

Copolyester Studies. IV. Dyeing Behavior of Drawn and Undrawn Fibers Derived from Tetramethylene Terephthalate–Tetramethylene Sebacate Copolymers

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Synopsis

Drawn and undrawn fibers of tetramethylene terephthalate–tetramethylene sebacate copolymers, containing up to 20 mol % of the latter, have been dyed in an infinite dyebath with a disperse dye. The dyeing process has been interpreted in terms of the equilibrium dye absorption, the half-time of dyeing, and the diffusion coefficient. Increasing sebacate content has been found to have a marked effect on the rate and level of dye uptake. Deviations from Fickian behavior have been observed for the drawn fiber and related to presence of voids.

INTRODUCTION

In previous papers we reported the preparation and characterization¹ of tetramethylene terephthalate–tetramethylene sebacate copolymers containing up to 20 mol % tetramethylene sebacate. The melting and crystallization behavior of these systems was described,² as was their conversion into fibers by melt spinning and drawing and subsequent mechanical testing.³

We now report studies on the dyeing behavior of drawn and undrawn fibers of these copolymer systems and of the homopolymer, poly(tetramethylene terephthalate) 4GT.

In the context of increasing energy costs, pressure dyeing in aqueous media at temperatures above 100°C is becoming an increasingly less viable commercial operation. The dye uptake of polyester may be increased, and this can be accompanied by a reduction in dyeing temperature if certain copolymer systems are employed.⁴

This series of copolymers has been prepared and studied to evaluate the effects on physical properties and dyeing behavior consequent to the incorporation of roque tetramethylene sebacate units into a tetramethylene terephthalate chain.

EXPERIMENTAL

Materials

The copolymers were prepared, characterized, converted into fibers, drawn, and mechanically tested as previously described.¹⁻³ Undrawn and drawn fibers of draw ratio³ of approximately 3.7 were used in dyeing experiments.

Dyeing was performed in an infinite dyebath using Dispersol Orange AG (C.I. No. 11005) supplied by ICI Ltd. The commercial dyestuff was separated from

diluents and dispersing agents by Soxhlet extraction with distilled acetone. The acetone was removed, and the remaining diluent and dispersing agent was removed by Soxhlet extraction of the dye with distilled water. After drying the dye overnight at 60°C/1 mm Hg, it was recrystallized from AR toluene, yielding red needles (mp 215°C lit.⁵ 215°C).

Apparatus

The apparatus used was that designed by Weinberg⁶ and Gur-Arieh⁷ and has been reported in detail elsewhere. Stirring was arranged such that the rate of dye uptake was independent of the stirring rate.

Dyeing Procedure

Fibers were pretreated prior to dyeing in boiling, distilled water for 2 hr and then maintained in the wet state until dyed. The dye solution was prepared in the following manner to avoid the presence of dye crystallites in the dye liquor. An accurately weighed quantity of dye (2–5 mg) was dissolved in distilled acetone (5 ml), and this solution was added to water (5 l.) maintained at 65°C. The aqueous solution was heated to boiling, left for 5 min and then filtered into the preheated dyeing vessel through glass filter papers. The dye solution was allowed to cool to the dyeing temperature with constant stirring. The vessel was maintained in a thermostatted bath, and the temperature in the dyeing vessel was maintained $\pm 0.2^\circ\text{C}$.

For each rate-of-dyeing experiment, 12 bundles of fibers (total weight approximately 120 mg) were used. Dyeing times ranging from 1 min to 34 hr were employed. On removal from the dyebath, the fibers were washed with warm water (<40°C), dried between filter papers, and finally dried at 50°C/1 mm Hg for 24 hr.

Dye absorption was measured by dissolving a known weight of fiber in freshly distilled *m*-cresol, followed by determination of the optical density of this solution at 432 nm in 1-cm pathlength cells using a Hilger Uvispek spectrophotometer. Application of the Beer-Lambert law yielded the concentration of dye in solution.

RESULTS AND DISCUSSION

The presence of dye crystallites in the dye liquor has been shown to lead to error by initiating further crystallization. In order to avoid this, the procedure reported in the experimental section was adopted. With adequate stirring all the solutions employed in this study were maintained as true solutions over time periods in excess of those used in dye-uptake studies.

