

The Effect of Structural Changes on Dye Diffusion in Poly(ethylene Terephthalate)

J. H. DUMBLETON, J. P. BELL, and T. MURAYAMA,
Chemstrand Research Center, Inc., Durham, North Carolina 27702

Synopsis

The diffusion of a disperse dye, 1-amino-4-hydroxyanthraquinone (C.I. Disperse Red 15) into poly(ethylene terephthalate) fibers has been studied as a function of heat-setting temperature and draw ratio. It was found that the dynamic loss modulus E'' , measured under the dyeing conditions, was related to the dye diffusivity D . This indicates that the diffusion is controlled by the mobility of the polymer chain segments. Both the diffusivity and dye saturation values do not vary monotonically with heat-setting temperature but exhibit a minimum at a heat-setting temperature near 175°C. X-ray diffraction measurements were used to show that this behavior is attributable to crystallinity and crystal size changes resulting from heat-setting.

INTRODUCTION

Fujita et al.¹ have shown that above the glass transition the diffusion coefficient D of organic liquids in an amorphous polymer, poly(methyl acrylate), is related to the steady-state viscosity η by the equation

$$\ln D_T/RT = -B \ln \eta + C \quad (1)$$

where B and C are constants; their experimental results indicate that B is near unity.

The shear viscosity η may be replaced by E''/ω , where E'' is the tensile dynamic loss modulus measured at frequency ω and at temperature T .^{2a} Since E'' is the tensile loss modulus, the quantity E''/ω is equivalent to the tensile viscosity η_T , which is equal to 3η . Substitution of E''/ω in eq. (1) leads to

$$\ln D_T/RT = -B \ln E''/\omega + (C - B \ln 1/3) \quad (2)$$

Strictly speaking this replacement is rigorous only for E'' measured at zero frequency. The validity of the substitution is further discussed in the appendix.

Equation (1) with E''/ω substituted for η was applied to the diffusion of acid dyes in drawn nylon 66 fibers by Bell.³ It was assumed that a measurement frequency of 11 cps was low enough for the substitution to be valid.

A relation

$$\ln D_T/RT = -4.5 \ln E''/\omega + C' \quad (3)$$

was found to exist, where E'' was measured under dyeing conditions. The fact that the value of B was 4.5 instead of near 1 was attributed to the fact that the polymer was oriented (E'' was necessarily measured parallel to the fiber axis, whereas diffusion takes place primarily perpendicular to the fiber axis) and semicrystalline and also, possibly, to the substitution of E''/ω for η .

It was of interest to establish whether eq. (2) was valid for dye diffusion in polymers in which the crystallinity could be more easily varied than in nylon 66. Because of the possibility that B was a function of physical structure it was desirable to choose a polymer that could be obtained in a wide variety of crystallinities and orientations. Poly(ethylene terephthalate) is such a polymer, and further work on the connection between structure and dyeing was carried out with this polymer. This work is described herein.

EXPERIMENTAL

Preparation of Samples

Unoriented PET yarn (birefringence 0.004) was used as the starting material. Yarns with draw ratios of $3\times$ and $4.25\times$ were obtained by drawing the spun yarn over a hot pin at 80°C . Samples with different degrees of heat-setting were obtained by freely suspending skeins of yarn in an evacuated oven for periods of 6 hr. It had been previously determined that no further changes in crystallinity occurred after 6 hr, so that the structures could be assumed dependent only on the temperature of heat-setting and not the heat-setting time. This heat-setting treatment was followed by a 1 hr boiling in water, during which time the samples were again free to relax. The water treatment was given so that no structural changes due to water would take place during the dyeing experiments. X-ray crystallinities were found unchanged for longer times of boiling after the initial hour. The structural measurements were then made before dyeing.

It may be remarked that two types of structural change may be envisaged during dyeing, namely, irreversible and reversible changes. The conditioning treatment will eliminate the need for consideration of the former change but not the latter. If consideration of reversible changes is necessary, then x-ray measurements under the dyeing conditions (100% R.H.) must be carried out.

Structural Measurements

X-ray measurements were made after winding the yarn samples on aluminum frames. Crystallinities were measured on a Norelco diffractometer by the method of Dumbleton and Bowles.⁴ Crystallite orientations

were obtained from azimuthal diffractometer scans on the ($\bar{1}05$) plane. Crystal size determinations perpendicular to the fiber axis (for drawn samples) were obtained from 2θ scans on the (010) plane. The instrumental broadening was obtained from the width of the diffraction peaks of a sample of hexamethylene tetramine. The gaussian form of the instrumental broadening correction was used.⁵ Small-angle measurements were made on a Kratky camera with slit collimation and on a pinhole small-angle camera. The small-angle data were used to obtain crystal sizes along the chain axis for the drawn samples.⁶ The orientation of the fibers was also judged from birefringence measurements which, when combined with the x-ray data, yielded the orientation in the noncrystalline regions.⁷

Dynamic measurements were made on a Vibron (Toyo Measuring Instruments, Ltd., Tokyo, Japan) direct-reading viscoelastometer (Model DDV-II), which was operated at a frequency of 11 cps. Measurements were made with the sample in a nitrogen atmosphere at 0% R.H. and at 100% R.H. The modulus E' and the loss factor $\tan \delta$ were measured at 5°C intervals, with smaller intervals near the transition region. Samples were allowed to equilibrate for 5 min at each temperature before the measurements were taken.

