

Copolyester Studies. VII. The Dyeing Behavior of Undrawn Fibers Derived from Tetramethylene Terephthalate: Poly(tetramethylene Oxide) Random Block Copolymers

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Synopsis

A series of copolymers based on poly(tetramethylene terephthalate) containing poly(tetramethylene oxide) blocks whose molecular weights ranged from 1000 to 5000 in concentrations from 10 to 30% by weight was prepared. The polymers were melt spun into fibers and the undrawn fibers dyed with a disperse dye at three temperatures. The equilibrium adsorption and diffusion coefficient of the dye increased with both the molecular weight and concentration of the polyether. The equilibrium adsorption varied linearly with both the molecular weight and concentration. It has been assumed that the equilibrium dye partition coefficient K_M gives a parameter of the accessibility, V , of the fiber for dye. If the diffusion coefficient D_M is given by $D_M = VD_0/\tau$, where D_0 is the diffusion coefficient of the dye in the amorphous regions and τ is a tortuosity factor, a good correlation can be obtained between K_M and D_M , suggesting that changes in D_0/τ vary in a systematic fashion.

INTRODUCTION

In previous articles^{1,2} we reported the preparation and characterization of random copolymers made from tetramethylene terephthalate and poly(tetramethylene oxide). In that work, emphasis was placed on the relationships between the physical properties and the composition of the polymer and the size of the poly(tetramethylene oxide) block. The polymers were fabricated into fibers by melt spinning, and the mechanical properties of the filaments so obtained were determined. This study is concerned with an examination of a further property which is sensitive to the structure of the fiber, namely, the adsorption of dyes.

EXPERIMENTAL

Materials

The preparation and characterization of the polymers and their conversion into fibers have been described previously.^{1,2} Undrawn fibers which were formed under gravity from a rod spinner were dyed in an "infinite" dyebath of concentration 9 mg/L. The dye used was Dispersol Orange AG (Disperse Orange 3)

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supplied by I.C.I. (Organics Division). It was purified by recrystallization giving red needles,³ lit.⁴ mp 215°C.

Dyeing Procedure

Small samples of the fiber (24 mg) were contained in stainless steel cages; these were immersed in the dye liquor contained in a 5-L round-bottom flask. The stirring was adequate to ensure that the rate of dyeing was independent of the rate of agitation.

Prior to dyeing, the fibers were preheated in boiling distilled water for 2 h and kept in the wet state until they were dyed: this was to ensure that the fiber had achieved a stable structure and prevented structural changes occurring during the dyeing process.⁵ The preparation of the dye solution has been described elsewhere.³ The fiber samples were withdrawn and washed and the dye concentration measured optically with the aid of a Hilger Uvispek spectrophotometer after dissolution in freshly distilled *m*-cresol.

The undrawn fibers examined contained different amounts of the polyether block which were themselves of differing molecular weight (1000–5000).

RESULTS AND DISCUSSION

The equilibrium adsorption and rates of dyeing given by the time of half-dyeing are reported in Tables I, II, and III. From plots of C_t/C_∞ vs. $t^{1/2}$, the diffusion coefficients D were calculated using eq. (1) valid for the initial dyeing rates:

$$\frac{C_t}{C_\infty} = 4\sqrt{\frac{Dt}{\pi r^2}} \quad (1)$$

where C_t and C_∞ are the amounts of dye taken up at time t and at equilibrium and r is the radius of the fiber. A typical plot is given in Figure 1.

