The poly(ethylene terephthalate) fibers and filaments used in textiles are normally oriented and semicrystalline. Apart from their dependence on external conditions and nature of dye-stuff, the diffusion and uptake of dye molecules in the polymer are governed by structural parameters such as relative amounts of amorphous and crystalline regions, states of orientation of amorphous regions, and morphology of crystalline regions. Thus, the dyeability of PET is, as discussed in Chapter I, consider-
ably influenced by its fine structure which, in turn, depends on the history of the polymer. It is known that the glass transition temperature (T_g) of oriented and crystalline PET is high (100–130 °C) and the dyeing rate will be appreciable only after the dyeing temperature has well exceeded the T_g. Therefore, polyester is commercially dyed at high temperatures, namely, 200–230 °C in thermosol dyeing and 120–135 °C in High-temperature dyeing. Carrier dyeing is carried out at 100 °C but the method suffers from economic and technical disadvantages. No method is yet known to dye polyester at lower temperatures.

As discussed in Chapter I, it is recently reported that the dyeability of polyester is modified by pretreatment of the material with certain organic solvents. However, not much information is available in this new field. The objective of the work presented in this chapter is critically discussed in Chapter I. Attempts have been made to develop a solvent system with which PET filaments can be treated at relatively low temperatures so as to improve the dyeability without affecting the mechanical properties appreciably. The kinetics and equilibrium studies of dyeing of solvent-treated PET have been carried out. Mechanism of dye-diffusion has been discussed. Attempts have been made to understand the modification of dyeability of PET in the light of solvent-induced structural changes as discussed in Chapter III.

A number of organic solvents having different degrees of interaction with PET were selected. A list of these solvents is given in Chapter II. The filaments were solvent-treated in slack condition by immersion at a given temperature for a fixed time.
Two sets of the treated samples were prepared: Set-Rt contained samples which retained 14% of the solvent (o.w.f.) prior to dyeing; Set-Rm contained samples from which the solvent was removed prior to dyeing. The samples were dyed with the disperse dye C.I. Disperse Orange 3 from finite dyebath (liquor to goods ratio, 100) under different conditions of temperature, time, and dye concentration. The dyed samples were soaped, washed, and dried before determining the dye uptake by extraction method. The detailed experimental methods and methods of data analysis are given in Chapter II.

FACTORS INFLUENCING DYEABILITY

Effect of Solvent Nature. In Table 1 is given the dye uptake data for samples solvent-treated for 10 min at 65 °C and dyed for 35 h at 65 °C and 98 °C from dyebaths containing 5.0 gpl of the dye. It is found that a number of solvents, namely, perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride, and chlorobenzene do not influence dyeability. Methyl salicylate, dimethylformamide, dichloromethane (treated at boil, 40 °C), and benzyl alcohol increase the dye uptake to a small extent. In contrast, however, it is found that nitrobenzene (NB) and s-tetrachloroethane (TCE) increase the dye uptake severalfold as compared to the control (untreated PET) and the heat-treated sample in silicone oil under identical conditions. TCE improves the dye uptake more than NB. It can be seen from Table 1 that the presence of small amounts of the solvent in the treated samples (Set-Rt) results in a slightly higher dye uptake as com-
Table 1. Dyeability of solvent-treated PET filaments.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dye Uptake, g/kg (o.v.f.)</th>
<th>Dyeing Temperature 65 °C</th>
<th>Dyeing Temperature 65 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Set-Ra</td>
<td>Set-Rt</td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td>1.96</td>
<td>3.78</td>
</tr>
<tr>
<td>Heat</td>
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<tr>
<td>Perchloroethylene</td>
<td></td>
<td>1.98</td>
<td>1.93</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td></td>
<td>2.10</td>
<td>2.20</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td></td>
<td>1.96</td>
<td>1.99</td>
</tr>
<tr>
<td>s-Tetrachloroethane</td>
<td></td>
<td>17.0</td>
<td>21.6</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td></td>
<td>2.00</td>
<td>2.01</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td></td>
<td>2.49</td>
<td>2.82</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td></td>
<td>2.40</td>
<td>2.53</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td></td>
<td>12.1</td>
<td>16.8</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td></td>
<td>1.61</td>
<td>1.78</td>
</tr>
<tr>
<td>Methyl salicylate</td>
<td></td>
<td>2.22</td>
<td>2.80</td>
</tr>
<tr>
<td>Benzy alcohol</td>
<td></td>
<td>3.01</td>
<td>3.28</td>
</tr>
</tbody>
</table>

