

Polymeric Dye Receptors for Disperse Dyeable Polypropylene Fibers

H. DAYIOGLU

Department of Textile Engineering, Istanbul Technical University, Gümüşsuyu, Istanbul, Turkey

SYNOPSIS

Polypropylene fibers containing various amounts and different types of 2-vinyl pyridine/styrene (2VP/St) copolymer in terms of molecular weight and molar ratio were prepared, and the disperse dyeability of these fibers were investigated. In addition, the disperse dyeability of 2VP/St copolymer alone was also studied. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene is a hydrocarbon in composition; therefore, the fibers are definitely hydrophobic. Its strength properties are quite good, being comparable to polyamide and polyester. It is highly crystalline, and its specific gravity is the lowest of any fiber. It is also highly resistant to all chemicals at room temperature. With these properties, polypropylene has found a great number of applications. The main restrictions on the use of polypropylene fiber are its low softening temperature, which makes it difficult to iron, and its lack of dyeability.

Polypropylene fibers are difficult to dye by conventional dyeing techniques due either to lack of dye receptor sites in their molecular structure to which the dye molecules may become attached, or to difficulty of penetration of certain types of dye molecules into the structure.¹⁻⁵ Although the diffusion coefficient of disperse dyes into polypropylene is quite high, the saturation values are very low.⁶⁻⁹

It should be emphasized that the mass pigmentation is still the most widely used coloration method for polypropylene fibers. However, development of various conventional dyeing techniques is in progress. The efforts have been concentrated on three different directions:

- a. Dyeing of unmodified polypropylene fibers by conventional techniques involving suitable dyes such as vat, azoic, and hydrocarbon-sol-

uble dyes, carriers, high temperature dyeing, fiber swelling agents, and other treatments. This approach was previously successful for cellulose acetate and polyester fibers.

- b. Copolymerization or graft copolymerization of polypropylene with dye-receptive monomers. This process has been successfully used for polyacrylonitrile fibers.
- c. Introduction of additives to polypropylene has been suggested. Basic dyeability can be accomplished by spinning with a polymer containing basic groups such as copolymer of ethylene with potassium acrylate; mordant dyeability with nickel phenolates, phosphates, salts of fatty acids, triazole complexes; disperse dyeability with copolyesters, copolyamides, copolymers of vinyl pyridines with styrene, copolyesters of ethylene with alkylacrylates and acid dyeability with polyvinyl pyridines, polyamides, polyamines, polyureas, polyacrylamides, copolymers of ethylene with alkylaminoalkylacrylates.¹⁰⁻²¹

From various publications, some of which were cited previously, it may be noted that the dye sites in the fiber has been given primary consideration. Quite often, the importance of diffusion of the dye into the fiber seems to have been neglected. It is obvious that even if sufficient dye sites are present in the fiber, the fiber may not be satisfactorily dyeable. This occurs when the dye molecules are unable to diffuse into fiber. Coupled with ease of diffusion, a uniform dispersion of dye sites in the fiber is, of

course, essential in order to render the material with a desirable color intensity.

The present work aims at investigation the effect of the 2-vinyl pyridine/styrene (2VP/St) copolymer, which has been incorporated in polypropylene at various molecular weights and molar ratios, on disperse dye absorption of modified polypropylene fiber. Besides, disperse dyes being very hydrophobic with high molecular weight and relatively more hydrophilic with low molecular weight have been selected in order to investigate their effect on dye absorption.

EXPERIMENTAL

Materials

Monomers of 2-vinyl pyridine (2VP) and styrene (St) were purified by distillation under vacuum at 79–82°C and 50–51°C, respectively, to remove polymerization inhibitor. Azo-bis-isobutyronitrile (AIBN) as an initiator was purified by recrystallizing from toluene and dried under vacuum at 20°C. Ethyl 2-mercaptoacetate (E2MA) as a chain transfer agent was of commercial grade. Polypropylene as a basic polymer for fiber production used was of 35 MFI (230°C, 2.16 kg). The dyes used were Foron Navy S-2GL (very hydrophobic and high molecular weight) and Foron Yellow E-RGFL (more hydrophilic and low molecular weight). Dyes and auxiliaries used were of commercial grade. With the exception of cyclohexanone and benzene, which were of Analar grade, chemicals were general-purpose grade. Great care was taken while working with benzene because of its known toxicity.