Dyeing Rate Measurements

Dyeing rate and saturation measurements were made without carriers or other dye bath additives; dyeing rates were relatively low. No difference in dyeing rate or dye absorbed at saturation was found between samples that had been boiled for 1 hr in distilled water and samples that were given a scour after the boil-off; it was concluded that the additional scour was unnecessary, and it was discontinued. Before the dyeing the fiber samples were conditioned at 21°C and 65% R.H.

The dye used was purified Eastman C. I. Disperse Red 15, 1-amino-4-hydroxy anthraquinone. The dye was purified by crystallization from acetone, as previously described by Bowers and Wright.⁸ In this procedure the commercial dyestuff was added to hot acetone in the ratio of 1 part dyestuff to 16 parts acetone. The solution was filtered twice while hot through a fine sintered-glass filter. The resulting solution was boiled, to increase the dye concentration, and then cooled slowly to room temperature. The crystals were allowed to grow from 12 to 16 hr at 0°C and were then filtered from the solution and washed with distilled water. The crystals were then redissolved in acetone, and the entire procedure was repeated until crystals of suitable purity were obtained. Purity measurements were made on crystals that had been dried at 70°C for several hours. Samples that had a melting temperature of 213°C and a maximum extinction coefficient above 44.0 were considered acceptable. These conditions were usually met after five or six crystallizations.

The dye bath was prepared by adding 4.5 g of the purified dye to 3 liters of distilled water. A fiber sample, weight 0.200 g, was placed in a 250 ml

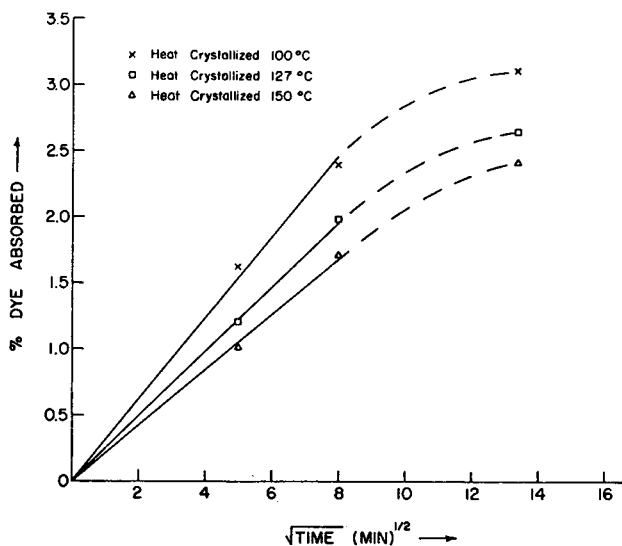


Fig. 1. Per cent dye on fiber versus $(\text{time})^{1/2}$ for undrawn fibers.

bottle together with 120 ml of the dye solution. The bottle was quickly capped and submerged in an oil bath at the dyeing temperature. Dyeings were made at 100°C, with the exception of a few measurements at 80°C, on undrawn yarn. The bottles were rotated within the bath in such a manner that they were completely inverted during each revolution. The speed of rotation was 36 rpm. Dyeing times of from 25 min to 70 hr were used. These times do not include the 4 min required for the dye bath to reach temperature. At the end of the dyeing the bottles were removed from the oil bath and cooled in tap water. The fiber sample was removed from the bottle and washed, first in water and then in acetone, to remove surface dye. For the acetone wash the fiber was placed in a sample bottle with acetone and shaken vigorously. This rinsing was carried out five times, after which the fiber was dried, conditioned at 21°C and 65% R.H., and reweighed. The dye was extracted from the fibers with hot dimethylformamide at 95°C. Five extractions were made on each sample, the first three being for 5 min and the last two for 15 min. The extract was brought to 100 ml with dimethylformamide, and the optical density of the extract was measured with a Cary Model 11 spectrophotometer. The per cent dye on the fiber was calculated from the following formula:

$$\% \text{ dye absorbed} = \frac{(\text{optical density} \times \text{extract volume} \times \text{dilution} \times 100)}{(\text{extinction coefficient} \times \text{dyed sample weight} \times 1000)}$$

Since there was more than enough dye to saturate the dye bath under the conditions used, the dyeings can be considered as occurring in an "infinite" dye bath in which the dye concentration does not change. The dye concentration for the 80°C dyeings was lower because of the lower solu-

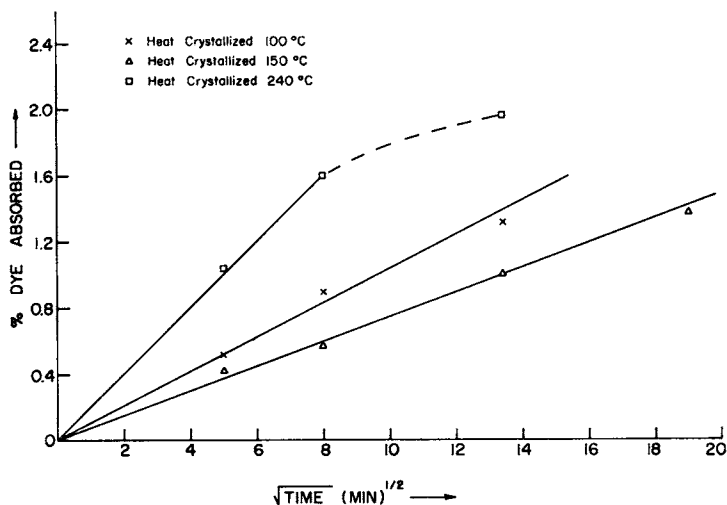


Fig. 2. Per cent dye on fiber versus $(\text{time})^{1/2}$ for fiber drawn 4.25 \times .

bility at that temperature. This is compensated by the lower saturation value, C_{∞} , used in the diffusion constant calculations.