a. Dyeing time, 35 h.
Set-Ra, solvent removed prior to dyeing.
Set-Rt, 14% solvent (o.v.f.) retained prior to dyeing.
pared to the samples from which the solvent was removed (set-Ht).
On the basis of this preliminary study, two solvents tetrachloro-
ethane and nitrobenzene were selected for further investigation.

Comparison of dyestability. Solvent treatment was carried
out for 10 min at 65 °C with NB and TCE. The solvent-treated and
untreated samples were dyed for 1 h at 65 °C and 98 °C and the
practical dye exhaustion curves were obtained as shown in Figure
1. The untreated samples were also dyed by the standard carrier
dyeing method. Figure 1 shows that both the rate and extent of
exhaustion at 65 °C are higher for the TCE-and NB-treated samples
(set-Ht and set-SB) (curves E and C) as compared to the untreated sample
dyed with carrier (curve G) and without carrier (curve A) under
identical conditions. The curves E and C are comparable with the
curve F which represents the carrier dyeing at 98 °C. The curves
(D and B) for the TCE-and NB-treated samples of set-Ht lie below
those (curves E and C) for the samples of set-Ht, but still the
curves D and B fall above the curves G and A which correspond to
the untreated samples dyed at 65 °C with and without carrier,
respectively.

Effect of Solvent Retained in the Fiber. The samples treat-
ed with NB and TCE for 10 min at 65 °C were allowed to retain dif-
ferent amounts of the solvent prior to dyeing. The samples were
dyed for 1 h at 65 °C under identical conditions. Figure 2 shows
the dye uptake as a function of the amount of solvent retained in
the sample. It is found that the curves pass through a maximum.
The presence of NB in an amount over 20 % (o.w.f.) and TCE over
Fig. 1 Dye exhaustion curves for PET filaments at dyeing temperatures indicated in parenthesis: A, Control (65 °C); B, NB-treated (Set-Rm) (65 °C); C, NB-treated (Set-Rt) (65 °C); D, TCE-treated (Set-Rm) (65 °C); E, TCE-treated (Set-Rt) (65 °C); F, Untreated carrier-dyed (98 °C); G, Untreated carrier-dyed (65 °C); H, TCE-treated (Set-Rt) (98 °C); K, NB-treated (Set-Rt) (98 °C).
Fig. 2 Variation of dye uptake with the amount of solvent retained in the treated fiber prior to dyeing. (a) NB-treated. (b) TCE-treated.

Fig. 3 Dependence of dye uptake on the time of solvent-treatment of PET filaments at 65°C. (a) NB-treated (Set-Rt). TCE-treated (Set-Rt).
25 % (o.w.f.) in the sample reduces the dye uptake. It is clear therefore that the presence of solvents in the sample up to a maximum limit increases the dye uptake. The solvent present in excess of this limit probably remains on the surface of the fiber and dissolves some dyestuff in itself, thereby preventing the latter from penetrating the fiber matrix in a given time.

**Effect of Treatment Time.** Figure 3 shows the dependence of dye uptake as a function of the time of treatment for samples of Set-R treated with NB and TCE at 65 °C. It is found that the dye uptake initially increases and then levels off after an optimum time depending upon the nature of the solvent and the treatment temperature. The optimum time of treatment with TCE and NB at 65 °C is found to be 2 and 6 min, respectively. This suggests that the structural changes favorable to dyeability are brought about faster in the case of TCE than NB. Based on these results, the treatment time of 10 min at 65 °C was chosen for the detailed investigation of the solvent-treated samples.