The methods used in evaluating dye uptake are standard and based on the Beer-Lambert law. The wavelength and magnitude of maximum absorption of the dye in *m*-cresol solution was unaffected by the presence of polymer molecules.

When polymers are dyed at elevated temperatures, structural changes occur, generally as a result of crystallization processes. Such changes can interfere with dye diffusion and lead to erroneous results. Thus in order to minimize such

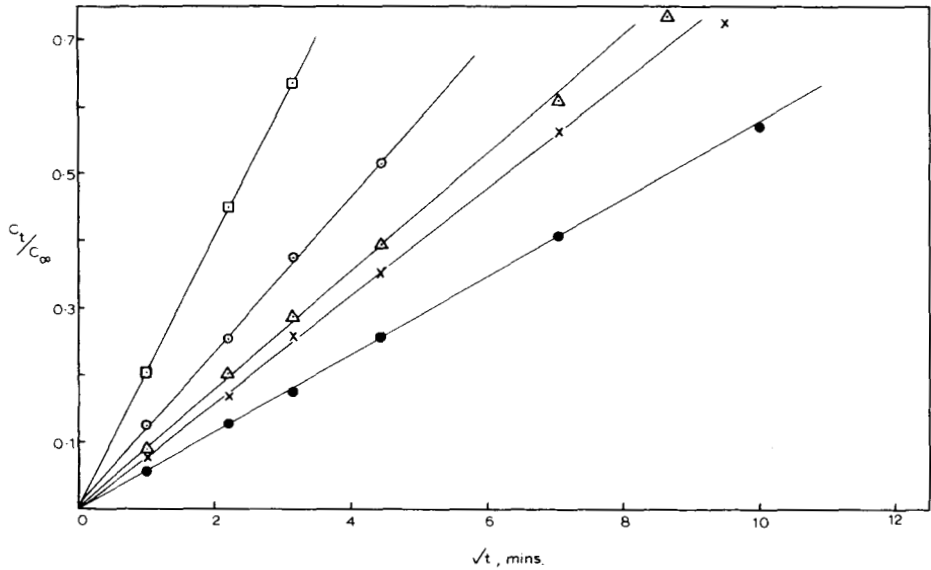


Fig. 1. The initial stages of dyeing for drawn fibers: ●, 4 GT; and ×, 5; Δ, 10; ○, 15; ◻, 20 mol % sebacate copolymer.

changes the fibers were subjected to a standardized pretreatment in a more drastic environment than the dyebath prior to the dyeing process.

Pretreatment of polyester fibers before dyeing can result in a marked reduction in diffusion rate,⁸ but it is obvious that such pretreatments are necessary. The reduction in diffusion rate is probably associated with crystallization, since Dumbleton et al.⁹ have shown that amorphous poly(ethylene terephthalate) 2GT when boiled in water for 1 hr yields a material having a degree of crystallinity of 37%. The consequence of such an increase in crystallinity may be an increase

