

## The Mechanism of Carrier Dyeing

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### Synopsis

The accelerated rate of diffusion of disperse dyes into synthetic fibers caused by various dyebath additives ("carriers") has been correlated with their plasticizing action. The rate of change in length of Acrilan filaments with temperature under dyebath conditions enabled the effects of the carrier on the  $T_g$  of the filaments to be measured, and the results for different concentrations of carrier at one temperature could be superimposed on a common curve by employing suitable shift factors. The shift factors, as well as the variations of the diffusion coefficients of dyes with temperature and carrier concentration, both matched a WLF relationship, confirming that the dyeing process is controlled by the segmental mobility of the polymer. Indirect experimental evidence suggests that the same relation will describe the effect of carriers on the dyeing of poly(ethylene terephthalate) substrates with disperse dyes.

### INTRODUCTION

Earlier difficulties associated with the coloration of synthetic fibers made from polyacrylonitrile and poly(ethylene terephthalate), using nonionic dyes, were due to the unacceptably slow rate of diffusion of the dyes into the fiber. These practical problems were eventually overcome by applying the dyes in specially developed pressurized machines which operate at temperatures greater than 100°C, or by the addition to the dyebath of organic compounds such as phenols, primary amines, hydrocarbons, and esters, which have the effect of increasing the rate of diffusion of the dyes in the fibers to an acceptable level of temperatures below 100°C. The latter compounds are referred to as "carriers" and their mode of action is discussed in this report.

Various aspects of the action of "carriers" have already been examined in an attempt to elucidate the mechanism by which they operate and various theories have been put forward. Some workers<sup>1</sup> suggest that the enhanced rate of dyeing is a result of an increase in the low solubility of the disperse dyes in the dyebath, while others<sup>2</sup> claim the action of water-insoluble carriers to be due to the formation of a surface layer of carrier around the fiber in which the dye is very soluble and from which movement into the fiber is rapid due to the intimate contact between dye and fiber. It has also been noted that some carriers cause swelling of the fibers, and this leads to the theory that a more vigorous movement of the fibrous

polymer molecules is made possible which is associated with easier penetration of the dye into the fiber.<sup>3</sup>

All these earlier arguments have been reviewed,<sup>4,5,6,7,8</sup> but so far no one theory has provided a comprehensive basis upon which carrier action may be adequately represented. Nevertheless, the available experimental evidence suggests that the most likely action of the carriers is associated with their effect on the physical properties of the fiber.

One approach has been to examine the energy requirements necessary for separating the polymer chains to allow ingress of the dye, by matching the solubility parameters of the carrier and fiber.<sup>9,10</sup> However, the solubility parameters of the carriers and fibers do not correlate well, and the inadequacy of the solubility parameters to describe the specific interactions between polar groups and the effects of orientation and crystallinity of the fiber polymer molecules may be the reason for the lack of correlation.<sup>11</sup> Nevertheless, the physical properties of the fibers are changed in the presence of carriers. Rawicz and Gates<sup>12</sup> found that all compounds which were effective dyebath additives in the dyeing of polyester fibers with disperse dyes also caused shrinkage of the fibers, and on the basis of shrinkage measurements Fujino et al.<sup>13</sup> demonstrated the existence of a transition temperature which could be lowered progressively by increasing the carrier content of the fiber, suggesting that the glass transition temperature ( $T_g$ ) of the fiber was being lowered.

Direct proof of a connection between the plasticizing effects of the carriers and the accelerated rate of diffusion of dyes is not easy to obtain using the published data, because generally the relevant changes in physical properties have not been measured under dyebath conditions. More recently however, Rosenbaum<sup>14,15</sup> has demonstrated a connection between the diffusion coefficient of the dye Malachite Green, at different temperatures, into acrylic fibers and the glass transition temperature. The latter was detected by measuring the extension of the fibers at different temperatures when subjected to a small tension under dyebath conditions. Using arguments based on free volume, he showed that the variation of the diffusion coefficient of the dye with temperature  $T$  was related to the glass transition temperature  $T_g$  by the variable  $T - T_g$  by an equation of the same form as the Williams, Landells, and Ferry equation, i.e.,

$$-\ln a_T = \ln \frac{D_T}{D_{T_g}} = \frac{A(T - T_g)}{B + T - T_g} \quad (1)$$

where  $a_T$  is the shift factor for the viscoelastic properties of the fiber,  $A$  and  $B$  are constants, and  $D$  is the diffusion coefficient at the temperature indicated by the subscript.

