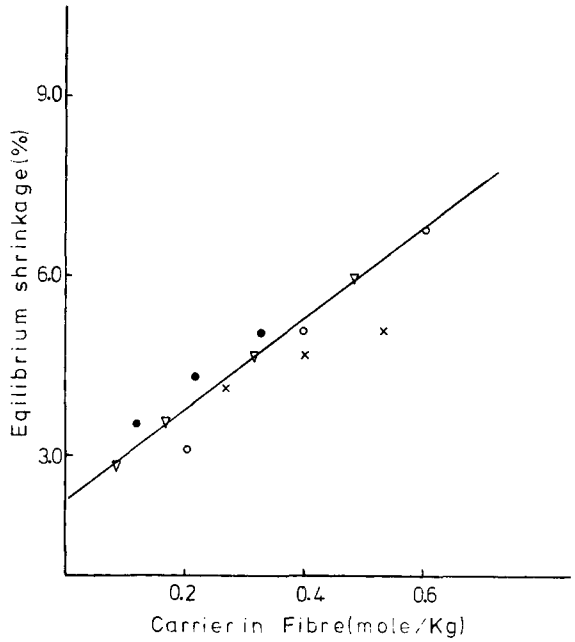

Fig. 4. Effect of carriers on equilibrium shrinkage of poly(ethylene terephthalate) filaments (D.R. 5:1): (○) phenol; (×) benzylamine; (●) nitrobenzene; (▽) benzyl alcohol.

swell in aqueous solutions of carrier[9] but the drawn fiber does (Fig. 2). Control of the mechanical and thermal history of the poly(ethylene terephthalate) filaments is obviously important in these studies, and most of the work described here concentrates on the properties of drawn filaments.

The results give additional strength to the argument that dispersion forces are dominant in the plasticization of poly(ethylene terephthalate) by carriers. Equivalent concentrations in the fiber of each of the carriers used give equivalent effects on the physical properties. Inspection of the solubility parameters of the carriers (Table I) reveals that all have a dispersion solubility parameter close to that for PET but the values for the association solubility parameter differ from one another. Therefore, if polar forces were dominant, the effects of equivalent concentration of carrier in the fiber would be different, as found for polyacrylonitrile fibers.[8] Since each carrier appears to act with the same intensity and the values of their dispersion solubility parameter are very similar, it is concluded that the dispersion forces dominate the carrier action.

Equivalence in the activity of each carrier in the drawn filaments extends to birefringence (Fig. 3) diameter swelling (Fig. 2) and equilibrium shrinkage (Fig. 4). The one exception encountered was with the changes in swelling and birefringence caused by *m*-cresol at the higher concentrations used. They are higher than expected when compared with the general trend for other results. However, it is believed that this compound will penetrate the crystalline regions of poly(ethylene terephthalate)[25] and the discrepancy may be due to the greater disruption of the molecular arrangement of the polymer.

Unlike the properties shown in Figures 2–4, the crystallinity as reflected by the density does not change over the whole range of carrier concentrations used (Fig. 1), and therefore other molecular events take place even when the percentage crystallinity remains constant.

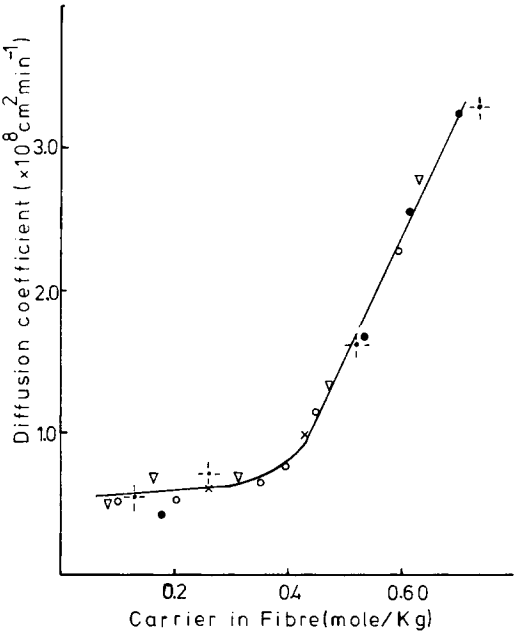

Fig. 5. Effect of carriers on diffusion coefficient of CI Disperse Orange 3 into poly(ethylene terephthalate) filaments (D.R. 5:1) at 95°C: (○) phenol; (▽) benzyl alcohol; (–¦–) 2-phenoxy ethanol; (●) nitrobenzene; (×) benzylamine.