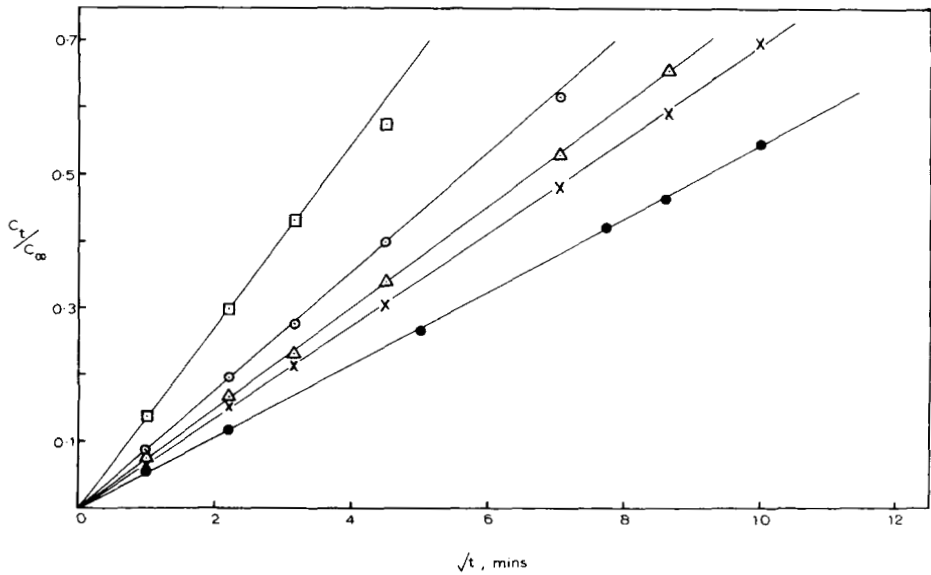


Fig. 2. The initial stages of dyeing for undrawn fibers. ●, 4 GT; and ×, 5; Δ, 10; ○, 15; ◻, 20 mol % sebacate copolymer.

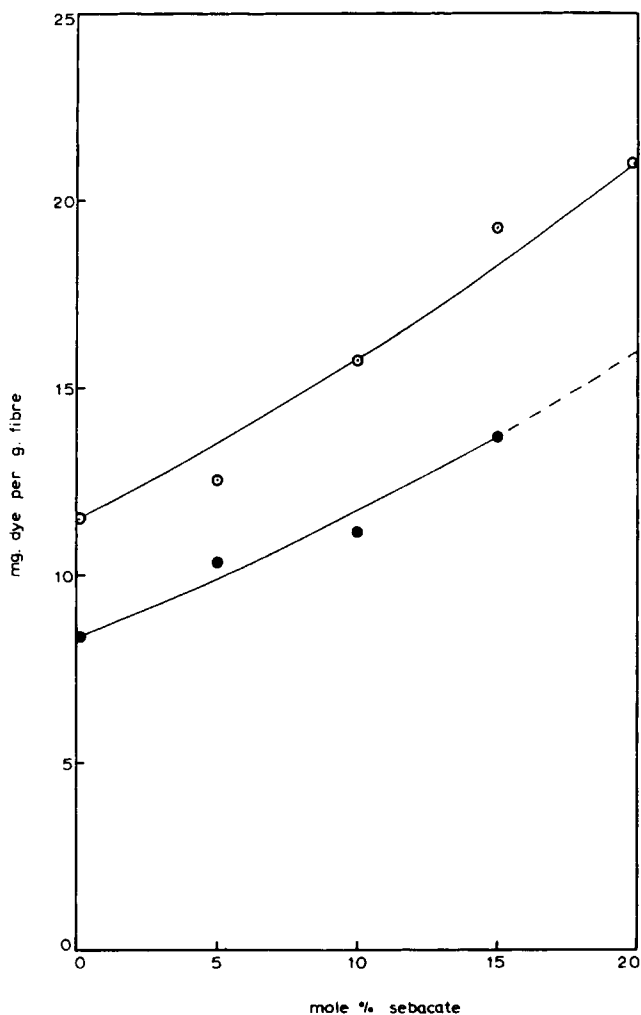


Fig. 3. Equilibrium absorption of drawn and undrawn fibers at 70°C: ●, drawn; ○, undrawn.

in the glass-transition temperature (T_g). Thus amorphous 2GT has a T_g of approximately 80°C, whereas moderately crystalline samples have T_g 's approaching 100°C.

In the present study the pretreatment afforded to the fibers should result in marked increases in crystallinity.^{1,2} Thus undrawn fibers of 4GT would be expected to attain crystallinity levels of approximately 30%.¹ However, in previous studies² we reported that the incorporation of sebacate units causes a marked attenuation in the rate of crystallization and the level of crystallinity attained. Thus for the copolymers the level of crystallinity produced by pretreatment should decrease slightly with increasing sebacate content.

In the context of the dyeing process, the predominant effect of fiber pretreatment would be to increase the T_g , which would restrict segmental mobility, thereby decreasing the rate of diffusion of the dye.

In direct opposition to this pretreatment effect will be the plasticization effect of the aqueous dyeing medium on the T_g of the polymers. Thus Dumbleton et al.⁹ have shown that water can decrease the T_g of pretreated 2GT fibers by 10°C

per percent of water absorbed. Similarly, Howard and Williams¹⁰ have found that the figure for nylon 66 is 15°C per percent water absorbed. Liw¹¹ has obtained results that indicate that similar water absorption levels are to be expected for 4GT and 2GT, suggesting that a similar depression of T_g in aqueous media will occur. The presence of sebacate units may be expected to increase water absorption only slightly at the level of incorporation under investigation.