Adherence of the variation of the diffusion coefficient with temperature to eq. (1) demonstrates that the segmental mobility of the polymer chains, which controls the viscoelastic properties, also controls the movement of dye through the substrate. Consequently, eq. (1) should also be applicable when the glass transition temperature is reduced by the incorporation of

"carrier" into the polymer, providing this plasticizing action is responsible for the enhanced uptake of dye by the fiber.

The work presented here shows how the correlation indicated by eq. (1) has been achieved for the accelerated diffusion of nonionic dyes, caused by carrier-like compounds into polyacrylonitrile fibers. An indication of the applicability of eq. (1) to poly(ethylene terephthalate) films is also given.

## EXPERIMENTAL AND RESULTS

### Materials

**Substrates.** Bright "Acrilan" 3-denier monofilament, supplied by Monsanto Ltd., was used as a polyacrylonitrile substrate.

Before use, the filaments were washed at 40°C in a solution containing a nonionic detergent (0.5 g/l. Dispersol VL) and trisodium phosphate (0.5 g/l.), for 150 min. Washing was followed by successive rinses in distilled water until no change in the pH value of the rinse water was observed.

Polyester films (Melinex type 442) were supplied by I.C.I. (Plastics Division). They contained no additives and were either 8 or 12  $\mu$  thick.

**Carriers.** Phenol (A.R. grade) was the principal "carrier" used. It was chosen because it is soluble in water and therefore does not present the experimental difficulties that are associated with the very low water solubility of commercial carriers, which are applied as emulsions. A few comparative experiments were also made using nitrobenzene, toluidine, and dimethylformamide.

**Dyes.** The two commercial dyes which were used were Dispersol Fast Orange G (I.C.I.) (CI Disperse Orange 3) and Dispersol Fast Scarlet B (I.C.I.) (CI Disperse Red 1). *p*-Aminoazobenzene was also used as supplied by B.D.H. Purification of the commercial dyes was carried out by hot-water extraction of the commercial powder followed by successive crystallizations from toluene, until a constant melting point the product was obtained. The melting points were 218°C for CI Disperse Orange 3 and 160°C for CI Disperse Red 1 (literature values were 215°C and 163°C, respectively).

### Examination of the Effect of Carriers on the Properties of Acrilan

The work involved a study of two different aspects of the same problem: (i) the effect of aqueous solutions of phenol on the mechanical properties of the filaments, and (ii) the dyeing properties of the fibers after treatment with phenol.

### Location of Glass Transition Temperature $T_g$

The glass transition temperature was determined from the change in the length of a filament which occurred at different temperatures ranging from 20°C to 95°C. The apparatus used was similar to that used by Rawicz.<sup>12</sup>

In order to eliminate the possibility of misleading effects arising from the diffusion of phenol into the filaments during measurement, the filaments were conditioned for 2 hr at 95°C in a phenol solution of appropriate concentration. The slight tension produced by a 3-mg weight secured on the free end of the filament kept the filament taut during the pretreatment.

#### Procedure and Results

The pretreated 3-denier filament of length 50–60 cm with a load of 0.097 g attached at one end was clamped by the other end in a vertical, thermostatically jacketed glass column containing the appropriate solution of phenol. The lengths of the filament were determined accurately as the