Preparation and Characterization of 2VP/St Copolymers

Freshly distilled 2-vinyl pyridine and styrene in molar ratio of 30/70, 50/50, and 70/30 were placed in sealed glass tubes with AIBN and E2MA under nitrogen in a temperature-controlled water bath for 20 h. At the end of this time, the products were purified by dissolving them in toluene and precipitating the copolymers from the cold solutions by addition of petroleum ether (bp 80–120°C) as a nonsolvent for 2VP/St copolymers. Finally, the copolymers (white in color) were dried at 60°C under vacuum for 3 h. Various batches of 2VP/St copolymer with different molecular weights were also prepared by varying the concentrations of AIBN and E2MA.

Solution viscosity measurements of 2VP/St co-

polymers were carried out using an Ubbelohde type viscometer at $25 \pm 0.1^\circ\text{C}$. Solutions of concentrations 0.1, 0.4, 0.7, and 1.0% (w/v) were prepared separately by dissolving the copolymer in benzene at the boil. Limiting viscosity numbers $[\eta]$ were obtained by extrapolation of the viscosity number data to $c = 0$ using least squares method.

Preparation of 2VP/St Copolymer in Film Form

About 0.4 g of 2VP/St copolymers was dissolved in toluene and poured on to separate flat glass plate of area 13×13 cm in order to get a thickness of 26 μm , which is similar to the fiber diameter. These solutions were kept on the glass plate for 20 h to evaporate toluene, and then the copolymer films were removed using a razor blade. The measured thicknesses of the above prepared films were between 24 and 33 μm .

Preparation of Samples for Melt Spinning

The 2VP/St copolymer was dissolved in toluene and then the solvent was evaporated to get a concentration of between 3 and 5% (w/v). At the end of this procedure, polypropylene was added to the above-prepared solution, and 2VP/St copolymer was precipitated by addition of petroleum ether to the mixture while agitating continuously. Then the polymer mixture was dried in a vacuum oven at 100°C for 4 h.

Melt Spinning and Drawing

A MK-3 rod type melt-spinning apparatus, made by ICI (England) was used to convert the polymers into the filament form. There was no problem when spinning polypropylene alone and a mixture of low molecular weight 2VP/St copolymer and polypro-

Table I The Relationship between the Polymerization Conditions and the Limiting Viscosity Number

AIBN (w/v %)	E2MA (v/v %)	Monomer Molar Ratio (2VP/St)	$[\eta]$
0.15	0.00	50/50	2.29
0.20	0.45	50/50	1.83
0.44	1.46	50/50	1.41
2.14	3.55	50/50	0.78
2.14	3.55	70/30	0.83
2.14	3.55	30/70	0.88

Table II The Tensile Properties of Fibers Containing Different Amounts of Low Molecular Weight 2VP/St Copolymer^a

Copolymer Content (% o.w.f.)	Decitex per Filament	Load at Break (g)	Extension (E) at Break (%)	Tenacity (T) (g/dtex)	Tensile Factor $T \cdot E^{1/2}$
0.00	5.02	26.62	32.3	5.30	30.1
2.30	5.81	24.70	30.0	4.25	23.3
2.71	5.81	28.00	24.2	4.82	23.7
5.07	6.82	27.76	28.9	4.07	21.9
6.01	6.04	24.16	30.0	4.00	21.9
8.03	6.32	25.03	27.1	3.96	20.6

^a 2VP/St molar ratio = 70/30, $[\eta] = 0.83$.

pylene, whereas when a mixture of high molecular weight 2VP/St copolymer and polypropylene was used with an additive concentration above 4%, the filaments broke during spinning. Melt spinning was carried out using a spinneret with 10 holes each of 0.325 mm in diameter at 260°C. A laboratory scale drawframe was used to draw the spun filaments at a draw ratio of 1 : 5 at 120°C.

