

Diffusion of Dyes in Polyester Fibers. IV. Anomalous Sorption of Disperse Dye Synthene Scarlet P3GL

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Synopsis

The investigations on dyeing of poly(ethylene terephthalate) fibers with disperse dye Synthene Scarlet P3GL have revealed anomalous sorption of the dye in heat-treated samples. In the mathematical solution of the process it has been assumed that anomalous sorption can be treated as superposition in time of two stages of Fickian sorption. The contents of absorbed dye at quasiequilibrium C_I , at the final equilibrium C_{II} , and the apparent diffusion coefficients D_I and D_{II} have been calculated using Hill's equation.

INTRODUCTION

For poly(ethylene terephthalate) (PET) the lack of "sites" able to bind the dye molecules and hydrophobicity of the polymer chains favors dyeing with nonionic disperse dyes. The dyeing itself may be regarded as the dissolution of dye molecules in a polymer, proceeding through diffusion of a penetrant within a fiber.¹ According to Dumbleton et al.,² the diffusion of large disperse dyes within PET is controlled by the segmental motion of a polymer, and it may be considered as type B of the nonideal Fickian diffusion.³ For this type the diffusion coefficient of a penetrant is concentration-dependent.⁴ However, this concentration dependence does not influence markedly the shape of rate-of-dyeing curves and a reasonable fit could be obtained between the experimental curve and the one calculated with the linear Fick's law.⁵ This makes possible the calculation of an apparent diffusion coefficient on the basis of the rate-of-sorption curve.

The poly(ethylene terephthalate) fibers show a high affinity to disperse dyes; however, the dye diffusion coefficients are low, being of the order of 10^{-10} – 10^{-13} $\text{cm}^2\text{-s}^{-1}$. For a particular dye a diffusion coefficient may vary in relation to the crystallinity and the orientation of a fiber.

It is known⁶ that the diffusion of some dyes, such as disperse dye Synthene Scarlet P3GL in PET fibers, are susceptible to variation in the internal structure of the polymer. As we have stated, the rate-of-dyeing curves of this dye in the heat-treated fibers differ from those known for many other dyes as they represent the so-called anomalous (non-Fickian) sorption. This type of sorption has been reported for some organic solvents in amorphous polymers at the temperature below T_g , but not until now for dyes in crystalline polymers.

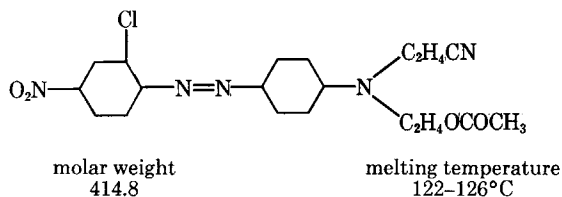
In this paper we present an attempt to describe quantitatively the anomalous sorption of disperse dye Synthene Scarlet P3GL in PET fibers. In the calculations of diffusion coefficients it has been assumed that each of the two stages of sorption proceeds according to the linear Fick's law. Such an assumption made

possible the calculations of dye contents at the quasiequilibrium and final equilibrium states as well as the apparent diffusion coefficients for both stages of the sorption.

EXPERIMENTAL

Materials. A multifilament poly(ethylene terephthalate) (PET) yarn (75 denier 36 filaments) manufactured by Chemitex Elana, Poland, was used as starting material. Fibers were drawn at the rate of 438 m/min to draw ratio 3. Samples of a different degree of crystallinity were obtained by heat treating of freely suspending skeins of native yarn in a silicone oil bath maintained at a fixed temperature within $\pm 2^\circ\text{C}$. The fibers were put to heat treating at 147°C , 165°C , 182°C , 200°C , and 220°C . After holding the sample in an oil bath for 30 min at a constant temperature, it was taken out and cooled rapidly with cold water, then washed thoroughly in *n*-heptane and dried in air. Before dyeing the untreated and heat-treated fibers were purified with a solution of the nonionic surface active agent NNO (produced by Rokita, Poland) of the concentration 2 g/dm^3 , at 85°C , then washed with distilled water and dried in air.