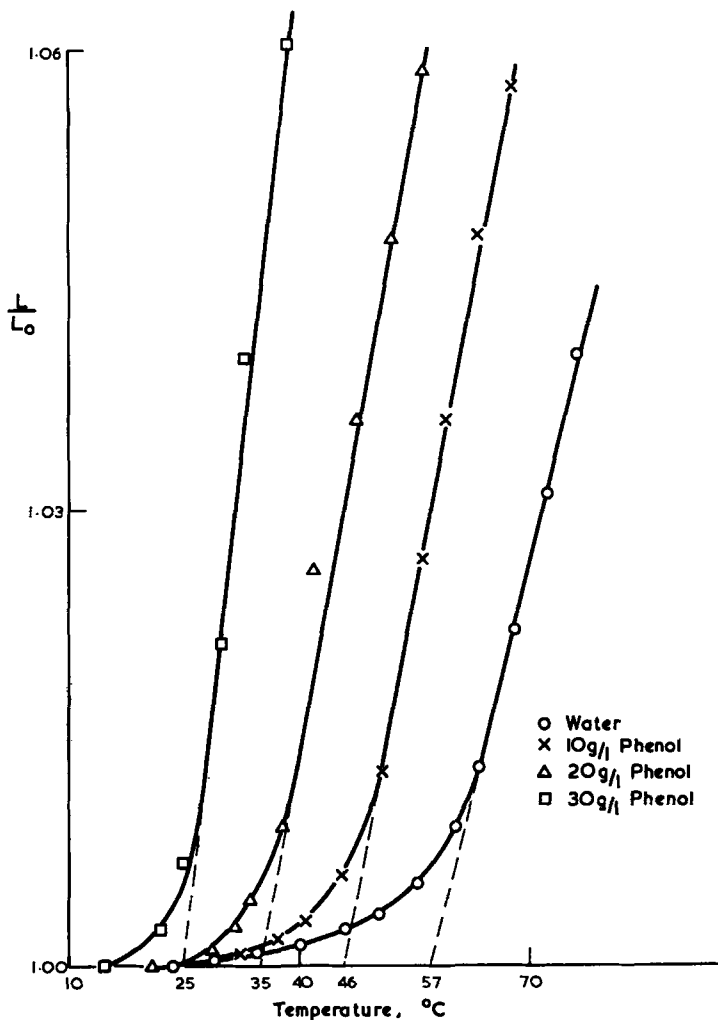


Fig. 1. Effect of temperature on the fractional increase in length of Acrilan filaments immersed in solutions of phenol.

TABLE I  
Glass Transition Temperatures of Acrilan  
Filaments When Immersed in Different Solutions

Solution	Concentration, g/l.	$T_g$ , °C
Water	—	57.0
Phenol	10	46.0
Phenol	20	35.0
Phenol	30	25.0
Toluidine	2.3	43.0
Nitrobenzene	1.0	52.5
Nitrobenzene	2.0	49.5
Dimethylformamide	10	53.0

temperature was raised from room temperature in 5°C steps to 95°C. Below  $T_g$ , the rate of change of length was very low and the length was recorded after 30 min. The temperature was then raised by 5°C and the new length recorded. Above  $T_g$ , the rate of change of length became rapid, and the length was recorded when the rate of extension became small enough to be regarded as negligible within the time scale of the experiment.

The results, presented in Figure 1 as a plot of the ratio of the new ( $l$ ) to the original length ( $l_0$ ) against temperature, reflect those obtained by Rosenbaum<sup>14</sup> for the linear and axial expansion of acrylic fibers at different temperatures. They show a marked increase over a very narrow temperature range, and the  $T_g$  was taken as the intercept of the steep linear portion of the plot on the abscissa. The values so obtained for the filaments immersed in different solutions are given in Table I.

#### Partition of Phenol Between Water and Acrilan Filaments

Changes in the distribution of phenol in the system with changing temperature have no significant effect on the recorded values of  $T_g$ , because it was established from the linear isotherms obtained over a concentration range of 5–50 g/l. of phenol that the partition coefficient was not markedly affected by temperature.

The experimental results are summarized in Table II. They were obtained by equilibrating separate 1-g samples of Acrilan filament in the phenol solutions of different concentration at various temperatures.

The quantity of phenol absorbed was determined from the changes in optical density of the solutions, using a value of  $1.585 \times 10^3$  for the extinc-

TABLE II  
Effect of Temperature on the Partition of Phenol Between Acrilan and Water

Temperature, °C	Partition coefficient
95	2.5
80	2.2
65	2.6

tion coefficient of phenol at 270 nm.<sup>16</sup> The time taken to reach equilibrium increased as the temperature approached the  $T_g$  of the filaments in water (60°C). Below this temperature, there appeared to be a threshold concentration below which the rate of uptake of phenol became so slow that measurements were impracticable.