Diffusivities were calculated from graphs of percent dye on fiber versus time by the method of Hill.⁹ Theory states that when the sample is not near dye saturation there should be a linear relation between per cent dye on the fiber and the square root of the time. In Figures 1 and 2 data for the undrawn yarn and yarn drawn 4.25 \times are plotted. It is seen that the graphs are linear, as expected.

RESULTS

Spun Yarn

X-ray results for the conditioned, heat-crystallized, spun PET yarn are given in Table I. The crystal sizes shown in the table were obtained from the integral breadth of the 010 reflection.

TABLE I
X-Ray Results for Undrawn, Heat-Crystallized PET Fibers

Temp., °C	X-ray crystall. X, %	Long period, Å	Cryst. size, Å	Cryst. vol. v , Å ³	X/v ($\times 10^7$), Å ⁻³
As-spun	37	87.0	66.8	296,000	12.5
100	39	87.0	66.8	296,000	13.2
112	41	87.2	66.5	293,000	14.0
127	43	87.2	67.7	309,000	13.9
150	44	87.5	68.0	312,000	14.1
175	46	96.0	73.0	386,000	11.9
200	47	99.0	76.5	447,000	10.5
220	50	108.1	80.9	525,000	9.5

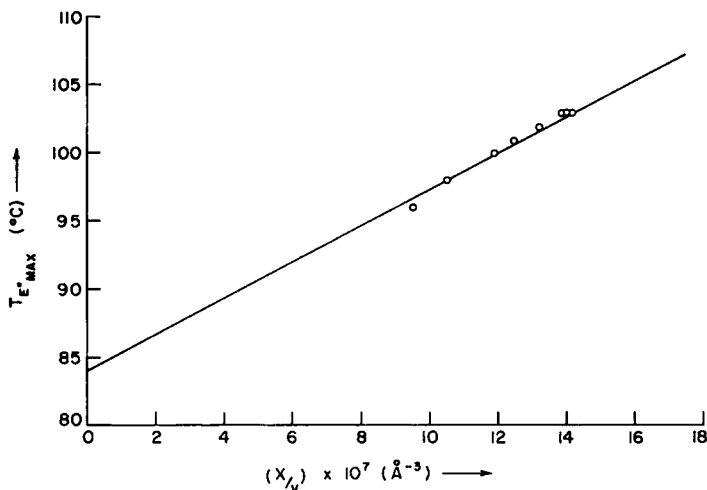


Fig. 3. $T_{E^{\max}}$ vs X/v for undrawn, heat-crystallized PET fibers.

The crystallinities increase with an increase in annealing temperature, although the range of crystallinities is small when compared with the range of crystallinities obtained for heat-crystallized spun PET samples that have not been boiled in water.¹⁰ A 1 hr boil in water for an as-spun PET yarn produces a crystallinity of 37%. To obtain this crystallinity by using dry heat only requires an annealing temperature of approximately 125°C. Thus immersion in water appears to be equivalent to an increase in annealing temperature of about 25°C. This figure is close to the decrease in the glass transition temperature of undrawn PET by water,^{11,12} which implies that the crystallization temperature is fixed relative to the glass transition temperature. The ultimate attainable crystallinity does not seem to be affected by the boiling-water treatment, since maximum crystallinities of 50% are found both in the present work and in a previous publication in which dry heat was used.¹⁰

The long period increases with annealing temperature but is lower than the corresponding values before the water-boil treatment. The intensity of the small-angle maximum is also much lower after the water treatment. This indicates that boiling does not simply increase the crystallinity but causes a decrease in the crystal size. Possibly a large range of crystal sizes is present, since this could account for the low intensity under the small-angle maximum.

Earlier work by Dumbleton and Murayama¹⁰ on undrawn, heat-crystallized PET has shown that the position of the α transition (glass transition) depends on crystallinity, crystal size and, in particular, the number of crystals, which may be represented by X/v , where X is the crystallinity and v the volume of a crystal. In the earlier work a graph of the glass transition temperature versus X/v was linear. It is interesting to see whether the present samples obey this relation. The X/v values are shown

TABLE II
Vibron Data for Undrawn, Heat-Crystallized PET Fibers

Temp., °C	At 0% R.H.		At 100% R.H.		
	$T_{E''_{max}}$, °C	E''_{max} ($\times 10^{-8}$), dyn/cm ²	$T_{E''_{max}}$, °C	E''_{max} ($\times 10^{-8}$), dyn/cm ²	$E''_{100^{\circ}C}$ ($\times 10^{-8}$), dyn/cm ²
As-spun	101	1.01	80	1.22	2.8
100	102	1.22	84	1.43	5.6
112	103	1.34	83	1.52	5.8
127	103	1.30	85	1.31	6.4
150	103	1.23	85	1.23	6.0
175	100	1.20	80	1.50	8.0
200	98	0.98	80	0.85	5.5
220	96	0.94	75	0.60	4.3

in Table I. The crystal volume was obtained by cubing the crystal size obtained from the (010) measurements. The glass transition temperatures, which were taken as the temperature at which the maximum in E'' (loss modulus) occurred, and which were obtained from Vibron measurements at 0% R.H., are given in Table II. Figure 3 shows the graph of X/v versus glass transition temperature. The points fit the line that was obtained in the previous work. This further substantiates the earlier claim that in unoriented PET the glass transition temperature is determined by the number of crystallites.