**Effect of Treatment Temperature.** Figure 4 shows the dependence of relative dye uptake on treatment temperature for the samples of Set-R treated with the solvent for 10 min. The relative dye uptake is expressed as a ratio of the dye uptake of the sample to that of the untreated sample dyed under identical conditions. This method of representing dye uptake, as suggested by Berndt and Loers, eliminates the difficulties due to nonreproducibility of dye uptake values which is generally experienced in dyeing polyester fibers with disperse dyes. The dye uptake of samples heat-
Fig. 4 Dependence of dye uptake on the solvent-treatment temperature.
A, NB-treated (Set-Hm). B, TCE-treated (Set-Hm).
treated in silicone oil for 10 min at different temperatures. is also plotted in Figure 4. It is found that treatment with TB and TCE at temperatures below 40 °C has no influence on the dye uptake. At higher temperatures the dye uptake increases rapidly with increasing temperature up to about 80 °C in the case of TCE and about 100 °C in the case of NB, and then slows down. In contrast, it is found that heat-treatment in silicone oil does not influence the dyeability up to a treatment temperature of about 120 °C. Then the dye uptake decreases slightly with increasing temperature reaching a minimum around 150-170 °C. From 200 to 240 °C the dye uptake increases to a value which is slightly higher than that of the untreated sample. This suggests that there is a considerable negative shift in treatment temperature, that is, from 200 to 40 °C, for increasing the dye uptake by solvent treatment as compared with heat treatment. Furthermore, it is remarkable that the increase in dye uptake due to solvent treatment at temperatures above 40 °C is much more than that due to the heat treatment at 240 °C.

Dyeing Behavior and Structural Changes. The dyeing behavior of the heat-treated and solvent-treated PET can be explained in terms of structural characteristics as discussed in the last chapter. The dyeing behavior of PET of thermally annealed PET was observed by previous workers\textsuperscript{264,284} to be similar to that reported above. Marvin\textsuperscript{284} presumed that increase in dye uptake above that of the un-set fabric at setting temperatures of 200 °C and above is associated with disorientation of the fiber. Later, Fumbleton et al.\textsuperscript{264} showed that the minimum in the dye uptake against
annealing temperature curve is due to the restraints imposed by
the number of crystallites. They argued that the number of crys­
llites is at the maximum just at the annealing temperature which
gives the minimum in dye uptake. The workers believed that the lar­
ger the number of crystallites, higher the Tg and hence lower seg­
mental mobility which would restrict the dye diffusion. In the same
study, however, Bumbleton et al. observed that there is no chan­
ge in the orientation of amorphous or crystalline regions of the
4.26 x drawn PET filaments on annealing at temperatures 100-240 °C.
This is surprising because it has been shown by many workers286
that air-annealing and oil-annealing of drawn PET fibers results
in significant disorientation of the amorphous regions which is
reflected in shrinkage. It appears therefore that the explanation
by Bumbleton et al.264 of the dyeing behavior in terms of change
in the number of crystallites may be only partially applicable.
Since it is the amorphous regions of PET where the dye molecules
enter any change in the structure of amorphous regions would be
expected to influence the dyeing behavior. Moreover, disorientation
of amorphous regions would enhance the segmental mobility which
would promote dye diffusion. Indeed, it is found, as discussed in
the last chapter, that treatment of drawn PET with nitrobenzene,
s-tetrachloroethane, and other solvents bring about considerable
disorientation of the amorphous regions. Furthermore, it is also
shown that the Tg of the polymer is reduced as a result of solvent
treatment. On the other hand, it is found from wide-angle x-ray
scattering that there is no significant change in the number of
crystallites under the above conditions of solvent treatment. These
arguments lead one to believe that the increase in dye uptake and dye diffusion, as will be discussed shortly, by solvent treatment is essentially due to disorientation of the amorphous regions.

Figure 5 gives a pictorial representation of the changes in fine structures of oriented PET fibers on solvent treatment at low temperatures. Figure 5a shows that the amorphous regions in the untreated polymer are highly oriented resulting in a compact structure and hence poor dyeability. The disorientation of the amorphous regions upon solvent treatment, as shown in Figure 5b, makes the structure more accessible to dye molecules. Figure 5c shows that in the case where some solvent is present in the fiber prior to dyeing and the solvent molecules are physically bound to the disoriented amorphous structure the chain segments might be slightly pushed apart and the polymer matrix is kept in a swollen state. This swollen matrix will have increased surface area and hence shows more dye accessibility. It is, however, pointed out above that the role of solvent molecules present in the polymer structure in enhancing the dyeability may be explained better in terms of the reduced glass transition temperature of the PET-solvent system. As discussed in Chapter III, it is shown that solvent-induced shrinkage (i.e., disorientation) can take place at low temperatures without any significant crystallization. At higher temperatures disorientation and crystallization take place concomittantly. It therefore appears that disorientation plays a major role in increasing the dyeability by treatment with solvents at low-temperatures. The influence on the dyeing behavior by high-temperature solvent treatment may be complicated by crystallization.
Fig. 5