The accuracy of the measurements was not high because the decrease of the concentration of phenol in solution was low and individual values at a particular temperature differed by  $\pm 10\%$ . However, the numerical values obtained are similar to the result of Takoaka and Aki,<sup>17</sup> quoted in the literature as 3.0 at 80°C and 90°C, respectively. From the combined results of Tables I and II, it is apparent that effects arising from a change in the distribution of phenol brought about by changes in temperature, on the values of the  $T_g$  recorded in Table I are likely to be small, since a change of concentration of phenol in solution of 10 g/l. is required to produce a shift in the  $T_g$  of approximately 10°C.

The results emphasize the need for pretreatments to be carried out at a temperature well above the  $T_g$  of the untreated filaments to ensure an equilibrium distribution of carrier before making measurements.

### Significance of Measured Changes in Length

It is unlikely that the changes in length represent an absolute measurement of a specific property since they may embody contributions from linear axial thermal expansion and permanent deformation as well as from creep. Nevertheless, the properties measured in this way do appear to consist of an overwhelming contribution from viscoelastic properties, since at the magnitude of stresses applied in these experiments, the slope of the elongation-versus-temperature relationship, was proportional to the load

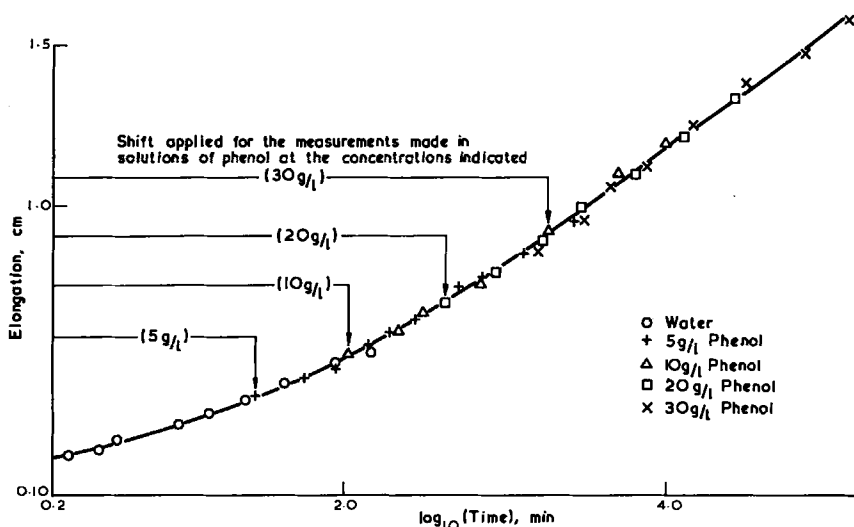


Fig. 2. Superimposition of the rate of elongation of Acrilan filaments using measurements made in phenol solutions of different concentration at 70°C.

TABLE III  
Shift Factors Used to Superimpose the Rate of Elongation Onto a Common Curve

Concentration of phenol in solution, g/l.	Shift factor $\log_{10} a_T$
0.00	0
5.00	-1.46
10.00	-2.04
20.00	-2.64
30.00	-3.25

applied to the filaments. Furthermore, the values extrapolated for the glass transition temperature from these experiments did not vary by more than  $\pm 2^\circ\text{C}$ , which is within the limits of accuracy that could reasonably be expected for the semiquantitative method employed.

The dependence of the results on segmental mobility was confirmed by showing that the rates of extension measured in phenol solutions of different concentrations were superimposable. Plots of elongation against log time at  $70^\circ\text{C}$ , for appropriately treated filaments, could all be superimposed on a common master curve by a common shift of points from each experiment along the log time axis (Fig. 2). The shift factors  $a_T$ , obtained using the untreated filaments as a reference, are given in Table III. It is possible to match these shift factors to those calculated from the WLF relationship using the values of  $T_g$  given in Table I. The calculated curve for the WLF equation using values for the constants  $A = 10.8$  and  $B = 28.5$ , corresponding to the values used by Rosenbaum,<sup>18</sup> and the plot of the experimental points are given in Figure 4.

The results described so far, therefore, show that the effect of the carrier is to increase the segmental mobility of the polymer chains in the filaments at a given temperature, and it remains to correlate the physical properties of the fiber with the diffusion of dyes through the molecular structure.

### Dyeing Properties

Rates of uptake of dye were determined using a bath containing the appropriate concentration of carrier in the filaments which had already been pretreated with carrier; under such circumstances, the diffusion process can be expected to be governed by a constant diffusion coefficient.