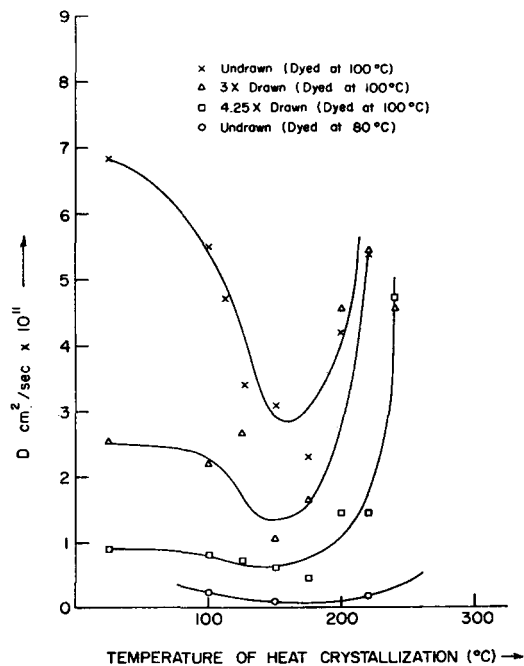


Fig. 4. D versus annealing temperature.

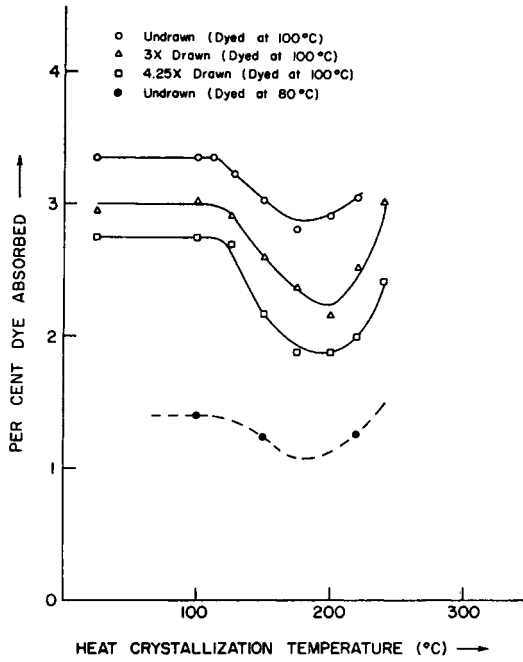


Fig. 5. C_{∞} vs. annealing temperature.

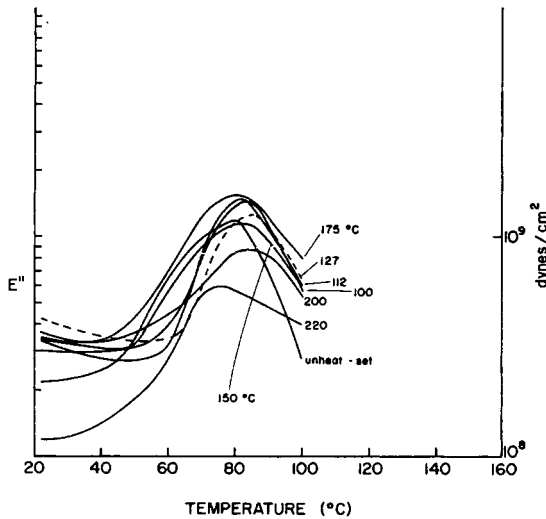


Fig. 6. E'' vs. T for undrawn yarn.

The dyeing results are shown in Figures 4 and 5. In Figure 4 the diffusivity D is plotted against annealing temperature, and Figure 5 shows the equilibrium dye uptake C_{∞} versus annealing temperature. Both D and C_{∞} exhibit a minimum at an annealing temperature near 175°C.

The diffusivity and dye uptake are much higher for the 100°C dyeing than for the 80°C dyeing. The reason for the much lower D values obtained for 80°C dyeing is evident from the curves of E'' versus temperature in Figure 6. It is seen that 80°C is the glass transition temperature and corresponds to a maximum value in E'' . The E'' curves fall quite steeply above 80°C, leading to a lower value of E'' at 100°C and, hence, a high value of D . Alternatively, it may be said that at 100°C the chain segments have a relatively high freedom of movement, and dye molecules will easily penetrate the polymer, whereas at 80°C the polymer is almost in the glass region, and molecular motion is much more difficult.