Dyeing. Fibers were dyed with disperse dye Synthene Scarlet P3GL manufactured by Zachem, Poland. According to Color Index this dye corresponds to Disperse Red 54. The chemical structure of the dye is:



Because of low solubility of Synthene Scarlet P3GL in water the dye was used as a commercial product in stabilized form. The fibers were dyed in a water bath of the composition: dye 1.5 g/dm^3 ; dispersing agent NNO 2 g/dm^3 ; carrier Dilatin OD (Sandoz, Basel) 2 g/dm^3 , formic acid to maintain pH 5–6. For dyeing, the fibers were placed in a bottle equipped with a reflux condensor. The bottle was rotated within an oil bath kept at appropriate temperature. Dyeing was carried out for 10 min to 40 h at 100°C mainly, and for some samples at 86°C and 94°C .

The concentration of the dye in a dye bath (1.5 g/dm^3) and the ratio of the volume dye liquor to the weight of fibers (1000:1) secured the stability of the bath composition during dyeing. Dyeing under such conditions can be considered as occurring in an "infinite" dye bath. At the end of dyeing the fibers were removed from a dye bath, cooled rapidly in water, and washed in cold acetone to remove adhering dye.

For the quantitative determinations the absorbed dye was extracted from the fibers with hot eluent of the composition: 40% dimethylformamid, 59% ethylene glycol, and 1% formic acid at $110\text{--}120^\circ\text{C}$.⁷ The eluted dye was determined spectrophotometrically at 480 nm. The amount of dye taken up by the fibers was expressed in the weight of dye (mg) per g of the fiber.

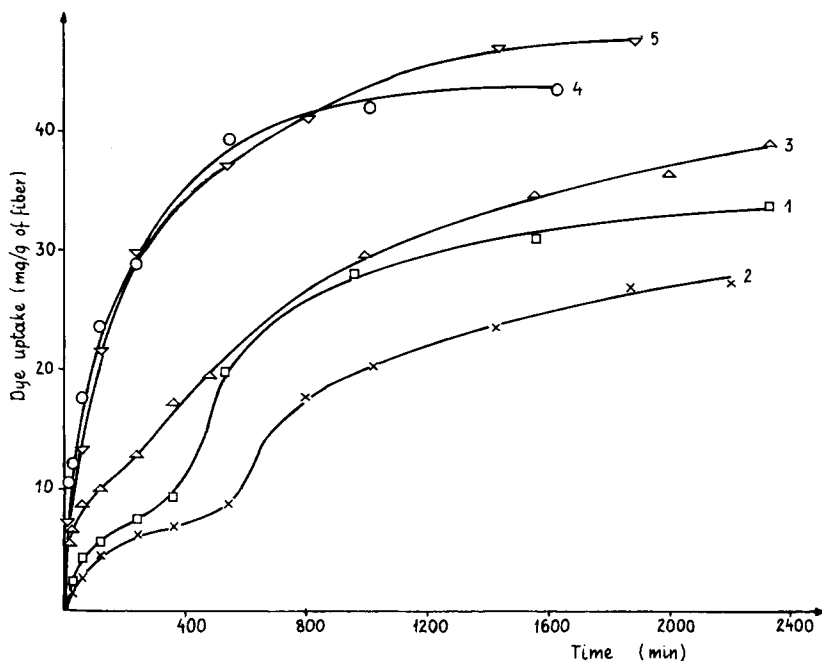


Fig. 1. Experimental rate-of-dyeing curves of the poly(ethylene terephthalate) fibers heat-treated at 147°C (1), 165°C (2), 200°C (3), 220°C (4), and untreated (5). Dye: Synthene Scarlet P3GL. Temperature of dyeing 100°C.

RESULTS AND DISCUSSION

Rate-of-Dyeing Curves

In Figure 1 the rate-of-sorption curves of Synthene Scarlet P3GL in the untreated and heat-treated polyester fibers are shown. According to the plots, at an early stage of dyeing the dye contents in the fibers heat-treated at 147°C, 165°C, and 200°C are below those for the untreated fiber and below that of the sample which has been heat-treated at the highest temperature 220°C. These results are in accordance with the data published by Dumbleton et al.² Some explanations concerning this relation will be presented in a forthcoming paper taking into account the structure of fibers.

The interesting fact, not described earlier, is that the rate-of-sorption curves of Synthene Scarlet P3GL in the PET fibers heat-treated at 147°C, 165°C, and 200°C (low sorption) differ in their shape from the others in the appearance of the inflection point characteristic for anomalous (non-Fickian) sorption. In those fibers the sorption seems to proceed in two stages: at the first stage the quasiequilibrium is obtained, whereas at the second stage the final equilibrium is attained. The establishment of an apparent equilibrium takes the longest time in the fiber heat-treated at 165°C, in which the uptake of dye is the lowest.