### Preparation of Dyebaths

Dye solutions of sparingly soluble nonionic dyes were prepared from purified material to avoid complications likely to arise from the use of dispersions. Para-Aminoazobenzene was dissolved (30 mg/l.) in water or the appropriate solution of phenol at  $90^\circ\text{C}$ , filtered hot through a G4 sintered crucible to remove any undissolved particles, and divided into aliquots of suitable volume ready for dyeing in a finite dyebath.

A stock solution of Disperse Red I (0.86 g/l.) was prepared by dissolving the dye in a 3:1 acetone:water mixture. When preparing the infinite

dyebaths, 1750 ml water or phenol solution at 95°C was added to 10 ml of the prepared stock solution. A clear colored solution resulted after a period of vigorous stirring.

### Dyeing from Dyebaths

Preliminary estimates of the effect of plasticizing agents on the diffusion coefficient of a dye in acrylic fibers were obtained using finite dyebaths with *p*-aminoazobenzene as dye. The use of the latter had the advantage of a relatively high solubility even at room temperature, but the disadvantage that the temperature range over which the diffusion coefficient could be measured in the presence of plasticizing agents was very narrow because once the temperature was raised very far above the  $T_g$ , the rate of dyeing became too fast to measure.

The pretreated dried fiber (1.0 g) was entered into the solution of dye and carrier (150 ml) contained in a quickfit tube at the appropriate temperature and secured on a suitably thermostated agitation device set at 70°C. The rate of dye uptake was measured by removing and weighing aliquots (2 ml)

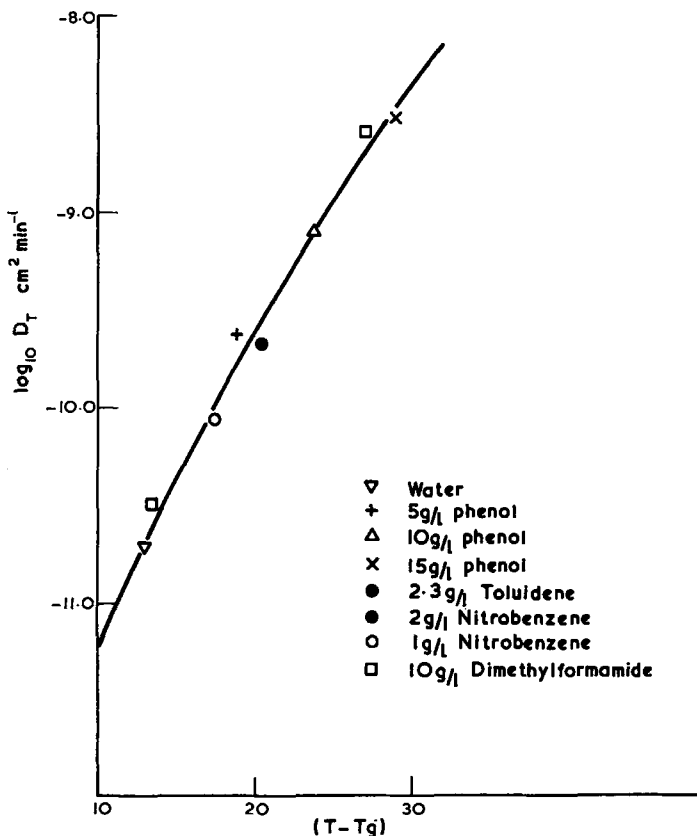


Fig. 3. Effect of different carriers on the diffusion coefficient of *p*-aminoazobenzene in Acrilan fiber at 70°C, expressed as a function of  $T - T_g$ .

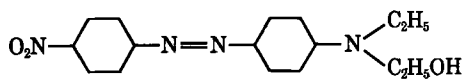


of the dyebath after timed intervals and estimating colorimetrically after suitable dilution to give a final solution of dye in a 50:50 acetone:water mixture.

After establishing the linear dependence of  $C_t/C_\infty$  on  $t^{1/2}$ , where  $C_t$  = dye absorbed after time  $t$ ,  $C_\infty$  = dye absorbed at equilibrium, and  $t$  = time, the solution of Fick's second equation proposed by Crank<sup>20</sup> and Wilson<sup>21</sup> for use in a finite dyebath was used to calculate the apparent diffusion coefficient.