Estimation of the Amounts of 2VP/St Copolymers in the Fiber

A potentiometric titration method was undertaken to estimate the amount of 2VP/St copolymer in the modified polypropylene fibers. The fibers were dissolved in cyclohexanone at the boil and titrated with 0.1N hydrochloric acid using a pH meter to detect the end point in order to calculate the amount of 2VP/St copolymer present in the sample of fiber.

Dyeing Procedure

The Rotadyer MK-I, made by John Jeffreys Ltd., (Rochdale, England) consists of a temperature con-

trolled water bath with two electrically heated elements. A rotating clamp with up to 14 tubes each of 100 mL capacity was used to carry out the dyeing experiments.

The dyeing recipe used was:

- Fiber, 2 g (0.4 g. for copolymer films)
- Dye, 12.5% o.w.f. (30% for copolymer films)
- Ammonium acetate, 3% o.w.f.
- Dispersol AC, 2.5% o.w.f.
- Liquor ratio, 50 : 1 (100 : 1 for copolymer films)

Dyeing was started at 40°C, reached the boil (98°C) in 20 min time and continued at this temperature for 70 min.

The amounts of dye used in the dyebath were quite high to prevent the dyebath from exhausting, in order to be able to compare the dye absorption results of dyed samples.

Wash-Off

Washing solution containing 0.5% (w/v) standard washing soap was used at a liquor ratio of 50 : 1 at

Table III Tensile Properties of Fibers Containing Different Molecular Weight of 2VP/St Copolymers of 30/70, 50/50, and 70/30 Molar Ratios

$[\eta]$	Copolymer Content (% o.w.f.) [2VP/St molar ratio]	Decitex per Filament	Load at Break (g)	Extension at Break (%)	Tenacity (g/dtex)	Tensile Factor $T \cdot E^{1/2}$
2.29	3.02 [50/50]	6.03	20.13	22.13	3.34	15.7
1.83	2.14 [50/50]	6.53	22.60	27.4	3.46	18.1
1.41	3.44 [50/50]	6.10	26.20	22.5	4.30	20.4
0.78	3.60 [50/50]	5.92	27.41	26.4	4.63	23.8
0.83	2.71 [70/30]	5.81	28.00	24.2	4.82	23.7
0.88	3.03 [30/70]	6.22	27.69	22.9	4.45	21.3

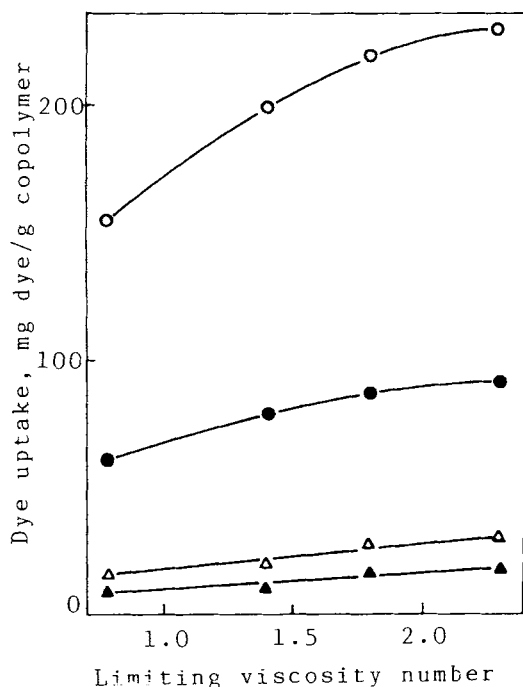


Figure 1 The effect of molecular weight of 2VP/St copolymer film on dye absorption: (○) commercial Foron Yellow E-RGFL; (●) pure Foron Yellow E-RGFL; (△) commercial Foron Navy S-2GL; (▲) pure Foron Navy S-2GL.