The equilibrium dye uptake increases linearly at the three temperatures used with both the quantity of polyether contained within the fiber and with the molecular weight of the polyether block when the polyether concentration is maintained constant (Figs. 2 and 3). This suggests that the accessibility of the polymer increases with increasing amount or size of the polyether block. The

TABLE I
Dyeing of the Undrawn Fibers 4GT/PTHF 1000

PTHF (wt %)	Dyeing temperature (°C)	Fiber radius (cm)	Equilibrium absorption (g/kg)	Partition coefficient (L kg ⁻¹ × 10 ⁻³)	Diffusion coefficient (cm ² min ⁻¹ × 10 ⁸)	Half-dyeing time (min)
10	70	0.0052	11.01	1.22	2.17	46
20	70	0.0044	13.64	1.52	7.45	12
30	70	0.0052	15.66	1.74	18.09	7
10	80	0.0052	10.55	1.17	6.82	25
20	80	0.0044	12.72	1.42	16.78	8
30	80	0.0052	15.21	1.69	32.13	4
10	85	0.0052	10.36	1.15	11.94	15
20	85	0.0044	12.53	1.39	24.63	5
30	85	0.0052	15.00	1.67	42.17	3

TABLE II
 Dyeing of the Undrawn Fibers 4GT/PTHF 2000

PTHF (wt %)	Dyeing temperature (°C)	Fiber radius (cm)	Equilibrium absorption (g/kg)	Partition coefficient (L, kg ⁻¹ × 10 ⁻³)	Diffusion coefficient (cm ² min ⁻¹ × 10 ⁸)	Half-dyeing time (min)
10	70	0.0050	11.58	1.29	2.76	40
20	70	0.0047	14.10	1.57	10.26	10
30	70	0.0050	16.33	1.81	20.11	5
10	80	0.0050	11.10	1.23	7.52	22
20	80	0.0047	13.75	1.53	21.36	6
30	80	0.0050	16.02	1.78	34.41	3
10	85	0.0050	10.79	1.20	12.12	13
20	85	0.0047	13.51	1.50	29.67	4
30	85	0.0050	15.60	1.73	44.18	2

diffusion coefficient also increases markedly with concentration (Fig. 4) but less so with increase in molecular weight of the polyether block.

Increases in the dyeing temperature decrease the amount of dye taken up at equilibrium, but simultaneously the rate of dyeing increases, from which data activation energies may be calculated (Table IV). These show a decrease in magnitude not only as the concentration of polyether is increased but also as the size of the polyester block is increased (at constant % incorporation).

The dyeing behavior of random copolymers prepared from poly(tetramethylene terephthalate) containing (a) isophthalic and (b) sebacic acid as the comonomer^{3,6} has also been studied. With both these systems, increases in the comonomer content increased both the rate of dyeing and the quantity of dye taken up at equilibrium. The increase in rate of dyeing can be explained in a qualitative sense by the more rapid segmental motion resulting from the decrease in glass transition temperature as the comonomer concentration increased; in addition, the volume available for dye adsorption becomes larger, thereby increasing accessibility presumably from disruption of the structure by the increasing quantity of comonomer.

 TABLE III
 Dyeing of Undrawn Fibers Containing 10% by Weight of PTHF

PTHF mol. wt.	Dyeing temperature (°C)	Fiber radius (cm)	Equilibrium absorption (g/kg)	Partition coefficient (L kg ⁻¹ × 10 ⁻³)	Diffusion coefficient (cm ² min ⁻¹ × 10 ⁸)	Half-dyeing time (min)
1000	70	0.0052	11.02	1.22	2.17	46
2000	70	0.0050	11.58	1.29	2.76	40
3000	70	0.0048	12.23	1.36	2.95	38
4000	70	0.0047	12.64	1.40	3.23	36
5000	70	0.0048	13.17	1.46	4.71	33
1000	80	0.0052	10.65	1.18	6.72	22
2000	80	0.0050	11.13	1.24	7.46	17
3000	80	0.0048	11.58	1.29	7.79	14
4000	80	0.0047	12.12	1.35	8.20	11
5000	80	0.0048	12.57	1.40	10.86	9
1000	85	0.0052	10.36	1.15	11.95	15
2000	85	0.0050	10.79	1.20	12.12	13
3000	85	0.0048	11.44	1.27	12.56	11
4000	85	0.0047	11.70	1.30	13.12	9
5000	85	0.0048	12.41	1.38	15.90	6