For undrawn fibers, therefore, it has been assumed that the increase in T_g resulting from pretreatment is balanced by the plasticizing effect of water, and the T_g used in the dyeing experiments was that determined previously¹ by dynamic mechanical measurements (E''_{\max}).

For the drawn fibers the situation is more complex, since during drawing both orientation and stress crystallization occur and the T_g of the drawn fibers will be higher than the E''_{\max} value. Pretreatment, however, will have little effect, since the fibers are already highly crystalline. The major effect on T_g will therefore result from plasticization by water in the dyeing medium. If the depression in T_g is of a similar order to that for undrawn fibers, then the effective dyeing T_g may be similar to the temperature of E''_{\max} .

To determine the effects of the incorporation of sebacate units on the dyeability of the polymers, each fiber was dyed at the same relative temperature ($T_g + X^\circ\text{C}$). This temperature, where X was an arbitrary value so that a relatively rapid rate of dyeing could be achieved, was chosen because of the known dependence of the rate of dyeing on the difference between the dyeing temperature T_d and T_g .^{4,12,13} In addition, all the fibers were dyed at 70°C, since one of the predominant features of the incorporation of sebacate units into the terephthalate chain is the reduction in T_g of the copolymer.¹ It would be expected that dyeing at the same temperature should reveal marked increases in the rate of dyeing with increasing sebacate content.

Tables I–IV show the results obtained from dyeing experiments on undrawn and drawn fibers at $T_g + X^\circ\text{C}$ and at 70°C. Results are expressed in terms of equilibrium absorption, the amount of dye absorbed by the fiber when equilibrium has been established; the half-time of dyeing $t_{1/2}$, defined as the time to reach half the equilibrium absorption, and the diffusion coefficient D .

The diffusion coefficient was calculated by the application of the equation for short dyeing times for infinite cylinders,¹⁴

$$C_t/C_\infty = 4\sqrt{(D_t/\pi r^2)}$$

where C_t is the amount of dye absorbed by the fiber in time t , C_∞ is the amount of dye absorbed by the fiber at equilibrium, and r is the radius of the fiber.

Typical plots of C_t/C_∞ vs the square root of the dyeing time for the initial stages of dyeing are shown in Figs. 1 and 2 for drawn and undrawn fibers at $T_g + 39^\circ\text{C}$. Similar results were also obtained at 70°C. It is indicative of the Fickian nature^{14,15} of the dyeing mechanism that in the initial stages of dyeing such plots give straight lines passing through the origin.

The general trends in dyeing properties with increased sebacate content at $T_g + 39^\circ\text{C}$ are shown in Tables I and II and indicate that

- (1) the rate of dyeing increases markedly,
- (2) the rate of diffusion of dye increases substantially, and
- (3) more dye is taken up by the fiber.

Such increases reflect the "opening" of the structure of the polymer as sebacate

TABLE I
 Dyeing of Undrawn Fibers at $T_g + 39^\circ\text{C}$

Composition, mol % sebacate	Dyeing temperature, $^\circ\text{C}$	Fiber radius, cm	Equilibrium absorption, mg/g	Diffusion coefficient, $\text{cm}^2 \text{min}^{-1}$ $\times 10^8$	Half- dyeing time, min
0	95	0.0078	7.53	3.482	87
5	89	0.0076	8.74	5.396	53
10	78	0.0080	12.96	6.970	46
15	73	0.0072	15.80	8.660	32
20	62	0.0042	22.11	7.851	14