40°C for 30 min under continuous agitation (ISO test no. 1) to remove unfixed surface dye.

Measurement of Dye Content of Dyed Samples

The dye uptake (defined as mg dye/g fiber or mg dye/g copolymer) was estimated by extracting a known amount of dyed sample in pyridine and then measuring the optical density using a UV spectrophotometer (Philips Pye Unicam SP 1800) and fi-

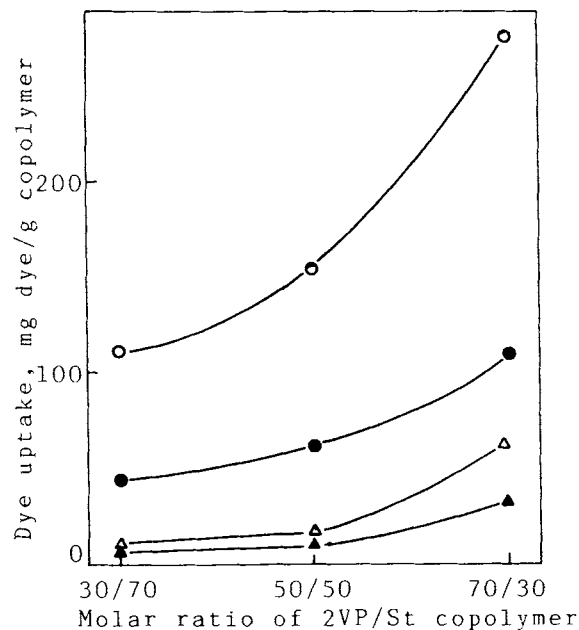


Figure 2 The relationship between the molar ratio of 2VP/St copolymer film on dye absorption: (○) commercial Foron Yellow E-RGFL; (●) pure Foron Yellow E-RGFL; (△) commercial Foron Navy S-2GL; (▲) pure Foron Navy S-2GL.

nally comparing the results with the calibration graphs of the dyes in commercial and pure form. The dye uptake results are given in commercial (unpurified original dye) and pure dye (purified dye) form in order to compare the dye uptake results with industrial dyeing scale. The absorbance measurements were carried out at 598 nm for Foron Navy S-2GL and 470 nm for Foron Yellow E-RGFL. Commercial grade dyes were purified by dissolving them in acetone, then filtering off, and finally evaporating the acetone. The dried form of this dye is believed to be pure.

Table IV Effect of Molecular Weight of 2VP/St Copolymer (in 50/50 Molar Ratio) within Fiber on Dye Absorption

[η] (Additive Content, % o.w.f.)	Dye Uptake (mg dye/g fiber)		Dye Uptake (mg dye/g additive)	
	Pure Foron Yellow E-RGFL	Commercial Foron Yellow E-RGFL	Pure Foron Yellow E-RGFL	Commercial Foron Yellow E-RGFL
2.29 (3.02)	6.5	16.6	215.2	549.7
1.83 (2.14)	4.7	12.0	219.6	560.7
1.44 (3.44)	7.0	17.9	203.5	520.3
0.78 (3.60)	10.1	25.8	208.6	716.7

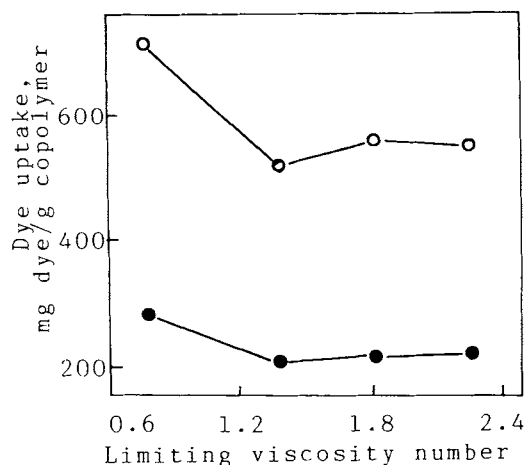


Figure 3 Effect of molecular weight of 2VP/St copolymer in the fibre on dye absorption, calculated per g of additive: (○) commercial Foron Yellow E-RGFL; (●) pure Foron Yellow E-RGFL.