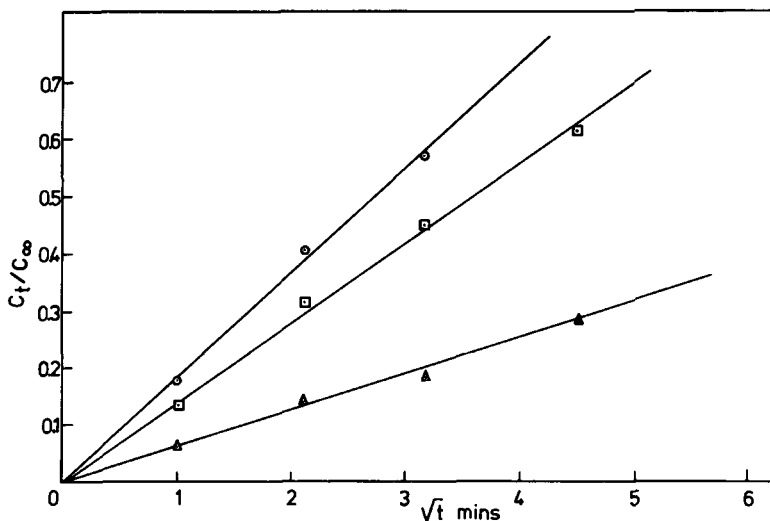


Fig. 1. Dyeing behavior at 70°C for copolyesters derived from poly(tetramethylene oxide) MW 1000. Weight % poly(tetramethylene oxide): (○) 10%; (◻) 20%; (△) 30%.

The structure of the polyether/polyester polymers used in the present work may be regarded as one in which the polyether blocks are embedded in a polyester matrix which is the first crystalline component to form when the melt is cooled. If the concentration or the molecular weight of the polyether is high enough (concentrations larger than 10% and polyether molecular weight greater than 2000), there is clear evidence from WAXS and DSC that crystallization of the polyether occurs.¹ Since the melting points of the polyether are in the region of 30–35°C, the polyether component will melt under dyeing conditions (ca. 70–85°C). For this reason, it is not possible to correlate dyeing data with properties such as initial modulus or T_g , which are determined by measurements at lower temperatures; hence, the dyeing data will be considered and discussed in isolation.

Equilibrium Data

The data for the equilibrium uptake of dye at three different temperatures is shown in Figure 2. It is seen from these data that there is a linear relationship with composition (by weight). Such observations have been made using other

TABLE IV
Activation Energy for Undrawn Fibers

Polymer code	E (cal/mole)
4GT/PTHF 1000 10%	27,700
4GT/PTHF 1000 20%	19,450
4GT/PTHF 1000 30%	13,800
4GT/PTHF 2000 10%	24,100
4GT/PTHF 2000 20%	17,300
4GT/PTHF 2000 30%	12,800
4GT/PTHF 3000 10%	23,600
4GT/PTHF 4000 10%	22,800
4GT/PTHF 5000 10%	19,800

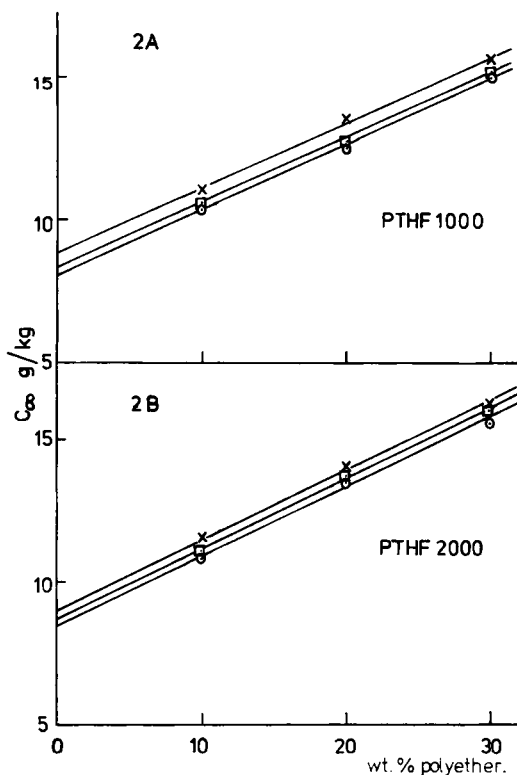


Fig. 2. Absorption of Dispersol Orange AG by the copolyesters derived from poly(tetramethylene oxide) MW 1000 (PTHF 1000) (a) and MW 2000 (PTHF 2000) (b). Dyeing temperature: (x) 70°C; (□) 80°C; (○) 85°C.