 TABLE II
 Dyeing of Drawn Fibers at $T_g + 39^\circ\text{C}$

Composition, mol % sebacate	Dyeing temperature, $^\circ\text{C}$	Fiber radius, cm	Equilibrium absorption, mg/g	Diffusion coefficient, $\text{cm}^2 \text{min}^{-1}$ $\times 10^8$	Half- dyeing time, min
0	95	0.0040	6.36	1.057	80
5	89	0.0040	6.38	2.059	38
10	78	0.0042	9.45	2.742	33
15	73	0.0037	11.49	3.869	17
20	62	0.0024	20.04	4.588	6

units are introduced. These units are accommodated within the amorphous regions, and their relative flexibility and the ease of rotation of bonds will increase segmental mobility above the T_g with respect to 4GT. An increase in sebacate content also increases the amorphous content of the polymers² and results in a reduction in the size of the crystalline regions as indicated by the lowering in melting point.¹ As a result of these factors both the dye uptake and the diffusion coefficient of the dye are increased (Figs. 3 and 4) to substantial extents. Such data stress the importance of the fractional volume of the amorphous regions and the mobility of the chains in those regions.

The dyeing behavior at 70°C of drawn and undrawn fibers (Tables III and IV) reveals similar trends to those determined at $T_g + 39^\circ\text{C}$. The behavior observed is much more pronounced, since $T_d - T_g$ now increases with increasing sebacate content.

The data presented in Tables I-IV also indicates a faster rate of dyeing for drawn fibers relative to undrawn fibers, even though the rate of diffusion of dye within the drawn fibers is slower. Sprague⁸ has found similar effects in studies of cellulose acetate fibers, which was attributed to the increased surface area per unit weight of the drawn fibers of reduced fiber diameter being exposed to the dye solution. Similar effects have been observed for nylon 66 by Munden and Palmer,¹⁶ for 2GT by Cegarra and Puente,¹⁷ and for polyacrylonitrile by Rosenthal.¹²

In addition to the increased surface area per unit weight presented to the dye bath, other factors are also operative in the present study. Thus Figure 5 shows a graphical representation of Crank's solution of Fick's equation as a solid unbroken line. This solution applies to the dyeing of an infinite cylinder in an infinite dye bath, and the systems under study should fit the curve closely if the

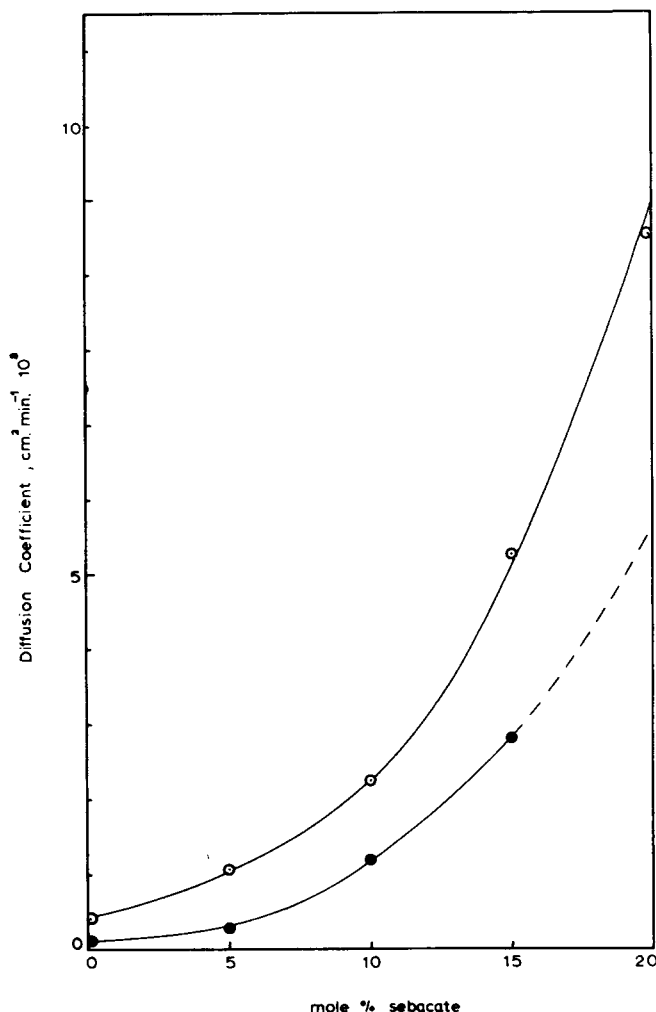


Fig. 4. The effect of composition on the diffusion coefficient for drawn and undrawn fibers: ●, drawn; ○, undrawn.

absorption is Fickian. Typical curves obtained from all the undrawn and drawn fibers are shown for the 5% copolymer in Figure 5. It can be seen that the drawn fibers show a marked departure from Fickian behavior.