Dyebaths containing various plasticizing agents were used, the effect of which on the glass transition temperature had been determined.

In Figure 3, the values obtained for the diffusion coefficient  $D$  are plotted against  $T - T_g$  to show the expected dependence of  $D$  on  $T - T_g$ . Since these results represent a  $T - T_g$  range of only 20°C, it is impossible to tell if the adherence of the results conforms to the calculated WLF relationship, and consequently further experiments were conducted using an infinite dyebath and a dye, CI Disperse Red 1, which has a slower rate of diffusion than *p*-aminoazobenzene at comparative temperatures:



CI Disperse Red 1

The apparatus used was similar to that described elsewhere.<sup>22</sup> The samples of filament (0.1 g) were contained in small, stainless steel wire cages secured on a stainless steel rod.

The rate of dyeing was plotted and the diffusion coefficient calculated according to Hill's equation for diffusion into a semi-infinite cylinder.<sup>23</sup> The radius of the 3-denier filaments was calculated assuming a density of 1.17 g/cc and that the adsorption of phenol did not result in a change in the radius of the fiber.

### Dyeing Poly(ethylene Terephthalate) Film

Samples of poly(ethylene terephthalate) film, secured in stainless steel frames, were dyed in a infinite dyebath after a pretreatment at 95°C for 24 hr in a blank dyebath of appropriate composition. Vigorous agitation of the dyebath during dyeing ensured that the necessary linear relationship between  $C_t$  and  $t^{1/2}$  was maintained. After dyeing, the dyed films were weighed, dissolved in metacresol or orthochlorophenol, and the dye content estimated colorimetrically. The diffusion coefficients were determined from the rate of dyeing data using McBaine's equation.

## DISCUSSION

The concept upon which this investigation into the mechanism of carrier dyeing is based, relates the increase in the rate of dyeing to the additional free volume which the carrier introduces into the fiber. The associated increase in segmental mobility of the polymer chains in the fiber may then

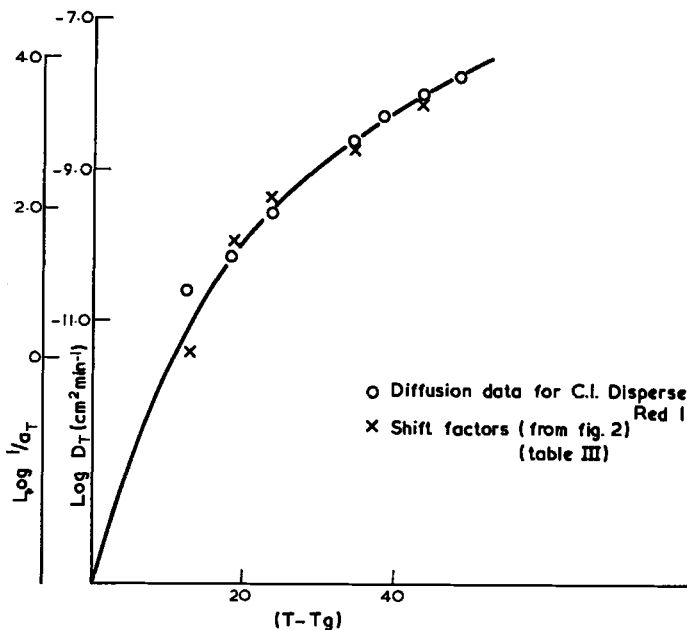


Fig. 4. Acrilan filament: matching the diffusion data and the physical properties to the WLF equation, Eq. (1), using  $A = 10.8$  and  $Y = 28.5$ .

be expected to lead to an increase in the rate of diffusion of dyes into the fiber, providing the diffusion is controlled by the segmental mobility. The viscoelastic properties are also governed by segmental mobility, and a connection between the physical properties of fibers and the diffusion properties of dyes has already been shown for the diffusion of Malachite Green into acrylic fibres<sup>18</sup> and disperse dyes into polyester<sup>24</sup> and nylon.<sup>25</sup>

The equation through which the diffusion coefficient of dyes and the physical properties may be related, eq. (1), states that the changes in properties with temperature are related to  $T - T_g$ . Consequently, the diffusion coefficient should increase, either when the temperature is raised, or when the temperature is kept constant and the  $T_g$  is lowered by the addition of carrier. Moreover, any changes in the physical properties of the fiber which occur when the carrier is added to the dye bath should also be described by eq. (1).