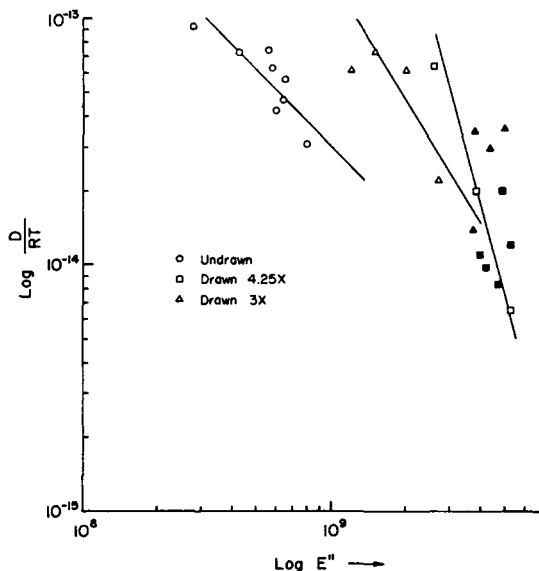


Fig. 7. $\log D$ vs. $\log E''$ (solid points denote $T_g > 100^\circ\text{C}$).

Values of E'' at 100% R.H. and 100°C were taken from Figure 6 by extrapolation to 100°C. The presence of water decreases the glass transition by some 20°C, but the height of the E'' maximum is not appreciably altered. Since the height of E'' is often taken as a measure of the crystallinity, this constancy implies that the crystallinity of the boiled and conditioned samples does not change on immersion in water.

As PET absorbs approximately 2% water, the change in glass transition is some 10°C/% water, a value which is not very different from the 15°C/% found in nylon 66.¹³ This is perhaps surprising since the molecules in PET are bound to each other by van der Waals forces, whereas in nylon 66 hydrogen bonds play a large part in intermolecular bonding. In fact, the great difference between these two polymers is in the *amount* of water that is absorbed. Water is just as effective in lowering the T_g of PET as in nylon 66, but PET absorbs much less water than does nylon 66.

TABLE III
X-Ray Data for 4.25× Drawn, Heat-Crystallized PET Fibers

Heat set temp., °C	Crystallinity X, %	f_c	f_{am}	Long period d	Cryst. size chain axis, Å	Cryst. size from (010), Å	Cryst. vol., Å ³ ($\times 10^{-1}$)	X/ρ ($\times 10^7$), Å ⁻³
4.25×	38	0.92	0.68	108.6	79	32	6,350	60
100	40	0.93	0.68	108.6	81.5	31	6,150	65
125	42	0.92	0.64	106.6	77.1	32	6,250	67
150	45	0.92	0.67	112.5	76.5	32	6,150	73
175	47	0.93	0.69	115.9	78.7	39	9,400	50
200	51	0.94	0.72	124.3	90.5	46	15,000	34
220	53	0.93	0.73	127.3	91.7	46	15,250	35
240	57	0.93	0.70	137.7	98.4	50	19,300	29

Figure 7 shows $\log D/RT$, the molecular mobility, plotted against $\log E''$. A linear relationship was found with the slope of the line near unity, as found by Fujita et al.¹

Yarn Drawn 4.25 \times

Table III shows the x-ray data for the PET yarn drawn 4.25 \times and annealed at various temperatures and then given a 1 hr boil in water. The data show a similar trend to those obtained for the undrawn yarns in that the crystallinity and long period increase with an increase in annealing temperature. The crystal sizes, both along the chain axis and perpendicular to the chain direction, increase in a similar fashion with annealing temperature. Since crystal size measurements were made both along and perpendicular to the chain axis, the crystallite volume was calculated on the assumption that the crystals were cylinders, the axis of the cylinder coinciding with the c axis. If the crystals were some other shape, say rectangular parallelepiped, the crystal volumes would be changed by a constant factor. This would not affect conclusions drawn on the basis of crystal size changes.

The eorientation of the crystals, as measured from the orientation of the $(\bar{1}05)$ plane, shows little change with annealing temperature, and comparison of the orientation values with those from previous work⁶ indicates that the boiling-water treatment did not change the crystallite orientation. The orientation of the noncrystalline regions was calculated from the following equation:

$$\Delta = (X)f_c\Delta_c^\circ + (1 - X)f_{am}\Delta_{am}^\circ$$

where Δ is the measured birefringence, X the crystallinity, f_c the crystallite orientation, and f_{am} the orientation of the noncrystalline regions. The

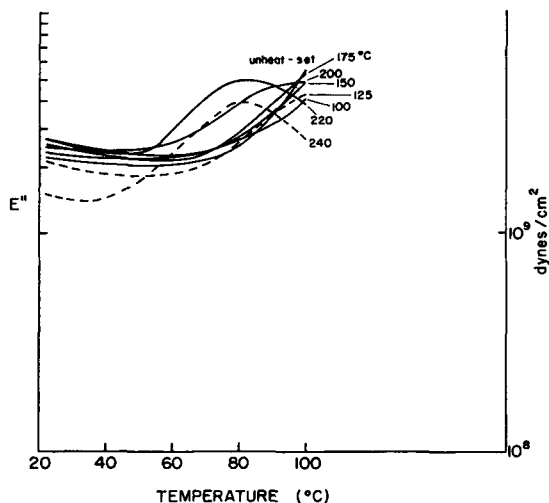


Fig. 8. E'' vs. temperature for 4.25 \times drawn samples.

quantities Δ_c° and Δ_{am}° are the intrinsic birefringences of the crystalline and noncrystalline regions and have been evaluated by Dumbleton.⁷ It will be seen that the orientation of the noncrystalline regions is lower than that in the crystalline regions. Again, however, there is no change in orientation with annealing temperature.