In studies^{18,19} on the diffusion of gases into polymers, similar non-Fickian adsorption has been described. Such behavior has been interpreted in terms of a "dual sorption" mechanism involving normal Fickian absorption and not of the filling of holes or voids in the polymer.²⁰

In a previous paper³ we reported that on drawing, voiding occurred as evidenced by an anomalously low density and shown by electron microscopy. It is suggested, therefore, that the behavior of the drawn fibers results from a mechanism similar to that proposed for gas absorption above. In our studies on voiding and void formation,³ it was shown that voiding occurred in the center of the fiber and was surrounded by a skin of unvoided material.

The dyeing of drawn fibers can thus be interpreted in the following manner by reference to Figure 6, where the voided center of a fiber is represented as a

TABLE III
Dyeing of Undrawn Fibers at 70°C

Composition, mol % sebacate	Fiber radius, cm	Equilibrium absorption, mg/g	Diffusion coefficient, cm ² min ⁻¹ × 10 ⁸	Half- dyeing time, min
0	0.0078	11.50	0.405	800
5	0.0076	12.55	1.088	282
10	0.0080	15.73	2.268	138
15	0.0072	19.28	5.276	48
20	0.0046	20.99	9.536	10.5

TABLE IV
Dyeing of Drawn Fibers at 70°C

Composition, mol % sebacate	Fiber radius, cm	Equilibrium absorption, mg/g	Diffusion coefficient, cm ² min ⁻¹ × 10 ⁸	Half- dyeing time, min
0	0.0040	8.36	0.102	480
5	0.0040	10.35	0.292	290
10	0.0042	11.17	1.206	74
15	0.0037	13.69	2.822	24.5
20 ^a	—	—	—	—

^a Dyed too rapidly to make meaningful measurements.

single, large cavity. In the initial stages of dyeing, dye diffuses through the solution and is adsorbed on the surface of a fiber [Fig. 6(a)] and then diffuses from the surface inside the fiber [Fig. 6(b)]. Dye then diffuses through the fiber until the central voided region is reached [Fig. 6(c)]. The process up to this point is similar to that obtaining in an undrawn fiber and is Fickian.

When the surface of a void is reached, diffusion into the void is then extremely rapid, and if many voids are present, the rate of dyeing increases rapidly [Fig. 6(d)].

It has been suggested by Ludewig²¹ that voids are not separate entities within the fiber, but are interconnected by capillaries forming a network. Such a network could thus be filled with dye solution, and a situation can be envisaged where dye adsorption could occur from the surface of the fiber towards the center, and from the surfaces of voids towards the outside of the fiber. However, such a situation is only likely to occur to a limited extent, since the dye liquor in a voided network is likely to be stagnant and diffusion slow. The mechanism suggested can be used to explain the behavior shown in Figure 5. The diffusion coefficient was determined during the initial stages of the dyeing process when Fick's equation applies. However, the rate of dyeing was determined as the half-time of the process, by which time stage d (Fig. 6) had been reached, and the rate of diffusion inside the fiber and overall rate of dyeing was extremely rapid due to diffusion of the dye into the voids.

The effect of temperature on the dyeing properties of the undrawn fibers is readily seen from Table V. Both the dyeing rate and the diffusion rate are markedly increased as the temperature of dyeing is raised.