Effect of Carriers on Dyeing Properties

Kinetics

Equal concentrations of carrier in the fiber also have equal effects on the diffusion coefficient of dyes into drawn fibers (Fig. 5). This has been reported for a few carriers before,[25–27] but the pattern of the change in the diffusion coefficient with concentration of carrier in drawn fibers has not. There is a pronounced break in the relationship between a concentration of about 0.35–0.45 mole carrier/kg fiber which may reflect the onset of some form of molecular rearrangement inside the fiber. In Figure 6, a record is given of the change in length of the drawn filament under a slight tension with temperature when immersed in solutions of 2-phenoxy ethanol. No change in length is detected at any temperature until a sufficiently high concentration of carrier is used. Then a small but definite increase in length occurs at a certain temperature. This temperature decreases with further increases in carrier concentration.

The minimum concentration of 2-phenoxy ethanol in solution required to produce the changes in length shown in Figure 6 is of interest. Using the partition coefficient to convert this concentration to the concentration expected in the fiber at 95°C shows that the latter falls within the concentration range which produces an abrupt change in the diffusion coefficient of the dye (Fig. 5).

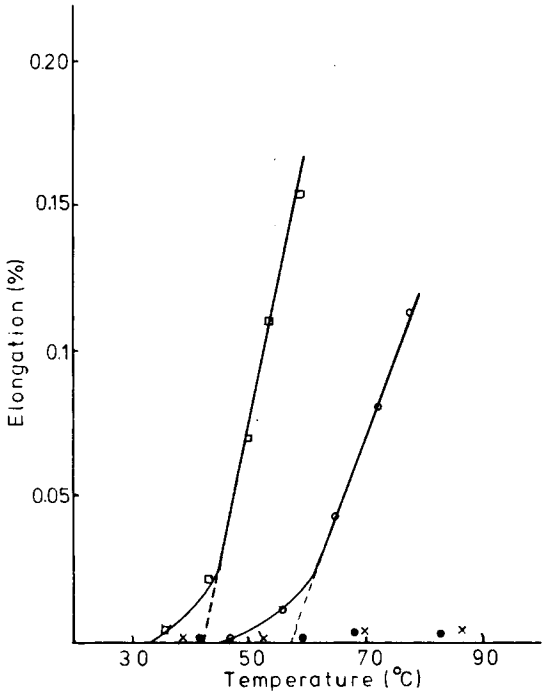

Fig. 6. Effect of 2-phenoxy ethanol and temperature on length of poly(ethylene terephthalate) filaments (D.R. 5:1): (+) 0.1 mole/l. 2-phenoxy ethanol; (●) 0.2 mole/l. 2-phenoxy ethanol; (○) 0.3 mole/l. 2-phenoxy ethanol; (□) 0.5 mole/l. 2-phenoxy ethanol.

Equilibrium Uptake of Dye in the Presence of Carriers

So far, all the results discussed have dealt with properties that are affected in the same way by all the carriers examined. They are all properties directly related to the molecular structure of the filaments. However, the relationship between the equilibrium uptake of the dye and the concentration of carrier in the fiber is more complicated, and the effect of carriers on the equilibrium uptake of dye varies from carrier to carrier. The effects of several carriers on the equilibrium uptake of CI Disperse Orange 3 were examined using concentrations of carrier in aqueous solution up to saturation; the results produced for each carrier were different (Fig. 7).

The effects are not limited to CI Disperse Orange 3; and in Table III the values are given for the diffusion coefficient and equilibrium uptake of three different dyes on drawn poly(ethylene terephthalate) filaments containing equal molecular concentrations of carrier. Changing the carrier does not affect the diffusion coefficient significantly, but there is a significant change in the equilibrium uptake of two of the dyes.

Since mole for mole the effects of all the carriers on those properties of the filament examined that reflect changes in molecular structure are identical, the conclusion is drawn that the results originate from an interaction between the dye and the carrier.

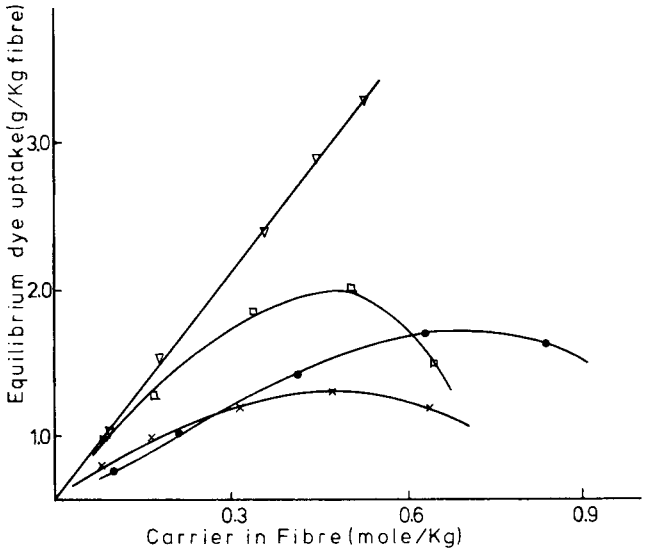

Fig. 7. Effect of carriers on equilibrium uptake of CI Disperse Orange 3 on poly(ethylene terephthalate) filaments (D.R. 5:1) at 95°C: (▽) nitrobenzene; (□) 2-phenoxy ethanol; (●) phenol; (×) benzyl alcohol.