Calculations of Equilibrium Contents and Diffusion Coefficients of Dye at Anomalous Sorption

It is generally accepted that in dyeing of polyester fibers the rate of dyeing depends on the rate of diffusion of dye in a polymer. This is correct if the rate of diffusion of dye molecules in the aqueous liquor toward the fiber surface and the rate of passage of dye across the interface are higher than the rate of penetrant diffusion in the fiber itself.⁸ Then the concentration gradient of dye within the fiber causes its diffusion from the surface to the center.

For the quantitative description of the diffusion of dyes in fibers, Hill's equation⁹ is most often employed. This equation presents the solution of the Fick's law for the radial diffusion in a cylinder of radius r . This equation permits to calculate the apparent diffusion coefficient at constant concentration of dye in a liquor, when the equilibrium content of dye within the fiber C_∞ is known. In Hill's equation

$$C_t = C_\infty \left[1 - \frac{4}{r^2} \sum_1^n \frac{1}{\alpha_n^2} \exp(-D_{\text{app}} \alpha_n^2 t) \right] \quad (1)$$

C_t and C_∞ denote dye concentrations in the fiber at time t and at saturation, D_{app} is an apparent diffusion coefficient, r is the radius of a fiber whereas α_n are the positive roots of the Bessel function of the first kind of order zero, $I_0(r\alpha_n) = 0$.

From Figure 1 it is seen that for the system studied, time of dyeing up to 40 h is not sufficient for the establishment of equilibrium. It is sometimes difficult to obtain accurate values of C_∞ experimentally owing to the degradation of the polymer substrate during sorption. Consequently, C_∞ has been calculated by means of eq. (1) taking four roots of the Bessel function: $\alpha_1 = 2.4048/r$, $\alpha_2 = 5.5201/r$, $\alpha_3 = 8.6537/r$, and $\alpha_4 = 11.7815/r$.

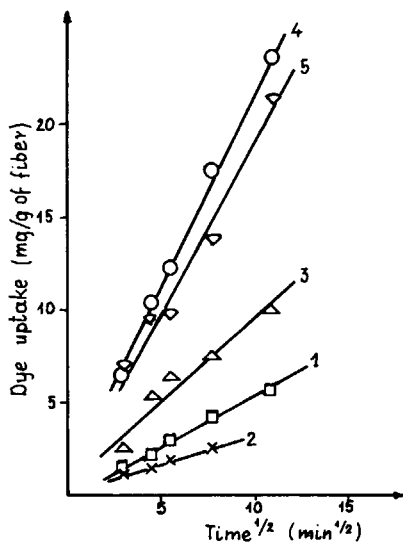


Fig. 2. Reduced sorption curves of Synthene Scarlet P3GL in poly(ethylene terephthalate) fibers heat-treated at 147°C (1), 165°C (2), 200°C (3), 220°C (4), and untreated fiber (5).

TABLE I
 Equilibrium Contents and Apparent Diffusion Coefficients of Disperse Dye Synthene Scarlet P3GL in Untreated and Heat-Treated Poly(ethylene Terephthalate) Fibers (Temperature of Dyeing 100°C)

Temperature of fiber treatment (°C)	Equilibrium contents of dye (mg/g fiber)		Apparent diffusion coefficients $\text{cm}^2\text{-s}^{-1} \times 10^{12}$		Standard deviation	
	Total C_∞	Stage I C_I	Stage I D_I	Stage II D_{II}	Stage I	Stage II
		Stage II C_{II}				
Untreated	48.2	—	3.7	—	0.0052	—
147	36.5	13.2	3.5	2.3	0.0110	0.0069
165	35.6	11.1	2.9	1.2	0.0264	0.0016
182	—	12.9	3.4	—	0.0142	—
200	56.9	14.5	14.2	0.4	0.0185	0.0339
220	43.9	—	5.9	—	0.0039	—

The equilibrium concentration C_∞ and the diffusion coefficient D_{app} have been calculated numerically applying the least squares method:

$$S = \sum_1^m (C_{t_i, \text{calcd}} - C_{t_i, \text{exptl}})^2 \quad (2)$$

In eq. (2) m means a number of dye content determinations C_t after time t , whereas $C_{t, \text{calcd}}$ is defined by eq. (1). The standard deviation of the fit to the experimental points, σ , has been obtained by calculating S from eq. (2) and using that value in the following expression:

$$\sigma^2 = S/(m - 2) \quad (3)$$

The equilibrium concentrations of dye in the untreated fiber and the samples heat treated at 220°C have been computed with this procedure (Table I). In these fibers the sorption is Fickian and there is no inflection point on the rate-of-sorption curves. Another procedure is needed for calculations of C_∞ and D_{app} for anomalous sorption.