MODEL STRUCTURES OF SOLVENT-TREATED PET FIBERS

a. untreated

b. solvent removed

c. solvent retained (•)
Effect of Dyebath Concentration and Dyeing Temperature. Figure 6 shows the building-up isotherms for samples treated with TCE and BB for 10 min at 65 °C and dyed for 1 h at 50, 65, and 85 °C. It is found that the dye uptake generally increases with increasing dyebath concentration and finally levels off. The dye uptake also increases with increasing dyeing temperatures. It is apparently seen that dye saturation is reached in 1 h time at 50 °C. However, this is not actually the case. The reason is that at low temperatures the diffusion of dye molecules from the surface to the inner fiber structure is restricted. At higher temperatures the surface dye molecules diffuse faster into the fiber, and hence no saturation is observed in the practical dyeing time. It is found that there is a considerable increase in exhaustion in 1 h at 65 °C as compared to 50 °C. The increase in exhaustion from 65 °C to 85 °C is relatively less. This effect is more marked with TCE-treated sample than with NB-treated sample. It is found that at higher dyeing temperatures the nonequilibrium concentration isotherms tend to become linear. It shows that the dyeing process has reached near equilibrium in 1 h at 85 °C. It is therefore concluded that the filaments treated with NB or TCE at 65 °C for 10 min can be dyed satisfactorily at temperatures of 65 to 85 °C.

KINETICS AND EQUILIBRIUM THERMODYNAMICS OF DYING

The kinetics of dyeing and equilibrium dyeing of the control (the untreated PET) and the samples treated with NB and TCE for 10 min at 65 °C were studied at different temperatures.
Fig. 6 Building-up isotherms of dyeing at different temperatures. (a) NB-treated (Set-Rt). (b) TC2-treated (Set-Rt).
Rate of Dyeing. Figures 7A-7E show the rate of dyeing curves for the samples at different temperatures. However, a convenient method for studying the dyeing rate involving no assumption as to mechanistic models is to determine the time of half-dyeing.286 The reciprocal of the time of half-dyeing ($t_\frac{1}{2}$) together with the corresponding values of equilibrium dye sorption ($\xi$) would give a clearer picture of the dyeing rate. For the present systems, the time of half-dyeing was calculated graphically by the method described in Chapter II. The values of $t_\frac{1}{2}$ and $\xi$ are given in Table 2. It is found that at any given temperature the solvent-treated samples dye at much faster rate than the control. The rate of dyeing of solvent-treated samples of Set-Rt is slightly more than that of the samples of Set-Rm.

Dye-Diffusion Coefficient and Activation Energy. Table 2 shows the apparent dye-diffusion coefficients ($D$) for the samples at different temperatures. It is found that the diffusion coefficient is considerably increased as a result of treatment with both NB and TCR. The diffusion coefficient increases with increasing temperature in all cases. Figure 3 shows a plot of $\ln D$ against $1/T$. It is found that the relationship is nonlinear in most cases. Such nonlinear dependence of diffusion coefficient on temperature has also been reported by Rosenbaum178 and other workers. The deviation from linearity probably occurs when the transition temperature of dyeing is exceeded.178 This shows that the activation energy of dye diffusion is not constant over the entire temperature range. Therefore the values of the apparent activation energy of diffusion ($r_a$)
Fig. 7A Rate of dyeing curves of PET filaments at different temperatures. Control.
Fig. 7B Rate of dyeing curves of PET filaments at different temperatures. NB-treated (Set-Rm).

Fig. 7C Rate of dyeing curves of PET filaments at different temperatures. NB-treated (Set-Rm).
Fig. 7. Rate of dyeing curves of PET filaments at different temperatures. TCE-treated (Set-Rt).