TABLE III
Effect of 0.5 mole Carrier/kg Fiber on the Diffusion Coefficient and Equilibrium Uptake of Different Dyes on Poly(ethylene Terephthalate) Filaments (D.R. 5:1)[a]

	Equilibrium dye uptake, g/kg			Diffusion coefficient $\times 10^8$, cm^2/min		
Carrier	A	B	C	A	B	C
Phenol	2.40	1.58	2.63	9.67	4.71	8.82
Aniline	1.80	1.62	2.18	9.72	4.65	8.47

[a] A = 4-Hydroxyazobenzene; B = 4-aminoazobenzene; C = azobenzene.

CONCLUSIONS

The effect of carriers on the swelling birefringence and equilibrium shrinkage of drawn poly(ethylene terephthalate) filaments support the conclusion that dispersion forces govern the plasticization mechanism.

For all the carriers examined, equal concentrations of carrier in the substrate had equal effects on the diffusion coefficient of dyes. However, the effect of carrier concentration on the equilibrium uptake of dye varied from carrier to carrier. This is taken as evidence for interaction between the carrier and the dye.

References

1. V. S. Salvin, *Am. Dyestuff Rep.*, **49**, 600 (1960).
2. A. A. T. C. C. Piedmont Section, *Am. Dyestuff Rep.*, **48**, 23 (1959).
3. A. A. T. C. C. Piedmont Section, *Am. Dyestuff Rep.*, **48**, 37 (1959).
4. A. H. Brown and A. T. Peters, *Am. Dyestuff Rep.*, **57**, 281 (1968).
5. A. Murray and R. Mortimer, *Rev. Prog. Colour.*, **2**, 67 (1971). Published by Society of Dyers and Colourists.
6. W. Ingamells, R. H. Peters, and S. R. Thornton, *J. Appl. Polym. Sci.*, **17**, 3733 (1973).

7. W. Ingamells and R. V. Narasimham, *J. Appl. Polym. Sci.*, **20,** 2271 (1976).
8. Z. Gur-Arieh, W. Ingamells, and R. H. Peters, *J. Appl. Polym. Sci.*, **20,** 41 (1976).
9. (a) A. M. Yabani, Ph.D. Thesis, Victoria University of Manchester, 1976; (b) W. Ingamells and A. M. Yabani, *J. Soc. Dyers Colour.*, **93,** 417 (1977).
10. A. N. Derbyshire and R. H. Peters, *J. Soc. Dyers Colour.*, **71,** 530 (1955).
11. C. J. Hansen, *J. Paint Technol.*, **39,** 104 (1967); *ibid.*, **39,** 505, 511 (1967).
12. J. L. Gardon, *Encyclopedia of Polymer Science and Technology,* Vol. 3, Interscience, New York (1966).
13. D. M. Koenhen, *J. Appl. Polym. Sci.*, **19,** 1163 (1975).
14. J. H. Hildebrand and R. Scott, *The Solubility of Non-Electrolytes,* Reinhold, New York, 1949.
15. R. F. Blanks and J. M. Prausnitz, *Ind. Eng. Chem., Fundam.*, **3,** 1 (1964).
16. I. Marshall and A. B. Thompson, *J. Appl. Chem.*, **4,** 145 (1954).
17. N. H. Harts and A. Stuart, *Crystals and The Polarizing Microscope,* Arnold, London, 1960.
18. R. D. Andrews, *J. Appl. Phys.*, **25** 1223 (1954).
19. F. M. Rawicz, D. M. Cates, and H. A. Rutherford, *Am. Dyestuff Rep.*, **50,** 320 (1961).
20. J. Crank, *Mathematics of Diffusion,* Oxford Clarendon Press, London, 1956, p. 66.
21. W. R. Moore and R. P. Sheldon, *Polymer,* **2,** 315 (1961).
22. J. Kolb and E. F. Izard, *J. Appl. Phys.*, **20,** 571 (1949).
23. W. R. Moore and R. P. Sheldon, *J. Text. Inst.*, **51,** T438 (1960).
24. W. Ingamells and K. V. Narasimham, *J. Soc. Dyers. Colour.*, **93,** 306 (1977).
25. R. Rochas and M. Courmont, *Bull. Inst. Text. France,* **86,** 15 (1960).
26. O. Glenz, W. Beckman, and W. Wunder, *J. Soc. Dyers Colour.*, **75,** 141 (1959).
27. M. J. Schuler, *Text. Res. J.*, **27,** 352 (1957).
28. Z. Gur-Arieh, W. Ingamells, and R. H. Peters, *J. Soc. Dyers Colour.*, **92,** 332 (1976).
29. D. Balmforth, C. A. Bowers, W. J. Bullington, T. H. Guion, and T. S. Robers, *J. Soc. Dyers Colour.*, **82,** 405 (1966).

Received March 11, 1977