The physical properties of the Acrilan-phenol-water system examined here (Fig. 4 and Table III) did in fact fit very well into a WLF type of relationship in which  $\log a_T$  was calculated using the values of  $A = 10.8$  and  $B = 28.5$ . The experimentally determined values of  $a_T$ , when plotted against corresponding experimentally determined values of  $T - T_g$ , fit very closely to the calculated relationship. The values taken for  $A$  and  $B$  were the same as those calculated by Rosenbaum using data based on acrylic fibers having different values of  $T_g$ , but these are different from those widely used to describe the viscoelastic behavior of amorphous polymers ( $A = 40$ ,  $B = 52$ ). This is not surprising since the fibers are very different

TABLE IV  
Effect of Phenol on the Activation Enthalpy ( $-\Delta H$ ) for the Diffusion of  
*p*-Aminoazobenzene Into Acrilan in the Presence of Phenol

Phenol concentration, g/l.	Calculated value of $\Delta H^*$ , kcal/mole
0	72.5
5	61.4
10	54.4
15	46.0
20	44.2

from amorphous polymers being quasi-crystalline with molecules oriented preferentially along the fiber axis. Such considerations must affect the distribution of the space available for the diffusion of dyes, and movement of polymer chains in such cases could be regarded as producing spaces with cross sections elongated in the fiber axis direction. Theories based on free volume do not consider such constraints, and this point has been discussed elsewhere.<sup>26</sup>

From the described effects of phenol on the physical properties of Acrilan, it is clear that the segmental mobility of the polymer chains is enhanced by the presence of phenol, and it is now necessary to relate this observation with effects of phenyl on the rate of dyeing.

The assumption is made that the diffusion process takes place by a series of jumps of the dye molecule from one location to another and that the rate of diffusion is governed by the rate of occurrence of vacancies next to the dye molecule created by the movement of adjacent polymer segments. It follows, then, that the variations in the diffusion coefficient are related to changes in the viscoelastic properties, because both phenomena are governed by segmental mobility. In such circumstances, the shift factor may be represented by  $\ln(D_T/D_{T_g})$ , eq. (1). Unfortunately,  $D_{T_g}$ , the diffusion coefficient at  $T_g$ , is not amenable to experimental determination because it has a very low value. Moreover, because of the experimental limitations on the range of values of  $T - T_g$  which could be used, it was unreasonable to use a standard reference temperature instead of  $T_g$ . For this reason,  $D_{T_g}$  was taken as constant and a comparison made between the plot of  $\log D_T$  against  $T - T_g$  and  $-\log a_T$  against  $T - T_g$ . By a simple shift of the ordinate, the dyeing data can be made to fit onto the same curve as the results of the mechanical data (Fig. 4).

Further favorable evidence for a connection between the diffusion coefficient of a dye and  $T - T_g$  for *p*-aminoazobenzene in the presence of other compounds showing carrier activity is presented in Figure 3. Unfortunately, the very fast rate of diffusion of the above dye restricted measurements to a very narrow temperature range which made it impossible to obtain conclusive fit of the data for this dye to eq. (1). Nevertheless, values of activation enthalpy for the diffusion process measured in the usual way and quoted in Table IV show the reduction in value expected when the  $T_g$  is lowered.

On the basis of the evidence presented, therefore, it may be concluded that the accelerated rate of dyeing of Acrilan is due to the enhanced segmental mobility arising from the presence of the carrier.

### Dyeing of Poly(ethylene Terephthalate)

Unfortunately, the mechanical methods used for the determination of the  $T_g$  of Acrilan filaments in a dyebath were not feasible for poly(ethylene terephthalate) in film form. Nevertheless, it was possible to produce indirect evidence that the mechanism of dyeing for poly(ethylene terephthalate) was also dependent upon segmental mobility. This was accomplished by assuming that the lowering of the  $T_g$  caused by the incorporation of phenol in the dyebath was directly proportional to the concentration of phenol in the bath and then matching a plot of  $\log D$  against phenol concentration to a curve of  $\log a_T$  against  $T - T_g$ , calculated using eq. (1). Once the appropriate scale for the concentration of phenol had been chosen, only a vertical shift of the experimental points was needed to fit them on to the WLF curve (Fig. 5).