copolymer systems, namely, copolyesters of poly(tetramethylene terephthalate) containing various quantities of sebacic acid.⁷ It is not possible to relate the dye uptake to physically measurable parameters of the fiber structure, e.g., crystallinity, because of the uncertainty of knowing what fraction of the noncrystalline region is available to accommodate the long, stiff dye molecule. A very simplistic approach to the data is however possible.

It can be assumed that the quantity of a disperse dye adsorbed by a hydrophobic polymer, C_F , is linearly related to the concentration of dye in solution, C_B , through a partition coefficient K_T :

$$K_T = \frac{C_F}{VC_B} \quad (2)$$

where C_F is measured in grams (or moles) per kg of polymer and C_B is given in grams (or moles) per liter; V is the volume given in liters per kg of fiber and represents the volume of the polymer accessible to dye. On the assumption that, to a first approximation, K_T does not change with copolymer composition, the measured partition coefficient C_F/C_B is a parameter of the change of accessibility of the copolymer.

On this basis, the increase in accessibility occurs as a result of the disruption of the structure of the polyester matrix. The volume available in the polyester is reduced by the factor $(1 - x)$, where x is the weight fraction of the polyether,

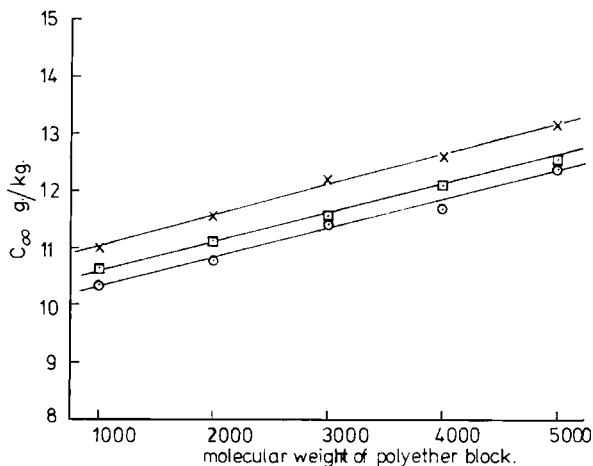


Fig. 3. Adsorption of Dispersol Orange AG by copolyesters derived from poly(tetramethylene oxide) of varying molecular weights, containing 10 wt % of the polyether block. Dyeing temperature: (x) 70°C; (□) 80°C; (○) 85°C.

but increased by an amount proportional to x . On this basis, the new accessibility is given by $V(1 - x) + kx$, where k is the proportionality constant, i.e., the volume produced by a unit weight of polyether. Hence, the measured partition coefficient K_M is given by

$$\frac{C_F}{C_B} = K_M = K_T[V + x(k - 1)] \quad (3)$$

Equation (3) shows that K_M or, in the experiments presented here, C_F , since C_B is constant, increase linearly with x .

A second feature of the present systems is the variation in the molecular weight of the block. Increases in this parameter increase the quantity of dye adsorbed at the same weight concentration of polyether, suggesting that either structural disruption increases or the polyether forms a well-defined phase which may adsorb dye to a greater extent than the polyester. In fact, copolymers of the type discussed here are expected to have a structure in which the polyester forms crystalline lamellae interspersed with polyether/noncrystalline polyester regions.⁹⁻¹¹

The increase in dye uptake with increasing molecular weight of the polyether block when the weight concentration of the latter is maintained constant presumably arises from structural distortions of the polyester matrix caused by the decrease in volume when the polyether crystallizes within the already crystallized polyester. Moreover, in reaching the dyeing temperature, melting of the polyether occurs with consequent increase in volume. Such observations indicate that the higher-molecular-weight polyether blocks will result in an increased quantity of amorphous regions and hence greater accessibility to dye. The alternative that the polyether, at least at the higher molecular weights, forms a separate molten phase at the dyeing temperature is an additional explanation for increased dye uptake. A simple distribution experiment of the dye between a high-molecular-weight polyether at the dyeing temperature gave a fairly large partition coefficient of 3×10^3 .