In Figure 8 curves of E'' as a function of temperature for the 4.25 \times sample are shown. The measurements were made at 100% R.H. It is clear that, at least for the low annealing temperatures, the dyeings (100°C) were carried out in the neighborhood of the glass transition of the samples. The values of E'' at the dyeing temperatures are given in Table IV.

TABLE IV
Vibron Data for 4.25 \times -Drawn, Heat-Crystallized PET Fibers

Temp., °C	At 100% R.H.	
	$E''_{100^\circ\text{C}} (\times 10^{-9}),$ dyn/cm ²	$T_{E''_{\text{max}}},$ °C
4.25 \times	5.3	>100
100	4.0	>100
125	4.2	>100
150	4.7	>100
175	5.3	>100
200	4.9	100
220	3.8	85
240	2.6	80

The dyeing results are included in Figures 4 and 5. The saturation values and diffusivities both exhibit minima in the region of the 175°C annealing temperature, and the curves are similar to those found for the undrawn yarns, except that both D and C_∞ are reduced in magnitude. In Figure 7 the values of $\log D/RT$ are plotted against $\log E''$. A linear relation is found, but the slope of the line is much steeper than for the undrawn samples. Since the relation between D and E'' should only hold above the glass transition, there is some doubt whether points below the transition should be included on the graph. The points obtained at the low annealing temperatures, however, are reasonably in line with the rest of the data.

Yarn Drawn 3 \times

Since the diffusivity and saturation curves were similar for the undrawn and the 4.25 \times drawn yarns, except for the difference in magnitude, it was decided to examine a yarn of intermediate draw ratio; a yarn of draw ratio 3 was chosen. Curves showing the diffusivity and saturation versus the temperature of annealing are given in Figures 4 and 5. Both curves exhibit a minimum near 150°C and are intermediate in magnitude between the data for the undrawn and the 4.25 \times drawn samples. Curves of E'' versus temperature were obtained at 100% R.H., and a plot of $\log E''$ versus

$\log D$ was made; see Figure 7. Although there is more scatter on the graph, a straight line may be drawn through the data; the slope of this line is intermediate between that of the line for the undrawn samples and the line for the 4.25 \times drawn samples. Although an extensive x-ray study was not carried out on these samples, crystallinity and orientation values were obtained (Table V). The crystallinity increases with increased

TABLE V
X-Ray and Vibron Data for 3 \times -Drawn, Heat-Crystallized PET Fibers

Temp., °C	Crystallinity, %	f_c	f_{am}	At 100% R.H.	
				$E''_{100^\circ\text{C}} (\times 10^{-9}),$ dyn/cm ²	$T_{E''_{\text{max}}},$ °C
3 \times	33	0.91	0.53	3.8	>100
100	33	0.92	0.54	4.4	>100
125	32	0.92	0.54	5.0	>100
150	38	0.91	0.57	3.7	>100
175	43	0.92	0.57	2.7	100
200	56	0.92	0.56	2.0	88
220	57	0.91	0.56	1.5	80
240	59	0.91	0.54	1.2	72

annealing temperature. The crystallite orientation is little different from that in the 4.25 \times drawn yarns. However, the orientation in the non-crystalline regions is significantly lower in the 3 \times series than in the 4.25 \times series.

DISCUSSION

Consideration of the variation of E'' with temperature at 100% R.H. gives a good indication of how a PET fiber will dye. The diffusivity depends on the difference between the dyeing temperature and the glass transition temperature T_g . For a fixed dyeing temperature D is dependent on the structure of the fiber, since T_g depends on orientation, crystallinity, and other structural parameters.¹⁰ Usually an increase in orientation or crystallinity will increase the T_g . The T_g may be decreased by chemical modification of the polymer or by the use of carriers (swelling agents) in the dye bath, and such a change can be considered equivalent to an increase in the dyeing temperature. It should be pointed out that it does not necessarily follow that a continual increase in the dyeing temperature will always continually increase D . The temperature at which PET will crystallize is related to the glass transition temperature, and if the temperature of dyeing is above the crystallization temperature T_c , then crystallization will occur during dyeing, which can decrease D by increasing T_g . As an example, consider undrawn, amorphous PET, which has a T_g of 80°C, measured at 0% R.H. on the Vibron, and a T_c of 98°C. The presence of water lowers T_g and T_c by some 20°C, and so dyeing at 100°C will cause crystallization. The T_g after crystallization is near 100°C (again, when

measured at 0% R.H. on the Vibron), and so the D will be lower than if the dyeing had been carried out at a somewhat lower temperature than that at which crystallization occurred. In drawn yarns the T_g is greater than 100°C, and so crystallization will not occur at 100°C in water; e.g., the T_g of the 4.25 \times yarn is 130°C at 0% R.H. However, dyeing must be carried out under pressure, or the T_g must be lowered, in order to get reasonable diffusivity, and so the problem of crystallization again arises.