Light Fastness

A Xenon Arc type (Xeno Test 150 S, Heraurs) light fastness instrument was used to check the light fastness of dyed polypropylene fibers. The light fastness measurement was carried out on the specially selected samples of containing various amounts of 2VP/St copolymer, assuming that there would not almost be differences between all types of dyed samples on light fastness results.

RESULTS AND DISCUSSION

In order to prepare 2VP/St copolymers with different molecular weight, the amounts of AIBN and E2MA were varied according to the molecular weight required. It is seen from Table I that the limiting

viscosity number of copolymer was decreased by increasing the amounts of both AIBN and E2MA. The viscosities of copolymers with low molecular weights which were prepared under similar conditions in 70/30, 50/50, and 30/70 molar ratio were slightly different, presumably due to minor variation in polymerization parameters.

The tensile testing results in Table II suggest that the tenacity and the tensile factor were decreased with increasing concentration of 2VP/St copolymer in the fiber. It is seen from Table III that the reduction was greater on the fibers containing high molecular weight 2VP/St copolymer than at low molecular weight. With blends containing greater than 4.0% (o.w.f.) of copolymer with high molecular weight, the fibers broke during spinning. The better tensile properties correlate well with the improved dispersibility of the low molecular weight 2VP/St copolymer in polypropylene.

The absorption of disperse dyes by 2VP/St copolymers in film form was studied in order to see the effect of molar ratio of the monomers and molecular weight of copolymers. It is seen from Figure 1 that the dye absorption was increased by increasing the molecular weight of 2VP/St copolymer. It is also seen from Figure 2 that, as the monomer molar ratio increased in favor of 2-vinyl pyridine, the dye absorption also increased.

The amount of dye absorbed by copolymer film was much higher where low molecular weight and more hydrophilic Foron Yellow E-RGFL dye was used than with high molecular weight and very hydrophobic Foron Navy S-2GL. The dye absorption of fibers containing different molecular weights of 2VP/St copolymer was determined and the results are shown in Table IV and Figure 3. The amounts of 2VP/St copolymer in the fibers were different in each case. The difficulty in preparing a sample with

Table V The Relationship between the Molar Ratio of 2VP/St Copolymers with Low Molecular Weight within Fiber and Dye Absorption

2VP/St ([η], % Additive o.w.f.)	Dye Uptake (mg dye/g fiber)		Dye Uptake (mg dye/g additive)	
	Pure Foron Yellow E-RGFL	Commercial Foron Yellow E-RGFL	Pure Foron Yellow E-RGFL	Commercial Foron Yellow E-RGFL
70/30 (0.83, 2.71)	9.0	23.0	332.1	847.7
50/50 (0.78, 3.60)	10.1	25.8	280.6	716.7
30/70 (0.88, 3.03)	5.1	13.0	168.3	429.0