In Figure 2 the results of dye uptake determinations of Synthene Scarlet P3GL have been drawn in coordinates: the dye concentration (mg/g) of the fiber vs. the square root of time. It is seen that for the early stage of dyeing the relation is linear with correlation coefficients 0.92–0.99. These results confirm the fact that at the time below 2 h the sorption may be treated as being Fickian. Using experimental data for that time, the dye content at the quasi-equilibrium state C_I and a diffusion coefficient D_I have been calculated employing the method described above. Both values C_I and D_I describe quantitatively the first stage of sorption; the corresponding data are presented in Table I. Employing the same procedure the experimental rate-of-sorption curves have been divided into two parts, and the initial time of the second stage has been determined. This time is the longest one for the PET fibers heat-treated at 165°C. As we suppose, it is the time necessary for the relaxation of polymer chains, and it depends on the concentration of dye in the fiber. In Table I there are also presented dye equilibrium contents for the second stage C_{II} , calculated under the same assumption, i.e., that at the second stage the sorption is again Fickian.

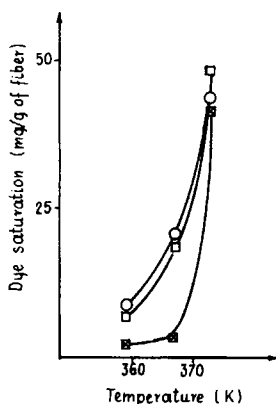


Fig. 3. Relation of dye uptake of Synthene Scarlet P3GL to temperature of dyeing for poly(ethylene terephthalate) fibers untreated (□) and heat treated at 165°C (■) and at 220°C (○).

The data of Table I show that the dye contents absorbed at stage I (C_I) in the fibers heat-treated at 147°C, 165°C, and 220°C are much lower than those at stage II (C_{II}). One can postulate that C_I corresponds to the volume of a polymer attainable for dye molecules at the beginning of dyeing whereas the C_{II} corresponds to the volume of restricted accessibility.

The apparent diffusion coefficients of Synthene Scarlet P3GL in the untreated and heat-treated fibers calculated with Hill's equation are inserted in Table I. With respect to the untreated fibers and the heat-treated ones at the highest temperature of 220°C, D_{app} values correspond to the mean rate of diffusion for the whole dyeing process. With respect to the fibers of anomalous sorption the diffusion coefficients at the first stage are higher than those for the second stage. This is consistent with the suggestion that at stage II the diffusion proceeds within the hardly attainable domains, presumably of the longest relaxation orientation. This is in agreement with the results of Blacker and Patterson,¹⁰ who found an increase of dichroism of dye molecules at the prolonged time of dyeing.

The Effect of Temperature on the Sorption of Dye

The drawings of Figure 3 present the variation of dye content in fibers with respect to temperature of dyeing. At the temperature interval 86–100°C the dye content increases considerably with the increasing temperature. On the basis of similar data, Tsubaki and Kitamura¹¹ determined the so-called "transition temperature for dyeing." The highest transition temperature for dyeing has been found for the fiber heat-treated at 165°C with the lowest dye content and anomalous sorption. For all samples the transition temperature exceeds T_g of semicrystalline PET ranging from 86°C to 94°C. This justifies the fact that the cooperative motion of a few polymer segments is necessary for the movement of large dye molecules.

CONCLUSIONS

The investigations on the sorption of Synthene Scarlet P3GL in PET fibers heat-treated at 147°C, 165°C, and 200°C reveal an anomalous type of sorption. In this paper we treat the observed sorption as the superposition of two stages displayed at the time scale. In each of them the nonideal Fickian diffusion proceeds with the apparent diffusion coefficients D_I and D_{II} and the equilibrium dye contents C_I and C_{II} . The comparison of the diffusion coefficients show that at both stages dye molecules diffuse in the domain of different segmental motions. Summing up the conclusions, the comparison of the equilibrium concentration at both stages points to the existence of noncrystalline domains of different accessibility and possibly different orientation within PET fibers.

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