In terms of the free-volume model of dye diffusion,²² this is in accord with a

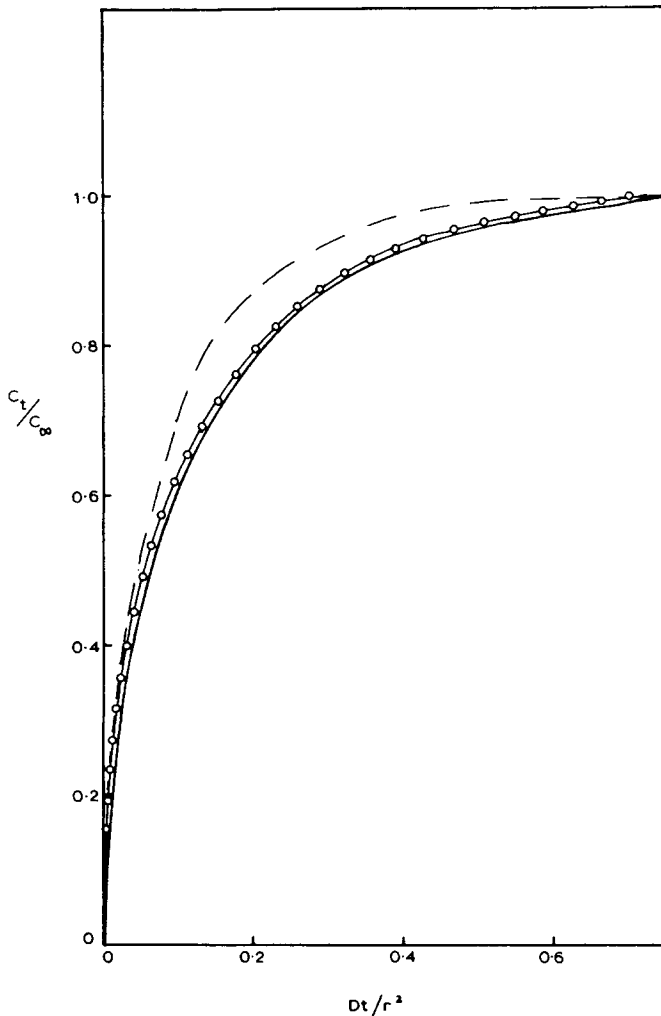


Fig. 5. Crank's solution of Fick's equation: —, Crank's solution (infinite cylinder, infinite dye-bath); ---, drawn 5 mol % sebacate copolymer; —○—, undrawn 5 mol % sebacate copolymer.

marked increase in segmental mobility, and hence free volume, with increased temperature. The decrease in equilibrium absorption observed with increased temperature is also to be expected in view of the exothermic nature of the dyeing process.

The temperature dependence of the diffusion rate can be expressed in a quantitative manner in terms of the activation energy of the diffusion process, which is determined from the equation $D_T = D_0 \exp(-E^*/RT)$, where D_T is the observed diffusion coefficient at an absolute temperature T , D_0 is a constant, E^* is the activation energy for diffusion, and R is the gas constant. The activation energy E^* may be calculated from the slope of the line obtained by plotting $\ln D_T$ against $1/T$, and results obtained for the undrawn and drawn fibers are shown in Table VI.

For the undrawn systems, it would be expected that the increased segmental mobility afforded by a reduction in T_g as compared with 4GT should lead to a gradual reduction in activation energy with increasing sebacate content.

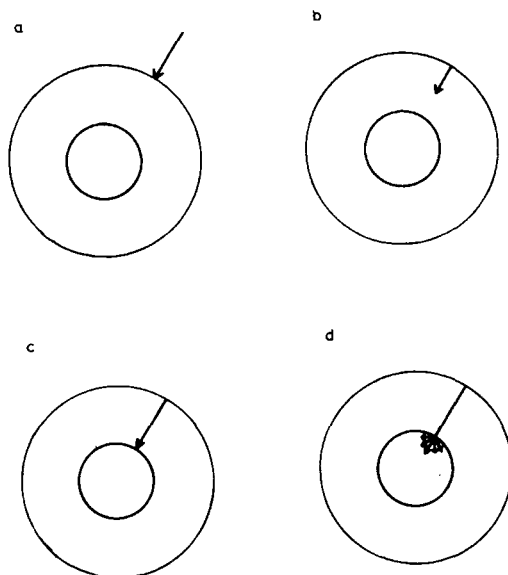


Fig. 6. Schematic representation of the dyeing mechanism in drawn voided fibers.

The trend is seen in part for 4GT, the 5 and the 20% copolymer. The 10% copolymer does not conform to such a pattern and the higher level of crystallinity observed in this fiber after pretreatment may be responsible. Thus the 10% copolymer had a crystallinity value of 23% compared with values of the order of 14% for other members of the series. This difference may hinder the movement of dye molecules within the fiber and increase the activation energy of the diffusion process. In addition, the 10% copolymer may also have a different crystallite size and distribution compared with the other systems, which may also affect the ease of diffusion of the dye molecules.