The observation that D is sensitive to T_g immediately implies that segmental motion in the polymer is the limiting factor in determining the dye diffusion. Presumably the dye molecules will readily penetrate the polymer when the chain segments move so as to produce spaces equal to the size of a dye molecule. It has been shown^{13b} that the glass transition temperature occurs when segmental motion is such that spaces of size equal to a chain segment occur. Since this size is roughly equal to the size of a dye molecule, the diffusivity would be expected to increase at the glass transition. Naturally, the larger the dye molecule is, the higher must be the dyeing temperature to enable spaces of sufficient size to be produced by segmental motion.

The position of T_g is not the only factor in determining D , since D depends on the value of E'' at the dyeing temperature and on the shape of the relation E'' versus temperature, which will change with changes in structure.

The theory relating E'' to D strictly only applies for the diffusion in amorphous polymers above T_g . It was found that for drawn nylon 66 the relation $\log D/RT = -B \log E''/\omega + C'$ was valid, but $B = 4.5$ instead of the value of unity predicted by the theory. There was the possibility that $B \neq 1$ because a semicrystalline and drawn material had been used or because the approximation $\eta = E/\omega$ was made. Since samples of widely differing structure were used in the present studies on PET, further insight is gained of the influence of structure on B . It is found that $B = 1$ for undrawn, semicrystalline PET (with $\eta = E''/\omega$), so that it appears that the reason $B \neq 1$ in nylon 66 was due to orientation. Indeed, for the drawn PET samples B is greater than 1, with a larger value of B for the 4.25 \times yarn than for the 3 \times yarn.

The curves of D versus annealing temperature have the same shape for all three series of yarns. Both the crystallite and amorphous orientation values are constant throughout the drawn series. The diffusivity is higher for the 3 \times samples than for the 4.25 \times , although the crystallite orientation is almost the same for both series. There is, however, a significant difference in the orientation of the noncrystalline regions for the 3 \times and 4.25 \times yarns. It is likely that the absolute level of curves of D versus annealing temperature depends on the degree of orientation in the noncrystalline regions. Since the minimum appears in all three curves, it does not depend on orientation, nor does it depend directly on crystallinity, since the crystallinity increases monotonically with annealing temperature. Earlier it was found that the position of T_g depended on the number of crystals;

the larger the number, the higher the T_g . This means that D will be influenced by the number of crystals. From Tables I and IV it is seen that for the undrawn and $4.25\times$ drawn samples the number of crystals is at a maximum just at the annealing temperature which gives the minimum in D . It is proposed that the restraints imposed by the number of crystals is responsible for the minima in all three series.

A similar argument should hold for the C_∞ curves, since these curves exhibit minima at the same annealing temperature, as do the D curves. It is proposed that certain parts of the noncrystalline regions are bound so tightly by neighboring crystallites that they cannot contribute to dye uptake. The magnitude of the curves is again influenced by orientation.

Earlier it was mentioned that there was a possibility that reversible structural changes took place during the dyeing. It now appears that these changes need not be considered, at least in a semiquantitative treatment of the dyeing process, since all the dyeing phenomena are explicable on the basis of x-ray measurements made at room temperature. It appears that the conditioning treatment was a satisfactory one.

CONCLUSION

It has been shown that dye diffusion in PET fibers is controlled by segmental motion. The curves of D versus annealing temperature and C_∞ versus annealing temperature have similar shapes for both undrawn and drawn yarns; these shapes are controlled by the number of crystals present. The absolute level of the curves is controlled by the orientation in the noncrystalline regions.

Appendix: The Validity of the Relations between D , E'' , and η

The equation of Fujita et al.,¹ which relates D to η is based on the concepts embodied in the W-L-F equation.¹⁵ If the behavior of a polymer does not follow the W-L-F relation, then there is also a good possibility that eq. (1) is not obeyed for this polymer. Although there are no data on the viscoelastic behavior of PET at 100% R.H., there is published work on the viscoelasticity of dry PET. Ward¹⁵ has shown that when his data on the creep of unoriented, semicrystalline PET is combined with the dielectric results of Reddish¹⁶ on similar material, the behavior of his samples follows the W-L-F representation. Indeed, in the present work it is found that eq. (1) holds with $B = 1$ for unoriented PET. There is some evidence to suggest that oriented, semicrystalline, dry PET does not follow the W-L-F relation.¹⁷ Accordingly, it might be suspected that eq. (1) would not hold for oriented samples. This is not the case, since eq. (1) still holds for the oriented PET samples examined here, but B is not 1; instead, B is near 4.

Granted the applicability of eq. (1), it is then of interest to examine the approximation involved in the substitution $\eta = E''/\omega$. As a first step, consider that the viscoelastic behavior of the polymer is represented by the

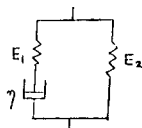


Fig. 9. Standard linear solid model.

standard linear solid,¹⁸ which consists of a Maxwell model in parallel with a spring (Figure 9). This model has a relaxation time $T_1 = \eta/E_1$ and a retardation time $T_2 = (E_1 + E_2)T_1/T_2$. If the stress is alternating of the form $\sigma = \sigma_0 \exp \{i\omega t\}$, then

$$E = E_2[(1 + \omega^2 T_1 T_2) + i\omega(T_2 - T_1)]/(1 + \omega^2 T_1^2) \quad (4)$$

Therefore

$$E'' = \omega E_2(T_2 - T_1)/(1 + \omega^2 T_1^2)$$

$$E''/\omega = E_1 T_1/(1 + \omega^2 T_1^2) \quad (5)$$

As $\omega \rightarrow 0$, so $E''/\omega \rightarrow E_1 T_1$, which is the steady-state viscosity η . Alternatively, if T_1 can be made sufficiently small (e.g., by increasing the temperature), so that $\omega^2 T_1^2 \ll 1$, then E''/ω is a good approximation to the steady-state viscosity. The latter approach is adopted here because the Vibron instrument is not designed to operate below $\omega = 3.5$ cps.