Fig. 7. Rate of dyeing curves of PET filaments at different temperatures. TCE-treated (Set-Rm).
Table 2. Fractional equilibrium exhaustion ($\epsilon_\infty$), half-dyeing time ($t_\frac{1}{2}$), and dye-diffusion coefficient ($D$) of PET filaments.

<table>
<thead>
<tr>
<th>Dyeing Temp. $^\circ$C</th>
<th>Untreated $\epsilon_\infty$</th>
<th>$t_\frac{1}{2}$ min</th>
<th>$D$ cm$^2$s$^{-1}$</th>
<th>Nitrobenzene Set-Rt $\epsilon_\infty$</th>
<th>$t_\frac{1}{2}$ min</th>
<th>$D$ cm$^2$s$^{-1}$</th>
<th>Nitrobenzene Set-Ea $\epsilon_\infty$</th>
<th>$t_\frac{1}{2}$ min</th>
<th>$D$ cm$^2$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.55</td>
<td>56.8</td>
<td>$6.24 \times 10^{-12}$</td>
<td>0.77</td>
<td>613</td>
<td>$1.18 \times 10^{-13}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>0.45</td>
<td>15.2</td>
<td>$3.09 \times 10^{-11}$</td>
<td>0.50</td>
<td>368</td>
<td>$1.14 \times 10^{-12}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>0.58</td>
<td>6.28</td>
<td>$5.10 \times 10^{-11}$</td>
<td>0.53</td>
<td>136</td>
<td>$2.00 \times 10^{-12}$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>85</td>
<td>0.50</td>
<td>1.94</td>
<td>$2.38 \times 10^{-10}$</td>
<td>0.51</td>
<td>19.6</td>
<td>$2.07 \times 10^{-11}$</td>
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<tr>
<td>90</td>
<td>0.15</td>
<td>1.15</td>
<td>$1.85 \times 10^{-3}$</td>
<td>0.48</td>
<td>1.64</td>
<td>$2.79 \times 10^{-10}$</td>
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<tr>
<td>95</td>
<td>0.48</td>
<td>1.09</td>
<td>$4.16 \times 10^{-10}$</td>
<td>0.48</td>
<td>1.64</td>
<td>$2.79 \times 10^{-10}$</td>
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<tr>
<td>100</td>
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<td>234</td>
<td>$6.91 \times 10^{-13}$</td>
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<td>1.10</td>
<td>$6.21 \times 10^{-10}$</td>
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<td>105</td>
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<td>80.6</td>
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<td></td>
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<td>110</td>
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<td>0.50</td>
<td>$1.38 \times 10^{-9}$</td>
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<td></td>
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<tr>
<td>115</td>
<td>0.50</td>
<td>15.0</td>
<td>$2.80 \times 10^{-11}$</td>
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<td>0.50</td>
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<td>0.50</td>
<td>$1.38 \times 10^{-9}$</td>
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<td></td>
</tr>
</tbody>
</table>

Contd...
<table>
<thead>
<tr>
<th>Dyeing Temp. °C</th>
<th>( \varepsilon_\infty )</th>
<th>( t_\frac{1}{2} ) min</th>
<th>( D ) cm(^2) s(^{-1})</th>
<th>( \varepsilon_\infty )</th>
<th>( t_\frac{1}{2} ) min</th>
<th>( D ) cm(^2) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.52</td>
<td>152</td>
<td>( 8.44 \times 10^{-13} )</td>
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<td>0.50</td>
<td>50.5</td>
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<td>0.79</td>
<td>105</td>
<td>( 9.33 \times 10^{-13} )</td>
</tr>
<tr>
<td>75</td>
<td>0.49</td>
<td>18.9</td>
<td>( 2.29 \times 10^{-11} )</td>
<td>0.52</td>
<td>93.9</td>
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<tr>
<td>85</td>
<td>0.50</td>
<td>4.51</td>
<td>( 9.29 \times 10^{-11} )</td>
<td>0.52</td>
<td>14.0</td>
<td>( 2.80 \times 10^{-11} )</td>
</tr>
<tr>
<td>95</td>
<td>0.52</td>
<td>3.13</td>
<td>( 1.25 \times 10^{-10} )</td>
<td>0.49</td>
<td>3.46</td>
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<td>1.06</td>
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<td>0.45</td>
<td>1.17</td>
<td>( 4.16 \times 10^{-10} )</td>
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<tr>
<td>115</td>
<td>0.33</td>
<td>0.52</td>
<td>( 1.35 \times 10^{-9} )</td>
<td>0.40</td>
<td>0.89</td>
<td>( 6.21 \times 10^{-10} )</td>
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Fig. 8 Temperature dependence of the diffusion coefficient of dyeing of PET filaments. A, Control; B, NB-treated (Set-Rm); C, NB-treated (Set-Ht); D, TCE-treated (Set-Rm); E, TCE-treated (Set-Ht).
obtained from the linear portions of the curves (Figure 2). The values are given in Table 3. It is found that the activation energy of diffusion is slightly reduced as a result of solvent treatment in the case of samples of Set-Ra. The reduction of $E_a$ is a little more for the samples of Set-Rt.