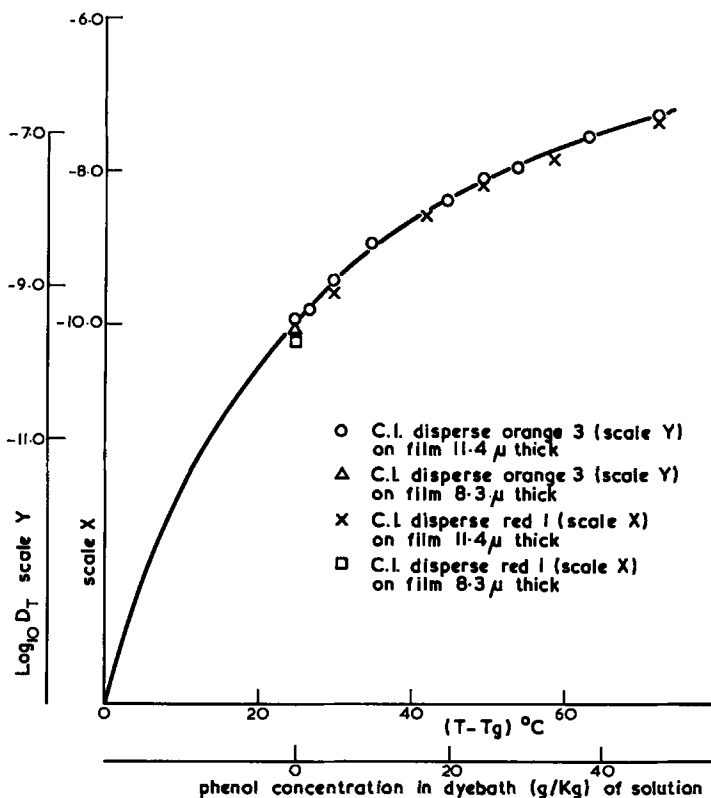


Fig. 5. Poly(ethylene terephthalate)film: matching the diffusion data for different dyes to eq. (1) using  $A = 10.8$ ,  $B = 28.5$ .

TABLE V  
Comparison of Predicted Values of  $T_g$  for Plasticized Poly(ethylene Terephthalate) Film with Experimentally Determined "Dyeing Transition Temperatures"

Dye	Concentration of phenol in the dyebath, g/l.	Transition temp., °C	
		Predicted values	Experimental values
<i>p</i> -Aminoazobenzene	0.0	70	70-75
	9.9	60	55-60
	19.6	50	46-51
	29.1	41	36-41
CI Disperse Orange 3	9.9	60	56-62
CI Disperse Red 1	19.6	50	45-50

Manipulation of the data in this way also enables a prediction of the  $T_g$  of the system to be made. These predicted values were confirmed empirically by separate experiments in which the film was dyed at different temperatures in the presence of phenol, for only 10 min. When the dye uptake was plotted against temperature, a clear indication of a dyeing transition temperature was obtained from the rapid increase in dye uptake which occurred over a very narrow temperature range. The dyeing transition temperature was taken as the intercept of the approximately linear portion of the curves on the temperature axis, and the agreement between the predicted values of  $T_g$  and the dyeing transition temperatures was very close (Table V).

The possible effects of any changes in crystallinity of the film being introduced during the pretreatment or during dyeing did not seem important, since within the limits of accuracy of infrared spectroscopy, the intensity of the band associated with the crystallinity occurring at  $973\text{ cm}^{-1}$  was not changed even by a 24-hr pretreatment of the film in phenol solution.

### CONCLUSIONS

The evidence presented confirms that the diffusion of disperse dyes into Acrilan filaments is controlled by the segmental mobility of the polymer chains and that in the presence of carriers, the segmental mobility is enhanced due to the associated increase in the free volume of the system.

Indirect experimental evidence suggests that even with a highly crystalline poly(ethylene terephthalate) substrate, the dyeing process, in the presence of carriers, may be expressed by a WLF relationship, suggesting that the dyeing process is governed by a small proportion of the polymer material not involved in a highly ordered molecular arrangement.

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