To a first approximation a change in temperature θ will produce a uniform shift of a logarithmic time scale.¹⁹ This is equivalent to saying that

$$T_1(\theta) = T_1(0) \exp \{ \Delta H/R\theta \} \quad (6)$$

where ΔH is the activation energy and θ the temperature.

From eq. (5) it may be shown that the maximum in E'' occurs when $\omega^2 T_1^2 = 1$. The maximum in $\tan \delta (=E''/E')$ occurs at $\omega^2 T_1 T_2 = 1$. Since $T_2 > T_1$, the temperature at which the maximum in $\tan \delta$ occurs is greater than that at which the maximum in E'' occurs.

Obviously, at the temperature of E''_{\max} the substitution for η of E''/ω is not valid, since $E''/\omega = E_1 T_1/2$, while $\eta = E_1 T_1$. However, the point of interest is to see how far above the temperature of E''_{\max} one has to go to be able to carry out the substitution. To investigate this point it is necessary to know the value of ΔH . This quantity is not available for PET at 100% R.H., but numerous values are given in the literature for PET under dry conditions and under unspecified moisture conditions. Illers and Breuer¹² have summarized the literature and conclude that the activation energy is little different whether crystalline or oriented samples are studied. The range of values is from 87 kcal/mol to 13 kcal/mol. For ease of calculation the value of ΔH will be taken as 100 kcal/mol. Then

$$T_1(\theta)/T_1(\theta_{E''_{\max}}) = \exp \{ (\Delta H/R)(1/\theta - 1/\theta_{E''_{\max}}) \}$$

$$T_1(\theta_{E''_{\max}}) = 1/\omega$$

Hence

$$T_1(\theta) = (1/\omega) \exp \{ 50,000(1/\theta - 1/\theta_{E''_{\max}}) \}$$

or

$$\omega^2 T_1^2(\theta) = \exp \{ 10^5(1/\theta - 1/\theta_{E''_{\max}}) \}$$

In the present case $\theta_{E''_{\max}}$ is taken at 373°K. Figure 10 shows a graph of $\omega^2 T_1^2(\theta)$ versus $\theta - \theta_{E''_{\max}}$, and it is seen that $\omega^2 T_1^2 \ll 1$ as long as $\theta - \theta_{E''_{\max}}$ is greater than 5°C. Thus the substitution of E''/ω for η is valid provided the temperature is more than 5°C above the temperature of E''_{\max} . Even down to within 2°C of the temperature of E''_{\max} the approximation is not grossly incorrect. It is well to emphasize the two regions of

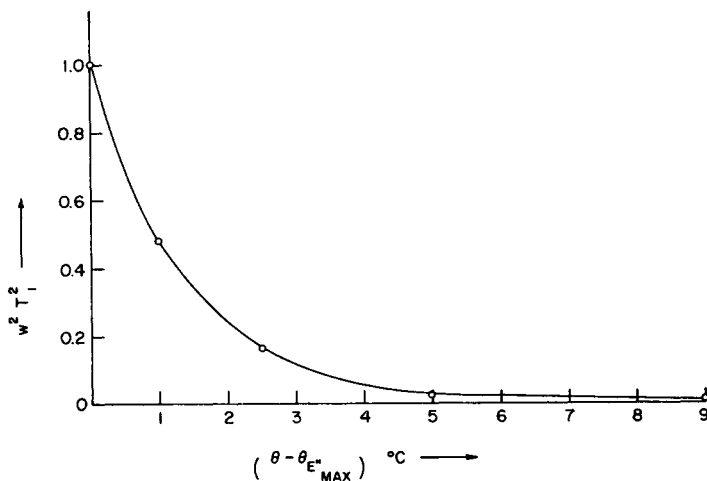


Fig. 10. Graph of $\omega^2 T_1^2$ as a function of $(\theta - \theta_{E''_{\max}})$.

validity of eqs. (1) and (2). Equation (1) is true above T_θ ; the same is true of eq. (2), but the subsidiary condition that the temperature be some 5°C above that at which E''_{\max} occurs is also required. Of course, in practice T_θ and the temperature at which E''_{\max} occurs are close together, and the distinction made above is somewhat academic.

Considering the present case of PET, it is clear that points on the graph of $\log D$ versus $\log E''/\omega$ collected for samples with T_θ greater than 100°C should not fall on the line predicted by eq. (2). These points were ignored in drawing the line through the data. However, it may be that the errors in measurement obscure to some extent the deviation caused by the invalidity of the substitution E''/ω for η .

Mention may be made that the conditions under which Bell³ substituted E''/ω for η were such that the substitution was valid; i.e., the dyeings were carried out at a sufficiently high temperature above T_θ .

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