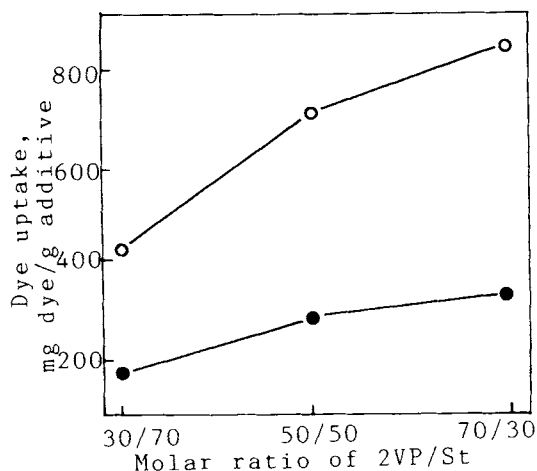


Figure 4 The effect of the molar ratio of 2-vinyl pyridine/styrene monomers within copolymers in the fiber on dye absorption, calculated per g additive: (○) commercial Foron Yellow E-RGFL; (●) pure Foron Yellow E-RGFL.

exactly the same amount of 2VP/St copolymer in each case arose partly from lack of insufficient degree of melt blending. Therefore, the absorption results were also calculated per g additive in order to compare the dye uptake values.

The results suggest that the dye uptakes generally increased on decreasing the molecular weight of 2VP/St copolymer. These results disagreed with the results obtained on 2VP/St copolymer alone. This may be explained by the fact that as the molecular weight of additive decreased the distribution of the additive within the fiber also improved, which leads to high dye absorption.²²

It is seen from Table V and Figure 4 that increased molar portion of 2-vinyl pyridine within 2VP/St copolymer also increased the dye absorption

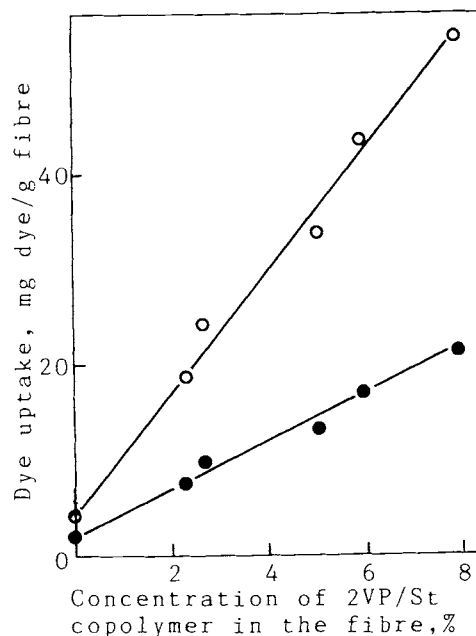


Figure 5 Effect of the concentration of 2VP/St copolymer in the fiber on dye absorption: (○) commercial Foron Yellow E-RGFL; (●) pure Foron Yellow E-RGFL.

of modified polypropylene fibers. This is attributable to the increased polarity of the additive.

The relationship between the amount of low molecular weight 2VP/St copolymer and the amount of dye absorbed appeared to be linear as shown in Table VI and Figure 5. Although the dye absorption of modified polypropylene fibers as mg dye of g additive decreased with increasing the amount of additive content, it is clearly seen that this decrease in the dye absorption was obtained due to the dye absorption values of unmodified polypropylene fibers. It is obvious from the table that, when the dye

Table VI Effect of the Amount of Additive Content on Dye Absorption and Light Fastness^a

Additive Content (%)	Dye Uptake (mg dye/g fiber)		Dye Uptake (mg dye/g additive)		Light Fastness
	Pure Foron Yellow E-RGFL	Commercial Foron Yellow E-RGFL	Pure Foron Yellow E-RGFL	Commercial Foron Yellow E-RGFL	
0.00	1.7	4.3	—	—	7
2.30	7.4	18.9	321.7	821.7	6-7
2.71	9.6	24.5	354.2	904.1	7
5.07	13.3	33.9	262.3	668.6	7
6.01	17.1	43.6	284.5	725.5	7
8.03	21.4	54.6	266.5	680.0	7

^a $[\eta] = 0.83$, 2VP/St molar ratio = 70/30.

uptake values of unmodified polypropylene fiber (1.7 mg dye/g fiber) were subtracted from the dye uptake values of modified polypropylene fibers, there is no significant differences between the dye uptakes of modified polypropylene fibers. Since the dye uptake values of Foron Navy S-2GL on modified polypropylene fibers were very low, they were not included in this paper. This low dye absorption could be attributed to the high molecular weight of Foron Navy S-2GL, leading to low diffusion rate into the fiber. It is also seen from Table VI that the light fastnesses of dyed fibers are extremely high.