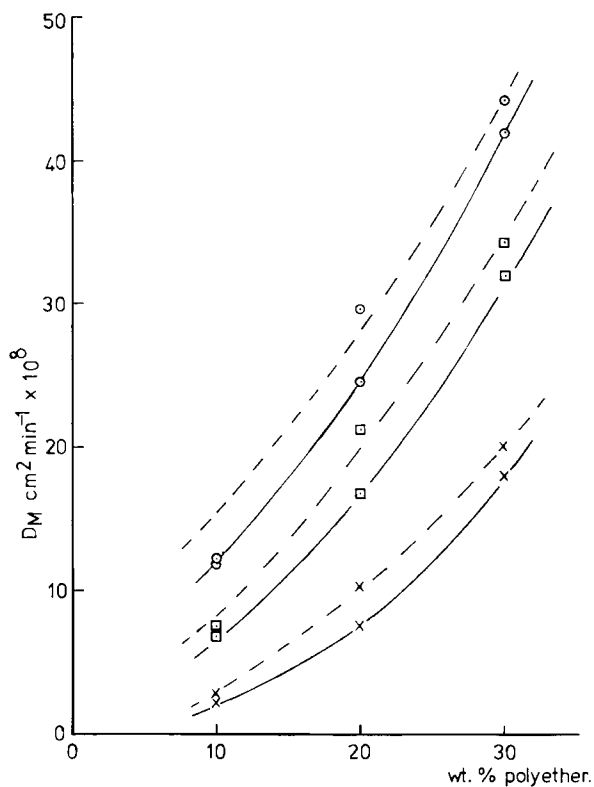


Fig. 4. Diffusion coefficients of Dispersol Orange AG: (—) PTHF 1000; (---) PTHF 2000. Dyeing temperature: (x) 70°C; (□) 80°C; (○) 85°C.

Diffusion Coefficient

The diffusion coefficients of the dye into fibers are shown in Figure 4. The diffusion coefficient increases at a greater rate than the partition coefficient. As indicated earlier, the diffusion coefficient cannot be correlated with the glass transition temperatures of the fibers since at the temperature at which these occur many of the samples show crystalline polyether components whose melting points are below the dyeing temperature. In view of this, the diffusion data have been correlated within itself by assuming that the equilibrium data give a parameter of the change in the accessibility.

If D_0 is the diffusion coefficient of the dye in the amorphous regions, the measured value D_M may be correlated with the accessibility α by

$$D_M = \frac{\alpha D_0}{\tau} \quad (4)$$

where τ is a tortuosity factor. This equation has been used with success for the diffusion of gases through polymer films¹²; and on the assumption that α may be equated to the amorphous fraction, values of τ have been obtained. The value of α can now be taken to be that given by eq. (3), whence

$$D_M = \frac{D_0 K_M}{\tau K_T} \quad (5)$$

If the assumption be made that D_0/τ varies monotonically with composition, then the measured diffusion coefficient will be correlated with K_M for any constant temperature. A plot of D_M vs. K_M (Fig. 5) shows a smooth curve at each temperature for samples containing polyether blocks of molecular weight 1000 and 2000, suggesting that the measured diffusion coefficient is correlated with the changing accessibility of the polymer.

The considerable increase in the diffusion coefficient as the concentration of polyether is increased must be due to changes in D_0 because of the increased segmental motion and also to the less tortuous nature of the diffusion path in the polymer as the concentration of polyether is increased, i.e., by a reduction in crystallinity.

Figure 6 shows the correlations for the samples of increasing molecular weight when it is seen that D_M does not increase as rapidly as predicted by the relation for the lower-molecular-weight products. This may be explained by the fact that increases in the molecular weight of the polyether block at constant-weight composition results in an increase in the degree of polymerization of the polyester component; this is again reflected in an increase in T_g and hence a lower value of D_0 must be expected.