The increase in diffusion coefficient with sebacate content shown in Tables III and IV for the drawn fibers is not reflected in the activation energy data presented in Table VI. These results show essentially the same activation energy for the fibers irrespective of composition. This suggests that ease of dye

TABLE V
Dyeing of Undrawn Fibers

Composition, mole % sebacate	Dyeing temperature, °C	Fiber radius, cm	Equilibrium absorption, mg/g	Diffusion coefficient, cm ² min ⁻¹ × 10 ⁸	Half- dyeing time, min
0	95	0.0078	7.53	3.482	87
0	85	0.0078	9.54	1.814	160
0	80	0.0078	9.82	1.339	290
0	70	0.0078	11.50	0.408	800
10	78	0.0080	12.96	6.970	46
10	70	0.0080	15.73	2.286	138
10	60	0.0080	18.44	0.554	446
20	70	0.0046	20.99	9.536	10.5
20	62	0.0046	22.11	7.851	14
20	50	0.0046	26.36	2.657	100

TABLE VI
Activation Energy for Dyeing Above the T_g

Composition, mol % sebacate	E^* , cal mole ⁻¹	
	Undrawn	Drawn
0	21,600	23,700
5	20,900	25,300
10	32,000	25,000
15	—	25,000
20	14,200	—

movement does not increase with increasing sebacate content in such systems.

One of the authors (WM) thanks the Department of Polymer and Fibre Science for a Research Studentship.

References

1. W. Marrs, R. H. Peters, and R. H. Still, *J. Appl. Polym. Sci.*, **23**, 1063 (1979).
2. W. Marrs, R. H. Peters, and R. H. Still, *J. Appl. Polym. Sci.*, **23**, 1077 (1979).
3. W. Marrs, R. H. Peters, and R. H. Still, *J. Appl. Polym. Sci.*, **23**, 1095 (1979).
4. R. H. Peters, *Textile Chemistry, Vol. 3. The Physical Chemistry of Dyeing*, Elsevier, Amsterdam, 1975.
5. C. L. Bird, *J. Soc. Dyers Colour.*, **70**, 68 (1965).
6. A. Weinberg, Ph.D. Thesis, Victoria University of Manchester, 1972.
7. Z. Gur-Arieh, Ph.D. Thesis, Victoria University of Manchester, 1973.
8. B. S. Sprague, *J. Polym. Sci., Part C*, **20**, 159 (1967).
9. J. H. Dumbleton, J. P. Bell, and T. Murayama, *J. Appl. Polym. Sci.*, **12**, 2491 (1968).
10. W. Howard and M. L. Williams, *Text. Res. J.*, **36**, 691 (1966).
11. P. H. Liw, Ph.D. Thesis, Victoria University of Manchester, 1972.
12. S. Rosenbaum, *J. Appl. Polym. Sci.*, **7**, 1225 (1963).
13. S. Rosenbaum, *J. Polym. Sci., Part A*, **3**, 1949 (1965).
14. T. Vickerstaff, *The Physical Chemistry of Dyeing*, Oliver and Boyd, London, 1954.
15. R. McGregor, *Text. Res. J.*, **35**, 279 (1965).
16. A. R. Munden and H. J. Palmer, *J. Text. Inst.*, **41**, 609 (1950).
17. J. Cegarra and P. Puente, *Text. Res. J.*, **36**, 134 (1966).
18. S. A. Stern, S. K. Ken, and A. K. Rao, *J. Macromol Sci., Phys.*, **B10**, 507 (1974).
19. H. Hoyo and W. N. Findley, *Polym. Eng. Sci.*, **13**, 255 (1973).
20. W. R. Vieth, C. S. Frangoulis and J. A. Ronda, *J. Colloid. Interface Sci.*, **22**, 454 (1966).
21. H. Ludewig, *Polyester Fibres: Chemistry and Technology*, Wiley-Interscience, 1971.
22. R. H. Peters and W. Ingamells, *J. Soc. Dyers Colour.*, **89**, 397 (1973).

Received October 5, 1977