CONCLUSION

When copolymers of 2-vinyl pyridine and styrene are dyed with disperse dyes, the dye uptake from an infinite dye bath is higher at higher vinyl pyridine/styrene ratio and slightly higher at higher molecular weight. When the same polymers are incorporated into polypropylene fibres by melt blending, the dye uptakes are again higher but slightly lower at high molecular weight. The dye uptakes are proportional to the amount of additive for a given copolymer.

The absorption of disperse dye with low molecular weight and relatively more hydrophilic properties is significantly greater than the type with high molecular weight and relatively high hydrophobic characteristics. Enhanced dyeability noted above is most likely related to better diffusion of low molecular weight dye (hence to its smaller molecular size) and hydrophilic group of the same dye (i.e., phenolic group in Foron Yellow E-RGFL) as well as greater interaction that would be expected between dye sites in copolymer (e.g., due to increasing 2VP).

Industrially acceptable shade level can easily be attained by selecting the amount, type of 2VP/St copolymer, and disperse dye in suitable combination. The light fastnesses of dyed modified polypropylene fibers are excellent. Spinability on a small scale is poor with the copolymers of higher molecular weight,

but satisfactory up to 8% of additive at lower molecular weight.

The author wishes to express his gratitude to the Department of Textile Industries at Leeds University for use of their facilities and Professor J. E. McIntyre of Leeds University and also to the British Council for financial support.

REFERENCES

1. J. G. Cook, *Handbook of Polyolefin Fibres*, Merrow, Watford, 1967.
2. H. P. Frank, *Polypropylene*, McDonald Technical and Scientific, London, 1969.
3. M. Farber, *Proc. Symp. on Polypropylene Fibers*, Southern Res. Inst., Alabama, 1964.
4. M. Ahmed, *Polypropylene Fibers—Science and Technology*, Elsevier, New York, 1982.
5. D. M. Nunn, *Dyeing of Synthetic Polymer and Acetate Fibers*, Dyers Co. Publ. Trust, Bradford, 1979.
6. C. L. Bird and A. M. Patel, *Journal of the Society of Dyers and Colourists*, **84**, 560 (1968).
7. DuPont, U.K. Pat. 932, 897, 1963.
8. ICI, U.K. Pat. 809,495, 1959.
9. K. L. Gardner and G. M. McNally, *Journal of the Society of Dyers and Colourists*, **93**, 4 (1977).
10. Toyo Rayon, U.S. Pat. 3,533,723, 1964.
11. Mitsubishi, U.K. Pat. 1,137,381, 1968.
12. Toyo Rayon, U.K. Pat. 1,069,890, 1967.
13. Montecatini, U.K. Pat. 1,009,661, 1965.
14. Sumitomo, U.K. Pat. 1,071,367, 1967.
15. C. Calde, *Tintoria*, **75**, 221 (1978).
16. B. G. Ferrini and H. Zollinger, *Helv. Chim. Acta*, **50**, 897 (1967).
17. A. Teiji et al., Sumitomo Chemical Co., Jpn. Pat. 7,414,861.
18. Sumitomo, U.S. Pat. 3,395,198, 1965.
19. Phillips, U.K. Pat. 1,394,459, 1975.
20. M. Farber, *Soc. Plast. Eng. J.*, **24**(8), 82 (1968).
21. J. E. McIntyre, *Progress of Applied Chemistry*, 1965, Vol. 50.
22. H. Dayioglu, Ph. D. thesis, University of Leeds, Dept. of Textile Industries, 1983.

Received March 18, 1991

Accepted January 27, 1992