The value of $D_0/K_T\tau$ given by D_M/K_M is thus dependent however on factors of polymer structure such as changes of crystallinity, increase in segmental

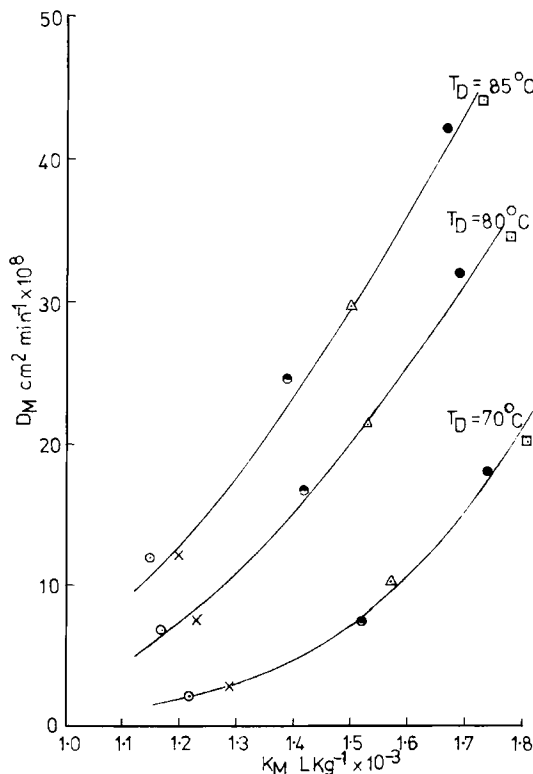


Fig. 5. Relationship between diffusion coefficient and partition coefficient for copolyesters derived from PTHF 1000 and PTHF 2000. % PTHF 1000 (by weight): (○) 10%; (●) 20%; (●) 30%. % PTHF 2000 (by weight): (×) 10%; (△) 20%; (□) 30%. T_D = Dyeing temperature.

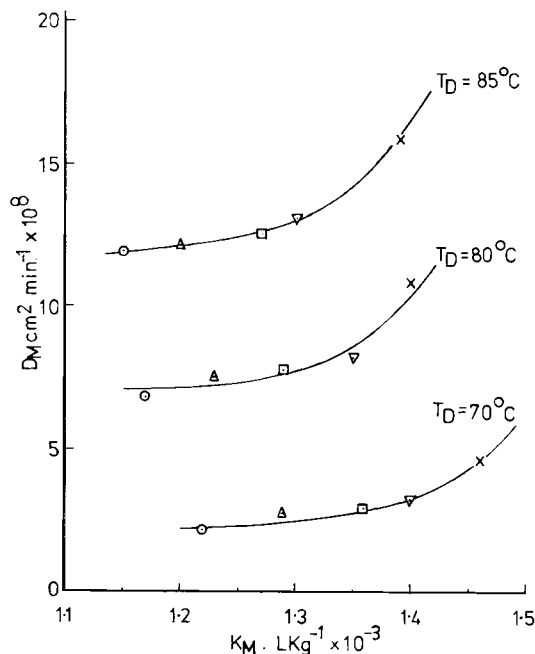


Fig. 6. Relationship between diffusion coefficient and partition coefficient for copolyesters containing 10 wt % of poly(tetramethylene oxide) of differing molecular weight. Molecular weight of PTHF block: (O) 1000; (Δ) 2000; (\square) 3000; (∇) 4000; (\times) 5000. T_D = Dyeing temperature.

motion, etc., as the percentage of the polyether increases. In the systems discussed in this report, further correlations with polymer structure are unfortunately not possible.

Conclusions

Both the dye uptake and the diffusion coefficients in the copolyether/esters increase as the quantity of the ether block increases. If the changes in the former be taken to reflect the changes in the accessibility, the latter is modified by other factors which would seem to be the improvement in tortuosity and the increased segmental motion resulting from increases in the polyether content.

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