**Mechanism of Dye Diffusion.** The mechanism of dye diffusion can be discussed in the light of the above results. As discussed in Chapter I, there are two mechanisms by which dye molecules can diffuse into a polymer. One is free-volume model\textsuperscript{177,178} and the other is pore model\textsuperscript{179}. According to the free-volume model, the diffusion of dye molecules occurs through formation of temporary holes in the polymer matrix due to segmental jumps. The formation of adequately-sized holes requires absorption of energy for sufficient segmental mobility. On the other hand, in the pore model it is assumed that the migration of dye molecules occurs through water-filled pores in the polymer matrix. It means that the activation energy of dye diffusion through the water-filled pores would essentially be the same as that for diffusion of dye in water. It is therefore expected that the activation energy of dye diffusion in the pore model should be lower than in free-volume model. In other words, if the mechanism of dye diffusion is changed from free-volume model to pore model, a considerable reduction in activation energy of diffusion should take place. However, as shown above, it is found that the activation energies of dye diffusion for both the control and the solvent-treated PET are of the same order of magnitude. It shows that the mechanism of dye diffusion is not changed as a result of the solvent
<table>
<thead>
<tr>
<th>Pretreatment of filaments</th>
<th>$E_a$ (Kcal/mol deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
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</tr>
<tr>
<td>Nitrobenzene (Set-Rt)</td>
<td>23.6</td>
</tr>
<tr>
<td>Nitrobenzene (Set-Rm)</td>
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</tr>
<tr>
<td>s-Tetrachloroethane (Set-Rt)</td>
<td>28.0</td>
</tr>
<tr>
<td>s-Tetrachloroethane (Set-Rm)</td>
<td>42.1</td>
</tr>
</tbody>
</table>
treatment. Since it is established\textsuperscript{177,178} that the free-volume mechanism of dye diffusion is applicable to PET, it is the same mechanism which is operative in the solvent-treated polymer also. Weigmann and co-workers\textsuperscript{13} first suggested that the dye-diffusion mechanism in PET treated with dimethylformamide is changed from free-volume model to pore model. However, later\textsuperscript{14} they also found that the mechanism is not changed as a result of solvent treatment.

It was shown earlier that the increased dye uptake of solvent-treated PET is due to disorientation of the amorphous regions. This also explains the increased diffusion coefficient of dye-diffusion in the solvent-treated fiber. However, it can be pointed out that the presence of small amounts of the solvent in the treated fiber prior to dyeing, as discussed above, results in higher diffusion coefficient and lower activation energy as compared with the fiber from which the solvent was removed before dyeing. It means that the solvent takes part in the transport of dye in some manner. It was shown from shrinkage measurements in Chapter III that the glass transition temperature (T\textsubscript{g}) of PET is considerably reduced in the presence of strongly plasticizing solvents such as TCE and IB. Therefore, although the role of solvent in the migration of dye is not very clear, it is speculated that the reduction in T\textsubscript{g} of the polymer-solvent system may be the major factor.

\textbf{Equilibrium sorption isotherms.} Figure 9 shows the representative sorption isotherms for equilibrium dyeing of untreated and solvent-treated PET filaments. In some cases a departure from linearity of the isotherms is observed. This is perhaps due to deviations
Fig. 9 Sorption isotherms of dyeing of PET filaments at different temperatures. (a) TCE-treated (Set-Rt). (b) NB-treated (Set-Rt).
from Henry's distribution law. The deviation observed at higher
temperatures might be due to breaking-up of dye aggregates. Never-
theless, since little aggregation will be expected at low dye con-
centrations, the standard chemical potential of dyeing ($\Delta/\mu$) can
be fairly accurately calculated from the slopes of the initial line-
ar portions of the sorption curves. In Table 4 are given the values
for equilibrium partition coefficient ($K$) and the thermodynamic
parameters ($\Delta/\mu$, $\Delta H^0$, $\Delta S^0$) obtained from the sorption isotherms.
The absolute values of these quantities may not be an exact measure
of the actual system because of the inherent difficulties with the
dyeing model, but a comparison of these values should serve to
establish the general trend.

**Equilibrium Partition Coefficient and Thermodynamic Para-

meters.** Since the dyeing process is one of the most complex and
difficult systems, McGregor pointed out that the conventional
standard affinity of dyeing ($\Delta/\mu$), which is a measure of the mean
driving force behind dyeing in an apparently unrealistic model of
the dyeing process, is more of a valuable theoretical tool than a
simple description of the "rate of dyeing" in the usual sense of
the term. Furthermore, since the standard free energy of dyeing
bears a logarithmic relationship with the partition coefficient
($K$), a considerable spread in $K$ values does not result in a large
spread in the values of $\Delta/\mu$. However, the apparent standard affinity
of dyeing is an important thermodynamic quantity because the
other thermodynamic quantities such as apparent standard heat of
dyeing ($\Delta H^0$) and the apparent standard entropy of dyeing ($\Delta S^0$)
### Table 4. Partition coefficient (K), standard affinity (Δμ°), standard heat (ΔH°), and standard entropy (ΔS°) of dyeing of PET filaments.

<table>
<thead>
<tr>
<th>Temp. of Dyeing (°C)</th>
<th>s-Tetrachloroethane Set-Ht</th>
<th>Set-Rm</th>
<th>Nitrobenzene Set-Ht</th>
<th>Set-Rm</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>Δμ Kcal/mol</td>
<td>ΔH° Kcal/mol</td>
<td>ΔS° 298.2°K Kcal/mol</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>176</td>
<td>1.31</td>
<td>-2.81</td>
<td>-2.95</td>
<td>-1.29</td>
</tr>
<tr>
<td></td>
<td>153</td>
<td>3.22</td>
<td>-2.78</td>
<td>-2.31</td>
<td>-1.36</td>
</tr>
<tr>
<td></td>
<td>81</td>
<td>2.61</td>
<td>-2.60</td>
<td>-2.55</td>
<td>-1.13</td>
</tr>
<tr>
<td>65</td>
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<td>-3.03</td>
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<td>-2.81</td>
<td>-1.36</td>
</tr>
<tr>
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<td>-3.36</td>
<td>-2.78</td>
<td>-2.31</td>
<td>-1.36</td>
</tr>
<tr>
<td></td>
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<td>2.73</td>
<td>-2.60</td>
<td>-2.55</td>
<td>-1.13</td>
</tr>
<tr>
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<td>-2.82</td>
<td>-1.59</td>
</tr>
<tr>
<td></td>
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<td>-3.94</td>
<td>-6.39</td>
<td>-11.9</td>
<td>-9.55</td>
</tr>
</tbody>
</table>
are calculated from it. The standard heat of dyeing ($\Delta H^\circ$) is a quantitative measure of the effect of temperature on dyeing equilibria. $\Delta H^\circ$ may be regarded as the sum of the heats of formation of the various bonds between the dye and the fiber. Figure 10 shows straight line plots of $\Delta \mu^\circ / T$ v. $1/T$ in all cases. The values of $\Delta H^\circ$ were therefore obtained from the slope of the curves. The standard entropy of dyeing ($\Delta S^\circ$) is a measure of the disorder of the dye molecules in solution and in fiber phases. The values of $\Delta S^\circ$ were obtained using Ciba-Helmholtz equation as discussed in Chapter II.

In Table 4 are given the values of partition coefficient ($K$), standard affinity of dyeing ($\Delta \mu^\circ$), standard heat of dyeing ($\Delta H^\circ$), and standard entropy of dyeing ($\Delta S^\circ$) for the untreated and solvent-treated samples. The negative sign of $\Delta \mu^\circ$ shows that the dye has spontaneous affinity for the samples. However, the magnitude of is found to decrease with increasing temperature of dyeing in all cases. This means that the dye has more affinity for water at higher temperatures than for the polymer. This fact is more clearly indicated by comparing the values of $K$ in Table 4. It is found that the standard affinity of dyeing increases at all temperatures as a result of solvent treatment. The increase of $\Delta \mu^\circ$ is more on treatment with s-tetrachloroethane than nitrobenzene. Furthermore, it can be seen that $\Delta \mu^\circ$ values are of the same order of magnitude for solvent-treated samples of both the Set-Rt and Set-Rm. It shows that the standard affinity of dyeing does not reflect on the role of the presence of small amounts of the solvent in the fiber prior to dyeing.
Fig. 10 Arrhenius dependence of the standard activation energy of dye-diffusion on temperature.
As shown in Table 4, it is found that $\Delta H^0$ is negative in all cases indicating thereby that equilibrium dye sorption has a negative temperature gradient. It is clear therefore that the process of dye sorption remains exothermic with solvent-treated PET as it is with the untreated polymer. Furthermore, it is found that the magnitude of $\Delta H^0$ is generally higher in the case of solvent-treated samples as compared to the control. Since $H^0$ is a measure of the strength of dye-fiber bonding, it means that the strength of dye-fiber bonds has slightly increased as a result of the solvent treatment. Indeed, it is found as has been discussed in the last chapter, that interaction of PET with some strongly interacting solvents such as TCE and NB results in considerable modification of the fiber fine structure. However, a clear picture of the change in the strength of dye-fiber bonding is not understood. It is found that $\Delta S^0$ is negative, and hence this decrease in entropy will not favor dye sorption. Nevertheless, since dye is sorbed, the driving force is mainly the large $\Delta H^0$. The decrease in entropy is caused by the reduced randomness, i.e., the more ordered packing of the dye molecules when sorbed by the polymer.

CONCLUSIONS

It is clear from the above discussion that the treatment of oriented and semicrystalline PET filaments with some organic solvents results in improved dyeability of the material. It is found that the treatment of PET with s-tetrachloroethane and nitrobenzene at low temperatures such as $65^\circ C$ increases the dye uptake and dye diffusion coefficient considerably. The dyeability of PET treated with these
solvents at 65 °C and dyed with a disperse dye from aqueous dye-bath without the addition of a carrier at 65 to 85 °C is (i) much more than the dyeability of the untreated PET dyed at 100 °C without the addition of a carrier and (ii) slightly less than the dyeability of the untreated PET dyed at 100 °C with the addition of a carrier (sodium salt of o-phenylphenol). As discussed in Chapter III, the treatment with these solvents at low temperatures such as 65 °C does not have a deleterious effect on the fiber mechanical properties. Although the solvent treatment at higher temperatures results in increasing dye uptake, the mechanical properties are increasingly affected. The improvement in dyeability by treatment at low temperatures is considered to be due to solvent-induced disorientation of the amorphous regions of the polymer. The solvent-induced disorientation of the amorphous regions results in increased segmental mobility as shown by the reduction in the glass transition temperature of the polymer. The dyeing behavior of PET treated with the solvents at higher temperatures may be influenced by crystallization.

The presence of small amounts of the solvent in the solvent-treated fiber prior to dyeing influences the dyeing behavior. The solvent present in the fiber up to a maximum limit of 20 % o.w.f. in the case of nitrobenzene and 25 % o.w.f. in the case of 1,4-dichloroethane increases the dye uptake and dye diffusion coefficient. However, the presence of the solvent in excess of the maximum limit reduces the dye uptake. The increase in dyeability due to the presence of the solvent in the fiber is attributed to the lowering of the glass transition temperature of the PET-solvent system.
The mechanism of dye diffusion into the solvent treated PET is the same as it is in the untreated PET, i.e., the free volume mechanism.